

The electric field gradient in noncubic metals

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Electric field gradients present at the atomic nuclei in solids may be studied through the nuclear electric quadrupole interaction by several methods. In noncubic metallic systems, a large amount of data has become available and is critically testing our theoretical understanding of the sources of field gradients in these systems. After summarizing the relevant measurement techniques, we discuss the development of the existing experimental data base and the various theoretical approaches to explain it. Comprehensive coverage of the published literature extends through 1977.

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GLOSSARY OF SYMBOLS

Most symbols used are listed here with an indication of the approximate locations of their appearance in the text.

a	Lattice constant	Eq. (2.15)
$a(l), b(l)$	Constants depending on nuclear spin	Eq. (3.3)

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c	Lattice constant (along symmetry axis direction, if any)	Eq. (3.3)
	Also used as the speed of light where no confusion results	Eq. (3.5)
$d\Omega$	Differential solid angle	Eqs. (3.4a) and (3.7a)
e	Magnitude of electron charge	Eq. (2.2b)
$f^0(\mathbf{k}), f_n^0$	Occupation probability for the state $ \mathbf{k}\rangle$ or ψ_n	Eqs. (5.7) and (5.27)
g	Nuclear gyromagnetic ratio	Before Eq. (3.2)
h, \hbar	Planck's constant; $\hbar = h/2\pi$	After Eq. (2.10)
hcp	Hexagonal close-packed	
$j_l(qr)$	Spherical Bessel function of order l	Eqs. (5.14), (5.21) and (5.22)
\mathbf{k}	Electron crystal momentum	Eqs. (5.1)–(5.5) and (5.7)
k_B	Boltzmann's constant	Eqs. (3.3) and (3.4b)
k_F	Fermi momentum	Eqs. (5.7) and (5.8)
m	Index for components of spherical tensors	Eqs. (2.8) and (2.7)
m_e	Mass of the electron	Eq. (5.8)
q	Principal component of the electric field gradient: V_{zz}/e	After Eq. (2.10)
\mathbf{q}, q	Fourier variable conjugate to position vector \mathbf{r} , and its magnitude	Eq. (5.7) ff.
\mathbf{r}	General position vector with Cartesian components x, y, z and spherical components r, θ, ϕ	Eq. (2.8)
$\{\mathbf{r}^{(n)}\}$	Set of all ion position vectors	Eq. (6.1)
t	Time	Eqs. (3.7) and (6.1)
tcp	Tetragonal close-packed	
A_λ	Angular distribution parameters	Eqs. (3.4) and (3.7)
APW	Augmented plane wave	Sec. V. A. 3
B	Temperature-dependence slope parameter	Eq. (4.4)
B_λ	Orientation parameter	Eqs. (3.4) and (3.7)
$C_{n, \mathbf{k}, \mathbf{K}}$	Wave-function expansion coefficient	Eqs. (5.4) and (5.5)
C_Q	Nuclear quadrupole contribution to heat capacity	Eq. (3.3)
D	Macroscopic electric displacement field	Eqs. (5.9) and (5.10)
DWF	Debye-Waller factor	Eqs. (6.4)
	$W(\mathbf{K}, T)$ or interchangeably $e^{-W(\mathbf{K}, T)}$	and (6.5)

E	Macroscopic electric field	Eqs. (5.9) and (5.10)		Also used as lattice molar volume	Sec. IV. B. 4 and VI. B
E_F	Fermi energy	Eq. (5.6)	V_{ij}	Microscopic electric field gradient tensor—Cartesian components	Eqs. (2.1), (2.4) and (2.5)
E_M	Energy of nuclear sublevel	Eq. (2.10)			
E_γ	Gamma-ray energy	Eq. (3.5)			
$E(\mathbf{k}), E_n$	Energy of electron in state $ \mathbf{k}\rangle$ or ψ_n	Eqs. (5.7) and (5.27)	V_{ps}, V_{ps}^0 V_{zz}^{Cond}	Ionic pseudopotential	Eq. (6.4)
EFG	Electric field gradient			Principal component of the electric field gradient arising from conduction electrons	Eq. (5.25)
$G_{\lambda\lambda}$	Perturbation factor	Eq. (3.7)			
H	Magnetic field strength	Before Eq. (3.2)	V_{zz}^{Ext}	—from external source charge	Eq. (2.12)
H	Hamiltonian operator	Eqs. (2.1) and (2.7)	V_{zz}^{FS}	—from Fermi surface electrons	Eq. (5.6)
I	Nuclear-spin eigenvalue	Eq. (5.2)	V_{zz}^{Latt}	—from a point-ion lattice sum	Eq. (2.15)
I_j	Cartesian components of nuclear-spin operator	Eq. (5.2)	V_{zz}^{Local}	—from local electronic charge	Eq. (2.12)
IMPAC	Coulomb excitation recoil implantation PAC	Sec. III. D			
\mathbf{K}, K	Reciprocal lattice vector and its magnitude	Eqs. (5.4), (5.5), (6.4) and (6.5)	V_{Ext} V_{Total}	Macroscopic potential due to external charges	Eqs. (5.10) and (5.11)
	Also used as proportionality constant	Eqs. (4.2) and (4.3)		Macroscopic potential due to external and induced charges	Eqs. (5.10) and (5.11)
M	Nuclear-spin projection quantum number (eigenvalue of I_z)	After Eq. (2.3)	$V''(r)$ $V_{sc}(\mathbf{r})$	Second radial derivative of potential $V(\mathbf{r})$	Eqs. (5.16) and (5.19)
M_a	Mass of lattice ions	Eq. (6.2)	$V_{zz}^{Cond}(r)$	Potential at \mathbf{r} due to electronic screening charge	Eq. (5.12)
ME	Mössbauer effect	Sec. III. C		Electric field gradient density due to conduction electrons at r	Eq. (5.25)
NAR	Nuclear acoustic resonance	Sec. III. A			
NMR	Nuclear magnetic resonance	Sec. III. A			
NO	Nuclear orientation	Sec. III. B	$V_{zz}^{Core}(r)$	Electric field gradient density due to core electrons at r	Eq. (5.26)
NQR	Nuclear quadrupole resonance	Sec. III. A			
OAQ	Orthogonalized atomic orbitals	Sec. V. A. 1	$V_C(\mathbf{r})$	Bare ionic potential	Eqs. (5.12)–(5.14)
OPW	Orthogonalized plane waves	Sec. V. A. 2	$W(\mathbf{K}, T)$	Debye-Waller factor	Eqs. (6.4) and (6.5)
P	Hydrostatic pressure	Sec. IV. B. 4 and VI. B	$Y_{2m}(\theta, \phi)$	Spherical harmonic of order 2 and degree m	Eq. (2.8)
P_{un}	Uniaxial pressure	Sec. IV. B. 4	Z	Ionic valence	Eq. (2.8)
$P_2(\cos\theta)$	Second-order Legendre polynomial	Eq. (2.14)	α	Phenomenological anti-shielding enhancement factor	Eqs. (5.17) and (6.12)
PAC	Perturbed angular correlation	Sec. III. D	$\alpha(\mathbf{r}, \mathbf{r}')$	Generalized electron response function	Eq. (5.27)
PAD	Perturbed angular distribution	Sec. III. D	β	Temperature-dependence slope parameter of Jena	Eq. (6.7)
Q	Conventional nuclear quadrupole moment (barns)	Eq. (2.2b)	$\beta(r)$	Radially dependent anti-shielding factor of Lodge [dual of $\gamma(r)$]	Eqs. (5.25) and (5.26)
Q_{ij}	Nuclear quadrupole moment tensor—Cartesian components	Eqs. (2.1) and (2.2)	γ	Grüneisen parameter [not to be confused with Euler's constant in Eq. (A2)]	Eq. (6.13)
$Q_2^{(m)}$	Nuclear quadrupole moment tensor—spherical components	Eq. (2.3)	γ_∞	Sternheimer antishielding factor for external source charge	Eq. (2.12)
$Q^{cond}(r)$	Quadrupole moment density of conduction electrons at r	Eq. (5.25)	$\gamma(r)$	Radially dependent anti-shielding factor	Eq. (2.13)
$Q_i(r)$	Quadrupole moment density induced in ion core	Eqs. (2.13) and (5.24)	δ_{ij}	Kronecker delta: = 1 for $i=j$, = 0 for $i \neq j$	Eqs. (2.2) and (2.5)
QI	Nuclear quadrupole interaction		$\delta(\mathbf{r})$	Dirac delta function	Sec. II. D
R	Sternheimer atomic (local) shielding factor	Eq. (2.12)	$\epsilon(\mathbf{q}), \epsilon(q)$	Hartree dielectric function for the free-electron gas	Eqs. (5.7) and (5.8)
$S(\mathbf{q})$	Lattice structure factor	Eqs. (6.10) and (6.11)	η	Axial asymmetry parameter	Eq. (2.11)
SH	Nuclear specific heat	Sec. III. B	$\eta(E_F)$	Density of electron states at the Fermi surface	Eq. (5.6)
SOPAD	Stroboscopic observation of PAD	Sec. III. D	θ_D	Debye temperature	Eq. (6.2)
T	Temperature	Eqs. (3.3), (3.4b) and (4.4)	ν_L	Larmor precession frequency	Eq. (3.2)
TDPAC	Time differential PAC	Sec. VI. A	$\nu_{ M - M+1 }$	Transition frequency	Eq. (3.1)
TDPAD	Time differential PAD	Sec. III. D	ν_Q	Spin-independent quadrupole interaction frequency $\equiv e^2qQ/\hbar$	After Eq. (2.10)
TIPAC	Time integral PAC	Sec. III. D	$\rho(\mathbf{r})$	Total lattice charge density (excluding the ionic charge at the origin)	Eq. (2.14)
U_λ	Deorientation parameters	Eq. (3.4)			
V	Electrostatic potential	Eq. (2.4)			

$\rho_e(\mathbf{r})$	Total electronic charge density	Eq. (5.1)
$\rho_N(\mathbf{r})$	Total nuclear charge density	Eq. (2.2a)
ϕ_{ij}	Macroscopic electric field gradient tensor—Cartesian components	Eq. (2.5)
ϕ_{zz}^{sc}	Principal component of the electric field gradient from a static screened lattice sum	Eq. (6.12)
$\phi_2^{(m)}$	Macroscopic electric field gradient tensor—spherical components	Eq. (2.6)
$\phi(T/\theta_D)$	Debye integral	Eqs. (6.6) and (6.7)
$\phi_i(\mathbf{r})$	Single core state wave function: i = core state index	Eq. (5.3)
$\phi_{ik}^{TB}(\mathbf{r})$	Core level tight-binding Bloch wave function	Eqs. (5.2) and (5.3)
$\chi_k(\mathbf{r})$	Free-electron plane wave	Eq. (5.2)
$\psi_k^{OPW}(\mathbf{r})$	Single OPW wave function	Eqs. (5.2) and (5.4)
$\psi_n(\mathbf{r})$	One-electron wave function	Eq. (5.27)
ω	Fourier variable conjugate to the time t	Before Eq. (5.7)
ω_Q	Spin-dependent quadrupole precession frequency	Eq. (3.6)
ω_0	Fundamental precession frequency of radiation pattern	Eq. (3.6)
$\Delta x, \Delta x_u$	Lattice vibration amplitudes	Eqs. (6.1) and (6.8) ff.
$\langle(\Delta x)^2\rangle$	Mean square vibration amplitude	Eqs. (6.2) and (6.5)
ΔZ	Effective valence difference between host and impurity	Sec. IV. B. 2
Σ'	Sum over lattice points omitting the origin	Eq. (5.17)
$\Phi_{nk}(\mathbf{r})$	Electronic pseudowavefunction	Eq. (5.5)
$\Psi_{nk}(\mathbf{r})$	Electronic wave function: n = band index	Eqs. (5.1) and (5.4)
Ω, Ω_q	Symbol for spherical polar coordinates, θ and ϕ , of \mathbf{r} and θ_q and ϕ_q , of \mathbf{q} , respectively	Eqs. (5.13) and (5.14)

I. INTRODUCTION

The study of the interaction of the atomic nucleus with extranuclear fields has proven quite useful in many contexts. Nuclear resonance and spectroscopic techniques have, for example, been valuable in elucidating the nature of chemical bonding in molecules and compounds (Bray, 1961; Gülich, 1975; Weiss, 1974), in deciphering the structure of biological molecules (Johnson, 1975a; Trontelj *et al.*, 1974), and in characterizing the properties of magnetic materials (Grant, 1975). In nonmagnetic systems, the nuclear electric quadrupole interaction (QI) has had wide applicability as an aid to determine the distribution of electric charge surrounding a nuclear site. The experimental techniques most commonly used for this purpose are nuclear magnetic and quadrupole resonance (NMR and NQR). These are appropriate for measurements on the stable nuclear ground states of relatively abundant species in the sample under investigation. The principles of the reso-

nance techniques with emphasis on application to non-metallic materials have been reviewed in many texts and articles (see, e.g., Das and Hahn, 1958). Applications to metals have been reviewed by Rowland (1961) and Drain (1967). Quadrupole effects in metals include a variety of diverse topics such as quadrupolar relaxation in liquid metals and alloys (Sholl, 1974; Warren, 1974) as well as fields surrounding impurities and/or defects in cubic metals (Kanert and Mehring, 1971). Although similar experimental and theoretical considerations apply in some degree to all such systems, we shall confine ourselves here to the QI in solid noncubic metals. The most recent review dealing with this subject is due to Barnes (1970) which emphasizes applications of the NQR technique to pure systems. A short summary of the most recently observed systematic trends in experimental data and some of their ramifications has been given by Raghavan (1976).

It is particularly appropriate at this time to attempt to bring together information concerning the QI in noncubic metals. Within the past few years, a significant increase in the amount and kind of available experimental data has occurred. This is especially true with respect to measurements of the QI at dilute impurities which have used techniques such as the Mössbauer effect, perturbed angular correlations and distributions of emitted radiations, and low-temperature nuclear orientation. The quantity of data has become sufficient to permit recognition of empirical trends which are providing critical tests of our theoretical understanding. Below, after some preliminaries, we offer a summary of the present status of experimental work, emphasizing those observations which have pointed to the need for an improved theory. Following that, the various theoretical approaches employed so far and their degrees of success will be summarized.

II. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION

A. Formulation of the interaction

The following description of the nuclear electric quadrupole interaction will not provide a detailed and rigorous derivation of the basic theory since excellent and complete presentations are available in the literature (Cohen and Reif, 1957; Das and Hahn, 1958; Kopfermann, 1958; Lucken, 1969). It is necessary however, for the sake of subsequent clarity, to introduce some basic ideas and notation. The quadrupole portion of the interaction energy of the nuclear charge distribution in an external electrostatic field is given by the Hamiltonian operator

$$H = \frac{1}{6} \sum_{ij} Q_{ij} V_{ij}, \quad (2.1)$$

which is expressed here as the inner product of two second-rank Cartesian tensors. The nuclear quadrupole moment operator Q_{ij} is defined by the integral over the nuclear charge density $\rho_N(\mathbf{r})$

$$Q_{ij} \equiv \int \rho_N(\mathbf{r})(3x_i x_j - r^2 \delta_{ij}) d\mathbf{r}, \quad (2.2a)$$

or can be expressed in terms of the nuclear spin operators as

$$Q_{ij} = \frac{eQ}{I(2I-1)} \left\{ \frac{3}{2} (I_x I_j + I_j I_x) - \delta_{ij} I(I+1) \right\}, \quad (2.2b)$$

where eQ is the quantity conventionally referred to as the nuclear quadrupole moment. The components of the corresponding spherical tensor operator are (Bleaney, 1967)

$$Q_2^{(0)} = \frac{eQ}{2I(2I-1)} [3I_x^2 - I(I+1)] \quad (2.3a)$$

$$Q_2^{(\pm 1)} = -\frac{\pm\sqrt{6}eQ}{4I(2I-1)} (I_x I_{\pm} + I_{\pm} I_x) \quad (2.3b)$$

$$Q_2^{(\pm 2)} = \frac{\sqrt{6}eQ}{4I(2I-1)} I_{\pm}^2, \quad (2.3c)$$

where $I_{\pm} = I_x \pm iI_y$. It is clear from Eq. (2.3a) that the conventional moment eQ is just the expectation value of $2Q_2^{(0)}$ in a nuclear state with maximum spin projection quantum number $M=I$. Nuclear quadrupole moments, Q , generally range from a few tenths of a barn (1 barn = 10^{-24} cm²) in nearly spherical nuclei to several barns in highly deformed nuclei. A large number of moments are now known and are tabulated along with indications of the measurement method employed, by Fuller and Cohen (1969), Fuller (1976), and Shirley and Lederer (1977).

The field gradient tensor V_{ij} is defined as the second partial spatial derivatives of a classical electrostatic potential V evaluated at the nuclear site. Thus

$$V_{ij} \equiv \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_{\text{nucleus}} \quad (2.4)$$

where V_{ij} is clearly symmetric. At this point most authors have taken the microscopic point of view that all the relevant charge producing V is external to the nucleus. (This ignores electrons in an s state, but these are spherically symmetric and thus do not contribute to a field gradient.) It is from this assumption that Laplace's equation, $\nabla^2 V = 0$, is invoked to show that the trace of V_{ij} vanishes. In fact, the multipole expansion from which Eq. (2.1) is derived, is only valid when the charge producing V_{ij} does not overlap the nuclear charge distribution. Notwithstanding this point, we shall formally admit the possibility that $\nabla^2 V \neq 0$. This will allow us to discuss potentials from a macroscopic viewpoint in order to include effects such as charge screening in metals. The lack of rigor implied here will not be material since, for our purposes, the nucleus will be considered as a point, neglecting its finite spatial extent. If a new tensor is defined by (Sholl, 1967)

$$\phi_{ij} \equiv V_{ij} - \frac{1}{3} \delta_{ij} \nabla^2 V, \quad (2.5)$$

the form of Eq. (2.1) is left unchanged since the trace of Q_{ij} is zero. Henceforth both ϕ_{ij} and V_{ij} will be referred to interchangeably as the electric field gradient (EFG) tensor unless a distinction is needed in the case of a non-Laplacian potential. The spherical components of

ϕ are (Matthias *et al.*, 1963)

$$\phi_2^{(0)} = \frac{1}{2} \phi_{zz} = \frac{1}{2} (V_{zz} - \frac{1}{3} \nabla^2 V), \quad (2.6a)$$

$$\phi_2^{(\pm 1)} = -\frac{\pm 1}{\sqrt{6}} (\phi_{xz} \pm i \phi_{yz}) = -\frac{\pm 1}{\sqrt{6}} (V_{xz} \pm i V_{yz}), \quad (2.6b)$$

$$\phi_2^{(\pm 2)} = \frac{1}{2\sqrt{6}} (\phi_{xx} - \phi_{yy} \pm 2i \phi_{xy}) = \frac{1}{2\sqrt{6}} (V_{xx} - V_{yy} \pm 2i V_{xy}), \quad (2.6c)$$

and Eq. (2.1) can then be written as

$$H = \sum_{m=-2}^{+2} (-)^m Q_2^m \phi_2^{-m}. \quad (2.7)$$

The field gradient at the origin due to a point charge Ze at \mathbf{r} would be given, for example, by

$$\phi_2^{(m)}(\mathbf{r}) = Ze\sqrt{4\pi/5} \frac{Y_{2m}(\theta, \phi)}{r^3}, \quad (2.8)$$

where Y_{2m} is a spherical harmonic and r , θ , and ϕ are the spherical polar coordinates of \mathbf{r} .

B. Symmetries and energy levels

Here ϕ_{ij} is a symmetric (traceless) second-rank tensor and can therefore be diagonalized by transforming coordinates to a principal axis system. In this new coordinate system, $\phi_2^{(m)}$ has the form

$$\phi_2^{(0)} = \frac{1}{2} \phi_{zz}, \quad (2.9a)$$

$$\phi_2^{(\pm 1)} = 0, \quad (2.9b)$$

$$\phi_2^{(\pm 2)} = \frac{1}{2\sqrt{6}} (\phi_{xx} - \phi_{yy}). \quad (2.9c)$$

In an axially symmetric environment where the x and y directions are equivalent, $\phi_{xx} = \phi_{yy}$ and $\phi_2^{(0)}$ is the only nonvanishing spherical component. Under these circumstances, the matrix representation of the Hamiltonian is diagonal when referred to a set of nuclear basis states $|IM\rangle$ defined with the principal z axis as the axis of quantization. The eigenvalues of the Hamiltonian are given by

$$E_M = eQ \phi_{zz} \frac{3M^2 - I(I+1)}{4I(2I-1)}. \quad (2.10)$$

From Eq. (2.10) it is seen that the magnetic substates with $+$ and $-M$ projections remain degenerate and that the level splitting depends on the spin I (unlike the case for a magnetic interaction). The quantity ϕ_{zz} is referred to as the principal component of the field gradient and is frequently written as $eq = \phi_{zz}$ in the literature. (Since Q is in cm² and E_M has dimension e^2/r , q has the convenient units of inverse volume.) Use of the notation eq , rather than ϕ_{zz} (or V_{zz}), will be made below when it is desirable to display the electron charge factor explicitly. Experimental values for eq in the majority of metals are in the 10^{17} V/cm² range. Thus experimental QI energies, $e^2 Qq$, range from $\approx 10^{-8}$ to $\approx 10^{-6}$ eV, and corresponding interaction frequencies are of the order of $\nu_Q \equiv e^2 Qq/h \approx 1$ to 500 MHz.

The sign of the product e^2Qq determines whether the state of maximum or minimum $|M|$ value lies lowest in energy. Although the energy is independent of the sign of M , the sign does play a vital role in picturing the interaction of the nuclear quadrupole with the field gradient as a nuclear precession. In this context, the analogy to a classical quadrupole in a nonuniform electric field is valid (Kopfermann, 1958). That is, when the axis of the quadrupole (i.e., the spin direction) is $<90^\circ$ from the positive principal z axis of the field gradient, the sign of the torque on the quadrupole is opposite to that when the inclination is $>90^\circ$. Since the axis of symmetry of the nuclear quadrupole is the nuclear-spin direction, this implies that states of $+$ and $-M$ precess in opposite senses (just contrary to the case of a magnetic Larmor precession). In the usual case where the degenerate $\pm M$ pair are equally populated, no net precession occurs. Looking ahead therefore to the question of measurement of the sign of the quadrupole interaction, one of two criteria must be met. Either one must determine the value of $|M|$ corresponding to the state of lowest energy or one must in some way individually distinguish the $+$ or $-M$ levels and determine the sense of precession of nuclei in that specific substate.

Returning now to the effect of the symmetry of the environment on the QI, we first note that in the event of cubic point symmetry about the nuclear site, all three coordinate directions, x , y , and z , are equivalent. In this case, $\phi_{xx} = \phi_{yy} = \phi_{zz}$ and the traceless property of ϕ_{ij} then requires all components of ϕ_{ij} to be zero and no interaction can be observed. The case of axial symmetry described above will occur if the point symmetry includes at least one n -fold rotation axis where $n \geq 3$. The trigonal, hexagonal, and tetragonal symmetry groups fall in this category. Should the point symmetry be rhombic or lower, then in general $\phi_{xx} \neq \phi_{yy}$ and, even in the principal axis system, the Hamiltonian will not be diagonal in the $|IM\rangle$ representation. Off-diagonal elements of the form $\langle IM|H|IM \pm 2\rangle$ will be nonzero. Although the Hamiltonian can be diagonalized analytically for a few cases of low nuclear spin I (Gerdaud *et al.*, 1969; Lücken, 1969), in general, numerical methods are required. In this instance, the principal component $e q = \phi_{zz}$ is not sufficient to completely specify the interaction. Conventionally, the axial asymmetry parameter η is defined by

$$\eta = (\phi_{xx} - \phi_{yy}) / \phi_{zz} \quad (2.11)$$

where the principal axes are chosen such that $|\phi_{zz}| \geq |\phi_{yy}| \geq |\phi_{xx}|$. This guarantees that $0 \leq \eta \leq 1$ since $\nabla^2 \phi = 0$. The energy eigenvalues of the Hamiltonian will depend on η . Although M is no longer a good quantum number, no degeneracy is lifted by the presence of the axial asymmetry for the case of half-odd integral nuclear spin. For integral spins, the degeneracy is lifted, but the sign of the QI is still not made available by this effect. Figure 1 illustrates the variation of level splitting as a function of η for a few values of the spin I .

For rare-earth elements, where the effect of the crystal field in a solid on the open $4f$ electron orbitals is an important consideration, the quadrupole fields

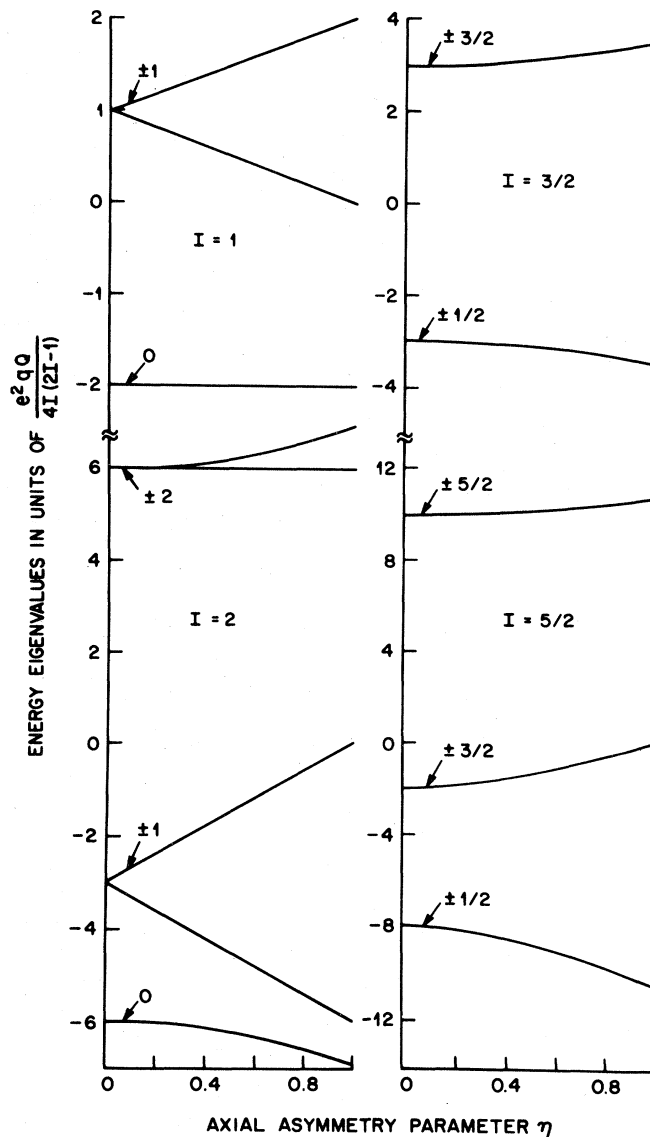


FIG. 1. Examples of the variation of the substate energies with the axial asymmetry parameter η , for spins $I = 1, \frac{3}{2}, 2,$ and $\frac{5}{2}$.

discussed above are but one element in the multipole expansion of the crystal field. The relationship of ϕ_{zz} and η to the conventional parameterization of crystal field theory has been given by Ofer *et al.* (1968).

C. Sternheimer antishielding

The term "antishielding" refers to the fact that the strength of the observed nuclear quadrupole interaction is influenced, and in most instances amplified, by the atomic electrons bound by the nucleus in question, compared to that anticipated were those electrons absent. The mechanism involved has been pictured in two rather different and complementary ways. Calculations following these two alternate approaches appear rather different in detail but yield identical results. Original

and many subsequent calculations have been done by Sternheimer (Das and Bersohn, 1956; Foley *et al.*, 1954; Sternheimer and Foley, 1953, 1956; Sternheimer, 1954a, 1954b, 1963a, 1963b, 1966, 1967a) and for that reason the antishielding factor is usually referred to as the Sternheimer factor. A rather complete tabulation of values, calculated using a relativistic Hartree-Fock-Slater electron theory, has been given by Feiock and Johnson (1969). A clear, albeit brief, description of the duality of viewpoints in this context has been given by Dalgarno (1962) and their equivalence has been demonstrated by Das and Bersohn (1956).

From the first and perhaps most physically appealing point of view, one pictures a source of electrostatic field, such as a point charge, outside the atom or ion of interest. The perturbing influence of the external potential on the electronic wave functions is computed. The resulting electronic charge distribution is thus pictured as being polarized by the external field and creates an additional field at the nucleus. When one expands the field in multipoles and examines the $l=2$ term, one finds that the additional field gradient at the nucleus is given by $-\gamma_\infty V_{zz}^{\text{Ext}}$. The Sternheimer factor γ_∞ is <0 for most ions and can be quite large. Antishielding factors for medium and heavy ions lie predominantly in the range $\approx 10 \leq -\gamma_\infty \leq \approx 80$ and can be as large as -400 in the iodine (-1) ion. The resulting total gradient at the nucleus is then $(1 - \gamma_\infty)V_{zz}^{\text{Ext}}$, representing a substantial enhancement due to the electron shells. Since the term "shielding" implies a reduction in the effect of the external field, the term "antishielding" was introduced to indicate the opposite result. A physically appealing explanation of why $(1 - \gamma_\infty)$ exceeds unity has been given by Cohen and Reif (1957). Usually the quantity $(1 - \gamma_\infty)$ is regarded simply as a factor which must be known in order to extract values of the V_{zz}^{Ext} arising from electrons and ions of a solid outside the atom or ion where the interacting nucleus resides.

In the event that the field sources are not wholly external to the electron shells, as in rare earths, for example, where nonspherical unfilled orbitals are present, the calculated shielding effects are less pronounced. Conventionally the Sternheimer factor R is associated with this field source (Sternheimer, 1950, 1951, 1952, 1954a, 1957, 1966, 1967b, 1972; Sternheimer and Peierls, 1971) and the gradient at the nucleus is written as $(1 - R)V_{zz}^{\text{Local}}$. R is usually found in the range $-0.2 \leq R \leq +0.2$. The foregoing ideas are responsible for the usual parameterization of the field gradient at the nucleus in the form

$$V_{zz} = (1 - \gamma_\infty)V_{zz}^{\text{Ext}} + (1 - R)V_{zz}^{\text{Local}}. \quad (2.12)$$

This formulation has been applied to insulators in general and the second term of Eq. (2.12) is appropriate, for example, to open $4f$ electron shells which are indeed localized, and to free ions in nonspherical excited states. It should be noted that R refers to atomic shielding of the EFG at the nucleus due to an unfilled atomic orbital and should not be confused with the shielding factor, usually denoted σ_2 , which is conventionally used to account for atomic shielding of a crystalline electric field gradient acting on the $4f$ shell itself (Barnes *et al.*, 1964; Müssbauer, 1964). As will become evident in

later sections, the use of Eq. (2.12) for metallic systems by many authors cannot be justified in light of recent experimental results. The underlying reason is that a large part of the field gradient is due to mobile electrons of a metal which cannot be properly categorized as purely external or purely local field sources. In fact, recent re-examination of the use of Eq. (2.12) for ionic solids has shown it to be inadequate when ion cores overlap (Beri *et al.*, 1978).

At the beginning of this subsection, a second possible viewpoint regarding antishielding effects was mentioned. In this approach one realizes that what is being measured in a QI experiment is the energy associated with the orientation of the nuclear quadrupole with respect to the external lattice. This energy will include not only that due to the nuclear moment itself, but will also involve orientational energy of the quadrupole moment induced by the nuclear quadrupole in the surrounding electronic shells. In other words, as the nuclear quadrupole precesses, the induced quadrupole distortion in the surrounding electronic charge, the orientation of which is tied to the nuclear orientation, also precesses, and it is the total energy of this combined effect which is observed. Whereas in the previous picture, it was the nucleus alone which interacted with all sources external to it, now the system consisting of nucleus plus atomic electrons, without regard for its internal structure, is the entity which interacts with an external field. When one computes the total moment induced in the electronic shells of an ion core by the perturbing influence of the nuclear moment Q at its center, one finds its value to be $-\gamma_\infty Q$ (Dalgarno, 1962; Hygh and Das, 1966). Thus the total interaction energy with an external field source again contains the factor, $(1 - \gamma_\infty)V_{zz}^{\text{Ext}}$.

In the more general case when at least some of the field sources may be inside the region of electronic charge associated with the ion, that portion would interact differently with the induced moment. The general expression for the radially dependent Sternheimer antishielding factor is then given by (Foley *et al.*, 1954; Hygh and Das, 1966)

$$\gamma(r') = \frac{-1}{Q} \left[\int_0^{r'} Q_i(r) dr + (r')^5 \int_{r'}^\infty Q_i(r) r^{-5} dr \right], \quad (2.13)$$

where $Q_i(r)$ is the induced quadrupole moment density due to the nuclear moment Q , and r' specifies the location of a point charge field source. The general expression for the observed principal component of the field gradient arising from a distribution of field source charge $\rho(r)$ would then be

$$V_{zz} = \int \rho(r) [1 - \gamma(r)] \frac{2P_2(\cos \theta)}{r^3} dr, \quad (2.14)$$

where P_2 is the second-order Legendre polynomial.

Unfortunately, discussions of the two alternative viewpoints for the understanding of antishielding effects, such as that given above, have sometimes contributed to misunderstanding of the actual physical processes involved. Denoting the first and second above-mentioned approaches as the total-gradient and total-moment methods,

respectively, the confusion arises when one asks why the effects of total gradient interacting with the nucleus and of total moment interacting with the external EFG do not add. This may seem plausible because the atomic electron distribution is certainly suffering simultaneous distortions induced by both nuclear moment and by external EFG. From the total-gradient viewpoint, it is indeed true that an additional EFG is present at the nucleus due to the nuclear induced distortion of the atomic electrons. However, this additional EFG displays an orientation which is fixed and identical to that of the nuclear quadrupole moment and therefore contributes a term to the interaction energy which goes as $\sum_{ij} Q_{ij} Q_{ij}$. Such a term is independent of nuclear orientation with respect to the external geometry and does not affect the splitting of the nuclear M substates. Analogously, from the total-moment viewpoint, the additional moment induced in the atomic electrons by the external EFG will have orientation fixed and identical to that of the external EFG and would add a term to the total energy which goes as $\sum_{ij} V_{ij}^{Ext} V_{ij}^{Ext}$. This term is clearly independent of the orientation of the nuclear moment and again does not contribute to the relative energies of the M substates. Thus, as long as one remains within the framework of a single viewpoint, the physical picture evoked by each is legitimate. Which view one prefers is largely a matter of taste. Statements in the literature which maintain that these viewpoints are fictitious (Cohen and Reif, 1957) or that one is more valid than another (Abragam, 1961) reflect individual preferences.

The conceptual confusion may be avoided by refraining from the artificial partitioning of the system reflected by the sole assignment of the atomic electrons to either the EFG source region or to the total observed moment. By considering the nucleus, atomic electrons, and external EFG as a single system and evaluating its total energy, one achieves a single picture which incorporates the interaction of both the nuclear moment with the externally induced atomic EFG as well as the external EFG with the nuclear induced atomic moment. These two interaction energies are indeed found to be equal and to yield, when added, a combined contribution to the interaction energy given by $-2\gamma_{\infty} Q V_{zz}^{Ext}$. But there is a third contribution to the total energy in this picture. That is an energy one can envision as being stored electrostatic energy of the atomic electrons. It arises from the interaction between the nuclear induced electronic distortion and the externally induced electronic distortion and is given by $+\gamma_{\infty} Q V_{zz}^{Ext}$ (Cohen and Reif, 1957). Thus the net result, $-\gamma_{\infty} Q V_{zz}^{Ext}$, is that expected from the other alternative approaches. An appendix to the paper of Das and Bersohn (1956) gives a clear exposition of the partial cancellation of interaction and stored energy which is a quite general feature of the second-order energy correction in perturbation theory. In the discussion of the preceding paragraph it was assumed that one is interested only in first-order quadrupole perturbations of the core electron wave functions. Beyond first order, the presence of a nuclear moment and/or external EFG explicitly influences the values of antishielding factors and only the total-energy viewpoint will yield correct results. The formalism for

the total-energy approach has recently been extended by Lodge (1976) to investigate the effects of induced moments in the ion core as well as in the mobile electron distribution in a metallic environment. This will be described in some detail in Sec. V.

D. The lattice sum

Although a discussion of the methods of calculation of the field gradient in metals will be deferred, it is worth mentioning here an idealized procedure which is admittedly unrealistic but which provides a point of reference that many investigators have used in discussing the implications of their experimental results. In this model the crystalline solid is regarded as an array of point ionic charges Ze situated at lattice sites. In a metal, the value of Z is usually taken to be the nominal valence of the metal ion and a uniform background of electronic charge is assumed to exist with a density chosen to guarantee electrical neutrality of the lattice as a whole. Since the electrons are assumed uniformly distributed, no contribution to a field gradient arises from them, and the computation reduces to the problem of summing the individual contributions of each point ion using Eq. (2.14), with $\rho(\mathbf{r})$ replaced by $Ze\delta(\mathbf{r} - \mathbf{r}_{ion})$, and $\gamma(r)$ replaced by γ_{∞} . A direct summation of these terms turns out to be only conditionally convergent in general.

Noting that the slow convergence of the direct lattice sum arises from the slow decrease with distance of the gradient due to point monopoles, an alternative direct-sum procedure was devised by Simmons and Slichter (1961). They subdivided the lattice into Wigner-Seitz polyhedra, each of which is electrically neutral, consisting of a point positive ion and a uniform electron density. The sum of the contributions from the multipole moments of each external cell was then evaluated and added to that explicitly computed for the electrons in the central cell.

Another rapidly converging summation procedure involving transformation to reciprocal lattice space was introduced by Ewald (1921). It was further developed by Nijboer and DeWette (1957, 1958) and applied to the specific case of field gradients by DeWette (1961) and DeWette and Schacher (1965; Dickermann and Schacher, 1967). The mathematics is completely analogous to the calculation of the electric field in a lattice of point dipoles. Typically, values obtained for the lattice contribution from a point-ion lattice sum are of the order of $V_{zz}^{Latt} \approx 10^{15}$ V/cm². The so-called ionic contribution, written as $(1 - \gamma_{\infty}) V_{zz}^{Latt}$, is often used as the first term of Eq. (2.12) and usually falls short of completely accounting for EFG's derived from experiment. In some instances minor modifications are introduced to the value of Ze to account for nonuniform electronic charge in the region of ions not at the origin (Pomerantz and Das, 1960). Contributions from nonuniform electronic charge within the lattice cell containing the origin are not accounted for here and are presumed to represent an additional gradient corresponding to the second term of Eq. (2.12). It is for this reason that measurements which yield values of the QI differing substantially from the point-ion lattice sum prediction have been taken as

evidence of the presence, and indeed importance, of a so-called local electronic contribution.

It is not necessary to repeat a lattice sum procedure for all cases. For a given lattice structure, the dependence of V_{zz}^{Latt} on lattice constants is fairly smooth and can be approximated by a simple functional form. For example, for hexagonal close-packed (hcp) structures of lattice constants a and c , Das and Pomerantz (1961) have given

$$V_{zz}^{\text{Latt}} = e/a^3 [0.0065 - 4.3584(c/a - 1.633)], \quad (2.15)$$

which is valid over the range of c/a shown in Fig. 2. An alternative formula has been presented by Das and Ray (1969). A broader view of the variation of V_{zz}^{Latt} with c/a for hcp and tetragonal close-packed (tcp) lattices is shown in Fig. 3. Additional corrections to the model by including point quadrupoles in addition to monopoles at the ion sites have been investigated (Das and Ray, 1969; Taylor, 1962; Taylor and Hygh, 1963) but do not result in significant changes of V_{zz}^{Latt} in the cases studied (Krien *et al.*, 1974b).

The ideas presented in this section will be drawn upon in later sections as the need arises. It should be noted that the fundamental theoretical points described above are well founded and are not those to be scrutinized in subsequent comparisons with experimental

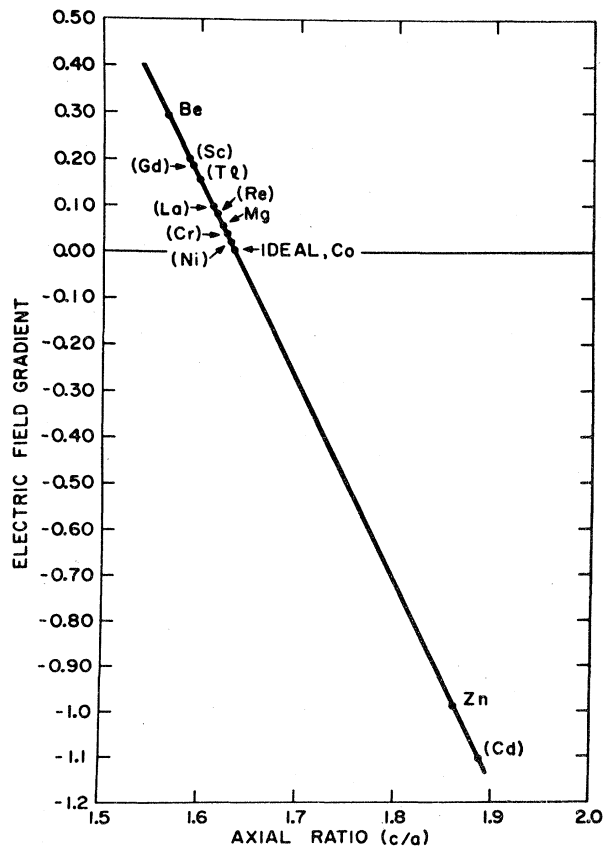


FIG. 2. The point-ion lattice sum contribution to the EFG in hexagonal close-packed metals as a function of axial ratio c/a . The EFG is expressed in the dimensionless form $a^3 V_{zz}^{\text{Latt}}/Z$. (Taken from Das and Pomerantz, 1961).

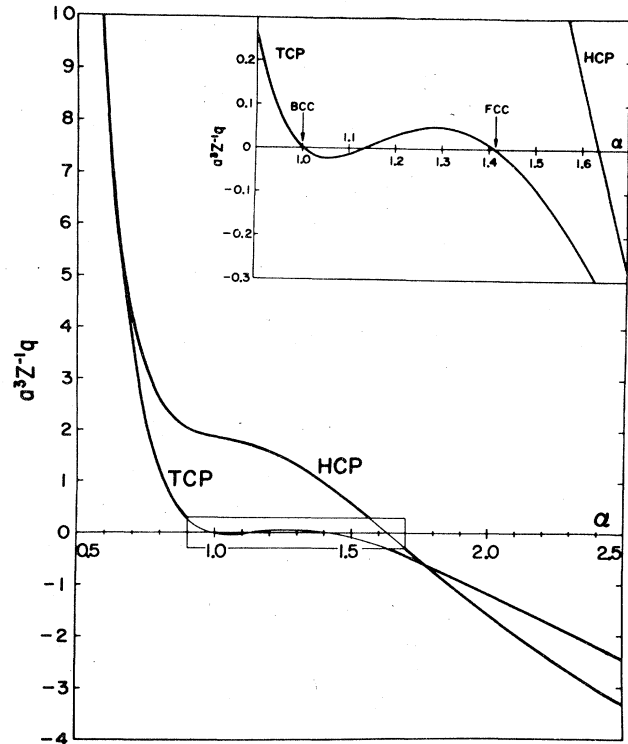


FIG. 3. The point-ion lattice sum contribution to the EFG in hexagonal (hcp) and tetragonal (tcp) close-packed lattices as a function of the axial ratio c/a over a wider range than in Fig. 2. The inset is an expanded view of the region enclosed in the rectangular box. The zero crossings for the tcp curve corresponding to cubic symmetry are shown. The third zero crossing of the tcp curve and the single crossing of the hcp curve are accidental and not due to an increase in lattice symmetry. EFG units are the same as in Fig. 2. (Taken from De Wette, 1961.)

data. Rather, it is the methods of applying these general concepts to the calculation and understanding of the QI in metals which will be the major theoretical problem raised.

III. MEASUREMENT TECHNIQUES

Corresponding to each technique capable of measuring the QI is a body of literature detailing the underlying physics and technical aspects of its use. Most of these methods are also appropriate for characterizing other properties of materials as well, such as magnetic interactions, to name one. We will here simply point out the various aspects of the techniques as they relate to the QI and emphasize the particular advantages of each.

A. Nuclear resonance

Nuclear resonance is perhaps the technique familiar to most. As mentioned in the introduction, nuclear quadrupole (NQR) and nuclear magnetic (NMR) resonance have been applied to a wide variety of systems. The basis of the technique is the application of a radio-frequency magnetic field which induces transitions

among the substates of a nuclear level that has been split by the electrostatic interaction. The occurrence of transitions is detected as an absorption of radiofrequency power when the applied frequency matches the transition energy divided by Planck's constant. In general, the nuclear absorption is extremely small and very sensitive spectrometers are required. It is for this reason that, by and large, these methods are applicable only to nuclear ground states of stable and relatively abundant nuclear species.

The great advantage of resonance methods is the obtainable precision which corresponds to the accuracy of a frequency measurement. As applied to metallic samples, however, one is often hampered by the limited penetration of radiofrequency power into the bulk of the sample material. It is usually necessary therefore to work with finely divided powdered samples. These have to be carefully annealed to remove inhomogeneities created in the powdering process which otherwise would severely broaden the resonance line. Measurements on highly perfect single crystals have, however, been possible in those cases where sensitivity is great enough to overcome the radio-frequency skin effect (Dougan *et al.*, 1969; Williams *et al.*, 1972).

For pure NQR, the substate transition energies are simply given by differences formed from Eq. (2.10) so that the frequency corresponding to a transition from $|M|$ to $|M+1|$ is given by

$$\nu_{|M|-|M+1|} = \frac{3e^2Qq}{4I(2I-1)\hbar} (2|M|+1). \quad (3.1)$$

NQR in metals was first observed in Ga metal by Knight, Hewitt, and Pomerantz (1956). An example of a NQR absorption spectrum for In metal is shown in Fig. 4. Since the observation of these resonant frequencies does not reveal the sublevel order, the sign of the interaction is not measured. Should an axial asymmetry be present ($\eta \neq 0$), it could (except for the special case of $I = \frac{3}{2}$ where only one transition is present) be determined from the level spacings. Use of single crystal samples allows

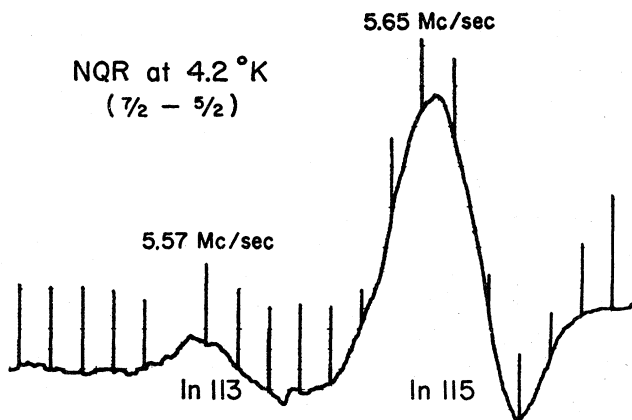


FIG. 4. NQR recorder trace for the $|M| = \frac{5}{2} - \frac{7}{2}$ transition in In metal at 4.2K, showing resonances for both ^{113}In and ^{115}In isotopes whose Q moments differ by $\approx 3\%$. (Taken from Hewitt and Taylor, 1962.)

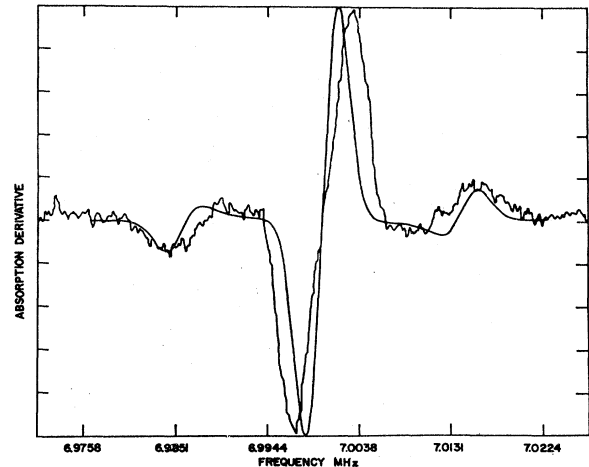


FIG. 5. Derivative of an NMR trace for ^9Be in Be metal in a magnetic field. The jagged curve is experimental and the smooth curve is a simulation. The central resonance at the Larmor frequency of ≈ 7 MHz is flanked on each side by quadrupole satellites. (Taken from Barnaal *et al.*, 1967.)

determination of the principal axes from line intensity measurements, and in this case the addition of a weak static magnetic field aids in localizing the axis directions. For the special case of $I = \frac{3}{2}$, the value of η can be extracted under these conditions as well (Lucken, 1969). The sign of e^2Qq is, however, still undetermined.

Here NMR also yields QI information. In this case a static magnetic field produces a Zeeman splitting which is substantially larger than that caused by the QI. In the absence of a QI, the M -level spacings are equal and a single resonance line at the Larmor frequency $\nu_L = gH/h$ is found, where H is the field strength and g is the nuclear gyromagnetic ratio¹ of the state. In a single crystal with a QI, this resonance is split so that a multiplet of frequencies is seen and is given to first order by

$$\nu_{M-M+1} = \nu_L + \frac{3e^2Qq}{4I(2I-1)\hbar} [3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi](M + \frac{1}{2}), \quad (3.2)$$

where θ , ϕ are the polar coordinates of the H field in the QI principal axis system. So in general, both e^2Qq and η can be determined. In a polycrystalline sample, angular averages must be performed but the resulting "powder pattern" in the resonance spectra can still be analyzed to yield QI information. The quadrupole satellites in a polycrystalline sample are illustrated for Be metal in Fig. 5. When a very large QI with some inhomogeneous broadening is present, a variation of the NMR method, which has been shown to overcome the difficulties one might expect in this

¹ In nuclear magneton units.

case, is based on observing the QI in second order at a resonance frequency approximately twice ν_L (Segel and Barnes, 1965).

Buttet and Bailey (1970) have demonstrated the feasibility of exciting the nuclear transitions through acoustic coupling in metals, thereby avoiding the radiofrequency skin effect. The imposed ultrasound couples to the nuclei via the induced EFG associated with the sound wave and the signal is observed as an attenuation of transmitted acoustic power. To our knowledge, only the original work in Re metal single crystals has used the nuclear acoustic resonance (NAR) technique for the QI measurement in a noncubic metal. The NAR method is also applicable to cubic metals in which case the sound wave itself produced a dynamic EFG at nuclear sites where no static EFG is present (Fischer *et al.*, 1978).

Although information on the sign of e^2Qq is normally not available with the nuclear resonance methods, in principle one could cause the level order to manifest itself in resonance spectra by forcing a nonuniform population of the levels by, for example, working at extremely low temperatures where the Boltzmann factor, $e^{h\nu/k_B T}$, is quite large. This is the basis of some QI sign measurements by other techniques, but has not to our knowledge been used in nuclear resonance. Abragam and Chapellier (1967) have however succeeded in modifying populations for this purpose by a double resonance method. The fundamental reasons for the accessibility of the QI sign to some, but not all, techniques for QI studies have been briefly but clearly explained by Raghavan *et al.* (1975b) and have been discussed on an elegant mathematical basis by Dubbers *et al.* (1978, and references therein).

B. Low-temperature methods

Low-temperature techniques for the detection of the QI are simply based, as mentioned above, on achieving a nonuniform population of the nuclear state sublevels through a Boltzmann factor $e^{-\Delta E/k_B T}$ which differs substantially from unity. Since various sublevels correspond to different values of the spin projection $|M|$, nonuniform population is synonymous with a non-random nuclear-spin orientation. Nuclear level splittings due to a QI are typically of the order of $\Delta E \approx 10^{-7}$ eV, therefore temperatures in the milli-Kelvin range are required. In practice these temperatures are reached by the adiabatic demagnetization of a paramagnetic salt or in a ^3He - ^4He dilution refrigerator. One method of sensing the nuclear level population is a measurement of the specific heat of the sample. Since at ultralow temperature, lattice and electronic contributions to the specific heat are frozen out, the small contribution arising from the orientational energy of the nuclear quadrupole moment in the presence of an internal electric field gradient can be detected calorimetrically. The nuclear contribution to the heat capacity of a nonmagnetic solid can be written as

$$C_Q = a(I) \left(\frac{e^2 Qq}{k_B T} \right)^2 + b(I) \left(\frac{e^2 Qq}{k_B T} \right)^3, \quad (3.3)$$

where a and b are spin-dependent constants. Thus at reasonably low temperature, the first term dominates and the magnitude of the QI can be obtained and, at still lower temperature, the second term becomes observable which, because of the odd power, can yield the sign of the QI. The magnitude of the QI was originally determined in this way in Re metal by Keesom and Bryant (1959). Gregers-Hansen *et al.* (1971) have extended this measurement to lower temperature and determined the sign of the QI in Re metal. Their data are shown in Fig. 6. The method is of course applicable only to the abundant species in the nuclear ground state and cannot easily distinguish among multiple species which each have ground-state quadrupole moments.

A second method, which is not limited to nuclear ground-state interactions or to the most abundant isotopes and can select specific nuclei in the presence of other interacting species, is the detection of low-temperature nuclear orientation by measurement of the spatial anisotropy of nuclear radiation. The method, conventionally referred to simply as "nuclear orientation" (NO), is made possible by the well-known dependence of the emission direction of a radiation, which carries with it angular momentum, on the orien-

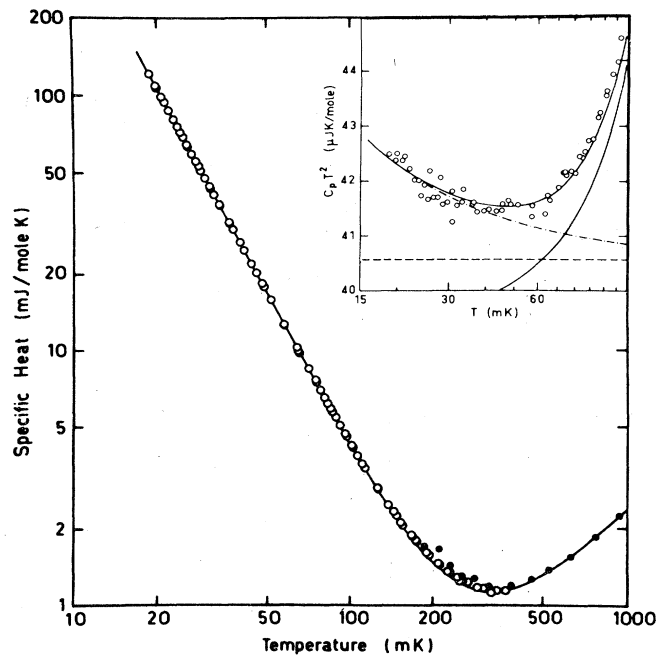


FIG. 6. The specific heat of Re metal as a function of temperature. Full circles are data of Smith and Keesom (1970) and open circles are those of Gregers-Hansen *et al.* (1971). The rising portion at low temperature due to the nuclear quadrupoles [according to Eq. (3.3)] is clearly visible above the rapidly decreasing electronic and lattice components. In the inset, the data are multiplied by T^2 . The solid line through the data is the theoretical fit to a negative value of e^2qQ/h while the lower solid curve is that for a QI of the same magnitude but positive sign. The individual contributions of the first and second terms of Eq. (3.3) are shown as dashed and dot-dashed lines, respectively. (Taken from Gregers-Hansen *et al.*, 1971.)

tation of the spin of the decaying nucleus. This is a direct consequence of the conservation of angular momentum and the fact that the angular momentum of the radiation (photons or β particles for example) is correlated with the direction of propagation. Since the nuclei are aligned with the principal component of the field gradient, it is necessary to use a single crystal sample in order to provide a unique orientation of the nuclei in the laboratory frame of reference. Detectors are placed at appropriate angles with respect to the alignment axis and the ratios of the radiation intensities in the various detectors, which are a measure of the anisotropic emission pattern, are observed as a function of temperature. In this way the degree of nuclear alignment is determined and the strength of the QI is extracted.

For an axially symmetric QI, the temperature-dependent rate of emission of radiation into a solid angle $d\Omega$ at an angle θ with respect to the alignment axis can be expressed as an expansion in Legendre polynomials as (Hamilton, 1975)

$$W(\theta, T) = \frac{d\Omega}{4\pi} \sum_{\lambda} B_{\lambda}(I) U_{\lambda}(x_1) \dots U_{\lambda}(x_{n-1}) A_{\lambda}(x_n) P_{\lambda}(\cos \theta), \quad (3.4a)$$

where

$$B_{\lambda}(I) = (\sqrt{2I+1} / \sum_M e^{-E_M/k_B T}) \sum_M (-1)^{I+M} \sqrt{2\lambda+1} \times \begin{pmatrix} I & I & \lambda \\ -M & M & 0 \end{pmatrix} e^{-E_M/k_B T} \quad (3.4b)$$

and the quantity in large brackets is an angular momentum coupling coefficient. The $B_{\lambda}(I)$ are orientation parameters for the initial state of spin I , $A_{\lambda}(x_n)$ are angular distribution parameters for the observed radiation x_n , and the $U_{\lambda}(x_i)$ are deorientation parameters to account for intervening unobserved radiations in the nuclear decay sequence. The information on the QI enters through the Boltzmann factors in $B_{\lambda}(I)$ where E_M is that of Eq. (2.10).

Since the nature of the anisotropy depends on the value of $|M|$ and the M sublevel lying lowest in energy is most strongly populated, it can be deduced whether the $|M| = I$ or $|M| = 0$ or $\frac{1}{2}$ level lies lowest. Thus the sign of the QI is also measured. An example of such data is given in Fig. 7. The analysis of the data depends on the nature of preceding nuclear decays, the spins and lifetimes of the nuclear levels involved, and the multipolarity of all emitted radiations. A summary of the details can be found in several texts (e.g., deGroot *et al.*, 1965). The prime requisite of the method is the existence of an appropriate radioactive isotope and a means of introducing it into the sample of interest.

This is the first technique mentioned thus far which is capable of measuring the QI using an extremely small number of interacting nuclei which need not be in the ground state. It is thus suitable for use in dilute alloys to determine the QI at impurities or in pure metals where abundant species do not possess measurable quadrupole moments. An interesting example is

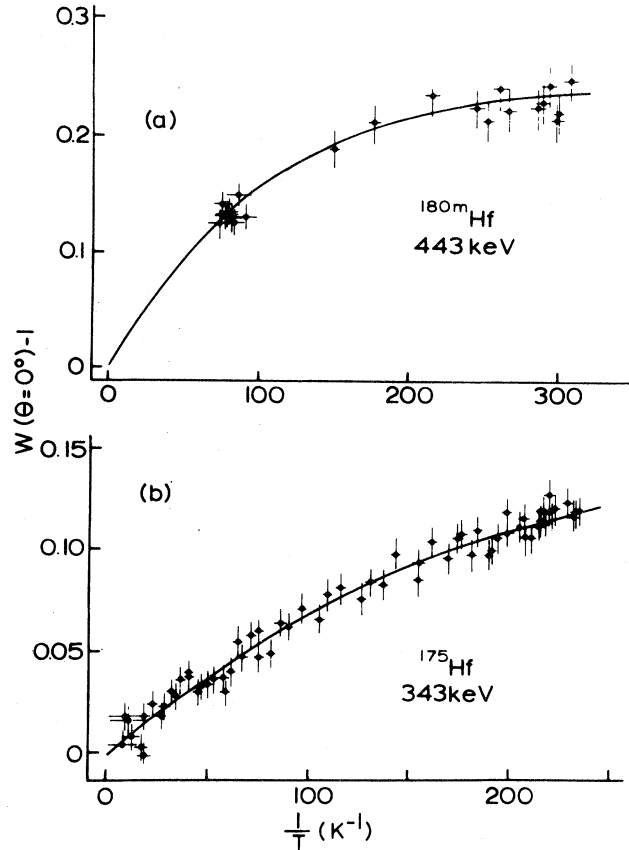


FIG. 7. Data illustrating the anisotropy of gamma radiation emitted by (a) the isomeric transition of ^{180m}Hf and (b) an excited state of ^{175}Lu , the daughter isotope of ^{175}Hf , which nuclei are aligned by the QI in a single crystal Hf metal sample at low temperature. The temperature dependence of the anisotropy is fitted to a function such as that of Eq. (3.4b). (Taken from Kaindl *et al.*, 1973.)

the QI measurement of Kaindl *et al.* (1973) in Hf metal, where NQR had been unsuccessful (see Fig. 7). It is the use of nuclear radiations from which these advantages are derived. Several additional techniques based on radiation detection to be described below thus have similar attributes. A recent variation on the NO technique involves the application of radio-frequency power in order to find the frequency at which induced transitions destroy the alignment and thus the anisotropy. Whereas the conventional NO method will measure an average effect in the event the radioactive nuclei are distributed among possibly nonunique sites, NMR on oriented nuclei (NMR/ON) can distinguish between different interaction strengths which correspond to different resonance frequencies. This technique has been applied to magnetic systems (Callaghan and Stone, 1972; Callaghan *et al.*, 1974; Herzog *et al.*, 1977b; Matthias and Holliday, 1966) but has not, to our knowledge, been used as yet to determine a QI in a noncubic metal. Although classical nuclear resonance techniques are limited to abundant species because the detection scheme relies on sensing absorbed power in the sample, these methods can be extended to dilute sys-

tems when the detection of resonance rests on observation of nuclear radiations.

C. The Mössbauer effect (ME)

Since its discovery in 1958 (Mössbauer, 1958), the Mössbauer effect (ME) has had wide use in the study of nuclear interactions, nearly approaching the more common NQR and NMR methods, and a similarly large body of literature is available on the subject. Wertheim (1964) and Gruverman (1967) have given summaries of the principles of the method. The basis of the effect lies in the existence of a finite probability that gamma radiation emitted or absorbed by a nucleus in a solid will not cause a nuclear recoil to occur. The energy of the gamma radiation emitted from a radioactive source in this way is thus precisely that of the nuclear transition with no deficit due to nuclear recoil. It is therefore possible for recoillessly emitted radiation, when incident on a target containing identical nuclei, to induce the reverse transition by being absorbed in a second recoilless process. Since the nuclei of the absorber are invariably in their ground states, this method is restricted to radiative transitions in the source which populate the ground state. In most applications, a varying Doppler shift of the gamma-ray energy is introduced by relative motion of the source and absorber and a radiation detector placed behind the absorber is used to detect a decrease in intensity of transmitted radiation when the energy of the incident gamma ray precisely matches the energy of the excited nuclear state in the absorber. In this way, small differences in the energy of the states in source and absorber arising from interactions of the nuclei with their surroundings can be measured. The available energy resolution ($\approx 10^{-8}$ eV) is so high that in a great many cases it is comparable to the QI splitting of the nuclear levels involved and transitions to individual substates can be observed. Although ground and excited states in both source and absorber may in general be split, leading to a rather complex absorption spectrum, the analysis, even in this case, is straightforward. Usually, however, a single line or unsplit source (or absorber) acts as an energy standard for finding the sublevel energy splitting in the absorber (or source). The splitting gives e^2Qq directly and (except for spin $I = \frac{3}{2}$) also yields a value of η . Since the gamma-ray energy provides an absolute standard, not only the sublevel energy differences but also the absolute energy of each sublevel is determined. Because the transition probabilities to each sublevel depend on the value of M , the level order and thus the sign of the QI can also be extracted (again with the exception of $I = \frac{3}{2}$) from the absorption line intensities, even for a polycrystalline sample. Full QI information for the case of $I = \frac{3}{2}$ (a very frequent case for the most commonly used isotopes) can be gained by use of single crystals or externally applied magnetic fields. This again takes advantage of the anisotropy of radiation intensity from or to a given M state with respect to a known quantization axis as in the NO technique, but low temperatures are not needed since the M states are individually resolved.

Value of e^2Qq derived from ME measurements are

commonly quoted in velocity units (usually mm/sec) which are related to frequency by

$$\nu_Q = \frac{e^2Qq \text{ (in velocity units)}}{h} \times \frac{E_\gamma}{c}, \quad (3.5)$$

where E_γ is the Mössbauer transition energy and c is the speed of light. When the interaction is measured in the absorber, a substantial fraction of the nuclei must be the resonantly absorbing species in order to see a signal. Measurement of the QI in the source, however, requires only enough of the isotope of interest to provide a sufficiently strong flux of radiation and thus very dilute systems can be handled by this method. A nice example of a particularly high resolution QI measurement is shown in Fig. 8 for a Ta impurity in a Re host lattice as done by Kaindl *et al.* (1972) and Kaindl and Salomon (1972).

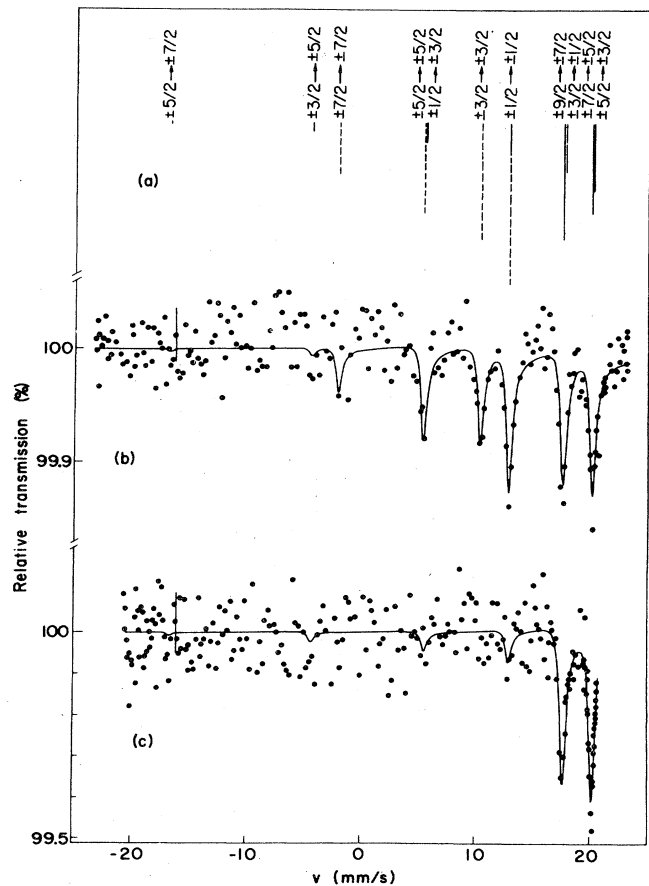


FIG. 8. Mössbauer absorption velocity-spectrum for the 6.2 keV gamma ray of ^{181}Ta taken using a ^{181}W in single-crystal Re metal source and a single-line Ta metal absorber. Spectra (b) and (c) represent gamma emission perpendicular and parallel to the QI symmetry axis, respectively. Part (a) gives the position and intensity expected for the various lines, labelling them with the values of the spin projection $|M|$ of the excited and ground states involved in each transition. (Taken from Kaindl *et al.*, 1972.)

D. Perturbed angular correlations (PAC) and distributions (PAD)

We have already seen the usefulness of the anisotropic radiation patterns from nuclei in systems prepared in such a way that M states can be separately identified. Now we present a class of methods also based on the observation of anisotropic radiation patterns but differing in a fundamental way from those mentioned previously. In this instance a nonrandom nuclear-spin orientation is provided by the detection of a preceding radiation. For just as the directional properties of radiation are influenced by the spin orientation, so can the spin orientation be determined by, or inferred from, radiation in a unique direction. One common utilization of this principle relates to nuclear excited states which are produced in a reaction initiated by a beam of accelerated particles impinging on a target from a unique direction (the beam line of the accelerator). Succeeding decay radiations will be anisotropic in general because spins of the nuclei in the excited states have been preferentially oriented in a plane perpendicular to the beam direction. Again the basic reason is conservation of angular momentum.

A second common approach is based simply on the observation of the direction of emission of radiation simultaneously depopulating one excited state and populating another excited state which then decays further by a second radiation. Then if one requires by suitable detection methods that the second radiation originated from the intermediate state of the same nucleus which emitted the first, the spatial distribution of the intensity of the second will be anisotropic with respect to the direction of the first (and vice versa). In this case, mere observation of one radiation direction selects an ensemble of nuclear states which are preferentially oriented. This is usually referred to as an "angular correlation" between two radiations whereas the accelerator technique is said to produce an "angular distribution" with respect to the beam. It should be noted that if an additional reaction product were detected from the same reaction as that emitting decay radiation, a "correlation" would be available in accelerator experiments as well. In some instances, this is advantageous because the additional constraints imposed by observation of a second radiation produce a stronger anisotropy in the correlation than was available from the corresponding distribution. Angular correlation techniques have been described in several texts (e.g., Frauenfelder and Steffen, 1965; Gill, 1975; Hamilton, 1975).

It must be emphasized that these methods of producing nuclear orientation and thus anisotropic radiation patterns are fundamentally different from NO or ME experiments because no extranuclear fields are employed and the nuclear states need not be split for the process to occur. If the intermediate nuclear level is split by a QI, for example, no effect of the QI on the radiation pattern would be observable if the symmetry axis of the QI were collinear with either radiation direction. In this event, the M -state populations are unaffected by the QI since they are stationary states when referred to the direction of propagation

of the radiation. If on the other hand the QI axis introduces a third unique direction in the system with respect to which the level splitting is referred, then the substates quantized along a propagation direction are nonstationary and their populations will evolve with a periodic time dependence. Classically, this evolution corresponds to a spin precession of the nuclei in each substate about the axis of the QI. We recall that substates with opposite signs of M precess in opposite directions under the influence of a QI. Thus if $+$ and $-M$ substates are equally populated in the intermediate state, one observes the sum of equal and opposite precessions of the associated radiation patterns and the sense of the precession and thus the sign of the QI cannot be measured. From the variation of intensity with time in a given detection direction, the QI frequency e^2Qq/h and, if present, η (except for $I = \frac{3}{2}$) can be determined. One often finds quoted in the literature, instead of the fundamental QI frequency, the fundamental angular precession frequency of the radiation pattern which is given by

$$\begin{aligned}\omega_0 &= 3\omega_Q \quad (I \text{ integral}) \\ &= 6\omega_Q \quad (I \text{ half odd integral}),\end{aligned}\tag{3.6}$$

where

$$\omega_Q = \frac{e^2Qq}{4I(2I-1)\hbar} = \frac{\pi}{2I(2I-1)} \nu_Q.$$

In order to measure the sign of the QI, one must employ a single crystal and the detection of the second radiation must select a particular sign of M , for instance by measuring the circular polarization of emitted gamma rays (Behrend and Budnick, 1962). Alternatively, the preparation of the nuclear intermediate state may be done in a way which leaves the populations of $+$ and $-M$ substates unequal (i.e., a polarization rather than an alignment). This can be achieved by circular polarization measurement of the first radiation, by utilizing an appropriate β decay as the first radiation (Raghavan *et al.*, 1973b) or in an accelerator experiment, by using either a spin polarized beam or measuring a correlation with a reaction product emitted in a direction not collinear with the beam (Klepper *et al.*, 1973).

When the lifetime of the intermediate nuclear level is shorter than or comparable to instrumental resolving times, only an average precession angle can be measured by observing a net attenuation of the anisotropy of the radiation and, if a sign is being measured, a net angular shift of the pattern. The accuracy under these circumstances is quite limited because attenuation can arise from many sources and only an average over possibly nonunique QI's at various nuclei is obtained. Such measurements are "time integral" (TIPAC) and suffer from the same sort of nonspecificity due to implicit averaging as do the previously mentioned techniques of NO and specific heat.

For sufficiently long nuclear lifetimes, however, the precession is observed as a modulation in intensity as a function of time and can in the best cases yield accuracies and uniqueness approaching that of nuclear resonance. These so-called "time-differential" mea-

surements (TDPAC and TDPAD) have yielded a great many valuable data recently on dilute-impurity systems. A summary of the TDPAD method using nuclear reactions has been given by Haas (1975). For a polycrystalline sample with an axially symmetric QI, the radiation pattern can be expressed as the Legendre polynomial expansion

$$W(\theta, t) = \frac{d\Omega_1 d\Omega_2}{16\pi^2} \sum_{\lambda} B_{\lambda}(x_1) G_{\lambda\lambda}(t) A_{\lambda}(x_2) P_{\lambda}(\cos \theta), \quad (3.7a)$$

which represents the rate of emission of radiation x_1 into solid angle $d\Omega_1$ and x_2 into $d\Omega_2$ which are separated by the angle θ . B_{λ} and A_{λ} are analogous to those in Eq. (3.4a), but here the B_{λ} describes orientation due to the observation of a radiation direction. The QI information is contained in the time-dependent perturbation factor

$$G_{\lambda\lambda}(t) = \sum_{M, M', q} \begin{pmatrix} I & I & \lambda \\ -M & M' & q \end{pmatrix}^2 e^{-i(E_M - E_{M'})t/\hbar}, \quad (3.7b)$$

where E_M is that of Eq. (2.10). Some examples are illustrated in Figs. 9, 10, and 11 where the data are proportional to the perturbation factor $G(t)$ appropriate to the experimental configuration in each case.

As in the case of NO, a NMR/PAC variation (Matthias *et al.*, 1966) has been found to be practical in a few systems. This method has been used, for example, on the light nuclei ^{12}B , ^{13}B , and ^{12}N where β -decay asymmetry, arising from ground-state polarization after a nuclear reaction, is destroyed by a radio-frequency field (Correll, 1978; Haskell and Madansky, 1973; Haskell *et al.*, 1975; McDonald and McNab, 1974; Minamisono *et al.*, 1971; Tanihata *et al.*, 1977; Williams *et al.*, 1972). A typical resonance spectrum is shown in Fig. 12. A complete elaboration of the theory of detection of NMR by means of nuclear radiation, including the NMR/PAC and NMR/ON methods, has been given by Matthias *et al.* (1971).

A second interesting variation employing an accelera-

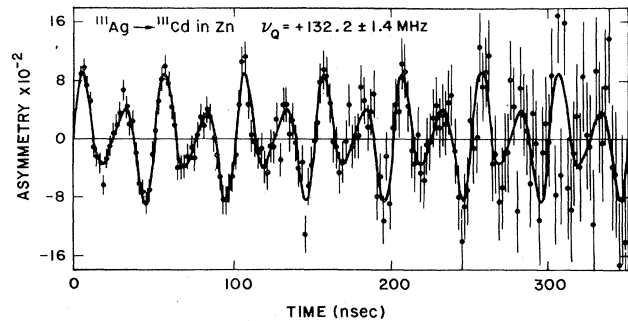


FIG. 10. An example of the use of beta-gamma PAC. The intermediate state is the same as in Fig. 9, but now populated from the beta decay of ^{111}Ag which is embedded in a Zn metal single crystal. Because parity is not conserved in the beta-decay process, the intermediate state has a net polarization and the perturbation factor is given by a sum of sines rather than cosines. The sign of the interaction (positive in this case) is thus available. (Taken from Raghavan *et al.*, 1976.)

tor-produced reaction uses a pulsed particle beam whose pulse repetition rate can be varied in order to bring it into synchronism with the nuclear precession. At this pulse repetition rate, nuclei excited by each subsequent pulse add coherently to the effects of nuclei excited in all preceding pulses, whereas in general, destructive interference destroys any net anisotropy. Thus by sweeping the pulse repetition rate through the critical value while monitoring anisotropy, a resonance-like behavior is seen and the nuclear precession frequency can be determined accurately (Schatz *et al.*, 1975). This method is called "stroboscopic resonance" for obvious reasons. In practice, varying the pulsing rate of an accelerator in a continuous way is not always straightforward. It has been common, therefore, in the case of interactions with external magnetic fields, to vary the field at fixed pulsing frequency in order to observe the resonance (Recknagel, 1971). An internal electric field gradient is of course not at the disposal of the experimenter for this purpose. A recent innova-

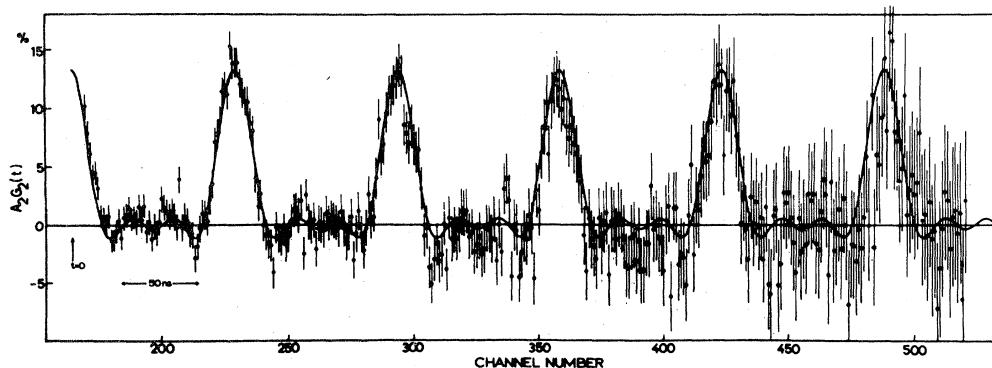


FIG. 9. An example of a spin-rotation spectrum obtained with the PAC technique. The data and fitted curve correspond to the time-dependent perturbation factor given by Eq. (3.7b) for the case of a gamma-ray cascade in the decay of $^{111}\text{Cd}^m$. The intermediate state at 247keV in ^{111}Cd , of spin $I = \frac{5}{2}$ and half-life $T_{1/2} = 84\text{ns}$, is embedded in a polycrystalline Cd metal sample at room temperature. In this case the modulation pattern corresponds to a sum of cosines of the fundamental precession frequency of Eq. (3.6) and two harmonics. (Taken from Raghavan and Raghavan, 1971b.)

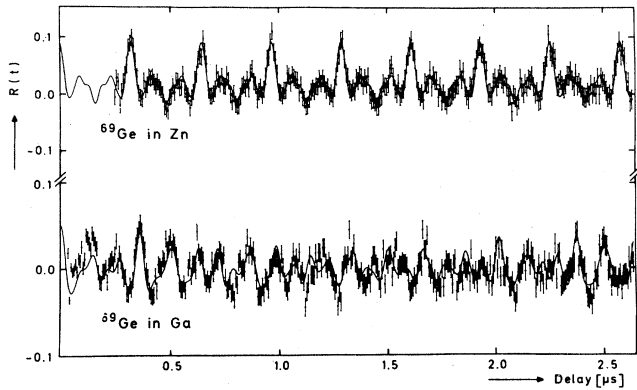


FIG. 11. Spin-rotation patterns obtained in PAD experiments using the $I = \frac{3}{2}$ isomeric state in ^{69}Ge with half-life $T_{1/2} = 2.8\mu\text{s}$. In the top spectrum, the isomer was produced by an (α, n) reaction on the Zn metal target and in the bottom spectrum, by a (p, n) reaction on the Ga metal target. In each case, the target temperature was just below the metal's melting point. The complex patterns are due to the presence of a larger number of harmonics of the precession frequency when the nuclear spin is high. Also evident is the aperiodic nature of the data for ^{69}Ge in Ga resulting from a nonzero axial asymmetry parameter η in orthorhombic Ga which causes the several precession frequencies involved to be incommensurate. (Taken from Haas *et al.*, 1973.)

tion by Raghavan and Raghavan (1977), in which a magnetic field is applied to the noncubic sample in order to produce beat frequencies in the nuclear precession between the magnetic Larmor and QI frequencies, has avoided this problem and increased the utility of stroboscopic resonance for QI measurements.

Complete and rigorous mathematical details concerning the anisotropy of nuclear radiations, their correla-

tions and distributions, and the influence of extranuclear perturbations can be found in several chapters of a text edited by Hamilton (1975).

IV. EXPERIMENTAL OBSERVATIONS

Although all of the experimental measurements known to the authors are listed in Appendix B, it would not serve our purpose here to attempt to provide descriptions and critiques of so large an amount of experimental data. Instead, we shall mention a few examples of measurements which epitomize the significant classes of results as they relate to the evolution of our understanding of the sources of the QI in noncubic metals.

A. Early experiments and interpretations

Eq. (2.12), as mentioned above, represents the conventional parameterization of the QI with which early experimental results have been compared. Unlike the case for free molecules or molecular solids where each electronic molecular orbital can be associated with a separate contribution to the QI (see Lucken, 1969, chapters 6 and 7), Eq. (2.12) contains only a rather phenomenological separation of contributions. An assumed calculable lattice sum portion, $V_{zz}^{\text{Ext}} = V_{zz}^{\text{Latt}}$, is computed as described in Sec. II.D and amplified by the Sternheimer factor $(1 - \gamma_{\infty})$. A local electronic term, $(1 - R)V_{zz}^{\text{Local}}$, is intended to account for all electronic effects and would be precisely calculable only given a complete knowledge of the electronic wave functions of all occupied states, a requirement which is rarely satisfied in practice.

Three aspects of early observations are particularly notable. The QI observed in noncubic metals yielded, in general, values for $|V_{zz}|$ which exceeded

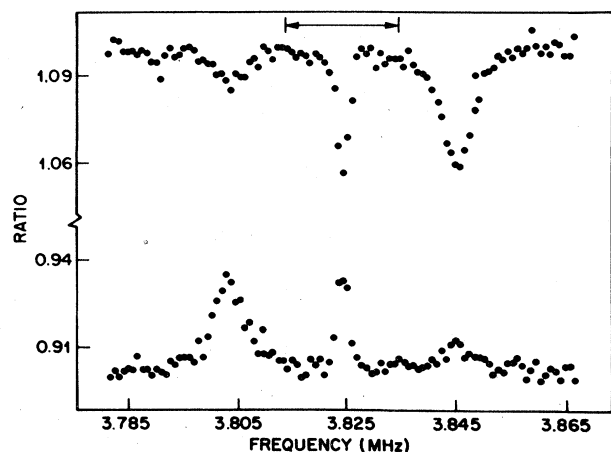
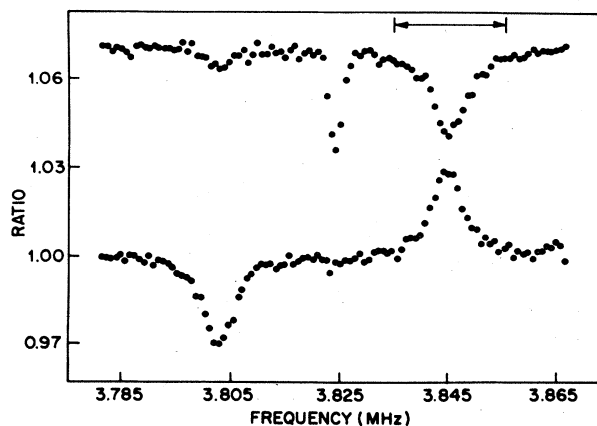


FIG. 12. Application of NMR/PAD method to ^{12}B nuclei, polarized in the $I=1$ ground state, which have recoiled after the $^{11}\text{B}(d, p)$ reaction into a Be metal single crystal. The $M=+1$ and -1 levels have been split by a static magnetic holding field and equally shifted by the QI. In each upper spectrum, the central line is a double-quantum transition ($M=-1 \leftrightarrow +1$) independent of the QI and the broader lines to the left and right sides are $\Delta M=+1$ and -1 transitions, respectively. The ordinate in these spectra is the asymmetry ratio for beta-particles emitted toward and away from the holding field direction (which is perpendicular to the QI symmetry axis). One sees that the amount of asymmetry is reduced when the applied rf field induces resonance depolarization. The lower spectra result from substate population inversions achieved by the adiabatic-fast-passage technique. (Taken from McDonald and McNab, 1974.)

$(1 - \gamma_\infty)V_{zz}$ | by large factors and thus implied substantial contributions due to local electronic charge (Das and Pomerantz, 1961). In Sn and Sb metals are specific examples (Hewitt and Taylor, 1962; Hewitt and Williams, 1963; Simmons and Slichter, 1961). In addition, when the temperature dependence of the QI was measured, it was found in general to be considerably stronger than that predicted by simply computing $V_{zz}^{Latt}(T)$ using tabulated lattice constants and thermal expansion coefficients (Hewitt and Taylor, 1962; Simmons and Slichter, 1961). Figure 13 exemplifies such observations. This was also frequently taken to imply a substantial temperature dependence arising from the local electronic contribution. For some time, the sign of V_{zz} was unavailable and only magnitudes could be compared. Early theoretical attempts to compute electronic contributions in the simplest of the metals [such as in Be (Mohapatra *et al.*, 1972; Pomerantz and Das, 1960) and in Mg (Jena *et al.*, 1973)] met with some success but depended on the use of approximately known wave functions using the orthogonalized plane-wave (OPW) method, for example (see Sec. V.A.2). Despite uncertainties in the quantitative results, it became clear that the total electronic contribution would result from the combined effects of electrons of differing orbital symmetry from each of the occupied energy bands and that these individual terms could be large and of opposite sign. A more phenomenological approach taken by Watson *et al.* (1965) to explain the QI in some metals and metallic compounds predicted that conduction electrons at the Fermi level would undergo a redistribution in the noncubic crystal field due to splitting of electronic sub-bands according to spatial symmetry (i.e., p_x , p_y , p_z or $d_{xy, yz, zx}$, $d_{3z^2-r^2, x^2-y^2}$, etc.). As a result, an "overshielding" factor is expected in p - or d -band metals which is negative and substantially large than unity, thus implying a sign change in the net QI (see Sec. V.B). This approach was also used by these authors to explain

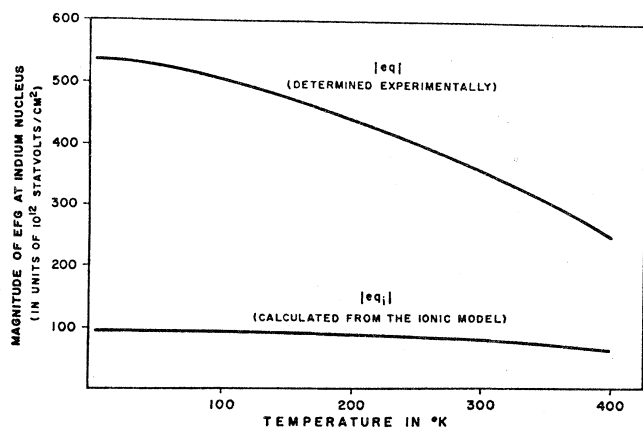


FIG. 13. Variation of the EFG at In in In metal, determined by NQR, with temperature, compared to the calculated variation of the point-ion lattice sum EFG with thermal expansion of the lattice. Note the stronger T dependence in the measured QI than would be expected based on the lattice contribution alone. The statvolt unit used on the vertical scale is equivalent to 300V. (Taken from Hewitt and Taylor, 1962.)

the possibility of a strong temperature dependence, due to Fermi-surface electrons, as a temperature-induced repopulation of states of differing spatial symmetry (see Sec. VI.A.1).

When Raghavan and Raghavan (1971b) found that, in Cd metal, the QI decreased strongly with rising temperature, whereas $V_{zz}^{Latt}(T)$ increased slightly, this anomaly was ascribed to just such a repopulation process (see Fig. 14). The picture that the Fermi-surface electrons of the metal are responsible for a strong temperature dependence of the QI would lead one to believe that, in dilute alloy systems, the dependence should be a unique property of the host metal. The first evidence that this was not generally true was provided by Kaufmann *et al.* (1974b) who showed that the temperature variations of the QI at Ta and Cd impurities in a Ti lattice differed significantly. A later measurement on Sc in Ti yielded a third unique dependence (Reno *et al.*, 1974). The data for impurities in Ti are shown in Fig. 15. In order to isolate the explicit dependence on temperature from that on lattice volume, pressure dependence studies have verified that the explicit dependence is substantial (O'Sullivan and Schirber, 1964a; Raghavan *et al.*, 1972). This is particularly evident for Cd in Fig. 16 where, in a plot of the pressure dependence results, data from temperature-dependence measurements are also plotted. The latter points are located in the figure at a pressure coordinate corresponding to that pressure which would have produced the same axial ratio change as did thermal expansion. More recent pressure-dependence studies have been summarized by Butz and Kalvius (1976; see also Ernst *et al.*, 1977). However, without knowledge of the sign of the QI, any specific hypotheses

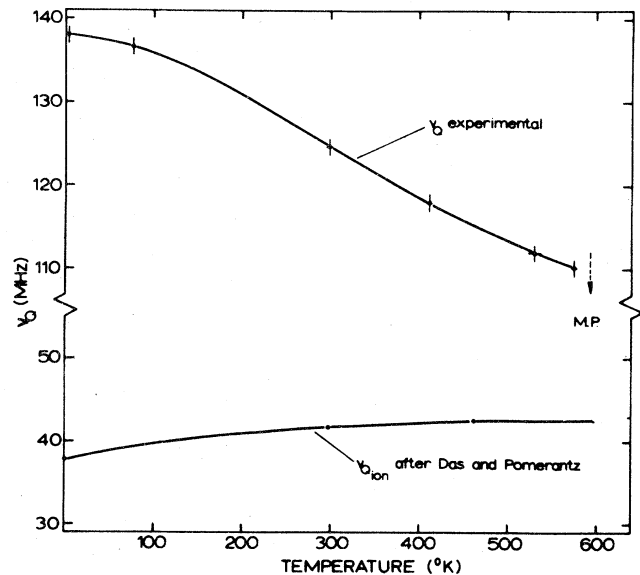


FIG. 14. The "anomalous" variation of the magnitude of the EFG at Cd in Cd metal discovered by Raghavan and Raghavan (1971b) using the PAC technique (see Fig. 9). Note that the experimental curve decreases strongly with temperature in opposition to the slow increase expected from a point-ion lattice sum EFG calculation. (Taken from Raghavan and Raghavan, 1971b.)

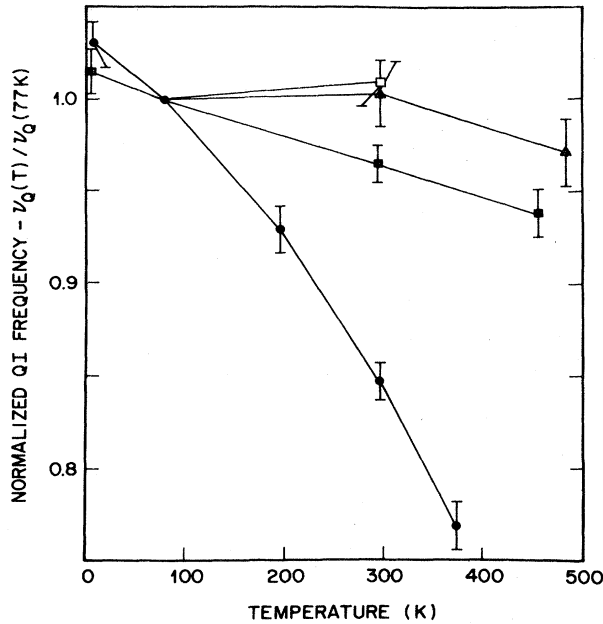


FIG. 15. The relative temperature dependence of the magnitudes of the EFG at Sc (Reno *et al.*, 1974), Ta, and Cd (Kaufmann *et al.*, 1974b) in a Ti host lattice. Data for Sc, Ta, and Cd are represented by triangles, squares, and circles, respectively. Full and open squares correspond to different Ta in Ti samples. The data, derived from PAC measurements, are normalized to liquid nitrogen temperature. This was the first explicit evidence that the slope of the temperature dependence of the QI was dependent on the identity of the impurity probe element.

remained speculative.

When early sign measurements began to appear no clear trend was obvious. For example, Thatcher and Hewitt (1970) were able to employ charge screening theory (Kohn and Vosko, 1960) to deduce that the sign of V_{zz} at In in In was negative, as is V_{zz}^{Latt} , by using NMR to determine the QI as a function of the concentration of various impurities. On the other hand, Gregers-Hansen *et al.* (1971) found in a nuclear specific heat measurement that the sign of V_{zz} at Re in Re metal was negative, in opposition to the sign of V_{zz}^{Latt} . In a similar vein, the field gradient at Hf in Hf metal was found by ME to agree with the positive lattice portion (Gerdau *et al.*, 1968) whereas at In and Cd in Cd metal, measured by β - γ PAC, a positive experimental value opposed the negative lattice result (Raghavan *et al.*, 1974a and 1973b). Sign reversal in Re, a transition metal, could be taken as support for the overshielding hypothesis of Watson *et al.* (1965); however, the Hf metal result raises questions in this regard. A microscopic calculation for Cd metal using a pseudopotential-OPW method by Mohapatra *et al.* (1973) predicted a sign reversal as was observed; however, the predicted magnitude of V_{zz} was not in good agreement with experiment. Agreement with microscopic calculations is certainly gratifying when it occurs; however, one might reasonably hope to find at least qualitative agreement with a more general theoretical picture which applies to large classes of systems without recourse to a detailed microscopic

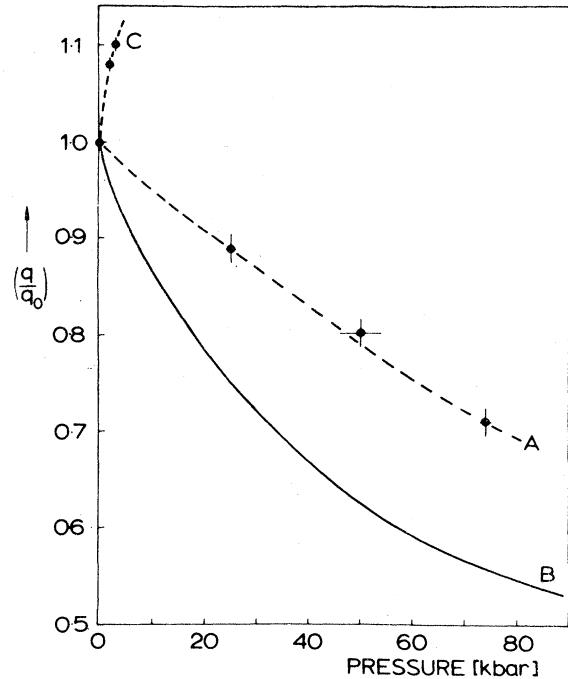


FIG. 16. Relative variation of the magnitude of the EFG at Cd in Cd metal as a function of pressure (curve A) as compared to that expected from a point-ion lattice sum calculation using known compressibilities (curve B). Curve C is data taken from the temperature variation measurement (shown as the two left-most points in Fig. 14) plotted at the pressure coordinate which would have produced the same lattice axial ratio change as did thermal expansion. The opposite behavior of the QI as the axial ratio changes, depending on whether pressure or cooling is used to alter the lattice constants, is striking. (Taken from Raghavan *et al.*, 1972.)

picture in each case. From the few results quoted so far, the sporadic agreement with various theoretical expectations was rather discouraging as far as this hope was concerned.

Although the magnitudes of the QI could not be predicted with confidence, several data suggested that in many systems, a proportionality of the total field gradient, V_{zz} , to the lattice part, V_{zz}^{Latt} , existed. That is, from a value of $|V_{zz}|$ at one impurity in one metal an estimate of $|V_{zz}|$ for a second impurity in a second metal could be made by

$$|V_{zz}(\text{imp2 in met2})| = |V_{zz}(\text{imp1 in met1})| \times \frac{1 - \gamma_{\infty}(\text{imp2})}{1 - \gamma_{\infty}(\text{imp1})} \times \frac{V_{zz}^{Latt}(\text{met2})}{V_{zz}^{Latt}(\text{met1})} \quad (4.1)$$

This relation held very approximately, for example, for Cd, In, or Fe impurities in Cd, In, or Ti metals (Bodenstedt *et al.*, 1972; Hewitt and Taylor, 1962; Kaufmann *et al.*, 1974b; Qaim, 1969; Raghavan and Raghavan, 1971a; Raghavan *et al.*, 1973b) (see Table I) and for the two inequivalent sites of Ta in ω -phase Zr (Kaufmann and McWhan, 1973) and of Cd in Be (Kaufmann *et al.*, 1975). In Table I, one sees that, although proportionality to $|V_{zz}^{Latt}|$

TABLE I. $|V_{zz}|$ observed in several systems ($\times 10^{17}$ V/cm²).

Impurity	Host		
	Cd	In	Tl
	$ V_{zz}^{\text{Latt}} = 1.2 \times 10^{16}$ V/cm ²	$ V_{zz}^{\text{Latt}} = 0.17 \times 10^{16}$ V/cm ²	$ V_{zz}^{\text{Latt}} = 0.46 \times 10^{16}$ V/cm ²
Cd			
$\gamma_{\infty} = -29.3$	6.71	0.93	1.48
In			
$\gamma_{\infty} = -25$	9.36	2.17	...
Fe			
$\gamma_{\infty} = -9.14$	2.59	1.37	0.48

seems to hold, the dependence on γ_{∞} is reversed for Cd and In impurities. Possible reasons for this are discussed in Sec. IV.B.2. From the form of Eq. (2.12), which separates the lattice and electronic contributions, it is difficult to understand exactly how the total field gradient should be proportional to only the lattice term. The observations implied therefore that the size of the electronic contribution is in some sense proportional to the degree of "noncubicity" of the lattice and thus also to V_{zz}^{Latt} .

In this subsection we have indicated some specific observations without offering an overall picture into which isolated results might fit. In the past few years, however, with the appearance of new data and, in particular, the re-examination of earlier data, several systematic trends have evidenced themselves and are discussed below.

B. Systematics of the QI

Empirically observed systematic trends in QI data which are known to date fall into three categories. The overall question of proportionality, as illustrated by Eq. (4.1) has been investigated by Raghavan *et al.* (1976 and 1975a). Correlations of the QI in impurity systems with impurity valence has been treated by Leitz *et al.* (1976) and Collins (1978). And similarities in the QI temperature dependence were originally noticed by Heubes *et al.* (1974) and discussed in more detail by Christiansen *et al.* (1976) [See note added in proof].

1. Proportionality

The first strong indication to workers in the field that the conventional parameterization of Eq. (2.12) was inadequate for metals was provided by Raghavan *et al.* (1976; 1975a). They found by entering all available data for which both the magnitude and sign of the QI were known onto a plot of the calculated point-ion lattice contribution against the so-called electronic contribution (derived by subtraction of the lattice field from the experimental value) that a strong and nearly universal correlation existed between the "electronic" and "ionic" terms. This is clearly visible in Fig. 17 where the figure of Raghavan *et al.* is reproduced. In addition to the above-mentioned data (solid points), data for which only QI magnitudes were available have also been plotted (open points) by choosing the sign, when no guidance from measurements in similar systems existed, so as to achieve best agreement with the observed trend. In the previous section we pointed out that it might not be unreasonable for the electronic contribution to be in

some way proportionate to the lattice field V_{zz}^{Latt} , but the revealed correlation indicates rough proportionality to the full ionic gradient at the nucleus, $(1 - \gamma_{\infty})V_{zz}^{\text{Latt}}$.

The possibility that the electronic contribution as represented by the second term of Eq. (2.12) is proportional to the Sternheimer antishielding factor, $(1 - \gamma_{\infty})$, of the ion containing the nucleus in question is not admitted by the assumptions entering Eq. (2.12). Thus the need for a radical alteration of our view of the role of the metallic electrons was established. The correlation among all data for both pure and impurity systems is quite striking and lends support both to the rough proportionality as indicated in Eq. (4.1) and to a general expectation that the so-called electronic

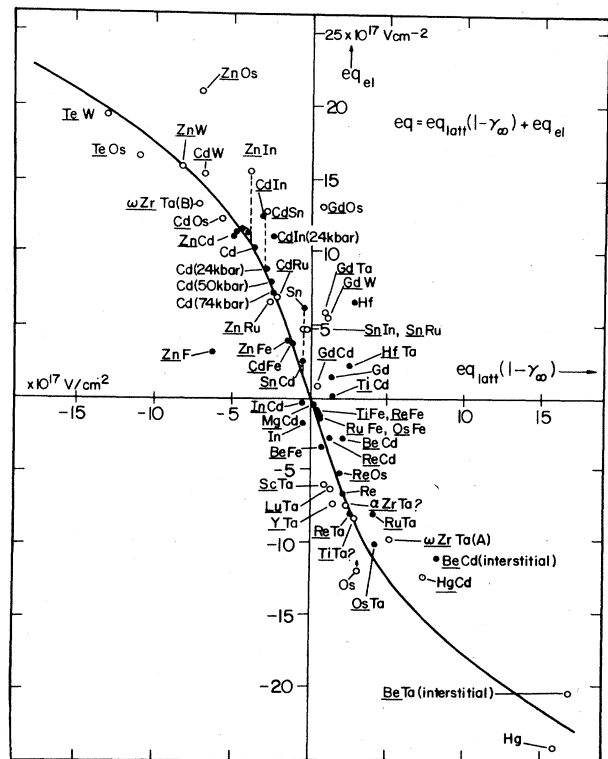


FIG. 17. The so-called "universal correlation" discovered by Raghavan *et al.*, (1975a, 1976) between the local electronic and lattice terms of Eq. (2.12) for several pure and impurity systems. Underlined symbols refer to the host metal. A and B refer to two inequivalent substitutional sites in ω -Zr. Filled circles indicate data for which the sign of the QI was known and open points, indicating cases where only magnitudes were available, are predictions.

contribution [as defined by Eq. (2.12)] is opposite in sign to the ionic gradient. Raghavan *et al.* gave the empirical expression (neglecting open-shell effects),

$$V_{zz} \cong -K(1 - \gamma_{\infty})V_{zz}^{Latt}, \quad (4.2)$$

as an approximate description of the universal correlation, where K is ≈ 2 . Comparing Eq. (4.2) with Eq. (2.12), one sees immediately that the basic assumptions upon which Eq. (2.12) were based are not completely applicable in a metal.

Omitted from the data displayed in Fig. 17 are the cases of rare-earth atoms with open $4f$ shells in which the major QI contribution arises from the $4f$ electrons. The rare-earths have been treated by Pelzl (1972) in this regard. He finds that, in addition to the $4f$ shell, an anomalously large ionic contribution is needed to explain experimental data and concludes that the value of γ_{∞} must be revised upward in a metallic environment. This corresponds then to the general observation that γ_{∞} must be involved in the "extra-ionic" or electronic contribution as in non-rare-earth systems.

Referring to Fig. 17, one sees that several points do lie off the curve. The extreme outlying point for F in Zn must be taken with caution since fluorine is a highly electronegative ion and may well be in a local compound coordination with the Zn. Therefore the fluorine may not be situated at the regular lattice site for which V_{zz}^{Latt} was calculated. In fact, a common caveat which must be invoked in many instances is possible ignorance of the exact lattice location of an impurity in a solid. For dilute alloy samples prepared by the usual metallurgical techniques, it is probably a reasonable assumption that the impurity resides substitutionally on regular host lattice sites. However, in recent years, much data has been accumulated for nominally insoluble impurities which have been energetically implanted into a noncubic host by an isotope separator or by recoil from a nuclear reaction. Care must be exercised in interpreting these data. In many cases, the impurity lattice location has been determined by ion beam channeling experiments (Kaufmann *et al.*, 1974a, 1975, 1976; Krien *et al.*, 1976) without which the implications of the QI data would not be subject to unique interpretation. The data in Fig. 17 (except for F in Zn) are relatively well characterized in this regard.

Several points lying off the main curve appear close to the curve in a graphical sense, but these deviations are not negligibly small and in some instances they lie in the first or third quadrant implying a breakdown in the general sign-reversal trend. Therefore the correlation must be considered to be approximate, pointing only to the dominant behavior but admitting significant variations for specific cases. Variations might arise, for example, from somewhat inappropriate choices for the lattice ionic charges, Ze , which were assumed in Fig. 17 to be the nominal integral valence of the host element in the metallic state. Corrections to Ze of the order of 10% to 20% have been invoked by some authors (Mohapatra *et al.*, 1972; Pomerantz and Das, 1960) to account for the effect of nonuniform distributions of distant electronic charge. A correction to Ze ,

however, would move a point in Fig. 17 along a 45° line roughly parallel to the curve and would thus not account for most of the deviations.

Another likely source of deviations for individual points from the curve in Fig. 17 which applies to the points corresponding to impurity systems is host lattice relaxation. It is in fact rather surprising that the relaxation of near-neighbor atom positions surrounding the impurity is not so significant an effect as to have completely blurred the observed correlation. In some sense, however, this effect may have been implicitly (and unintentionally) included in the correlation since it turns out that as one traverses the table of the elements a strong correlation is found between an element's atomic size and the value of $(1 - \gamma_{\infty})$ for the free ion (Sen and Narasimhan, 1976).

Available data not included in Fig. 17 have been plotted in a similar fashion in Fig. 18. The curve of

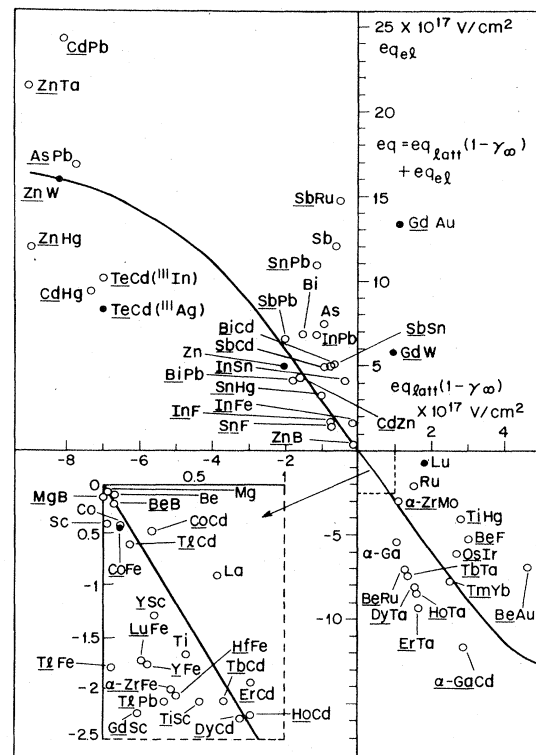


FIG. 18. Data not included in Fig. 17 have been plotted in a similar fashion here. The curve is identical to that in Fig. 17. Points lying close to the origin in the fourth quadrant have been plotted in the inset for clarity. Solid circles correspond to systems of known EFG sign and open circles are predictions as far as the sign is concerned. Experimental EFG values are listed in Appendix B and ionic gradients not tabulated in Raghavan *et al.* (1976) have been taken from Fechner *et al.* (1973) (rare earths), Taylor and Hygh (1963) (arsenic structure), Torgeson and Barnes (1964) (lanthanum), and Valic and Williams (1969) (gallium). Systems for which data are available but whose coordinates fall outside the range of this figure are: BeAu (interstitial site I) (-123, +162), (interstitial site II) (-12.9, +32.4); BeHg (interstitial) (-122, +118); HgPb (+16.4, -34.4); Te (-4.4, +83); TeI (-91, +115); SeTe (-13.3, +123); and SeI (-278, +353). The coordinates following each system are given in units of 10^{17}V/cm^2 .

Raghavan *et al.* has also been added to the figure. In most of these new cases, the sign of the EFG is not known and corresponding points have been plotted with a choice of sign such that best agreement with the curve is achieved. It is evident that the general trend is supported by this additional data.

A very recent NAR experiment on cubic Mo metal (Fischer *et al.*, 1978), has demonstrated that the same proportionality factor does not apply simultaneously to the EFG induced by different components of the acoustically applied stress tensor. Further experiments of this type could indicate how general the concept embodied in Eq. (4.2) is.

2. Impurity valence

An explanation for some of the deviations, suggested by Raghavan *et al.* (1976), relates to the character of the outer electronic shell of the probe ion. With this view, the increasing deviation of the points for Cd and Sn hosts as one goes through the series of impurity ions, Cd, In, and Sn, would be ascribed to the increasing number of outer *p* electrons in the series, i.e., Cd(5s²), In(5s²5p¹) and Sn(5s²5p²). Thus an additional local electronic contribution may be present due to non-spherically distributed valence electrons which remain spatially correlated to the impurity ion in the metal environment. This effect, which is relatively small on the scale of Fig. 17, would truly correspond to the second (or local) term of Eq. (2.12), and Eq. (4.2) may be modified as

$$V_{zz} \cong -K(1 - \gamma_\infty)V_{zz}^{Latt} + V_{zz}^{Local}, \tag{4.3}$$

which has the general form of Eq. (2.12), but the second term is now considered relatively small.

A third alternative viewpoint, which may be fundamentally identical to the above-mentioned valence electron idea, is the effective impurity charge picture. The impurity charge is simply defined to first order as the difference in impurity and host valence, $\Delta Z = Z_{impurity} - Z_{host}$. That is, under the assumption that the valence electrons are lost to the metallic energy bands, an apparent deficit or surplus of charge, ΔZ , relative to the background ionic charge, is present at the impurity site. Since a metal can be viewed as an electron gas, the mobile electrons will partially screen the impurity charge and in so doing redistribute themselves near the impurity in such a way as to influence the field gradient. A good deal more will be described below about the general implications of charge screening in this context (see Sec. V.C). For the time being, an empirical approach will suffice. One notices that the series of impurity ions Cd⁺², In⁺³, and Sn⁺⁴ would represent, respectively, ΔZ 's of 0, +1, and +2 in a Cd host and -2, -1, and 0 in a Sn host. Thus charge screening of ΔZ could equally well be responsible for the systematic deviation of these points from the universal correlation. Of course, one would expect the electronic screening charge to take anatomic-like wave function near the impurity which corresponds to the first empty orbits of the ion, and thus the valence electron idea and charge screening are in reality one and the same concept. The impurity charge screening

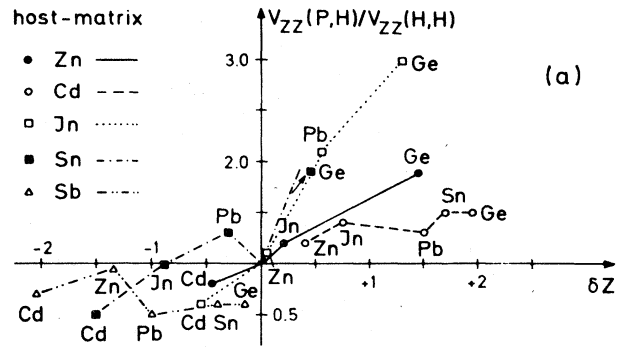


FIG. 19. The ratio of the EFG at impurities in several hosts to the EFG at the host nuclei themselves, plotted against the effective impurity charge, ΔZ , corrected for impurity size. A rough trend is seen which indicates an increasing EFG with increasing ΔZ . Lines connecting various points for a given host element are intended to guide the eye. (Taken from Leitz *et al.*, 1976.)

hypothesis has been systematically investigated by Leitz *et al.* (1976) who did indeed find that an empirical correlation between the QI and impurity charge [corrected for difference in impurity and host atomic volumes (Blatt, 1957; Farrell *et al.*, 1970)] existed among a large number of cases in *sp*-metal (i.e., nontransition metal) hosts. Their results are displayed in Fig. 19 where the ratio of impurity to host field gradients is plotted against ΔZ .

Recently Collins (1978) has studied the same correlation in a somewhat different way by plotting the electronic contribution to the EFG against impurity valence as shown in Fig. 20. The correlation is striking and demonstrates that, in the *sp* metals, the electronic EFG is approximately proportional to the number of conduction electrons screening the impurity.

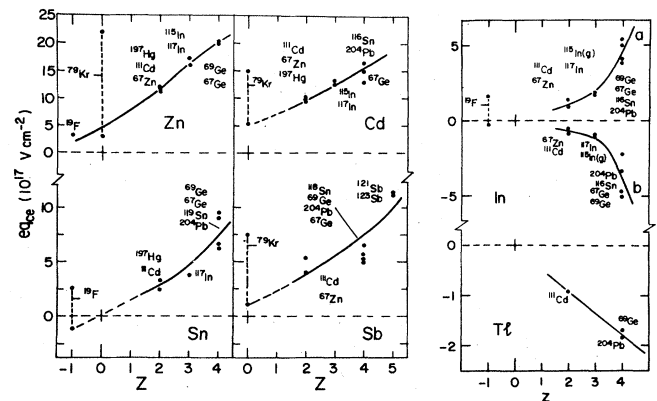


FIG. 20. Alternate display of the correlation between impurity EFG's and valence. Here, for six metallic hosts, the electronic contribution to the EFG [derived from Eq. (2.12)] is plotted against impurity valence. For positive valence impurities, the sign of the electronic EFG was taken opposite to the lattice EFG when QI sign data were unavailable. For impurities of $Z=0$ or -1 (Kr and F) and for all impurities in the host In, both choices of sign are shown. The clear correlation seen here supports the notion that the electronic contribution to the EFG is proportional to the number of conduction electrons screening the impurity in a given host. (Taken from Collins, 1978.)

3. The QI temperature dependence

As mentioned earlier, in the majority of cases studied, the temperature variation of the QI has been observed to be stronger than that expected on the basis of a point-ion lattice field varying with the thermal expansion of the lattice. One previously cited explanation for this was the possibility of a thermally induced repopulation of states of differing spatial symmetry by electrons at the Fermi surface (Watson *et al.*, 1965). These same authors used an order of magnitude argument to conclude that an electron-phonon interaction would be too weak to be responsible for this effect. On the other hand, thermal vibrations have long been known to account for the QI temperature dependence in ionic and molecular solids (Bayer, 1951; Kushida *et al.*, 1956). Their importance in metals remained in doubt until recently.

An unexpected discovery was presented for the first time by Heubes *et al.* (1974) who found that virtually all QI temperature-dependence data, including the most precise NQR data, could be described by the empirical relation

$$V_{zz}(T) = V_{zz}(0)(1 - BT^{3/2}). \quad (4.4)$$

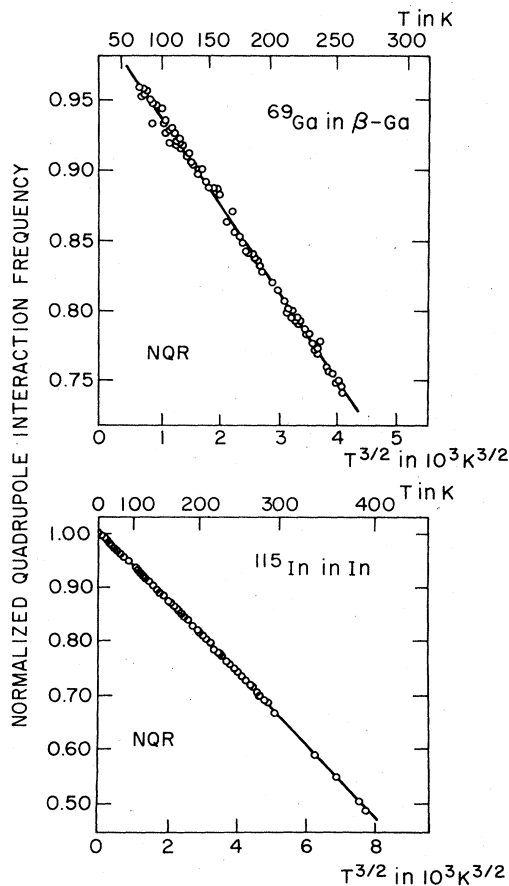


FIG. 21. The normalized temperature dependence of the EFG in metallic In (Hewitt and Taylor, 1962) (see Fig. 13) and β -Ga (Segel *et al.*, 1972) plotted against a $T^{3/2}$ scale. Note that the most accurate NQR data in these cases follow a linear dependence on $T^{3/2}$. (Taken from Christiansen *et al.*, 1976.)

A more complete description of these observations has been given by Christiansen *et al.* (1976). Aside from the trivial normalization factor $V_{zz}(0)$, only one parameter, the slope B , enters in Eq. (4.4) and this relation holds for pure systems as well as for impurity systems. In the latter type, the value of B was found in many cases to be different for different impurities in the same host. The data of Figs. 21 and 22 show the apparent linear behavior of $V_{zz}(T)$ when plotted against $T^{3/2}$. Attempts to fit the available data to alternate formulae, such as to the sum of terms linear and quadratic in T , led to poorer agreement. It was also noted that the slope parameter B , for a Cd impurity in several hosts, was greatest where the QI itself was smallest and vice versa.

The universal nature of Eq. (4.4) is yet another

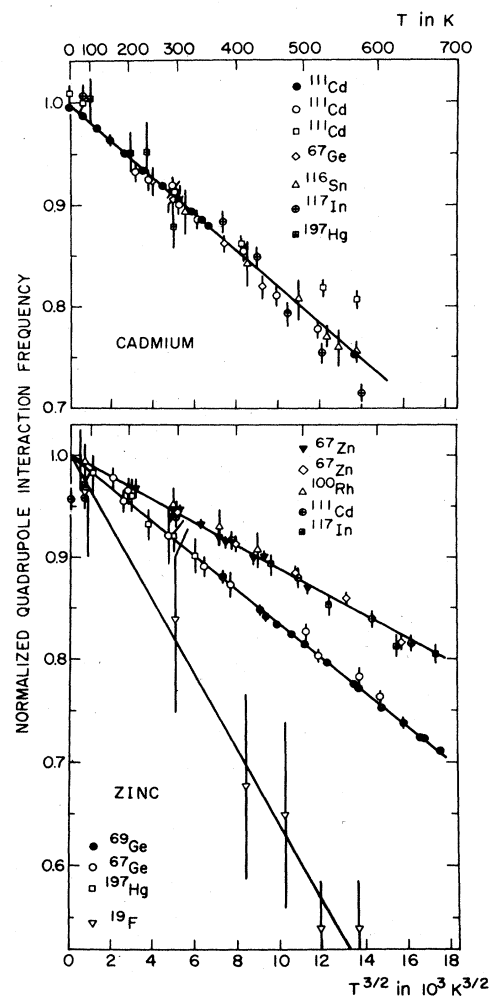


FIG. 22. The normalized temperature dependence of the EFG at host and impurity probes in Cd and Zn metals, plotted against a $T^{3/2}$ scale. Although some of the data are less accurate than that shown in Fig. 21, they are clearly consistent with the $T^{3/2}$ behavior. Note that the grouping of impurities with different T -dependence slope in the Zn host does not occur in Cd. [References to the individual measurements plotted here can be found in Christiansen *et al.* (1976) from whom this figure was taken.]

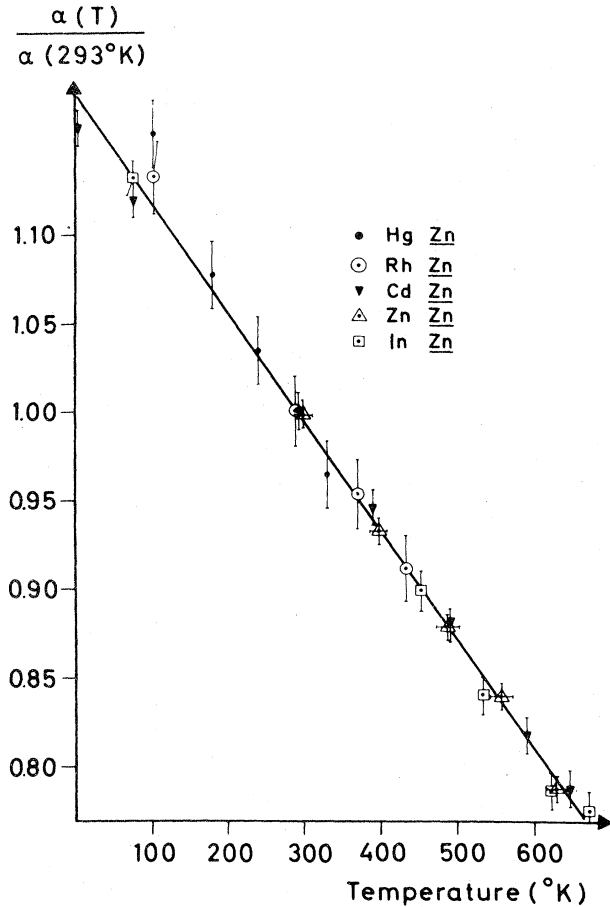


FIG. 23. The dependence on temperature, for impurities in Zn, of the so-called electronic enhancement factor, defined as the ratio of the experimentally determined EFG to the calculated lattice-sum contribution, normalized to the data at room temperature. The linear dependence of this ratio on T has not been explained. (Taken from Krien *et al.*, 1975a.)

indication that the conventional parameterization of Eq. (2.12) is not appropriate. For it would be difficult to believe that any fortuitous combination of circumstances could cause the temperature dependence of the lattice term and of the local electronic term to be essentially identical in the vast majority of cases. In fact a formulation similar to Eq. (4.2) or (4.3), with only a single dominant term, would seem more compatible with the simplicity of Eq. (4.4). Several hypotheses, put forward to explain, at least in part, the temperature-dependence question, will be discussed in a later section (see Sec. VI A).

One additional puzzling aspect of the temperature dependence of the QI has been pointed out by Krien *et al.* (1974b, 1975a) who found that in some systems the so-called electronic enhancement factor, i.e., $V_{zz}^{Exp}/V_{zz}^{Latt}$, shows a linear dependence on T . Some of the data upon which this observation is based are shown in Fig. 23. No specific explanation has been proposed for this effect as yet.

4. The QI pressure dependence

It was recognized early that measurement of the pressure dependence of the QI could provide direct information on the variation V_{zz} with changing lattice parameters (O'Sullivan and Schirber, 1964a). Further, it was demonstrated by Raghavan *et al.* (1972), that such results in combination with temperature-dependence data could be used to isolate the explicit effect of the temperature on V_{zz} from the changes caused by thermal lattice expansion.

To separate the dependence of V_{zz} on a given number of different lattice parameters, an equal number of independent experiments is usually required. In the case of hcp and tcp lattices, the structure can be completely described by only two lattice parameters. The volume V and the axial ratio c/a of the unit cell are convenient choices. The dependence of V_{zz} on these parameters can then be determined by observing the variation of the QI in a single crystal subjected to a hydrostatic pressure P and an uniaxial compression P_{un} . The measured pressure dependences can be decomposed as follows:

$$\left(\frac{\partial \ln V_{zz}}{\partial P}\right)_T = \left(\frac{\partial \ln V_{zz}}{\partial \ln V}\right)_{T, c/a} \left(\frac{\partial \ln V}{\partial P}\right)_T + \left(\frac{\partial \ln V_{zz}}{\partial \ln c/a}\right)_{T, V} \left(\frac{\partial \ln c/a}{\partial P}\right)_T \quad (4.5)$$

$$\left(\frac{\partial \ln V_{zz}}{\partial P_{un}}\right)_T = \left(\frac{\partial \ln V_{zz}}{\partial \ln V}\right)_{T, c/a} \left(\frac{\partial \ln V}{\partial P_{un}}\right)_T + \left(\frac{\partial \ln V_{zz}}{\partial \ln c/a}\right)_{T, V} \left(\frac{\partial \ln c/a}{\partial P_{un}}\right)_T \quad (4.6)$$

Here the logarithmic derivatives have been used to avoid normalization factors and the subscripts T , V , and c/a indicate constant temperature, pressure, and c/a ratio, respectively. If the explicit dependences of V and c/a on P and P_{un} are known, e.g., from compressibility data, values for $(\partial \ln V_{zz}/\partial \ln V)_{T, c/a}$, the variation of V_{zz} under congruent compression, and $(\partial \ln V_{zz}/\partial \ln c/a)_{T, V}$, the variation of V_{zz} under an isochorus change of c/a , can be derived from Eqs. (4.5) and (4.6).

In the majority of experiments, only the dependence of V_{zz} on hydrostatic pressure has been studied. It was found that, over the experimentally covered pressure range in sp metals, (DaJornada *et al.*, 1978; Hwang *et al.*, 1977; O'Sullivan and Schirber, 1964a, 1964b; Raghavan *et al.*, 1972) as well as for a Ta impurity in several transition metals (Butz and Kalvius, 1976), V_{zz} varies essentially linearly. In a recent study of α -Ga (Hwang *et al.*, 1977), the slope of the pressure dependence of V_{zz} was found to vary considerably with temperature. All values available for $(\partial \ln V_{zz}/\partial P)_T$ are listed in Table II along with the corresponding $(\partial \ln V_{zz}/\partial T)_P$ results.

The experimental observations show a clear deviation from point-ion lattice sum calculations of V_{zz} , using the appropriate lattice constants. This is evident in Fig. 16. Furthermore, the lattice sum predicts, for the congruent compression coefficient $(\partial \ln V_{zz}/\partial \ln V)_{T, c/a}$, a value of -1 . As shown in Fig. 24, this is in systematic disagreement with experimental results derived, with

TABLE II. Pressure dependence coefficients of the EFG; the corresponding temperature dependence coefficients are included in the table.

System	$\left(\frac{\partial \ln V_{zz}}{\partial P}\right)_T$ [10 ⁻³ kbar ⁻¹]	Ref.	$\left(\frac{\partial \ln V_{zz}}{\partial T}\right)_P$ ^a [10 ⁻⁴ K ⁻¹]	Ref.
⁵⁷ Fe in Be	+0.8(3)	Janot and Delcroix, 1972	-5.5(3)	Janot <i>et al.</i> , 1974
⁶⁹ Ga in α-Ga	+1.5(-)	Kushida and Benedek, 1958 Hwang <i>et al.</i> , 1977	-2.5(-)	Valic and Williams, 1969
⁶⁹ Ga in β-Ga	+5.7(-)	Brown and Segel, 1975	-22.9(3)	Segel <i>et al.</i> , 1972
¹¹¹ Cd in Zn	-5.6(4)	DaJornada <i>et al.</i> , 1978	-3.0(3)	Raghavan <i>et al.</i> , 1974c
¹¹¹ Cd in Cd	-4.3(3)	Raghavan <i>et al.</i> , 1972 Butz, 1978b	-5.1(1)	Christiansen <i>et al.</i> , 1976
¹¹¹ Cd in Sn	+4.1(4)	DaJornada <i>et al.</i> , 1978	-9.2(1)	Christiansen <i>et al.</i> , 1976
¹¹⁵ In in In	+13.3(4)	O'Sullivan and Schirber, 1964a	-25.1(3)	Hewitt and Taylor, 1962
¹²¹ Sb in Sb	-8.29(20)	O'Sullivan and Schirber, 1964b	-3.69(3)	O'Sullivan and Schirber, 1964b
¹⁸¹ Ta in Sc	+8.0(3)	Butz <i>et al.</i> , 1976	-3.4(-)	Butz and Kalvius, 1974
¹⁸¹ Ta in Y	+9.2(6)	Butz <i>et al.</i> , 1976	-6.9(1)	Butz and Kalvius, 1974
¹⁸¹ Ta in Tb	+6.9(22)	Butz, 1978b	...	
¹⁸¹ Ta in Lu	+10.2(13)	Butz <i>et al.</i> , 1976	-4.4(12)	Butz and Kalvius, 1974
¹⁸¹ Ta in α-Zr	+3.9(3)	Butz <i>et al.</i> , 1974	-3.8(1)	Kaufmann and McWhan, 1973
¹⁸¹ Ta in ω-Zr(A)	-1.1(3)	Butz <i>et al.</i> , 1975	+0.9(4)	Kaufmann, 1973a
¹⁸¹ Ta in ω-Zr(B)	+6.0(4)	Butz <i>et al.</i> , 1975	-1.3(4)	Kaufmann, 1973a
¹⁸¹ Ta in Hf	+6.3(7)	DaJornada <i>et al.</i> , 1974 Ernst <i>et al.</i> , 1977	-2.5(1)	Lieder <i>et al.</i> , 1971 Unterricker, 1974
¹⁸¹ Ta in Re	+0.9(2)	Butz and Potzel, 1975	-0.7(2)	Netz and Boderstedt, 1973 Butz and Potzel, 1975

^aDerivative taken near room temperature.

the help of Eq. (4.5), using compressibility data and an estimate for $(\partial \ln V_{zz} / \partial \ln c/a)_{T,V}$ given by Butz and Kalvius (1976). From these discrepancies, a strong influence of band structure variations caused by an increase in the average conduction electron density was inferred (Ernst *et al.*, 1977; Raghavan *et al.*, 1972).

As mentioned above, knowledge of the coefficients $(\partial \ln V_{zz} / \partial \ln V)_{T,c/a}$ and $(\partial \ln V_{zz} / \partial \ln c/a)_{T,V}$, derived from the pressure-dependence measurements, also makes it possible to separate $(\partial \ln V_{zz} / \partial T)_{V,c/a}$, the explicit temperature dependence of V_{zz} , from the effects of thermal lattice expansion, since

$$\left(\frac{\partial \ln V_{zz}}{\partial T}\right)_P = \left(\frac{\partial \ln V_{zz}}{\partial \ln V}\right)_{T,c/a} \left(\frac{\partial \ln V}{\partial T}\right)_P + \left(\frac{\partial \ln V_{zz}}{\partial \ln c/a}\right)_{T,V} \left(\frac{\partial \ln c/a}{\partial T}\right)_P + \left(\frac{\partial \ln V_{zz}}{\partial T}\right)_{V,c/a} \quad (4.7)$$

To solve this equation for $(\partial \ln V_{zz} / \partial T)_{V,c/a}$, the thermal expansion coefficients of the lattice must also be known. It was found that the explicit dependence of V_{zz} on temperature for Ta embedded substitutionally in several transition metals is very small (Butz and Kalvius, 1976; Ernst *et al.*, 1977), whereas, in the *sp* metals In and Cd, a strong explicit temperature dependence has been observed (Butz and Kalvius, 1976; Raghavan *et al.*, 1972). As mentioned in the previous section, a thermally induced repopulation of conduction electron states has been invoked to explain this behavior (Raghavan *et al.*, 1972; Watson *et al.*, 1965).

V. THEORY OF THE QI IN METALS

Where the need arose in earlier sections, some aspects of various theoretical approaches have already been mentioned, primarily to highlight the major points of agreement and lack thereof with experiment. It is clear from those discussions that the failures of early theory to adequately account for particular observations largely shaped the course of subsequent experimental investigations, leading to the recognition of systematic trends as described in the previous section. Not merely for aesthetic reasons is a comprehensive theory required, but, with such a theory, extraction of valuable information on the structure of metals and alloys from QI data would be inevitable. The utility of QI data for incisive tests of our knowledge of the elec-

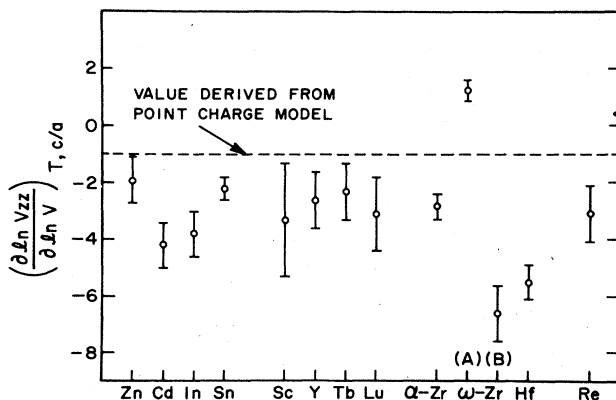


FIG. 24. Fractional change in EFG with fractional change in lattice volume, $(\partial \ln V_{zz} / \partial \ln V)_{T,c/a}$ derived, as discussed by Butz and Kalvius (1976), from pressure-dependence studies. The obvious deviation from the value -1, expected from the point-ion lattice sum results, indicates the importance of the electronic contribution to the dependence on volume changes.

tronic structure of metals can in fact be greater than that of data from, for example, deHaas-van Alphen or cyclotron resonance measurements, which are sensitive only to energy band structure and Fermi-surface shape. Even Knight shift data pertain only to electrons near the Fermi surface, although in this case electronic wave functions are explicitly involved. The QI, on the other hand, is determined by the total spatial distribution of electronic charge and therefore requires knowledge of wave functions for electrons throughout the entire occupied region of momentum (k) space. The QI thus provides a severe test of any model purporting to describe the complete electronic structure of a metal and, conversely, is therefore a most difficult quantity to accurately calculate from first principles.

The categorization of various theoretical approaches is somewhat problematic. Even the simplest of metals is too complex to be amenable to "exact" numerical calculations. Some approximations and assumptions are needed to make the problem tractable and which of these are reasonable to invoke in a particular case depends on the specific metal involved. The ultimate goal of any such calculation is the determination of the electronic charge density $\rho_e(\mathbf{r})$ for inclusion in Eq. (2.14) for the field gradient. The general form of $\rho_e(\mathbf{r})$ would be given formally by

$$\rho_e(\mathbf{r}) = 2e \sum_n \int |\Psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}, \quad (5.1)$$

where the wave function $\Psi_{n\mathbf{k}}(\mathbf{r})$ depends on the band index n and the electron crystal momentum \mathbf{k} . The sum extends over all occupied bands and the integral over all occupied regions of \mathbf{k} space. The crucial aspects of attempts to evaluate Eq. (5.1) lie in the proper representation of the $\Psi_{n\mathbf{k}}$ functions and in the proper evaluation of the integral by approximate numerical methods. Rather than to attempt to describe in great mathematical detail methods applied in any individual case, we have chosen to survey the general approaches taken so far, ordering the presentation by beginning with methods relying on use of microscopic wave functions and then proceeding to those which are more phenomenological.

A. Microscopic approaches

The most fundamental, and therefore the most tedious and least physically intuitive, method of computing the QI in a metal is of course the evaluation of electronic wave functions which approximate as closely as possible the real metal. In most such studies, the intention has been to compute the sum of explicit contributions to the EFG from the "conduction" electrons of each occupied energy band and then to add the point-ion-sum EFG amplified by the $(1 - \gamma_\infty)$ Sternheimer factor. Thus implicit in these approaches has been the assumption that the parameterization represented by Eq. (2.12) is appropriate. Although we have several times pointed to the inadequacy of Eq. (2.12) for a metal, the results of specific calculations in that context have, nevertheless, proved valuable, and some recent refinements in the theory have dealt with a more realistic separation of local and external field sources.

1. OAO

A useful point of departure for this discussion is a calculation by Hygh and Das (1966) for antimony. The semimetal character of antimony places it in an intermediate position between nonconducting solids and true metals. Characterizing the antimony lattice as an array of nonoverlapping ions and considering the five valence electrons per atom as forming five fully occupied energy bands bounded by a Fermi surface whose shape is that of the first Brillouin zone, these authors applied a tight-binding Wannier-function approach to the computation of the valence electron charge density. The Wannier functions were constructed from orthogonalized atomic orbitals (OAO) which accounted for orbitals of the central ion and the first near neighbors. An attempt to account for antishielding effects was also made by considering the general form for the antishielding factor given by Eq. (2.13). Thus different shielding effects for field sources originating at the central ion and at the near neighbors were included. The explicit values of these shielding factors, however, were only roughly estimated from calculations in the literature concerning values, for neighboring elements, of the Sternheimer factors $(1 - R)$ and $(1 - \gamma_\infty)$ of Eq. (2.12). The result obtained for the magnitude of the total field gradient was fortuitously close to the experimental value derived from NQR (Hewitt and Williams, 1963). The overall accuracy claimed was of the order of $\pm 20\%$. The major points to be stressed concerning this result are that the experimental observation of a gradient nearly an order of magnitude greater than the point-ion lattice sum prediction was successfully explained in terms of an overwhelming electronic contribution and that the quantitative success of the approach very likely arose from the use of Wannier functions, thus avoiding the need to explicitly sum contributions over all of \mathbf{k} space. In true metals where one cannot legitimately assume all bands are fully occupied, a different approach is required.

2. OPW

The approach taken in most cases to date is based on the orthogonalized plane-wave (OPW) method of representing conduction electron wave functions originally introduced by Herring, (1940). Progress in the implementation of this method to field-gradient calculations is epitomized by the work in beryllium metal which was initially attempted in 1960 (Pomerantz and Das) and very much advanced twelve years later (Mohapatra *et al.*, 1972). At the time of the earlier work, rather heuristic assumptions and approximations had to suffice in the evaluation of the relevant wave functions, with the end result that a wave function of essentially s -wave character was derived which yielded no local contribution to the EFG. The only modification of the point-ion lattice value arose from the influence of the calculated nonuniformity of electron density throughout the lattice on the appropriate effective value of ionic charge to be used in the lattice sum. An 8% increase in the calculated EFG was thus deduced. Since that time, the necessary prerequisites for an extended OPW calcula-

tion became available.

A single OPW wave function consists simply of a suitably normalized plane wave, as for a free electron, from which are subtracted the projections of that plane wave onto the core states of the metal ion so as to render the resulting function orthogonal to the core states. A schematic representation would appear as

$$\psi_{\mathbf{k}}^{\text{OPW}}(\mathbf{r}) = \chi_{\mathbf{k}}(\mathbf{r}) - \sum_t \langle \phi_{t\mathbf{k}}^{\text{TB}}(\mathbf{r}) | \chi_{\mathbf{k}}(\mathbf{r}) \rangle \phi_{t\mathbf{k}}^{\text{TB}}(\mathbf{r}), \quad (5.2)$$

where $\chi_{\mathbf{k}}(\mathbf{r}) \propto e^{i\mathbf{k}\cdot\mathbf{r}}$ is the plane wave, and the core states $\phi_t(\mathbf{r})$, enumerated by the index t , are contained in the tight-binding Bloch function

$$\phi_{t\mathbf{k}}^{\text{TB}}(\mathbf{r}) \propto \sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \phi_t(\mathbf{r} - \mathbf{r}_j). \quad (5.3)$$

Use of Eq. (5.3), where the sum runs over the atom sites at \mathbf{r}_j of the crystal lattice, allows orthogonalization to core states on the ion core at the origin ($\mathbf{r}_j = 0$) as well as to those on neighboring ions if necessary. The first requisite for this approach is then accurate core level wave functions which can reasonably be taken from free-ion calculations.

In general, a single OPW function is not adequate because the crystal potential seen by conduction electrons will mix such states. Therefore the OPW functions are used as a basis set for the construction of the actual wave functions as

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} C_{n, \mathbf{k}+\mathbf{K}} \psi_{\mathbf{k}+\mathbf{K}}^{\text{OPW}}(\mathbf{r}). \quad (5.4)$$

Here, \mathbf{K} is a reciprocal lattice vector and the coefficients $C_{n, \mathbf{k}+\mathbf{K}}$ are determined from a secular equation involving matrix elements of the crystal potential in the OPW basis. Thus the second requisite is an accurate form for the potential presented by the metal ion to the conduction electrons. Finally, the third requirement, once the wave function is known, is the shape and location of the Fermi surface so that in evaluating Eq. (5.1), the limits of integration are defined. In practice the integral is converted to a sum over an array of points in \mathbf{k} space within the Brillouin zone. The accuracy is therefore dependent on the coarseness of the coverage relative to the rapidity with which the charge density varies with \mathbf{k} .

All these prerequisites were met in the relatively simple metals, beryllium (Mohapatra *et al.*, 1972) and magnesium (Jena *et al.*, 1973) where good quantitative agreement was achieved with experimental EFG magnitudes. The signs of the EFG have not been determined experimentally. The variation of the local electronic EFG within various bands is illustrated in Fig. 25 where it is plotted along several symmetry directions in the Brillouin zone for two bands in magnesium. It is interesting to note that although the contributions to the EFG from the various bands were qualitatively similar in the two metals, the detailed cancellation of opposing contributions differed, leading to a negative net electronic contribution in beryllium and positive in

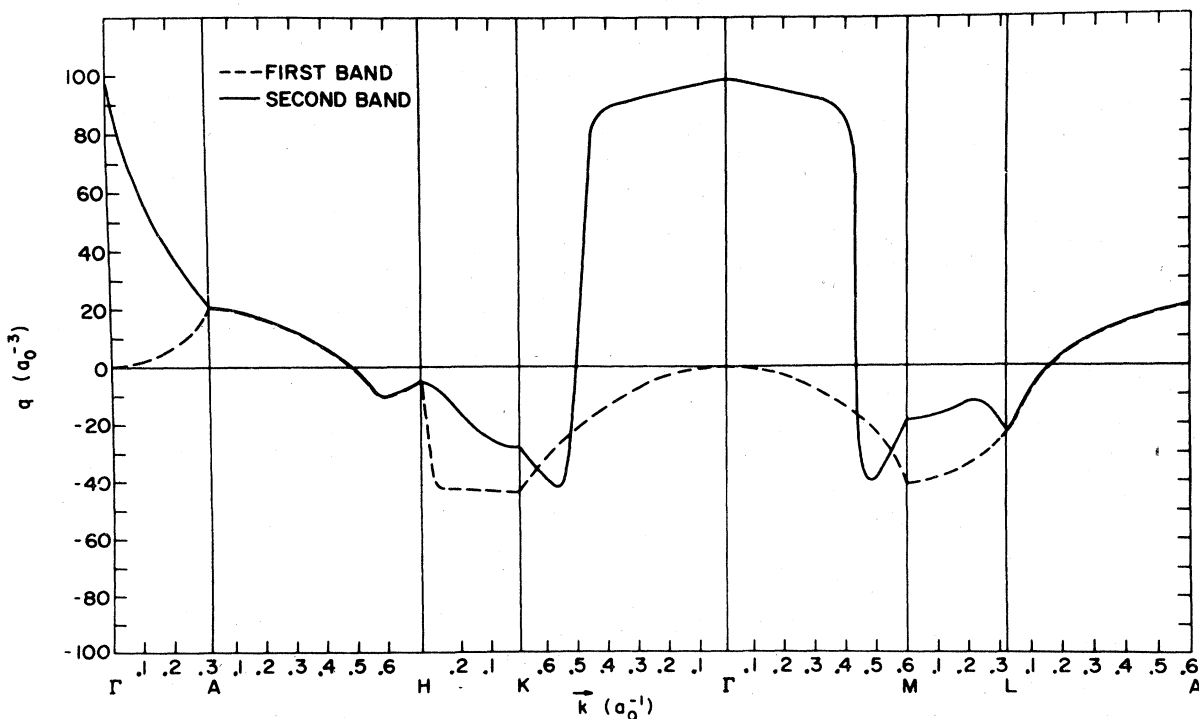


FIG. 25. The local electronic contribution to the EFG in Mg, computed by the OPW method, displayed as a function of location along symmetry directions in the Brillouin zone for two different bands. The units of the ordinate are arbitrary. (Taken from Jena *et al.*, 1973).

magnesium. In beryllium the electronic contribution was only 25% of the lattice field whereas in magnesium it was a factor of ≈ 2.5 greater than the lattice field.

Similar calculations in the hcp metals Zn and Cd have also been attempted. Here, although atomic wave functions and Fermi-surface information are available, no real crystal potentials existed in the literature. Thus an alternative approach to the evaluation of the $C_{n, \mathbf{k}+\mathbf{K}}$ parameters was needed.

The need to know a real potential is obviated through use of a pseudopotential (Harrison, 1966). As indicated above, the wave functions for mobile electrons of a metal may be considered as plane waves with the caveat that they be properly orthogonalized to the wave functions of the other electrons in the system, *viz.*, the core electrons. The orthogonalization modifies the conduction electron wave functions so as to reduce the density of these electrons within the ion cores. One can envision the effect of orthogonalization therefore as the response to a potential with a repulsive core. Thus if one substitutes for a real potential, a pseudopotential, which is formally considered as the combination of a real potential and a repulsive "orthogonalization potential," a pseudofunction for the conduction electrons can be defined as

$$\Phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} C_{n, \mathbf{k}+\mathbf{K}} \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}). \quad (5.5)$$

This is the analog of Eq. (5.4) and the coefficients $C_{n, \mathbf{k}+\mathbf{K}}$ are in fact the same as in Eq. (5.4). The coefficients can therefore be determined from matrix elements of the pseudopotential in the plane-wave basis, and the real wave functions $\Psi_{n\mathbf{k}}(\mathbf{r})$ will be obtained from Eq. (5.5) by replacing the plane waves $\chi_{\mathbf{k}}(\mathbf{r})$ with the OPW functions $\psi_{\mathbf{k}}^{\text{OPW}}(\mathbf{r})$.

Available pseudopotentials (Stark and Falicov, 1967) for Zn and Cd, which were appropriate for electrons in the vicinity of the Fermi surface, were extended to apply to the entire Brillouin zone and used to calculate the EFG by Mohapatra and co-workers (Das, 1975; Mohapatra *et al.*, 1973). Their results showed for both metals that the negative lattice-sum contribution (see Fig. 17) is expected to be overwhelmed by a large positive electronic contribution. Subsequent experimental sign determinations in Cd (Raghavan *et al.*, 1974a) and recently in Zn (Herzog *et al.*, 1977a) have verified their predictions. This agreement was, and remains, the only theoretical justification obtained to date for the sign-reversal trend in nontransition metals. Unfortunately, the nuclear quadrupole moments involved in the experimental measurements were not directly known from experiment. Signs and approximate magnitudes deduced from nuclear models and systematics were reasonably reliable, however. A quantitative agreement of theory and experiment in the case of Cd, for example, would have required a nuclear moment nearly three times that expected, thus implying a theoretical underestimate of the EFG. Recent more direct measurements of nuclear moments in Zn (Vetterling and Pound, 1977) and Cd (Echt *et al.*, 1976a; Raghavan *et al.*, 1973a) have verified this discrepancy.

A modified OPW calculation which included nonspheri-

cal effects in the magnetically ordered rare earths has been done by Devine and Dixon (1973). They computed the conduction electron plus lattice contribution to the EFG and claim agreement for these components (to within a factor of 5 to 10) with experiment. The validity of their experimental comparisons has been questioned recently by D'Onofrio and Iraldi (1977).

In response to the discovery of the universal correlation (Fig. 17), an attempt to incorporate more realistic shielding effects in the electronic contribution was recently made (Mohapatra *et al.*, 1977; Pattnaik *et al.*, 1977; Thompson *et al.*, 1978a and 1978b). In plotting the $l=2$ component of the conduction electron density (see Fig. 26), as determined from the OPW procedure (Mohapatra *et al.*, 1977) against radial distance from the nucleus, it was found that the density attributable to the plane-wave components of the OPW functions lay primarily outside the ion core and should therefore be shielded by a factor more like $(1 - \gamma_{\infty})$ than $(1 - R)$. By computing the effect of core orbital deformation due to the nuclear moment on the interaction energy of the core with the conduction electrons, it was found that an effective antishielding factor of about 65% of $(1 - \gamma_{\infty})$ was applicable to the plane-wave electronic contribution (Pattnaik *et al.*, 1977; Thompson *et al.*, 1978a and 1978b). Inclusion of this refinement yielded quantitative agreement with experiment in Cd and Zn.

The theoretical verification that antishielding effects similar to those applicable to the external lattice charges also applied in large measure to the "local" conduction electrons lends support to the systematic trend of Fig. 17, explaining, at least qualitatively, the

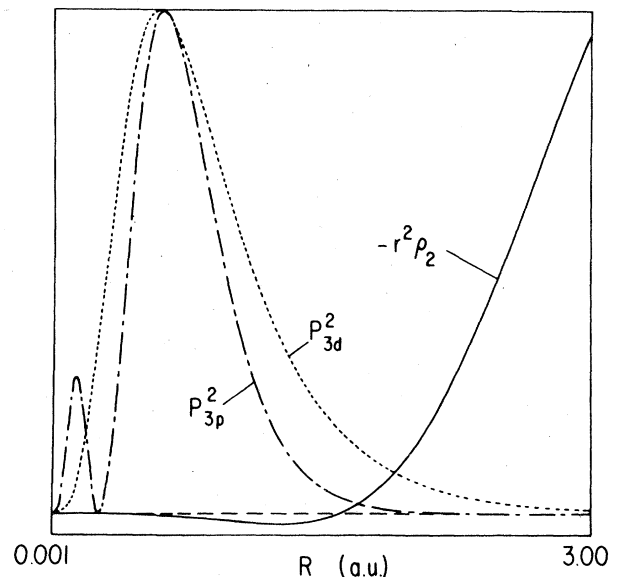


FIG. 26. Plot of the radial density of those conduction electrons which contribute to the EFG ($l=2$ component), separately for the plane-wave and core components of the OPW functions, as a function of distance to the nucleus in Zn. Note that a major fraction of the density for the plane-wave portion, which was heretofore considered to be essentially local, lies outside the maxima in densities attributable to the outer core states. (Taken from Mohapatra *et al.*, 1977.)

origin of the overall dependence of the EFG on the Sternheimer antishielding factor of the ion core at the origin. Future microscopic calculations must therefore avoid the automatic assumption of the separation of field sources which Eq. (2.12) implies.

No similar calculations dealing with impurity systems have as yet been attempted. The successful use of the empirical pseudopotential in pure systems, however, portends similar success for impurities, because the pseudopotential approach is easily applied to the description of the perturbing influence of an impurity in a metal.

3. APW

An alternative microscopic approach to the construction of electron wave functions in metals is the augmented plane wave (APW) method described by Loucks (1967) and by Mattheiss *et al.* (1968). The APW function consists of plane waves outside the so-called APW sphere, a mathematical construct, and solutions to the Schrödinger equation inside the sphere where a spherical muffin-tin potential is commonly assumed. The APW functions, suitably adjusted to satisfy continuity requirements at the sphere boundary, are used in a relation similar to Eq. (5.4) to form the required wave functions. To our knowledge, this technique has only been applied twice to the calculation of an EFG. It was found (Das and Ray, 1970) that in dysprosium metal, a substantial and sign-reversing contribution from the conduction electrons is to be expected. Comparison with experiment in this instance indicated that an additional antishielding enhancement was needed to explain observations. In Sn metal, similar calculations gave reasonable results (Collins, 1976), including a sign reversal, but comparison with experiment was difficult for lack of a firm experimental value of the nuclear Q moment involved. It is likely that use of non-spherical potentials in this method would enhance the reliability of the results.

B. Electrons at the Fermi surface

In the previous subsection we emphasized the need to include all occupied electron states in considering the electronic contribution to the EFG. It may be asked, however, whether electrons near the Fermi surface play any special role. This question was considered by Watson, Gossard, and Yafet (1965) after noting that experimental values for the QI at vanadium sites in V_3X type intermetallics scaled in rough proportion to the electronic density of states at the Fermi level. Figure 27 illustrates the observed trend. The metal was viewed by Watson *et al.* from the standpoint of a tight-binding APW model in order to conceptually separate a contribution from those charges within and outside of the APW sphere. The so-defined external charge was considered to be the source of the lattice field. The conduction electrons were assumed to occupy Bloch states, which are eigenfunctions of a crystal potential that is spherical within the APW sphere. An EFG would originate from the conduction electrons within the sphere since the Bloch states display the symmetry of the noncubic crystal environ-

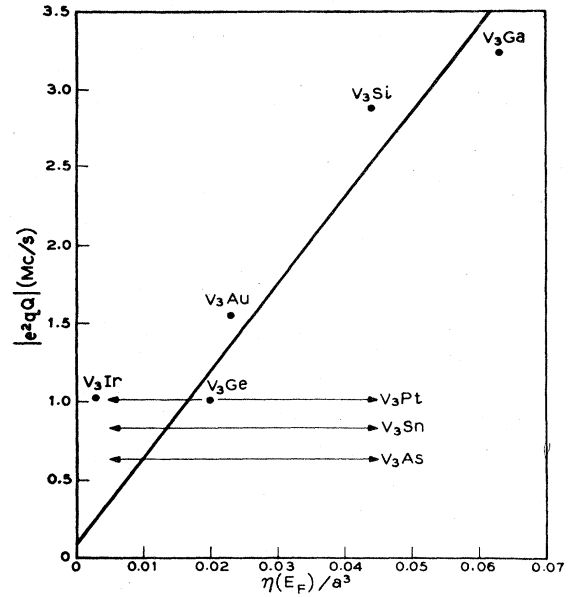


FIG. 27. Plot of the magnitude of the QI frequency for ^{51}V in several V_3X ($X=Si, Ge, Ga$, etc.) compounds against the electronic density of states at the Fermi level (normalized to lattice volume). Values of $\eta(E_F)$ for $X=Pt, Sn$, and As were not available. The apparent correlation seen here motivated Watson *et al.* to consider the specific influence of Fermi-surface electrons on the EFG. (Taken from Watson *et al.*, 1965.)

ment. In the absence of other effects, this would be the local electronic contribution. The question was then raised as to the effect on the EFG of the perturbing influence of the external field, V_{zz}^{Latt} , on the Bloch electrons within the atomic sphere. Two such effects were envisioned. First, all Bloch states would be spatially distorted by the external potential. And second, the energies of the Bloch states would be shifted in first order. The first effect is analogous to the orbital distortions from which the Sternheimer antishielding factor arises. The second effect would cause a redistribution of occupied states of various orbital symmetries in the vicinity of the Fermi level. It is the latter which Watson *et al.* concluded may dominate the EFG under suitable conditions. For this particular contribution to the EFG, they arrived at the expression,

$$V_{zz}^{FS} \approx -2e^2 V_{zz}^{Latt} \eta(E_F) \langle r^2 \rangle \langle r^{-3} \rangle \langle P_2(\cos \theta) \rangle^2, \quad (5.6)$$

after several simplifying assumptions. The angular brackets imply expectation values of the enclosed quantity to be taken over the orbital of appropriate symmetry (i.e., p -like, d -like, etc.) at the Fermi surface.

Several qualitative features of Eq. (5.6) should be noted. V_{zz}^{FS} is proportional to V_{zz}^{Latt} as would be expected, since V_{zz}^{Latt} is the source of the assumed perturbation. The individual factors multiplying V_{zz}^{Latt} are all positive, thus indicating an overall negative proportionality factor, i.e., a shielding effect. V_{zz}^{FS} is proportional to the density of states at the Fermi level, $\eta(E_F)$, and to the product of the radial expectation values $\langle r^2 \rangle \langle r^{-3} \rangle$ for the relevant orbitals. Finally, the rationale for considering this particular term as dominating other effects, if

$\eta(E_F)$ and $\langle r^2 \rangle \langle r^{-3} \rangle$ are sufficiently large, is that it arises from a "coherence" between the perturbing potential and the gradient operator since each contributes a $P_2(\cos \theta)$ factor.

By inserting experimental values of $\eta(E_F)$ from electronic specific heat data and values of the radial factors from atomic orbital calculations, values for the ratio $V_{zz}^{FS}/V_{zz}^{Latt}$ were obtained for p - and d -band metals which ranged from ≈ -10 to -650 . Thus a sizable "overshielding" of the lattice field was expected which could result in reversing the sign of the total EFG relative to the direct lattice contribution. Introducing effects of self-consistency in the model did not materially alter this conclusion. Table III lists the derived overshielding factors for several elements as corrected for self-consistency. Although quantitative accuracy is not claimed, the impressive size of the predicted effect would lead one to believe that the Fermi-level electrons are prime sources of the EFG.

No conclusive evidence in support of or against this model has been derived from experiments or other methods of calculation. In the microscopic calculations noted in the previous subsection on Mg, for example, the fraction of the total EFG attributed to electrons near the Fermi surface was only a few percent (Jena *et al.*, 1973). In fact reasonable agreement was obtained with experiment in those cases without inclusion of the perturbation introduced by Watson *et al.* It can be argued, however, that the metals Be, Mg, Zn, and Cd are not p - or d -band metals with large $\eta(E_F)$ and therefore do not provide a critical test of the Fermi-surface effects. A more damaging observation is the experimental result (Brewer and Kaindl, 1978; Thatcher and Hewitt, 1970) in In, a p -band metal, that V_{zz} has the same sign as V_{zz}^{Latt} , whereas the Fermi-surface overshielding factor was predicted to be -85 to -115 . Similar contradictions can be found in the d -band transition metals. Although sign reversals have been reported in Re, Ru, and Os (Greggers-Hansen *et al.*, 1971; Kaindl *et al.*, 1972; Kaindl and Salomon, 1972; Raghavan *et al.*, 1976), no

reversals were observed in Lu, Hf, or Ti (Brewer and Kaindl, 1978; Kaindl and Salomon, 1972; Kaindl *et al.*, 1973; Raghavan *et al.*, 1976). Finally, the original trend of the QI with $\eta(E_F)$ in V_3X compounds was found not to hold in a similar series of Nb_3X intermetallics (Ehrenfreund *et al.*, 1971).

Recently, Piecuch and Janot (1976, 1977) have reconsidered the calculation of the local electronic contribution to the QI in pure d -band transition metals. Considering the anisotropy of the crystal field as a perturbation on the tight-binding model, they derived expressions for the EFG arising from *both* the local crystal field integrals within the central cell as well as from the Coulomb transfer integrals between the central cell and nearest neighbors. The former resulted in an expression identical to Eq. (5.6) except for an additional factor accounting for the electronic Coulomb and exchange interactions which were omitted by Watson *et al.* The latter resulted in a new term, explicitly neglected by Watson *et al.*, which corresponds to the spatial polarization of the electronic charge density in the central cell due to crystal anisotropy. The new term turns out to have a magnitude comparable to that of the original term but is of opposite sign. In a first approximation, it is proportional to the density of d -electron states at the Fermi level but is not explicitly proportional to the lattice field gradient.

Rough quantitative estimates of the total EFG, including this new term, in several transition metals, was not in good agreement with experimental magnitudes (Piecuch and Janot, 1977). In two cases treated, Re and Hf, experimental signs are available. The known negative sign of the QI in Re was not reproduced because the calculated negative electronic contribution was not greater than the positive lattice gradient. In Hf, however, the net electronic contribution was found to be positive due to the dominance of the new term in the theory, and with a positive lattice gradient, yielded agreement with the experimental positive sign. It is likely that once the approach of Piecuch and Janot is applied with fewer approximations, it will represent an excellent foundation for the understanding of the QI in transition metals and of the importance of electrons at the Fermi surface. In a general schematic attempt to account for the systematics in impurity systems (i.e., Figs. 17 and 18), Kolk (1976) has shown that Fermi-surface effects, as presently understood, cannot account for observations.

D'Onofrio and Iraldi (1977) have investigated the contribution of Fermi-surface electrons from a somewhat different viewpoint. They dealt with rare earth metals where experiment has shown that the EFG due to the $4f$ electron shell is reduced by the combined contribution of the lattice and conduction electron EFG's. The reduction is about two orders of magnitude greater than expected from the lattice portion alone. By perturbing the Fermi-surface electrons through their interaction with the $4f$ electrons (which are aligned in the magnetically ordered rare earths), these authors found agreement with experiment in the sense that both the signs and approximate magnitudes of the contribution to the EFG from sources other than the $4f$ electrons were reproduced.

TABLE III. Self-consistent results for the overshielding factor $V_{zz}^{FS}/V_{zz}^{Latt}$ for various metals. [Taken from Watson *et al.* (1965)].

Metal	$V_{zz}^{FS}/V_{zz}^{Latt}$
Sc	-18
Ti	-7
Co	-10.5
Y	-28 to -30
Zr	≈ -10
Ru	-7
Nb in Nb_3Sn	-42
V in V_3Ga	-20
La	-220
Re	≈ -100
Os	-55
Ga	-16
In	-85 to -115
Sn	-100 to -125
Tl	-150 to -170
Bi	-8

C. Pseudopotentials and charge screening

We have already introduced the use of a pseudopotential as an empirical artifice to avoid the need to know actual crystal potentials. In the earlier context, a pseudopotential which had been effective in replicating properties of the metal, such as Knight shifts, phonon frequencies, etc., was used to construct explicit electron wave functions for the computation of the EFG. A further conceptual simplification consists in avoiding the explicit use of electron wave functions by describing the mobile electrons as a dielectric medium. In dielectric response theory, the behavior of the electronic charge in response to a perturbing potential is completely characterized by a single dielectric function $\epsilon(\mathbf{q}, \omega)$. The functional dependence on the Fourier transform variables \mathbf{q}, ω (momentum, frequency) determines respectively the spatial and time variation of the electron gas response. All effects of explicit wave functions, including correlation and exchange, can, in principle, be embodied in the dielectric function. Formally, the task of calculating the electric charge distribution reduces simply to a calculation of the screening response of the electron gas to an appropriately chosen pseudopotential for the metal ions.

The results of many-body theory, which one can find in several texts on the quantum theory of solids (e.g., Kittel, 1963; Ziman, 1972), yield the expression for the dielectric function of an electron gas,

$$\epsilon(\mathbf{q}) \equiv \epsilon(\mathbf{q}, 0) = 1 + \frac{4\pi e^2}{q^2} \sum_{\mathbf{k} < k_F} \frac{f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q})}{E(\mathbf{k} + \mathbf{q}) - E(\mathbf{k})}, \quad (5.7)$$

where k_F is the Fermi momentum and we have set $\omega = 0$ in the static limit. In practice $\omega \neq 0$ effects need only be considered when time variations in the optical ($\approx 10^{15}$ Hz) frequency range are relevant. In Eq. (5.7), $E(\mathbf{k})$ is the electron energy and $f^0(\mathbf{k})$ is the occupation probability of the state $|\mathbf{k}\rangle$. For a free-electron gas with spherical Fermi surface at absolute zero temperature, an evaluation of the sum over \mathbf{k} space yields the explicit formula (Harrison, 1966; Kittel, 1968),

$$\epsilon(q) = 1 + \frac{2m_e e^2 k_F}{\pi \hbar^2 q^2} \left[1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right]. \quad (5.8)$$

The quantity m_e is the electron mass. Note that the derivative of $\epsilon(q)$ has a logarithmic singularity at $q = 2k_F$.

In complete analogy to the classical treatment of electrostatics in polarizable media, the dielectric function relates the electric displacement field \mathbf{D} , which arises only from external charges, to the electric field \mathbf{E} , which arises from the combined action of both the external and induced charges. Their relationship, stated in terms of Fourier components, is

$$\mathbf{D}(\mathbf{q}) = \epsilon(\mathbf{q})\mathbf{E}(\mathbf{q}), \quad (5.9)$$

and using the definitions, $-\nabla V_{\text{Ext}} = \mathbf{D}$ and $-\nabla V_{\text{Total}} = \mathbf{E}$, for the associated potentials in the Fourier variable notation,

$$-iqV_{\text{Ext}}(\mathbf{q}) = \mathbf{D}(\mathbf{q}) \text{ and } -iqV_{\text{Total}}(\mathbf{q}) = \mathbf{E}(\mathbf{q}), \quad (5.10)$$

one arrives at the connection between applied and total potential,

$$V_{\text{Total}}(\mathbf{q}) = V_{\text{Ext}}(\mathbf{q})/\epsilon(\mathbf{q}). \quad (5.11)$$

Thus taking a bare potential for the metal ion as V_{Ext} , Eq. (5.11), in conjunction with Eq. (5.8), will provide the screened potential V_{Total} .

The classic application of this approach was developed to treat the problem of an impurity ion in a metal lattice (Friedel, 1954, 1958; Langer and Vosko, 1959). The impurity-host valence difference ΔZ creates an effective point charge whose Coulomb potential induces a redistribution in the electron density. It was found that the logarithmic singularity in the slope of $\epsilon(q)$ at $q = 2k_F$ was the source of a long-range oscillatory behavior in the induced potential, usually called Friedel oscillations (Blandin and Friedel, 1960; Kohn and Vosko, 1960). The long-range character accounted for the unusually strong effects of impurities on NMR results in cubic metals (Brettel and Heeger, 1967; Drain, 1968; Kanert and Mehning, 1971; Rowland, 1960; Sagalyn *et al.*, 1961; Sagalyn and Alexander, 1977; Titman and Kellington, 1967; Tompa *et al.*, 1967). In this instance, the net charge on the impurity (as well as lattice strain due to the impurity) produces an EFG at a large number of neighboring host ions, thus shifting the host NMR frequencies.

We are interested here, however, in the EFG at a host or impurity ion site due to the surrounding ions and electrons of an undisturbed noncubic host lattice. One must therefore return to the idea of a lattice sum. To each ion is assigned a bare potential, which may be taken as an empirical pseudopotential, or in the simplest approximation, as the Coulomb potential of a $+Ze$ point charge, Z being the metallic valence. Account is then taken of the electrons of the metal by first screening the bare potential and then summing the contributions of each screened ion potential at the point where the EFG is being evaluated.

One recognizes that the assumed bare potential is meant to describe the electron-ion interaction for electrons *outside* each ion core. In discussing this approach, we shall initially adopt the simplifying assumption of point ions. This will give the formal appearance that the electron density and associated potential are known throughout the entire lattice. Nevertheless, it must be remembered that the results apply only to the inter-ion-core regions and that, in particular, evaluation of the potential at the "origin" implies evaluation of the potential seen by the ion, not the nucleus, at the origin.

The screened potential at a distance \mathbf{r} from an ion whose bare potential is $V_C(\mathbf{r})$ is given by

$$V(\mathbf{r}) = V_C(\mathbf{r}) + V_{sc}(\mathbf{r}) = \frac{1}{8\pi^3} \int \frac{V_C(\mathbf{q})}{\epsilon(\mathbf{q})} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}, \quad (5.12)$$

where $V_{sc}(\mathbf{r})$ denotes the potential due to the electronic screening charge alone and $V_C(\mathbf{q})$ is the Fourier transform of $V_C(\mathbf{r})$. The spherical components of the corresponding EFG tensor are then found, using the definitions of Eq. (2.6), by differentiating Eq. (5.12). They are given by

$$\phi_2^{(m)}(\mathbf{r}) = -\frac{\sqrt{4\pi/5}}{24\pi^3} \int \frac{V_C(\mathbf{q})}{\epsilon(\mathbf{q})} q^2 Y_{2m}(\Omega_q) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}, \quad (5.13)$$

where the spherical harmonic Y_{2m} is a function of the angular variables in \mathbf{q} . Equation (5.13) may be alternatively regarded as the EFG tensor at the origin due to a screened ion at \mathbf{r} . If $V_C(\mathbf{r})$ is a central potential, then $V_C(\mathbf{q})$ depends only on $|\mathbf{q}|$, and one sees from Eq. (5.8) that this is also true for $\epsilon(\mathbf{q})$. The angular part of the integral in Eq. (5.13) can therefore be performed, yielding

$$\phi_2^{(m)}(\mathbf{r}) = \frac{\sqrt{4\pi/5}}{6\pi^2} Y_{2m}(\Omega) \int_0^\infty dq q^4 \frac{V_C(q)}{\epsilon(q)} j_2(qr), \quad (5.14)$$

where the spherical harmonic is now a function of real space angles, and j_2 is the spherical Bessel function. Equation (5.13) is more instructive for formal manipulations, whereas Eq. (5.14) is suited for actual evaluation of the $\phi_2^{(m)}$. The factorized form of Eq. (5.14), where angular and radial dependences are separated, can be rewritten as

$$\phi_2^{(m)}(\mathbf{r}) = \frac{1}{3} \sqrt{4\pi/5} Y_{2m}(\Omega) V''(r), \quad (5.15)$$

where $V''(r)$ is the second radial derivative of $V(r)$ of Eq. (5.12), i.e.,

$$V''(r) = r \frac{d}{dr} \left(\frac{1}{r} \frac{dV(r)}{dr} \right). \quad (5.16)$$

The total EFG would then result from the sum over all ions of the lattice at $\mathbf{r}_i \neq 0$;

$$\phi_2^{(m), \text{Total}} = \alpha(1 - \gamma_\infty) \sum_i' \phi_2^{(m)}(\mathbf{r}_i). \quad (5.17)$$

An antishielding factor is added to indicate that such a factor should be present since, within the point-ion approximation, all of the source charge producing $\phi_2^{(m)}(\mathbf{r}_i)$ is external to the ion at the origin. Whether γ_∞ is the appropriate factor or not will be discussed below. The prefactor α represents this uncertainty.

Because $\epsilon(q)$ is a slowly varying function in general, the main contribution to $V(r)$ at larger r (i.e., $r \gg k_F^{-1}$) arises from the singularity in $\epsilon(q)$ at $q = 2k_F$. Eq. (5.12) can therefore be evaluated in the asymptotic limit of large r (Langer and Vosko, 1959; Lighthill, 1962) and results in the potential

$$V(r) \approx \left(\frac{2m_e e^2 k_F^2 V_C(2k_F)}{\pi^2 \hbar^2 \epsilon^2(2k_F)} \right) \frac{\cos(2k_F r)}{(2k_F r)^3}. \quad (5.18)$$

Higher-order corrections to this result are given in Appendix A. It has been commonly assumed that the radial part of $\phi_2^{(m)}$ can then be found by differentiation of Eq. (5.18) according to Eq. (5.16) (Sholl, 1967, 1975). This procedure is not strictly correct since differentiation should precede an asymptotic expansion. The leading term in the result, however, is insensitive to this point and is given by

$$V''(r) \approx A(2k_F)^2 \frac{-\cos(2k_F r)}{(2k_F r)^3}, \quad (5.19)$$

where A is the prefactor in brackets in Eq. (5.18). Terms decreasing faster than $1/r^3$ would be incorrect if derived from Eq. (5.18). This is elaborated in Appendix A. The asymptotic form can be used to avoid the explicit integration in Eq. (5.14) when $|\mathbf{r}_i|$ is sufficiently large. Although nearest-neighbor distances are not

always large enough to ensure $k_F r_i \gg 1$, the asymptotic form alone has frequently been used in calculations. Figure 28 shows a comparison of the asymptotic expression for $V''(r)$ of Eq. (5.19) with that derived from Eq. (5.14) and with that from an unscreened Coulomb potential in the region of near-neighbor distances. One can see that the asymptotic expression should not be expected to provide quantitative accuracy in the near-neighbor region. The oscillatory behavior of $V''(r)$ indicates high sensitivity to the precise location of neighboring ions. Had a Thomas-Fermi approximation to $\epsilon(q)$ been employed, both the oscillatory and long-range nature of $V''(r)$ would have been absent.

Because charge screening of the lattice ions is so effective in metals, one might expect that ions distant from the origin would appear essentially neutral and therefore should not contribute strongly to the EFG at the origin. From the asymptotic form in Eq. (5.19), one sees, however, that the individual ion contributions fall off as $1/r^3$. Since the number of ions in any neighbor shell increases roughly as r^2 , the total contribution of shells of ions falls off only as $1/r$. Thus in practice, the lattice sum must extend over a considerable number of relatively distant ions.

To our knowledge, Sholl (1967) was the first to use this method to compute an EFG in a solid. The Coulomb-point-ion approximation was employed and only the asymptotic $V''(r)$ was used. The Coulomb potential and its Fourier transform are given respectively by

$$V_C(\mathbf{r}) = Ze/r \text{ and } V_C(\mathbf{q}) = 4\pi Ze/q^2. \quad (5.20)$$

Also computed were quadrupolar relaxation rates in the corresponding liquid metals by the same method of charge screening. After finding the effective amplification factors, α , for the solids In and Ga, by comparing experiment with Eq. (5.17), Sholl was able to use the same factors in the liquid metals to successfully explain the experimental relaxation rates (see also Schir-

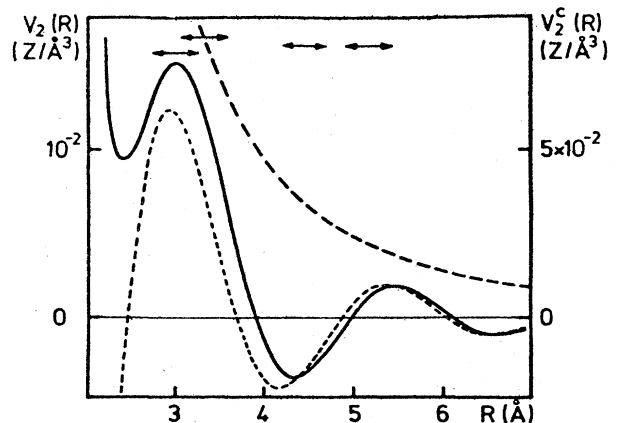


FIG. 28. A comparison of the radial derivative of the potential, as defined in Eq. (5.16), for a pure Coulomb potential (long-dashed line), the exact screened Coulomb potential of Eq. (5.12) (solid line) and the asymptotic approximation of Eq. (5.18) (short-dashed line). Values of parameters appropriate to Cd metal were assumed and the arrows in the figure indicate positions and vibration amplitudes of near neighbors in Cd. (Taken from Nishiyama and Riegel, 1978.)

macher, 1976; Sholl, 1976). The values of $|\alpha|$ ranged from ≈ 3 for Ga to 5 for In.

Nishiyama *et al.* (1976, 1977b) have also performed screened lattice sums for Coulomb point ions, without resorting however to the asymptotic approximation, and found nearly the same amplification factors $|\alpha|$, of the order of 6, for several simple metals. The near-constancy of α for simple group II, III, and IV metals was taken by Nishiyama *et al.* (1977b) to show that Eq. (5.17), involving the screened lattice sum, is more reliable than the empirical expression of Raghavan *et al.* (1976, 1975a) in Eq. (4.2). Sholl (1967) justifies these large α factors by pointing out that the γ_∞ values used are appropriate to free ions, whereas screened ions in a metal may be regarded as nearly neutral atoms for which antishielding factors are not generally available but are expected to be larger than for ions (Sen and Narasimhan, 1977; Sternheimer, 1967a). This implies that the screening charge about the ion at the origin, which is spherical in the above formulation, actually distorts and contributes to the EFG. The microscopic analog to this view is the incorporation of core distortion effects on the OPW wavefunctions by Das and co-workers (Mohapatra *et al.*, 1977; Thompson *et al.*, 1978a and 1978b). In the context of charge screening, Kaufmann and Vianden (1978), using Eq. (2.13), have computed the effective antishielding enhancement due to the screening charge about the origin by allowing that charge to distort from spherical symmetry under the influence of the ion core quadrupole moment. Their result was $\alpha = 1.7$, which is indicative of the expected effect but not large enough to explain experimental values. Thus, within the approximations used, the charge-screening approach has not satisfactorily accounted for the experimentally observed interaction strength. A recent summary of the charge-screening approach to the calculation of EFG's has been presented by Nishiyama and Riegel (1978).

One might have hoped that because of the oscillatory nature of the screened potential, the sign of the EFG due to various shells of neighbors might in some instances be reversed at the origin, thus accounting for the sign reversal trend as well. This has not been observed in general. Recently, however, Nishiyama *et al.* (1977a) have successfully reproduced an experimentally known sign change of the EFG at In in the compound InBi as a function of temperature (Radhakrishna and Mungurwadi, 1969), by applying the exact [i.e., derived from Eq. (5.14) rather than Eq. (5.19)] version of the screened lattice sum. One hopes therefore that suitable refinements of this approach will succeed in handling the EFG sign properly.

One attempt at using a more sophisticated screened pseudopotential, without invoking the point-ion assumption, has been made by Lodge and Sholl (1974) and provides a clue to the possible solution of the sign question. Although they did not achieve quantitative agreement with experiment, some aspects of their results for Be, Mg, Zn, Cd, and In lattices are indicative of the refinements needed in the charge-screening approach. They omitted from their calculation conduction electrons within the radius of the ion core at the origin. This is more realistic than the point-ion assumption

which essentially ignores the presence of finite ion core regions. They found in all cases that the EFG contributed by electronic screening charge was opposite in sign to that from the lattice of Coulomb point charges, but not large enough to reverse the sign of the net EFG. By comparison with experiment and with the available microscopic calculations in Be, Mg, and Cd, they concluded that, in most instances, the major contributor to the EFG must be the conduction electrons within the central core region which were not included in their study. They also found that in some cases their results were quite sensitive to the choice of pseudopotential.

Relaxation of the point-ion assumption can drastically alter the screened-ion lattice sum and is probably the explanation for the opposition in sign between electronic and lattice gradients found by Lodge and Sholl (1974). This is easily demonstrated by considering two simplistic alternatives to the Coulomb point-charge potential. For example, the Coulomb potential produced by a uniformly charged spherical shell of radius R_c and total charge Ze is given by

$$V(r) = \begin{cases} \frac{Ze}{R_c} & \text{for } r < R_c \\ \frac{Ze}{r} & \text{for } r > R_c \end{cases} \quad \text{and } V(q) = \frac{4\pi Ze}{q^2} j_0(qR_c), \quad (5.21)$$

or, for a charge Ze uniformly distributed throughout a spherical volume, by

$$V(r) = \begin{cases} \frac{3Ze}{2R_c} - \frac{Ze}{2R_c^3} r^2 & \text{for } r < R_c \\ \frac{Ze}{r} & \text{for } r > R_c \end{cases} \quad \text{and } V(q) = \frac{4\pi Ze}{q^2} \frac{3j_1(qR_c)}{qR_c}. \quad (5.22)$$

The additional oscillatory functions of R_c entering in $V(q)$ which do not appear in Eq. (5.20) can easily give rise to a change in sign in Eq. (5.13). This effect is due solely to relaxing the point-ion assumption for ions not at the origin.

When the ion at the origin is also considered to have finite spatial extent, the expression for the EFG tensor of Eq. (5.17) is no longer valid since it does not account for the possibility that the electronic screening charge due to ions at \mathbf{r}_i overlaps the ion core at the origin. One must therefore apply the concept of a radially dependent Sternheimer antishielding factor, $\gamma(r)$, as indicated in Eqs. (2.13) and (2.14). A straightforward consideration of this effect leads to the introduction of an additional q -dependent factor under the integral in Eq. (5.13) and (5.14) of the form

$$3 \int_0^\infty dr [1 - \gamma(r)] \frac{j_2(qr)}{r}. \quad (5.23)$$

With this modification, the $(1 - \gamma_\infty)$ factor in Eq. (5.17) would be omitted.

To summarize, we have noted that the charge-screening approach has not yet been successful in explaining either magnitudes or signs of the EFG. We expect that one primary difficulty has been the use of rather unrealistic simplifying assumptions and approximations, as evidenced above by the substantial change to be expected by, for example, allowing for finite ion cores, nonspherical screening charge, etc. Thus several refinements suggest themselves. With regard to contributions from ions truly distant from the origin ($k_F r \gg 1$), asymptotic expressions may be used, but bare pseudopotentials which include finite ion-core size should be employed. For near-neighbor shells, the exact screening integrals should be evaluated. For the ion at the origin in particular, a pseudopotential including orbital structure of the ion core as well as nonspherical components which influence antishielding effects should be used and radially dependent antishielding factors must be included to handle interpenetration of mobile and core electron distributions. The general question of antishielding in this context as well as in the context of microscopic calculations will be discussed further in Sec.V.D. Finally, it may be necessary to use a more sophisticated dielectric function which does not presuppose a free-electron gas with a spherical Fermi surface and linear superposition of screened ion potentials, assumptions which at first sight seem quite incompatible with the noncubic metallic environment. Correlation and exchange in the electron gas may also need to be considered in some instances, although Lodge and Sholl (1974) found these not to be important in the systems they studied.

Of course, the need to consider refinements of the sort enumerated above basically arises from the original desire to avoid explicit evaluation of electronic wave functions. The price of this simplification was loss of quantitative accuracy. The logical question to pose then is, "Why start with such a phenomenological model and then attempt to correct it for microscopic details when first-principles microscopic calculations, where they have been applied, have been reasonably successful?" In this regard, the justification arises first from the extremely successful application of the charge screening approach to explaining the dependence of the EFG on temperature, pressure, and alloy concentration. As described in the following section, a substantially broader insight into systematic trends has emerged from this approach than was possible from detailed microscopic investigations of specific systems. Secondly, the way in which this formulation combines lattice and electronic EFG's into a single source offers a way to avoid the artificial separation epitomized by Eq. (2.12). Thus one would like to retain these useful aspects of the approach and, at the same time, improve its capacity to quantitatively predict signs and magnitudes.

In a very recent work by Bodenstedt and Perscheid (1978), it has been demonstrated that a sign-reversal trend can indeed be predicted by a rather unsophisticated model of a noncubic metal. Through an *ad hoc* assumption that conduction electrons are concentrated primarily at the centers of the faces of Wigner-Seitz polyhedra, their contribution to the total EFG was computed by point-charge lattice-sum methods. The quan-

tity of charge centered between atomic planes relative to that within atomic planes was deduced by considering the electrostatic and elastic energies required to produce the known axial ratio, c/a , of the lattice. As simple as this model appears, it may present the basic reason for the sign reversal and should be verified by comparison with electronic charge density maps derived from experiment or microscopic methods of calculation.

D. Antishielding in metals

In Sec.II.C, the idea of antishielding was discussed in the context of free ions. The antishielding factor was introduced to account for the influence of the ion core electrons on the energy of interaction of the nuclear Q moment with charges other than those of the ion core. When source charges are completely external to the ion core, the factor, $-\gamma_\infty$, is involved. It was pointed out that this factor could be viewed in two ways, i.e., as indicating that the external charge interacts with an ion core moment $-\gamma_\infty Q$ or, alternatively, that the nuclear moment interacts with an amplified EFG, $-\gamma_\infty V_{zz}$. When the source charge is within the ion core region, the radially dependent factor $-\gamma(r)$ of Eq. (2.13) was appropriate. If one inserts Eq. (2.13) into Eq. (2.14), one finds the additional interaction energy due to the core goes as

$$QV_{zz} = \int d\mathbf{r} \left[\int_0^r Q_i(r') dr' \right] \left[\frac{2\rho(\mathbf{r})P_2(\cos\theta)}{r^3} \right] + \int d\mathbf{r} [2r^2\rho(\mathbf{r})P_2(\cos\theta)] \left[\int_r^\infty Q_i(r') r'^{-5} dr' \right]. \quad (5.24)$$

The integrands in these two terms have a natural interpretation. The first represents the interaction of the induced moment of the core electrons within radius r with the EFG due to source charge outside of r . The second accounts for the interaction of the quadrupole moment of the source charge within radius r with the induced EFG of the core electrons outside of r .

The situation becomes considerably more complex when the ion in question resides at a lattice site of a noncubic metal, but the basic notion of partitioning the various interaction energies involved into terms such as those of Eq. (5.24) can still be applied. The added complexity arises from the presence of conduction electrons. Two decisions must be made at the outset which actually bear on how the concept of antishielding shall be defined in the metal. Are the conduction electrons in the vicinity of the ion core at the origin to be viewed as an extension of the core and therefore be included in the calculation of an antishielding factor, or should these electrons be regarded as additional source charge for the EFG to be antishielded by the core? The former view is embodied in the approach of Kaufmann and Vianden (1978) while the latter fits better into a discussion based on an interaction-energy formulation, similar to Eq. (5.24). Taking the second alternative and realizing that antishielding is intended to elucidate the effect of the core electrons on the orientational energy of the nuclear moment with respect to the EFG source charge distribution, one must define the external source charge geometry with respect to which this orientation is to be referred. The natural choice is to use the surrounding lattice of ions as the frame of reference. The

task then is to enumerate the various contributions to the total energy of the system which depend on the relative orientation of the nuclear moment and the lattice, paying special attention to those terms which involve the influence of core electrons, as these are those which we have defined as antishielding contributions. The presence of conduction electrons not only contributes to such terms directly, as expected from Eq. (5.24), but also produces new terms, not previously considered, by virtue of their overlap and electrostatic interaction with the ion core.

The first, and so far the only, exposition of a general formalism has been presented by Lodge (1976). Below is reproduced Lodge's Eq. (78), with some alteration in notation. Lodge proposes that this expression represents, to first order, the total EFG at a nucleus in a metal

$$\begin{aligned}
 QV_{zz} = & QV_{zz}^{\text{Latt}} - \gamma_{\infty} QV_{zz}^{\text{Latt}} + QV_{zz}^{\text{Cond}} \\
 & - Q \int_0^{\infty} \gamma(r) V_{zz}^{\text{Cond}}(r) dr - V_{zz}^{\text{Latt}} \int_0^{\infty} \beta(r) Q^{\text{Cond}}(r) dr \\
 & - \int_0^{\infty} Q^{\text{Cond}}(r) r^{-5} \left\{ \int_0^r [\beta(r') + \gamma(r) - \gamma_{\infty}] r'^5 V_{zz}^{\text{Cond}}(r') dr' \right\} dr \\
 & - \int_0^{\infty} Q^{\text{Cond}}(r) \left\{ \int_r^{\infty} [\beta(r) + \gamma(r') - \gamma_{\infty}] V_{zz}^{\text{Cond}}(r') dr' \right\} dr.
 \end{aligned} \tag{5.25}$$

The various symbols are defined as follows: V_{zz}^{Latt} is the EFG due to the lattice of ion cores outside the central cell; V_{zz}^{Cond} is the total EFG due to the conduction electrons, assuming they are in the usual states determined by a lattice of spherical ions with the only quadrupole distortion due to the noncubic symmetry of the lattice; $V_{zz}^{\text{Cond}}(r) dr$ is the sum of that portion of V_{zz}^{Cond} arising from conduction electrons in the radial shell between r and $r + dr$ about the origin, plus any additional gradient induced in the conduction electrons by the lattice perturbation of the ion core; $Q^{\text{Cond}}(r) dr$ is the quadrupole moment of the conduction electrons situated between r and $r + dr$ which is induced (both directly and through distortions of the ion core) by the nuclear moment; $\gamma(r)$ is the radially dependent antishielding factor given in Eq. (2.13) with $\gamma(\infty) = \gamma_{\infty}$ and $\gamma(0) = 0$; and $\beta(r)$ is a new antishielding factor which can be considered the dual of $\gamma(r)$, with $\beta(0) = \gamma_{\infty}$ and $\beta(\infty) = 0$. The signs of $\gamma(r)$ and $\beta(r)$ have been taken opposite to that used by Lodge in order to be consistent with our use of $\gamma(r)$ elsewhere.

As formidable as Eq. (5.25) appears, Lodge's interpretation of the various terms is straightforward. In order of their appearance in Eq. (5.25), the terms represent contributions to the energy of orientation of the nuclear moment with respect to the lattice due to:

- (1) the lattice EFG acting on the nucleus;
- (2) the antishielded lattice EFG acting on the nucleus;
- (3) the usual-conduction-electron EFG acting on the nucleus;
- (4) the antishielded usual-conduction-electron EFG acting on the nucleus;
- (5) the lattice EFG acting on the antishielded [by $\beta(r)$]

nuclear-induced moment of the conduction electrons;

(6) the EFG due to the nuclear-induced distortion in the conduction electrons outside r acting on the moment of the usual-conduction-electron distribution inside r , considered in two forms with, respectively, the moment antishielded by $\beta(r)$ and the EFG antishielded by $\gamma(r)$, plus a correction for counting this interaction twice; and

(7) the EFG due to the usual-conduction-electron distribution outside r acting on the nuclear-induced moment in the conduction electrons inside r , considered in two forms with, respectively, the moment antishielded by $\beta(r)$ and the EFG antishielded by $\gamma(r)$, plus a correction for counting this interaction twice.

To avoid confusion, the distinction between $V_{zz}^{\text{Cond}}(r)$ and $Q^{\text{Cond}}(r)$ should be reemphasized. $V_{zz}^{\text{Cond}}(r)$ is the EFG due to that portion of the quadrupolar distortion of the conduction electrons which is attributable to the influence of the *lattice* geometry and is the quantity usually referred to as the local electronic contribution, i.e., the second term of Eq. (2.12). It is the quantity, for example, which includes results of OPW calculations. Also included in this quantity would be the perturbing effect of the lattice potential as, for example, considered by Watson *et al.* (1965). $Q^{\text{Cond}}(r)$, on the other hand, is the moment arising from that portion of the quadrupolar distortion of the conduction electrons which is induced, directly or indirectly by the *nuclear* Q moment. The presence of this effect has not been widely recognized, the fifth, sixth, and seventh terms of Eq. (5.25) being omitted from previous formulations. Attempts to at least partially include the influence of a distorted core on conduction electrons are represented by Das' and co-workers' (Pattnaik *et al.*, 1977; Thompson *et al.*, 1978a, 1978b) use of OPW wave functions to compute the interaction energy with deformed core orbitals and by the calculation of the induced moment in the screening charge about the origin by Kaufmann and Vianden (1978). Both of these attempts assumed a nuclear-induced core distortion and thus correspond only to the fourth term of Eq. (5.25). Nuclear-induced distortion of the conduction electrons interacting with lattice-induced core distortion was not considered. The separation of the conduction electron distortion into two additive terms, a lattice-oriented and a nuclear-oriented component, is valid within first-order perturbation theory.

Since Lodge considers the unperturbed-core and conduction-electron systems as initially spherical, the antishielding factors for the core and the moment densities of the conduction-electron distribution each arise from first-order perturbation of the corresponding electron states. The second and third terms of Eq. (5.25) are thus first order in core and conduction wave functions, respectively. The fourth and fifth terms are first order in both core and conduction-electron perturbations and thus are second order in the combined electronic states. Lodge's approximate treatment considers each system separately, however, with the understanding that repeated solutions for one set of electron states using revised results for the other set would eventually converge to self-consistency. In this way on-

ly first-order wave functions are employed and the radially dependent factors in Eq. (5.25) may be viewed as representing their final (and unknown) self-consistent counterparts. Terms which would have been of second order in either one or the other of the core or conduction states have been neglected. Somewhat in contradiction to this philosophy, the last two terms of Eq. (5.25) are of third order in the perturbing potentials for the joint core-plus conduction-electron system since there are two moment densities multiplying an antishielding factor. A large number of other third-order terms which one could formulate are omitted and the significance of these last two terms may be questioned.

The new antishielding factor, $\beta(r)$, is given by

$$\beta(r) = \frac{-1}{V_{zz}^{\text{Latt}}} \left[r^{-5} \int_0^r r'^5 V_{zz}^{\text{Core}}(r') dr' + \int_r^\infty V_{zz}^{\text{Core}}(r') dr' \right], \quad (5.26)$$

which is, formally, very much like Eq. (2.13) for $\gamma(r)$. In Eq. (2.13), $Q_i(r)dr$ represented the quadrupole moment induced by the nuclear moment in the core electrons between r and $r+dr$. Analogously in Eq. (5.26), $V_{zz}^{\text{Core}}(r)dr$ represents the EFG induced by the external lattice field in the core electrons between r and $r+dr$. [The distinction between the nuclear-induced core moment $Q_i(r)$ and the lattice-induced core EFG, $V_{zz}^{\text{Core}}(r)$, is completely analogous to the distinction between $Q^{\text{Cond}}(r)$ and $V_{zz}^{\text{Cond}}(r)$ discussed above.] Just as $-\gamma(r)Q$ can be considered as an additional effective moment to interact with the EFG due to source charge at r , so can $-\beta(r)V_{zz}^{\text{Latt}}$ be considered as an additional effective EFG to interact with the *moment* of the source charge at r . Since the conduction electrons have been assumed to have a nuclear-induced moment $Q^{\text{Cond}}(r)$, the $\beta(r)$ factor will enter into the expression for the nucleus-lattice interaction, as in Eq. (5.25). It is clear from the above summary of Lodge's approach that the statement in Sec.II.C concerning the identity of the two viewpoints of core distortions due to the nuclear moment or the external gradient is only true in the absence of the conduction electrons when the distinction between $\gamma(r)$ and $\beta(r)$ is lost. The basic notion, however, that, to first order, the total-gradient and total-moment viewpoints are each legitimate, is still true if one considers the core plus conduction electrons as a single system. In this context, the factor $\beta(r)$ would appear in the total-moment approach, but would be replaced by a conduction-electron analog of $\gamma(r)$ which provides antishielding of the lattice-induced EFG in the core, i.e., $V_{zz}^{\text{Core}}(r)$, in the total-gradient viewpoint. Lodge's contention that explicit consideration of nuclear-induced moments cannot be avoided results from his total-energy viewpoint. As Lodge himself points out, however, each term in Eq. (5.25) is proportional to Q and the net EFG is independent of Q as long as one does not go beyond first-order perturbations in the core or conduction states. Thus, just as in Eq. (2.13), the presence of Q arises from using the nuclear-induced-moment approach as an artifice for the evaluation of purely electronic properties. No atomic orbital calculations of $\beta(r)$ have appeared as yet. A detailed application of Lodge's antishielding theory must await calculations of

$\beta(r)$ as well as explicit expressions for the conduction-electron moment densities.

The importance of the fourth term of Eq. (5.25) containing $\gamma(r)$ has already been verified for Cd and Zn metals by Pattnaik *et al.* (1977). They demonstrated that a sizable portion of the lattice-oriented conduction-electron distribution lies outside the core and is effectively antishielded by 65% of γ_∞ rather than by the much smaller Sternheimer atomic shielding factor R . Their results are confirmed by nuclear moment values, derived from a comparison of measured QI frequencies with theory, which are in agreement with experiment for Cd (Raghavan *et al.*, 1973a) and Zn (Vetterling and Pound, 1977). The fifth term of Eq. (5.25) containing $\beta(r)$ may, however, represent a smaller effect because one expects the nuclear-induced moment density of the conduction electrons, $Q^{\text{Cond}}(r)$, will be largest at large r where the factor $\beta(r)$ tends to zero and smaller at small r where $\beta(r)$ reaches its maximum. Supporting this argument are calculations for ionic systems (Beri *et al.*, 1975; Ray *et al.*, 1975) where consistency corrections to account for the interaction of nuclear-induced moments in valence electrons with the lattice-oriented core amount to only $\leq 15\%$.

To this point, the discussion of antishielding in metals has been purely formal, indicating the relative interconnections between $l=2$ distortions of ion core and mobile electron charges, the former being cast in the form of antishielding factors for historical reasons. The appearance of the formal theory is certainly not restricted to that described above and, until actual numerical calculations appear, the most appropriate form is in question. The distinction between two groups of electrons is not formally necessary. One is simply interested in the response of all the electrons of the metal to a perturbation potential of $l=2$ character. If such a perturbation, written as $\delta V(\mathbf{r})$, is assumed to act on the one-electron states of the system, then the correction to the electronic charge density would be

$$\delta\rho_e(\mathbf{r}) = e \int d\mathbf{r}' \alpha(\mathbf{r}, \mathbf{r}') \delta V(\mathbf{r}'), \quad (5.27a)$$

where

$$\alpha(\mathbf{r}, \mathbf{r}') = \sum_{n, n' \neq n} \psi_n^*(\mathbf{r}) \psi_{n'}(\mathbf{r}) \frac{f_n^0 - f_{n'}^0}{E_n - E_{n'}} \psi_{n'}^*(\mathbf{r}') \psi_n(\mathbf{r}'). \quad (5.27b)$$

The ψ_n are unperturbed one-electron states of energy E_n and occupation probability f_n^0 and n runs over *all* electron states of the system. If this $\delta\rho_e(\mathbf{r})$ were used to compute the EFG due to $\delta V(\mathbf{r})$, the resulting electron-state scalar products would have the form of antishielding factors, not only for the core electrons, but for all electrons. Thus one could envision using the microscopically derived wave functions for the mobile electrons to compute the antishielding factor appropriate to them. It is also clear that $\alpha(\mathbf{r}, \mathbf{r}')$ is a generalized screening function since if one were to replace the ψ_n functions by plane waves, $\psi_n \rightarrow |\mathbf{k}\rangle$ and $\psi_{n'} \rightarrow |\mathbf{k}+\mathbf{q}\rangle$, then Eq. (5.27b) would have the form of a free-electron-gas dielectric screening function as in Eq. (5.7). Thus, in a general sense, the electron response can be formulat-

ed in the language of the charge-screening theory, or the microscopic theory, or a combination of both. Which terms are called antishielding terms and which are called screening terms is immaterial, since the two concepts are seen in fact to be one and the same for both core and conduction electrons. Of course, in actual computations, explicit assumptions for the ψ_n wave functions must be made, but the point to be stressed is that antishielding phenomena can be incorporated into any theoretical approach in a straightforward manner.

Primarily in the context of defect-created EFG's at host nuclei in cubic metals, another form of enhancement factor has been defined by Kohn and Vosko (1960). It is conventionally referred to as the Bloch enhancement factor, since it represents the ratio of the EFG computed with antishielding and periodic Bloch wave functions for the conduction electrons to that calculated for simple plane waves without antishielding. The connection between the Bloch enhancement factor and the Sternheimer antishielding factor has recently been discussed by Lodge (1977). In this paper, Lodge also discusses the effect of orthogonalization of conduction states to those of the ion core and, in a subsequent publication (Lodge, 1978), applies these concepts and a simplified version of Eq. (5.25) to computation of the EFG in several *sp* metals.

E. The EFG at impurities

No explicit calculations within either the microscopic or charge-screening framework have been reported for the EFG at an isolated nontransition-element impurity in an otherwise undisturbed noncubic host. One can envision, however, the necessary qualitative attributes which a proper theory must incorporate to handle the impurity problem and account for the trends discussed in the previous section. The correlation of the EFG to the value of $(1-\gamma_\infty)$ of the impurity suggests that the quadrupolar deformation of the impurity ion core must be considered. This implies orthogonalization to deformed core orbitals in the OPW method, nonspherical core potentials in the APW method, and nonspherically distributed screening charge about the origin in the charge screening method. These factors are of course also needed in pure systems. The correlation of the EFG to impurity valence also implies, in the charge screening context, that nonspherical screening charge is required, since additional screening charge needed to compensate the impurity ΔZ would not influence the EFG if it were spherically disposed. In microscopic approaches, use would have to be made of an impurity ion potential or pseudopotential which provides for the additional valence electron states at the impurity site. The coupling of the impurity to neighboring host ions would also be crucial since it determines the change in local geometry due to relaxation of the surrounding host lattice. Ion-ion pair potentials have been derived from screened pseudopotentials and in simple metals have successfully described known lattice-dynamical (Dagens *et al.*, 1975; Rasolt and Taylor, 1975) and impurity-diffusion properties (Schober *et al.*, 1975). These methods could be applied to the calculation of the EFG.

Nontransition metal hosts containing transition-metal

impurities have long been known to display interesting effects in their magnetic properties, electronic specific heats, and electrical resistivities. The theoretical description of these phenomena have been largely based on the Friedel-Anderson model (Anderson, 1961; Friedel, 1958) which describes the formation of a localized, virtually bound *d* state within the conduction band of the host. Recently Piecuch and Janot (1974, 1975) have used this theory to obtain an expression for the local electronic contribution to the EFG at transition-metal impurities in normal noncubic metals. Their result is formally identical to Eq. (5.6) where the density-of-states factor is to be interpreted as the density of *d* states, from the virtually bound level, at the Fermi surface, and expectation values are taken over the tight-binding *d* orbital of the impurity. The negative sign in Eq. (5.6) is consistent with experimentally observed sign reversals for an Fe impurity in Be (Janot *et al.*, 1974), Zn and Cd (Qaim, 1969) hosts. This agreement, however, can not yet be considered a conclusive verification of this approach, since nontransition impurities have also shown sign reversals in these hosts.

With the advent of large electronic computer facilities, it has also been possible to study metals by a cluster calculation technique where "exact" quantum-mechanical solutions for a limited number of ions in a cluster are obtained numerically (Bauschlicher *et al.*, 1975, 1976; Brewington *et al.*, 1976; Johnson, 1975b; Melius *et al.*, 1976). For the EFG problem, the subtleties of the quadrupolar distortions in ion cores and mobile electron distributions would be an added complexity in this method as well. By and large, the necessary theoretical tools applicable to the problem at hand have been used in other areas of physics and it remains to apply them here.

VI. APPLICATION TO SYSTEMATIC TRENDS

A. Temperature dependence

With regard to the EFG temperature dependence, an explanation is required for the qualitative experimental observations that the dependence is, in most instances, stronger than that anticipated from the effect of thermal lattice expansion on the point-ion lattice sum. Additionally, the quantitative $T^{3/2}$ behavior requires a theoretical explanation. In the context of the approaches to the calculation of the EFG described in the previous section, the problem of the temperature dependence has also been treated by several authors. The effects of Fermi-surface electrons are discussed below, followed by subsections describing the incorporation of thermal lattice vibrations into the theory.

1. Fermi surface electrons

Although thermal lattice and molecular vibrations were believed to account for the *T* dependence seen in nonmetals (Bayer, 1951; Kushida *et al.*, 1956), many believed for some time that this was not the case in metals, primarily because Watson *et al.* (1965) found that the electron-phonon interaction was not an important effect in this regard. Watson *et al.* were in fact only stating that phonons did not influence the Fermi-surface electron spatial character and therefore had no effect

on the contribution to the EFG represented by Eq. (5.6). For this contribution, they proposed that a significant T dependence would arise from a thermally induced repopulation of electron states of different symmetry at the Fermi surface. They arrived at an expression which related the T dependence to the curvature of the density of states, $\partial^2\eta(E)/\partial E^2$, evaluated at E_F . Since the importance of the Fermi-surface contribution in any specific case has not itself been definitely established, it is not possible at this time to decide whether the thermal repopulation hypothesis is needed to explain any particular result.

For the case of pure transition metals where Piecuch and Janot (1977) have elaborated the Fermi-surface-electron effects in more detail, qualitative predictions of the expected temperature dependence in the pure $3d$ -, $4d$ -, and $5d$ -metals were also made. In their formulation, all contributions to the local electronic EFG are proportional to the density of d states at the Fermi surface. The predictions are based on the known temperature variation of the magnetic susceptibility, which is proportional to the density of states, and on the relative size of the electronic and lattice contributions to the EFG. Unfortunately, no experimentally determined temperature-dependence data in these pure transition metals are available. In most instances, a decrease with temperature in the net EFG is expected. This is the usual observation in all metals and, as discussed below, could also be the result of thermal lattice vibrations. For Hf, Ru, and possibly Y, however, an increase with temperature is predicted by Piecuch and Janot. No other theoretical approach, to our knowledge, has made such a prediction, and measurement in these systems ought to provide a critical test of the sensitivity of the EFG to Fermi-surface effects. In sp metals for which data is currently available, recent successes in showing the importance of thermal lattice vibrations have demonstrated that the Fermi-surface effects are not a major contribution to the temperature dependence. The conditions under which Fermi-surface considerations are more or less significant compared to lattice vibrations has been discussed by Kolk (1976).

2. Lattice vibrations

Although several authors have mentioned thermal vibrations in the context of the EFG T dependence in metals, with varying degrees of faith in their importance, Quitmann *et al.* (1975) were the first to demonstrate that they could at least qualitatively account for the observed strong dependences. Their basic approach was to assume that the total EFG would be in some way proportional to the lattice contribution (a concept later supported by the universal correlation discussed in Sec. IV.B.1). The EFG tensor component V_{ij} , evaluated at the origin, is then a function of the instantaneous positions of the lattice ions, $\mathbf{r}^{(n)}(t) = \mathbf{r}_0^{(n)} + \Delta\mathbf{x}^{(n)}(t)$, where n enumerates the ions not at the origin, $\mathbf{r}_0^{(n)}$ are the equilibrium ion positions, and $\Delta\mathbf{x}^{(n)}(t)$ are the time-dependent ion displacements. Expanding V_{ij} in a Taylor series about equilibrium and taking a time average yields the relation

$$\langle V_{ij}(\{\mathbf{r}^{(n)}(t)\}) \rangle = V_{ij}(\{\mathbf{r}_0^{(n)}\}) + \frac{1}{2} \sum_{\mu, \nu, i, m} \frac{\partial^2 V_{ij}(\{\mathbf{r}^{(n)}\})}{\partial x_{\mu}^{(i)} \partial x_{\nu}^{(m)}} \Big|_{\{\mathbf{r}_0^{(n)}\}} \times \langle \Delta x_{\mu}^{(i)}(t) \Delta x_{\nu}^{(m)}(t) \rangle, \quad (6.1)$$

where the subscripts $\mu, \nu = 1, 2, 3$ refer to x, y, z components. The linear term is absent because the time average of $\Delta\mathbf{x}^{(n)}$ vanishes. The drastic assumption was then made that Eq. (6.1) could be replaced by $V_{ij} = V_{ij}^0 + C\langle(\Delta x)^2\rangle$ where the mean square vibration amplitude $\langle(\Delta x)^2\rangle$ was given in the harmonic Debye model as

$$\langle(\Delta x)^2\rangle = \frac{3\hbar^2}{M_a k_B \theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{z dz}{e^z - 1} \right]. \quad (6.2)$$

Here θ_D is the Debye temperature, k_B is Boltzmann's constant, and M_a is the ion mass. In this way, the T dependence of the EFG in In metal was fit reasonably well, but not precisely, by a Coulomb-point-charge lattice sum with the two adjustable parameters being the value of V_{zz} at $T=0$ and the coefficient C .

It should be noted that the replacement by $C\langle(\Delta x)^2\rangle$ of the second term in Eq. (6.1) is, strictly, not correct for a lattice of unscreened point charges with Coulomb potentials. This is easily seen by noticing that using a single $\langle(\Delta x)^2\rangle$ implies first that the lattice vibrations are considered uncorrelated, i.e., a lattice of independent and identical ions. Thus the factor $\langle \Delta x_{\mu}^{(i)}(t) \Delta x_{\nu}^{(m)}(t) \rangle$ reduces to $\langle \Delta x_{\mu}^{(i)}(t) \Delta x_{\nu}^{(i)}(t) \rangle \delta_{im}$, where δ_{im} is the Kronecker delta. In addition, isotropy in the vibrations is implied, further reducing this factor to $\langle (\Delta x_{\mu}^{(i)})^2 \rangle \delta_{\mu\nu} \delta_{im}$. Since $(\Delta x_1)^2 + (\Delta x_2)^2 + (\Delta x_3)^2 = (\Delta x)^2$ and each of the $(\Delta x_{\mu})^2$ are the same, we have $\langle (\Delta x_{\mu})^2 \rangle = \langle (\Delta x)^2 \rangle / 3$ and the second term of Eq. (6.1) becomes

$$\frac{1}{6} \langle(\Delta x)^2\rangle \sum_i \sum_{\mu} \frac{\partial^2 V_{ij}(\{\mathbf{r}^{(n)}\})}{\partial x_{\mu}^{(i)2}} \Big|_{\{\mathbf{r}_0^{(n)}\}}. \quad (6.3)$$

Since $V_{ij}(\{\mathbf{r}^{(n)}\})$ is the sum of the contributions of individual ions $\sum_m V_{ij}(\mathbf{r}^{(m)})$, one only has terms in the sum over l of the form $\sum_{\mu} \partial^2 V_{ij}(\mathbf{r}) / \partial x_{\mu}^2$. Remembering that V_{ij} is defined as $\partial^2 V / \partial x_i \partial x_j$, interchanging the order of the partial differentiation yields $\partial^2 / \partial x_i \partial x_j \sum_{\mu} V_{\mu\mu}(\mathbf{r})$. But $\sum_{\mu} V_{\mu\mu}$ is just the Laplacian, $\nabla^2 V$, of the potential which vanishes at the origin according to Laplace's equation since the charge producing the ionic potential is distant from the origin. Physically, this simply verifies that if a point charge vibrates isotropically so as to appear as a spherically distributed charge density, it still appears in the time average as a point monopole at the equilibrium position as far as fields external to the vibrating charge are concerned. This is of course the central idea, since in a real metal, the electronic charge which permeates the lattice may also be considered to "vibrate" with the ions. Thus the effective ion potential is not Coulombic and satisfies Poisson's equation, $\nabla^2 V \neq 0$, at the origin. It is this mechanism which would primarily account for the presence of a term containing $\langle(\Delta x)^2\rangle$ in the EFG, the importance of which Quitmann *et al.* demonstrated. Anisotropy and anharmonicity in the vibrations do in principle also dictate such a term, but those effects are not strong

enough alone to generate the sizable T dependence of the EFG.

Starting then from the recognition that it is the electrons of the metal which mediate the effect of lattice vibrations on the EFG, two distinct approaches to the elucidation of the T dependence have developed. A microscopic theory was arrived at independently by Jena (1976), who included temperature effects in the OPW approach, and later by Collins (1976) who used the APW method. In both instances explicit EFG computation was avoided in favor of finding only expected trends with temperature. The alternative approach, the charge screening formalism, is embodied in the work of Nishiyama *et al.* (1976).

3. Microscopic approaches

The microscopic approaches dealt solely with the local electronic term of Eq. (2.12), to which a lattice EFG (including effects of thermal expansion) is added. The influence of temperature on pseudopotentials was introduced by Kasowski (1969) who successfully explained the temperature variation of the Knight shift in Cd. The general result relating the matrix elements of the pseudopotential at finite temperature to those at $T = 0$ K is

$$\langle \mathbf{k} + \mathbf{K} | V_{ps} | \mathbf{k} \rangle = e^{-W(\mathbf{K}, T)} \langle \mathbf{k} + \mathbf{K} | V_{ps}^0 | \mathbf{k} \rangle, \quad (6.4)$$

where $W(\mathbf{K}, T)$ is the usual Debye-Waller factor (DWF) which is proportional to the mean square vibration amplitude of the lattice. It is given in the harmonic Debye approximation by

$$W(\mathbf{K}, T) = \frac{1}{2} K^2 \langle (\Delta x)^2 \rangle, \quad (6.5)$$

where $\langle (\Delta x)^2 \rangle$ is that of Eq. (6.2). Jena (1976) pointed out that it is just those matrix elements of Eq. (6.4) which enter directly into the determination of the coefficients in Eq. (5.5) for the electronic wave function and thus into the so-derived electronic charge density. He then expanded the exponential factor in Eq. (6.4), keeping only the first-order term in W , and arrived at the result for the charge density

$$\rho_e(\mathbf{r}) = \rho_e^0(\mathbf{r}) - \tilde{\rho}_e^0(\mathbf{r}) \phi(T/\theta_D), \quad (6.6)$$

where $\phi(T/\theta_D)$ is the quantity in brackets in Eq. (6.2) and contains the entire T dependence of the electronic charge density. Relating $\rho_e(\mathbf{r})$ to the EFG by Eq. (2.14), the EFG becomes

$$V_{zz}(T) = V_{zz}(0) [1 - \beta \phi(T/\theta_D)]. \quad (6.7)$$

This is essentially the expression of Quitmann *et al.* (1975), except that it is intended by Jena (1976) to apply only to the electronic contribution to the EFG. Nevertheless, a similar strong dependence on T was obtained which, when added to the lattice contribution, replicated, to within $\approx 5\%$, observations for Cd and Zn metals after normalizing to $V_{zz}(0)$ and fitting the slope parameter β to the data.

Jena also argued that over a substantial range of temperature the Debye integral, $\phi(T/\theta_D)$, yielded a $T^{3/2}$ dependence which, he contended, explained that quantitative feature of experiment. In fact, at low T , $\phi(T/\theta_D)$ approaches the zero-point value as T^2 , and at

high temperature increases linearly with T , thus passing through an intermediate region where a $T^{3/2}$ behavior is approximately followed. Despite the approximate nature of this observation, Jena factored out in a phenomenological way a $(T/\theta_D)^{3/2}$ from the $\phi(T/\theta_D)$ and, combining it with the prefactor of $\phi(T/\theta_D)$ in Eq. (6.2), deduced that the slope parameter β , in addition to depending on the band structure of the metal, would show a dependence on mass and Debye temperature according to $(M_a \theta_D^{5/2})^{-1}$. He claimed this was in rough agreement with observations for metals of similar band structure. Since the Debye temperature of a solid scales as $M_a^{-1/2}$, a predicted $M_a^{1/4}$ dependence on mass for β was expected. A crucial test of this hypothesis was provided by Raghavan and Raghavan (1978b) who searched for an isotopic mass effect in the T dependence for a ^{69}Ge probe in isotopically enriched host lattices of ^{114}Sn and ^{124}Sn . The expected effect was $\Delta V_{zz}(114-124)/V_{zz} = -0.41\%$, whereas a null result of $-(0.12 \pm 0.15)\%$ was found.

This result has now been understood by a closer examination of the $\phi(T/\theta_D)$ integral which demonstrates that factoring out $\theta_D^{3/2}$ was not correct. In fact, not only in the harmonic Debye approximation but also to all orders of anharmonicity (Maradudin and Flinn, 1963) one finds that, with the exception of the zero-point vibration term, all terms scale as powers of $(M_a \theta_D^2)$, implying that no isotopic mass effect should exist at elevated temperature. Thus the failure to verify this aspect of Jena's proposal does not vitiate his general result of the influence, through a DWF, of thermal lattice vibrations. A search for the zero-point isotopic mass effect by NQR in In metal is currently in progress (Kaufmann *et al.*, 1977).

Jena pointed out that a better fit to experimental T dependences might be achieved by incorporating effects of anharmonicity and realistic phonon frequency distributions into his model. Collins (1976), who arrived at a similar DWF dependence using an APW viewpoint, has shown that if one refrains from expanding the exponential factor in Eq. (6.4) and allows for a temperature-dependent Debye temperature $\theta_D(T)$, one can fit experimental data precisely. This result verifies the need to include real phonon frequencies and anharmonic effects, a T dependence in θ_D being one way to do so. A first-principles investigation of the individual contributions of the isotropic, anisotropic, and anharmonic lattice vibrations to the lattice and electronic EFG in Cd metal has been presented by Thompson *et al.* (1978a and 1978b). They found that the lattice EFG is primarily affected by the anharmonic phonons and also, to some extent, by the anisotropic phonons, but not at all by isotropic vibrations (as was shown above). On the other hand, the isotropic component almost entirely accounts for the variation of the electronic EFG. A recent OPW calculation of the EFG in Mg metal by Jena (1978) has yielded excellent agreement with experiment at $T = 0$ and 295K. However, when one considers the problem of accounting for the effects of vibrations of three types (i.e., isotropic, anisotropic, and anharmonic) on both the lattice and electronic contributions to the EFG, it is not surprising that an *ab initio* microscopic calculation has yet to yield a general and precise $T^{3/2}$ result.

In both the work of Jena and Collins, the multiplicative

factor K^2 in the DWF was taken to be the square of some sort of average effective reciprocal lattice vector of the order of the size of the first few Brillouin zones or, alternatively, the reciprocal radius of the Wigner-Seitz sphere. In matching data therefore it was included in the adjustable slope parameter of the models. This is one of the problems avoided by employing the more macroscopic approach of charge screening developed by Nishiyama *et al.* (1976).

4. Charge screening approach

Returning to Eq. (5.13) and (5.17) which express the EFG in terms of a lattice sum over ions (excluding the origin) located at positions \mathbf{r}_i , we see that thermal vibrations can be directly introduced by substituting $\mathbf{r}_i(t) = \mathbf{r}_i^0 + \Delta\mathbf{x}_i(t)$ and performing a time average. Assuming isotropic, independent, and uncorrelated vibrations, this reduces to the evaluation of the expression,

$$\sum_i' e^{i\mathbf{q}\cdot\mathbf{r}_i^0} \langle e^{i\mathbf{q}\cdot\Delta\mathbf{x}(t)} \rangle. \tag{6.8}$$

The quantity to be averaged in brackets above takes the form of a DWF and is given by (Maradudin *et al.*, 1963)

$$\langle e^{i\mathbf{q}\cdot\Delta\mathbf{x}(t)} \rangle = e^{-1/2\langle (\mathbf{q}\cdot\Delta\mathbf{x}(t))^2 \rangle} = e^{-q^2\langle (\Delta x)^2 \rangle/3}, \tag{6.9}$$

while the remaining factor

$$\sum_i' e^{i\mathbf{q}\cdot\mathbf{r}_i^0} = S(\mathbf{q}) - 1, \tag{6.10}$$

is the structure factor for the static lattice.

Introducing the above into Eqs. (5.13) and (5.17) yields for the principal component of the EFG,

$$\begin{aligned} \phi_{zz}(T) = 2\phi_2^{(0)} = \frac{-\alpha(1-\gamma_\infty)}{12\pi^3} \int \frac{V_c(\mathbf{q})}{\epsilon(\mathbf{q})} q^2 P_2(\cos\theta_q) \\ \times [S(\mathbf{q}) - 1] e^{-q^2\langle (\Delta x)^2 \rangle/3} d\mathbf{q}. \end{aligned} \tag{6.11}$$

One sees that the factor containing the $\langle (\Delta x)^2 \rangle$ depends on q^2 just as in the microscopic approaches it depended on K^2 . So in principle each component in the Fourier space shows a different T dependence. For precise comparisons, one may indeed have to evaluate Eq. (6.11) directly. It is very instructive, however, to write down the result of an asymptotic approximation to Eq. (6.11) which is derived as mentioned earlier by using the singular nature of $\epsilon(q)$ at $q=2k_F$ and noting that all other factors in the integral are smooth functions of q at $q=2k_F$. This results in the expression

$$\phi_{zz}(T) = \alpha(1-\gamma_\infty) \phi_{zz}^{sc}(T) e^{-4k_F^2\langle (\Delta x)^2 \rangle/3}, \tag{6.12}$$

where $\phi_{zz}^{sc}(T)$ is the static lattice sum of Eq. (5.17), including thermal expansion of the lattice, and now the DWF contains an explicit dependence on k_F , the Fermi momentum, rather than a more vaguely specified reciprocal lattice vector.

Aside from the prefactor, $\alpha(1-\gamma_\infty)$, Eq. (6.12) can be evaluated for a metal entirely from empirical data. Nishiyama *et al.* showed that by inserting known thermal expansion into the screened lattice sum, ϕ_{zz}^{sc} and known

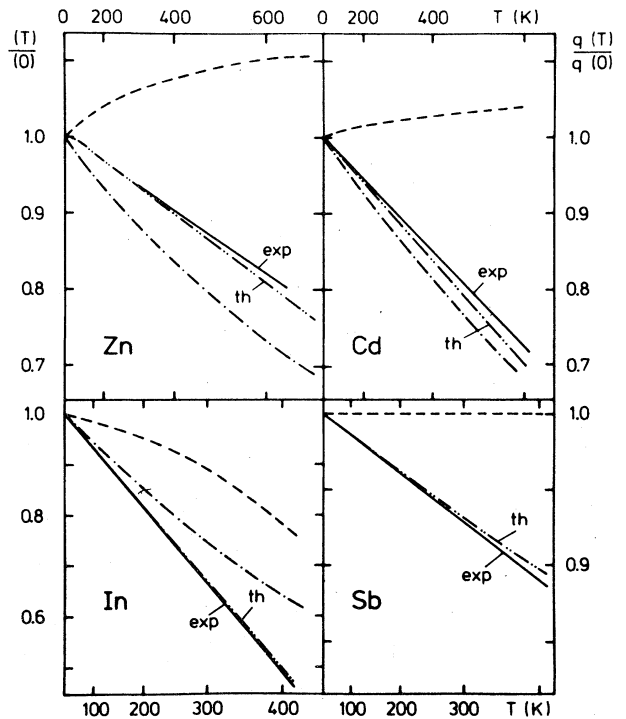


FIG. 29. Comparison of normalized experimental EFG temperature variation (solid line) with the charge-screening theory predictions (dot-dot-dash line), for Zn, In, Cd, and Sb, using Eq. (6.12). The dashed line is the screened lattice sum, $\phi_{zz}^{sc}(T)$, alone and the dot-dash line is the Debye-Waller factor alone. Note that the divisions along the temperature axis are scaled according to $T^{3/2}$. (Taken from Nishiyama *et al.*, 1976.)

values of k_F and $\langle (\Delta x)^2 \rangle$ as a function of temperature into the DWF, the normalized T dependence of the EFG in Zn, Cd, In, and Sb could be accurately matched with *no adjustable parameters*. Figure 29 demonstrates the excellent agreement with experiment. Figure 30 shows a similar result for Sn metal where data are available

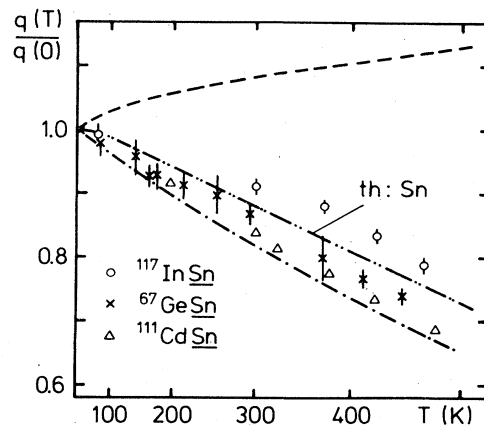


FIG. 30. Comparison of charge-screening theory prediction for the T dependence of the EFG in pure Sn metal with impurity EFG measurements. The meaning of the curves and the horizontal axis scale are the same as in Fig. 29. (Taken from Nishiyama *et al.*, 1976.)

for impurities. Here, although the general trend is reproduced, the data for the various impurities show significant deviation from the theory for pure Sn. At the present time, this represents the most successful attempt to quantitatively explain the EFG temperature variation. It was found that the dominant source of the strong T dependence arises from the DWF, but that it is essential to include the influence of lattice expansion embodied in $\phi_{zz}^{\text{sc}}(T)$ to obtain quantitative agreement. The theoretically predicted curves appear to precisely follow a $T^{3/2}$ dependence although this arises in no obvious analytical way. The fact that lattice and electronic contributions are united in a single term in Eq. (6.12) goes a long way toward justifying the universal nature of the $T^{3/2}$ law which was hard to understand in the context of Eq. (2.12).

The appropriateness of the DWF in Eq. (6.4) or (6.12) is strongly supported by the experimental observation of Torgeson and Borsa (1976) that the EFG at Nb in $2H-NbSe_2$, a quasi-two-dimensional layered inter-metallic compound, depended linearly on T . By examining the form of the Debye integral $\phi(T/\theta_D)$ for a quasi-two-dimensional case, they showed that a linear rather than $T^{3/2}$ dependence was to be expected. The outstanding problems remaining in the charge-screening formulation are the proper handling of the prefactor, $\alpha(1 - \gamma_\infty)$, to account for experimental magnitudes and signs and the explanation of why this approach yields an empirical $T^{3/2}$ power law.

It should be noted that an aesthetically pleasing alternative proposal to explain the $T^{3/2}$ law was put forth by Christiansen, Heubes, and co-workers (Christiansen *et al.*, 1976; Heubes, 1975). By drawing an analogy to spin-wave systems where low-temperature magnetic susceptibility varies as $T^{3/2}$ due to a collective excitation of the spin system (magnons) (Kittel, 1963, p. 56), they hypothesized a collective electronic excitation to account for the EFG variation. The model envisions the quadrupoles represented by the ion cores, distorted under the influence of the noncubic environment, as tending to align with the external EFG but fluctuating thermally about the fully aligned configuration. An

interaction between neighboring quadrupoles, mediated by the conduction electrons, would then allow a description in terms of collective excited modes ("quadrans") which, given the proper dispersion relation, would yield an analytic $T^{3/2}$ law for the EFG at nuclei. As elegant as this proposition may be, there is no quantitative estimate of the strength of the interquadrupole coupling and no evidence from, for example, specific heat measurements, that such excitations exist. One empirical observation is consistent with this model. That is the apparent trend that systems with large EFG's have weaker T dependence and vice versa. Figure 31 illustrates this for ^{111}Cd probes in various hosts. Considerably more information must be gathered, however, on the expected strength of this effect and its possible relation to thermal lattice vibrations before it can be taken as an alternative explanation to previously mentioned approaches.

5. Impurities

It is evident from Figs. 22 and 30 that the temperature dependence of the EFG at an impurity is not necessarily identical to that found for the pure host metal. The natural explanation for this, within the thermal vibration approach, is the existence of a local vibrational mode at the impurity site. A local mode may arise from the difference in mass of host and impurity. An impurity lighter than the host would show a greater vibrational amplitude (i.e., a lower effective Debye temperature) and thus a steeper temperature dependence. The data however do not scale in a simple way with impurity to host-mass ratio. An altered effective force-constant between the impurity and near-neighbor host atoms can also account for a local vibrational mode. This possibility has not been treated theoretically to explain EFG data. In principle, the pseudopotential methods of deriving impurity-host pair potentials could be used for this purpose.

Fermi-surface electrons may also be significant, particularly for the case of a transition-metal impurity. The specific case of an Fe impurity in Be metal epitomizes the dichotomy of views on the cause of the temperature dependence. The EFG at Fe decreases strongly with temperature whereas, at Be in Be, the dependence is quite weak (Janot *et al.*, 1974). Fe in Be is one of the few systems that does not follow a $T^{3/2}$ law well. At low T , a quadratic dependence is seen which goes over to a linear dependence at high temperatures. Piecuch and Janot (1974) have been able to explain this behavior convincingly by attributing it to the localized spin fluctuation attendant to the presence of a virtually bound $3d$ level which overlaps the Fermi level. Their viewpoint is strongly supported by the observation of similar temperature dependences in the electrical resistivity of normal metals with transition-element impurities, such as Mn in Al.

On the other hand, there is also evidence that a local vibrational anomaly may exist in this system. In addition to the QI, the Mössbauer effect measurements of Janot *et al.* (1974) determined the recoilless fraction for the Mössbauer gamma ray as a function of temperature, from which can be derived an effective Debye

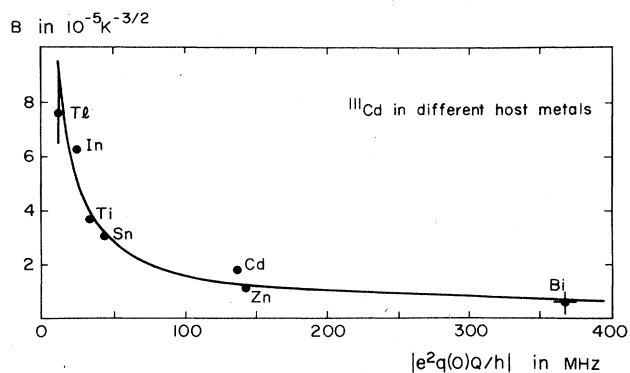


FIG. 31. For a Cd impurity in several hosts, the temperature-dependence slope parameter B of Eq. (4.4) is plotted against the $T=0\text{ K}$ value of the EFG $[V_{zz}(0)$ of Eq. (4.4)]. The inverse correlation of these parameters was taken as evidence in support of the "quadrans" hypothesis by Christiansen *et al.* (1976) from whom this figure is taken.

temperature and force-constant ratio for the impurity. Using an improved value for the host Debye temperature, Kaufmann and Vianden (1977) found that the Fe-Be force constant is substantially weaker than that of Be-Be. In addition, in the similar system of Os in Be, they found by ion-beam channeling that the Os is anomalously displaced from a substitutional lattice position at room temperature. If the Fe in Be also samples regions unusually far from the equilibrium substitutional site, this could account for the strong EFG temperature dependence. The choice of explanations, or combinations thereof, for the Fe in Be system in particular, and similar systems in general, must await more extensive and accurate experimental data.

B. Pressure dependence, etc.

The only microscopic calculation, to our knowledge which has been done to predict the EFG variation with hydrostatic pressure has been reported by Mohapatra *et al.* (1973) for Cd metal. Their result was later corrected slightly in Das (1975). By repeating the OPW-pseudopotential calculation using lattice parameters appropriate to a pressure of 50 kbar, a ratio $V_{zz}(P=0)/V_{zz}(50\text{kbar})=1.28$ was predicted, which compares favorably to the experimental value of 1.25 (Raghavan *et al.*, 1972). No explicit pressure dependence was assumed for the form of the pseudopotential in the calculation, all variation being derived from the change in lattice geometry alone.

Application of the free-electron charge-screening method (Nishiyama and Riegel, 1976) using Eq. (6.12) has been extremely successful in predicting pressure dependences and elucidating the main source of the observed variations. In Eq. (6.12), pressure enters through both the screened-ion lattice sum due to changes in lattice constants and k_F , and in the DWF by changes in k_F and $\langle(\Delta x)^2\rangle$. Lattice constant variation, obtained from x-ray diffraction and compressibility data, enters directly into the geometrical aspect of the lattice sum as well as into the form of the screened potential through the variation of k_F which is proportional to $[Z/V(P)]^{1/3}$, the cube root of the number of electrons per unit volume. $V(P)$ is the pressure-dependent atomic volume of the lattice. The DWF behavior can be estimated from $k_F^2 \propto V^{-2/3}$ and $\langle(\Delta x)^2\rangle \propto \theta_D^{-2}$, the latter being a result of the harmonic Debye model for $T \geq \theta_D$. These combine to yield

$$\frac{k_F^2(P)\langle(\Delta x)^2\rangle_P}{k_F^2(0)\langle(\Delta x)^2\rangle_0} = \left[\frac{V(P)}{V(0)} \right]^{2\gamma-2/3}, \quad (6.13)$$

where γ is the Grüneisen parameter, defined as $\gamma = -d \ln \theta_D / d \ln V$, which is known for many metals (Mahesh, 1967). In this way the normalized pressure dependence of the EFG in Cd and In metals was reproduced with no adjustable parameters. The relative importance of the lattice sum factor and the DWF is reversed here compared to the temperature-dependence investigation. From Fig. 32, one sees that, although the DWF is needed to get precise agreement, the screened lattice sum is most sensitive to pressure. Thus the pressure dependence is primarily due to change in lattice geo-

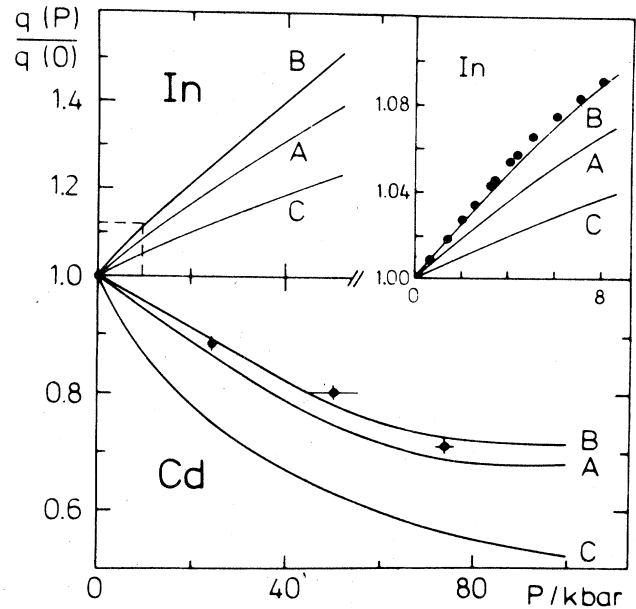


FIG. 32. Comparison of the charge-screening theory [Eq. (6.12)] prediction (curve B) for the normalized pressure dependence of the EFG in Cd and In metals with experiment (solid line). Curves A and C represent the variation of the screened lattice sum factor in Eq. (6.12) and of an unscreened Coulomb potential lattice sum, respectively. (Taken from Nishiyama and Riegel, 1976.)

metry. It is likely that this is why the microscopic calculation (Mohapatra *et al.*, 1973) which neglected thermal vibration effects in Cd was successful. Qualitative differences between the dependences of screened lattice sums on lattice geometry for close-packed and

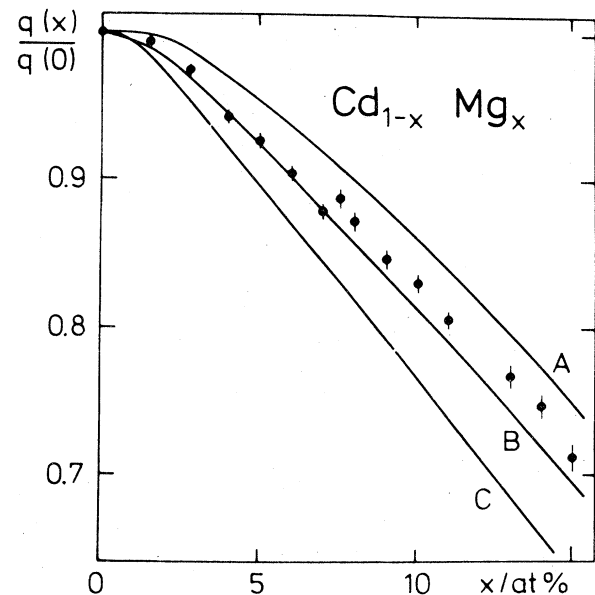


FIG. 33. Comparison of the charge-screening theory [Eq. (6.12)] prediction for the normalized variation of the EFG at Cd in CdMg alloys, as a function of Mg concentration. Curves have the same meaning as in Fig. 32. (Taken from Nishiyama and Riegel, 1976.)

open lattices have been pointed out by Butz (1978a).

Another successful application of charge screening has to do with the variation of the EFG, at host nuclei, with solute concentration in a noncubic binary alloy. This topic is, strictly speaking, not among those intended for this review, but rather relates to the problem of impurity-generated EFG's at neighboring host atoms, just as in cubic hosts. In the specific case, however, of a binary alloy of two isoelectric elements where the primary effects of varying concentration are lattice-constant and elastic-constant changes, one may test the theory intended for pure systems. Nishiyama and Riegel (1976) have done this for $\text{Cd}_{1-x}\text{Mg}_x$ alloys with $0 \leq x \leq 0.15$. Their results are shown in Fig. 33 where good agreement with experiment (Butz and Ernst, 1975) is evident.

Although a high degree of success has been noted for the charge-screening approach to T and P dependences, some as yet unsatisfactory aspects remain. We have already mentioned the need to clarify the situation for EFG sign and magnitude prediction. Other discrepancies have been found in specific cases. For example, this method has failed to correctly account for the axial asymmetry parameter η in the α and β phases of Ga metal (Dimmling *et al.*, 1977b). Also, the T dependence of the EFG in Be metal is found to be better reproduced by the approximate asymptotic expression of Eq. (6.12) than by the exact expression of Eq. (6.11), implying a need to revise the form of the screened potential (Dimmling *et al.*, 1977a). It is hoped that suitable refinements will be forthcoming in the near future.

VII. SUMMARY

There is now available a substantial amount of experimental data concerning the QI for host and impurity species in noncubic metals. The number of entries in the table of Appendix B attests to this fact and at this writing new results continue to appear. With the ever increasing sophistication in measurement and sample preparation techniques, it is likely that this data base will grow for some time. Perhaps each experimental result which lacks a corresponding quantitative theoretical justification should in principle be considered an unresolved issue which needs to be pursued. A more conservative and hopefully more readily attainable goal, however, would be the acquisition of a fundamental understanding of which properties of a noncubic metallic system are relevant to the EFG and of how one would incorporate these into a theoretical framework which explains some general trends and exceptions thereto without requiring quantitative precision. To expect such a development only four years ago seemed quite unrealistic. With the recognition of the empirical trends described in Sec. IV.B, which encompass a great deal of data, optimism in this regard now seems justified.

For pure sp metals, the theoretical outlook is most promising at present. The variations of the EFG with changes in lattice ion positions, whether due to thermal expansion, lattice vibrations, or hydrostatic compression, have been well reproduced in several cases by the simplified charge-screening approach. It has also been

demonstrated that accurate estimates of the EFG sign and magnitude can be achieved by a first-principles microscopic calculation in those simple metals where crystal potentials and band structures are known. An important recent refinement in the latter approach is the inclusion of Sternheimer antishielding effects in the electronic contribution to the EFG. These successes lend credence to the hope that the theory may be cast in a unified form, one in which a more sophisticated screened model-potential formalism allows retention of the general single-term appearance of the screening approach [as in Eq. (6.12)] that seems most appropriate to understanding observed empirical trends while retaining parameters which may be computed from first principles.

Similar successes in transition-metal hosts have yet to be realized. These metals provide a challenge in this regard. Of particular interest is the question of the EFG from Fermi-surface electrons, the importance of which has not been conclusively demonstrated. With a reliable theory, valuable information on the orbital symmetry of electrons in these cases may be gained.

Perhaps the most intriguing of the empirical trends is the $T^{3/2}$ dependence of the QI. Although replicated by the charge-screening approach to thermal lattice vibrations and expansion, the simple power law has not been fundamentally understood. Compounding this puzzle are observations that high-temperature electrical resistivity (Bastow, 1977) and the mean-square-vibration amplitudes themselves (Riegel *et al.*, 1977) appear to follow a $T^{3/2}$ law in many cases. One senses a common underlying phenomenon here, which is a general property of the anharmonic lattice dynamics of a solid, but no clear suggestion to account for a general $T^{3/2}$ behavior has been advanced.

Two very recent investigations have reported temperature dependence anomalies which bear further study. Herzog *et al.* (1978) have found in nuclear orientation experiments that the EFG at Hg in Zn, Cd, and Re hosts at very low temperature is several times that which would be predicted by a $T^{3/2}$ extrapolation of high-temperature data. No explanation is proposed. It would be worthwhile to confirm this unexpected result through measurements of the EFG at intermediate temperatures, since it may point to the presence of a new mechanism which is only operative at low temperatures. Rasera *et al.* (1978b) have found a significant deviation from a $T^{3/2}$ behavior for $T < \approx 300\text{K}$ in the EFG at Ta in Ho metal. They ascribe the anomaly to the influence of the crystal field on the unfilled $4f$ shell of near-neighbor Ho ions. That is, as the temperature decreases, the Ho $4f$ shell develops a nonzero average alignment with the lattice field and thus presents net ionic quadrupole moments which influence the EFG at the Ta site. This is an interesting observation since, as mentioned in Sec. II.D., a lattice sum over point quadrupoles yields an EFG contribution which is small compared to the monopole sum. Thus a new electronic enhancement factor associated with the quadrupole portion alone may have to be invoked to understand this result.

By far the majority of available data concerns the EFG at impurities. However, very little theoretical

effort has been expended on these systems. All of the aspects of the problem in pure systems apply here and in addition, several questions unique to impurities arise. The universal correlation of Sec. IV.B.1 shows clearly that the size of the *total* EFG depends on the impurity ion-core distortion. In addition, the different strengths of temperature dependences for different impurities in the same host raises questions of local lattice vibrational modes as well as virtually bound d states for transition impurities. Lastly, the correlation of the EFG with impurity valence (Sec. IV.B.2) demonstrates the importance of charge-screening concepts in these cases. There is thus an acute need for a theoretical framework to apply to the impurity system data from which information on the microscopic character of dilute alloys may be derived.

The impurity problem for noncubic hosts is closely related to impurities and defects in cubic systems as studied through the nuclear QI . Several such measurements have appeared (e.g., Baumvol *et al.*, 1978, 1977, Berthier and Minier, 1977; Butt *et al.*, 1977; Iglesias-Sicardi, 1978; Livi *et al.*, 1977, 1978; Minier and Dung, 1977; Pleiter, 1977; Rinneberg *et al.*, 1978; Weidinger *et al.*, 1978; Zawislak *et al.*, 1977). The difference here is the absence of an EFG from the lattice as a whole, since only local electronic and lattice distortions contribute to the EFG. A study of these cases may shed light on the local modifications needed to handle impurities in the noncubic case as well.

Although closing the gap in our theoretical understanding of the EFG in noncubic metals may appear to be a formidable task, a successful outcome to such a pursuit would certainly enhance our knowledge of the physics of metals and of defects in metals in general. Not the least of our objectives in preparing this review has been the opportunity to stimulate interest in this field within the physics community.

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Note added in proof: Systematic correlations of the EFG with extrinsic (T and P) as well as intrinsic material properties (lattice field, impurity charge, den-

sities of states) have been alluded to in the text. Recently, Machlin and Whang (1978) have uncovered two forms of correlation with material parameters qualitatively different from those considered previously. They find an empirical correlation between the elastic shear modulus, C_{44} , of a metal and the quadrupolar polarizability, α_q (as tabulated by Eieock and Johnson 1969) of the constituent ions. In retrospect, it is a quite plausible result since, whether the external stress applied to an ion is pictured as arising from an EFG or from a mechanically induced shear strain of the lattice, the resistance of the ion core to an ellipsoidal distortion ought to be similar. Thus one may expect elastic properties of a metal to be related to fields seen at the nuclei.

The correctness of this view is bolstered by a second observation of Machlin and Whang. For a series of Nb_3X and of V_3X compounds (such as shown in Fig. 27) which crystallize in the $A-15$ structure, they find it necessary to introduce a charge cloud shape parameter for the atoms at the chain sites (Nb or V) in order to successfully predict elastic and lattice constants and formation energies of these materials using a model potential theory. This implies that the resistance of the transition metal atoms to anisotropic deformation is a crucial factor in the stability of the compounds. It might have been argued that the introduction of a new parameter as an additional degree of freedom in the theory is merely an artifice to achieve agreement with experiment and does not necessarily require a true physical distortion of the atomic charge cloud. However, for the eleven compounds where QI measurements are available, the magnitude of the QI is strongly correlated to the charge cloud shape parameter. This demonstrates the reality of distortion effects.

The results of Machlin and Whang show that QI information can be useful in studies of the relationship of atomic properties of the elements to structural and mechanical properties of solids.

APPENDIX A. ASYMPTOTIC APPROXIMATION TO SCREENING INTEGRALS

The angular part of the integral of Eq. (5.12) can be performed, since $\epsilon(q)$ and $V_c(q)$ depend only on $|q|$, with the result,

$$V(r) = \frac{1}{2\pi^2} \int_0^\infty \frac{V_c(q)}{\epsilon(q)} q^2 j_0(qr) dq = \frac{1}{4\pi^2 r} \text{Im} \int_{-\infty}^\infty \frac{V_c(q)}{\epsilon(q)} q e^{i\sigma r} dq. \quad (A1)$$

The second form of the integral was obtained by noting that the integrand is even in q and expressing the Bessel function in terms of sinusoidal functions. To obtain the asymptotic form for $V(r)$, valid for $k_F r \gg 1$, one must expand $1/\epsilon(q)$ about the singular point at $q = 2k_F$ (or $q = -2k_F$). The contribution from $q = +2k_F$ and $-2k_F$ are identical, so only one point need be considered and a factor of 2 added. One sees from Eq. (5.8) that the singular terms in the expansion of $1/\epsilon(q)$ will have the form, $x \ln|x|$, to first order, and $x^2 \ln|x|$ and $x^2 \ln^2|x|$, in second order, where $x = 1 - q/2k_F$. By dis-

TABLE IV. Electric field gradients in noncubic metals.

Host	Probe	EFG [10^{17} V/cm ²]	Method	References	Remarks	Footnote		
Be	Be	$\pm 0.0483(31)$	NMR	*Barnaal <i>et al.</i> , 1967	EFG at 77 K	a		
			NMR	Alloul and Froidevaux, 1968				
			NMR	Knight, 1953				
	B	$\pm 0.134(13)$	NMR	McCart and Barnes, 1968				
			NMR/PAC	*Correll, 1978				
			NMR/PAC	*McDonald and McNab, 1974				
	N	$ \nu_Q $	NMR/PAC	*Williams <i>et al.</i> , 1972		xx		
			NMR/PAC	Correll, 1978				
	F	$\pm 2.2(4)$	IMPAC	Haskell <i>et al.</i> , 1975		c		
			ME	Budtz-Jorgensen <i>et al.</i> , 1976				
	Fe	$-2.2(15)$	ME	*Housley <i>et al.</i> , 1964	(T)	d		
			ME	*Janot <i>et al.</i> , 1974	(T)			
ME			Hoy <i>et al.</i> , 1977					
Ru	$\pm 5.9(13)$	TDPAC	Reno <i>et al.</i> , 1978		e			
Rh	$ \nu_Q $	TDPAC	Krien <i>et al.</i> , 1975b		xx			
		TDPAC	Krien <i>et al.</i> , 1976			(T)		
Cd	$-0.93(15)$	TDPAC	*Kaufmann <i>et al.</i> , 1975	Subst. site	f			
		TDPAC	*Raghavan <i>et al.</i> , 1974b					
		TDPAC	*Raghavan <i>et al.</i> , 1976					
	$\pm 3.1(5)$	TDPAC	*Kaufmann <i>et al.</i> , 1975	Interst. site	f			
		TDPAC	*Raghavan <i>et al.</i> , 1974b					
		TDPAC	Krien <i>et al.</i> , 1976			(T), interst. site		
Ta	$\pm 3.76(23)$	TDPAC	*Kaufmann <i>et al.</i> , 1976		g			
		TDPAC	Krien <i>et al.</i> , 1976			(T)		
Au	$\pm 2.18(9)$	ME	Perscheid <i>et al.</i> , 1978	Subst. site	h			
	$+39.3(10)$	ME	Perscheid <i>et al.</i> , 1978	Interst. site I	h			
	$+19.5(7)$	ME	Perscheid <i>et al.</i> , 1978	Interst. site II	h			
Hg	$\pm 4.8(6)$	TDPAC	Krien <i>et al.</i> , 1978	Interst. site	i			
		NMR/PAC	*Correll, 1978					
Mg	B	$\pm 0.134(13)$	NMR/PAC	*Haskell and Madansky, 1973		b		
			NMR/PAC	*Tanihata <i>et al.</i> , 1977				
			NMR/PAC	Correll, 1978				
	N	$ \nu_Q $	NMR/PAC	Haskell <i>et al.</i> , 1975		xx		
			NMR/PAC	Tanihata <i>et al.</i> , 1977				
			NMR/PAC					
	Mg	$\pm 0.053(-)$	NMR	*Dickson and Seymour, 1970	(T)	k		
			NMR	*Dogan <i>et al.</i> , 1969	(T)			
			NMR	*Drain, 1967	(T)			
	Cd	$-0.44(7)$	NMR	Rowland, 1961		f		
			TDPAC	*Raghavan <i>et al.</i> , 1976				
	S	Te	$+125(17)$	TDPAC	Andreeff <i>et al.</i> , 1974	(T)		
ME				Boolchand <i>et al.</i> , 1973	EFG at 4.2 K	l		
I	I	$+108(2)$	ME	Boolchand, 1978	EFG at 4.2 K	yy		
			NMR	*Barnes <i>et al.</i> , 1965		n		
Sc	Sc	$\pm 0.38(2)$	TDPAC	*Haas and Shirley, 1973		o		
			TDPAC	*Butz and Kalvius, 1974				
			TDPAC	Butz <i>et al.</i> , 1976			(P)	
Ti	Sc	$\pm 1.59(15)$	TDPAC	Reno <i>et al.</i> , 1974	(T)	o		
			Ti	$\pm 1.2(-)$	NMR	Narath, 1967	EFG at 4 K	p
			Fe	$-0.487(15)$	ME	*Wortmann and Williamson, 1975		d
β-Mn	Mn	$\pm 0.177(9)$	ME	Qaim, 1969		q		
			TDPAC	Devare and deWaard, 1977				
			TDPAC	*Kaufmann <i>et al.</i> , 1974b			(T)	
	Ta	$\pm 5.61(35)$	TDPAC	Raghavan <i>et al.</i> , 1976		g		
			TDPAC	*Kaufmann, 1973b				
			TDPAC	*Kaufmann <i>et al.</i> , 1974b			(T)	
Hg	$\pm 1.22(17)$	TDPAC	*Unterricker, 1974	(T)				
		TDPAC	Krien <i>et al.</i> , 1975a		i			
Co	Fe	$-0.32(2)$	NMR	*Drain, 1966	(T)			
			NMR	Jaccarino <i>et al.</i> , 1960				
			NMR	Masuda <i>et al.</i> , 1964		d		
Cd	Co	$\pm 0.29(2)$	ME	Perlow <i>et al.</i> , 1965	(T)	r		
			NMR	Kawakami, 1972	(T), EFG at 4.2 K	f		
Zn	B	$\pm 0.20(1)$	TDPAC	Lindgren and Bedi, 1977		b		
			NMR/PAC	*Correll, 1978				
			NMR/PAC	*Haskell <i>et al.</i> , 1975				
F	F	$-2.9(5)$	IMPAC	*Brenn <i>et al.</i> , 1973	Pos. QI sign det.	c		
			IMPAC	Brenn <i>et al.</i> , 1974				
			IMPAC	*Budtz-Jorgensen <i>et al.</i> , 1976				
			IMPAC	*Housley and Nussbaum, 1965				
Fe	$+2.63(17)$	ME	*Qaim, 1969		d			
		ME						
		ME	Kündig <i>et al.</i> , 1965			(T)		

TABLE IV. (Continued)

Host	Probe	EFG [10^{17} V/cm ²]	Method	References	Remarks	Footnote				
	Zn	+3.09(31)	TDPAD	*Bertschat <i>et al.</i> , 1974	(T)	dd				
			TDPAD	*Christiansen <i>et al.</i> , 1976	(T)					
			NO	Brewer and Kaindl, 1978	Neg. QI sign det.					
			NO	Herzog <i>et al.</i> , 1977a	Neg. QI sign det.					
			ME	Vetterling and Pound, 1977						
			ME	Potzel <i>et al.</i> , 1978						
			NQR	Kaufmann <i>et al.</i> , 1978						
			SH	Lien, 1960						
			SH	Phillips, 1958						
			SH	Seidel and Keesom, 1959						
			Ge	$ \nu_Q $			TDPAD	Christiansen <i>et al.</i> , 1976	(T)	xx
							TDPAD	Haas <i>et al.</i> , 1973	(T)	
							TDPAD	Rafailovich <i>et al.</i> , 1977	(T)	
SOPAD	Schatz <i>et al.</i> , 1975	(T)								
As	$ \nu_Q $		TDPAD	Feilitzsch <i>et al.</i> , 1974		xx				
			TDPAC	Haas, 1976						
Br	$ \nu_Q $		TDPAC	Haas, 1977		xx				
Ru	$ \nu_Q $	±3.8(8)	TDPAC	Haas and Shirley, 1973		e				
			TDPAC	Haas and Shirley, 1973						
Rh	$ \nu_Q $		TDPAC	Krien <i>et al.</i> , 1974b	(T)	xx				
			TDPAC							
Cd	+7.7(12)		TDPAC	*Haas and Shirley, 1973		f				
			TDPAC	*Raghavan <i>et al.</i> , 1976						
			TDPAC	Raghavan <i>et al.</i> , 1974c	(T)					
			TDPAC	DaJornada <i>et al.</i> , 1978	(P)					
In	±12.1(8)		TDPAC	Devare <i>et al.</i> , 1975	(T)	t				
			TDPAC							
I	+25.0(10)		TDPAC	*Ooms <i>et al.</i> , 1978b		m				
			TDPAC	*Ooms <i>et al.</i> , 1977						
Sm	±1.66(13)		IMPAC	*Rösch, 1975		u				
			IMPAC	*Rösch <i>et al.</i> , 1975						
Ta	±12.3(7)		TDPAC	Bedi <i>et al.</i> , 1978	(T)	g				
			IMPAC	*Rösch, 1975						
W	+7.65(45)		IMPAC	*Rösch, 1975		ww				
			IMPAC	*Rösch <i>et al.</i> , 1975						
Os	±13.2(15)		IMPAC	*Rösch, 1975		v				
			IMPAC	*Rösch <i>et al.</i> , 1975						
Hg	+2.92(38)		TDPAC	*Krien <i>et al.</i> , 1975a		i				
			NO	Herzog <i>et al.</i> , 1978	Pos. QI sign det.					
α -Ga	Ga	±5.33(-)	NQR	*Valic and Williams, 1969	(T)	qq w				
			NQR	Knight <i>et al.</i> , 1956						
			NQR	Hammond and Knight, 1960	(P)					
			NQR	Hwang <i>et al.</i> , 1977	(P)					
			NQR	Kushida and Benedek, 1958	(P)					
			TDPAD	Haas <i>et al.</i> , 1973						
			TDPAD	Echt <i>et al.</i> , 1976c						
			TDPAC	*Menningen <i>et al.</i> , 1977						
			TDPAC	Haas and Shirley, 1973						
			TDPAC	*Segel <i>et al.</i> , 1972	(T), EFG at 77 K					
β -Ga	Ga	±3.08(-)	NQR	Brown and Segel, 1975	(P)	w				
			NQR	*Bastow and Whitfield, 1976	(T)					
As	As	±6.5(-)	NQR	*Sharma, 1976	(T)	y				
			SH	Krusius and Pickett, 1971						
			SH	Taylor and Hygh, 1963						
			SH	Taylor, 1967						
			TDPAC	Haas and Shirley, 1973						
			TDPAC	Boolchand <i>et al.</i> , 1973	EFG at 4.2 K					
Se	Te	±110(15)	ME	Boolchand, 1978	EFG at 4.2 K	yy				
			ME							
Y	Sc	±0.99(5)	NMR	Barnes <i>et al.</i> , 1965		n d g				
			ME	Qaim, 1969						
			TDPAC	*Butz and Kalvius, 1974	(T)					
			TDPAC	Butz <i>et al.</i> , 1976	(P)					
α -Zr	Fe	±1.66(16)	ME	Qaim, 1969		d jj aa g				
			NMR	Hioki <i>et al.</i> , 1975	EFG at 4.2 K					
			TDPAD	Baba <i>et al.</i> , 1974						
			TDPAC	*Kaufmann, 1973a	(T)					
			TDPAC	*Unterricker, 1974	(T)					
ω -Zr	Ta	±4.59(24)	TDPAC	Butz <i>et al.</i> , 1974	(P)	g				
			TDPAC	Rasera <i>et al.</i> , 1978a	Hf alloys					
			TDPAC	*Kaufmann and McWhan, 1973	(T), site A					
			TDPAC	Butz <i>et al.</i> , 1975	(P), site A					
			TDPAC	*Kaufmann and McWhan, 1973	(T), site B					
			TDPAC	Butz <i>et al.</i> , 1975	(P), site B					

TABLE IV. (Continued)

Host	Probe	EFG [10^{17} V/cm ²]	Method	References	Remarks	Footnote	
Tc	Fe	-0.65(10)	ME	Takabatake <i>et al.</i> , 1978		d	
	Tc	$\pm 0.7(7)$	NMR	*Jones and Milford, 1962		bb	
Ru	Fe	-0.71(3)	ME	*Van Ostenburg <i>et al.</i> , 1962		d	
	Ru	$\pm 0.49(14)$	TDPAC	Wortmann and Williamson, 1975		e	
	Rh	$ \nu_Q $	TDPAC	Haas and Shirley, 1973		xx	
	Ta	-4.0(5)	ME	Kaindl and Salomon, 1972		cc	
Cd	Fe	+2.70(17)	ME	*Qaim, 1969		d	
			TDPAC	Deicher, <i>et al.</i> , 1977			
	Zn	$\pm 2.68(27)$	TDPAD	Bartsch <i>et al.</i> , 1974b		dd	
	Ge	$ \nu_Q $	TDPAD	Bartsch <i>et al.</i> , 1975		xx	
	Kr	$ \nu_Q $	TDPAC	Haas, 1977		xx	
	Ru	$\pm 4.6(10)$	TDPAC	Haas and Shirley, 1973		e	
	Rh	$ \nu_Q $	TDPAC	Krien <i>et al.</i> , 1975c	(T)	xx	
	Cd	+7.2(11)	TDPAC	*Bleck <i>et al.</i> , 1972		f	
			TDPAC	*Haas and Shirley, 1973			
			TDPAC	*Raghavan and Raghavan, 1971a	(T)		
			TDPAC	*Raghavan <i>et al.</i> , 1974a			
			TDPAC	*Bodenstedt <i>et al.</i> , 1972	(T)		
			TDPAC	*Christiansen <i>et al.</i> , 1976	(T)		
			TDPAC	*Raghavan and Raghavan, 1971b	(T)		
			TDPAC	*Raghavan <i>et al.</i> , 1972	(P)		
			TDPAD	Echt <i>et al.</i> , 1976a			
			TDPAD	Sprouse <i>et al.</i> , 1978			
			NO	Rosenblum and Steyert, 1975			
		In	+9.39(88)	TDPAC	*Christiansen <i>et al.</i> , 1976		t
				TDPAC	*Haas and Shirley, 1973		
				TDPAC	*Raghavan <i>et al.</i> , 1976	(P)	
				TDPAC	*Raghavan and Raghavan, 1972		
				TDPAC	*Raghavan <i>et al.</i> , 1973b		
			TDPAC	*Butt <i>et al.</i> , 1974	(T)		
	Sn	$\pm 7.9(17)$	TDPAD	*Bertschat <i>et al.</i> , 1976		ee	
			TDPAD	*Dimmling <i>et al.</i> , 1975			
			TDPAD	Vianden <i>et al.</i> , 1975			
			TDPAD	Christiansen <i>et al.</i> , 1976	(T)		
			TDPAD	Echt <i>et al.</i> , 1976b	(T)		
	Sm	$\pm 1.66(35)$	IMPAC	*Rösch <i>et al.</i> , 1975		u	
			IMPAC	*Rösch, 1975			
	W	$\pm 8.64(70)$	IMPAC	*Rösch <i>et al.</i> , 1975		ww	
			IMPAC	*Rösch, 1975			
	Os	$\pm 6.2(7)$	IMPAC	*Rösch <i>et al.</i> , 1975		v	
			IMPAC	*Rösch, 1975			
	Ir	$ \nu_Q $	TDPAC	Haas, 1976		xx	
	Hg	+2.0(3)	TDPAC	*Krien <i>et al.</i> , 1975a		i	
			NO	Herzog <i>et al.</i> , 1978	Pos. QI sign det.	qq	
	Pb	$\pm 16(-)$	TDPAC	Haas and Shirley, 1973		z	
In	F	$\pm 0.88(-)$	IMPAC	Budtz-Jørgensen <i>et al.</i> , 1976		c	
	Fe	$\pm 1.43(4)$	ME	*Flinn <i>et al.</i> , 1967		d	
			ME	*Qaim, 1969			
	Ge	$ \nu_Q $	TDPAD	Bartsch <i>et al.</i> , 1975		xx	
			TDPAD	Raghavan and Raghavan, 1978a			
	Cd	-1.02(16)	TDPAC	*Brandt and Rosenblum, 1973		f	
			TDPAC	*Budtz-Jørgensen <i>et al.</i> , 1973			
			TDPAC	*Haas and Shirley, 1973			
			TDPAC	Behrend and Budnick, 1962	Neg. QI sign det.		
			TDPAC	Lehmann and Miller, 1956			
			TDPAC	Bodenstedt <i>et al.</i> , 1972	(T)		
			TDPAC	Budtz-Jørgensen and Bonde-Nielsen, 1975	(T)		
			TDPAC	Christiansen <i>et al.</i> , 1976	(T)		
		TDPAC	Lindgren, 1978	(P)			
	In	-2.18(3)	NQR	*Hewitt and Taylor, 1962	(T)	j	
			NQR	*Simmons and Slichter, 1961	(T)		
			NQR	O'Sullivan and Schirber, 1964a	(P)		
			NQR	Thatcher and Hewitt, 1970	Neg. QI sign det.		
			NQR	Hewitt and Knight, 1959			
			NMR	Torgeson and Barnes, 1962			
			NMR	Adams <i>et al.</i> , 1966			
			TDPAC	Christiansen <i>et al.</i> , 1976			
			TDPAC	Haas and Shirley, 1973			
			NO	Brewer and Kaindl, 1978	Neg. QI sign det.		

TABLE IV. (Continued)

Host	Probe	EFG [10^{17} V/cm ²]	Method	References	Remarks	Footnote	
Sn	Sn	$\pm 3.7(14)$	TDPAC	Folle, 1974		ff	
	Pb	$\pm 5.7(-)$	TDPAC	Haas and Shirley, 1973		z	
	F	$\pm 1.7(-)$	IMPAC	Budtz-Jorgensen <i>et al.</i> , 1976		c	
	Ge	$ \nu_Q $		TDPAD	Bartsch <i>et al.</i> , 1975		xx
				TDPAD	Raghavan and Raghavan, 1977		
				TDPAD	Raghavan and Raghavan, 1978a		
				TDPAC	Haas and Shirley, 1973		e
	Ru	$\pm 4.3(10)$	TDPAC	Haas and Shirley, 1973		e	
	Cd	$\pm 2.08(32)$		TDPAC	*Budtz-Jorgensen and Bonde-Nielsen, 1975		f
				TDPAC	*Haas and Shirley, 1973		
TDPAC				*Raghavan <i>et al.</i> , 1976			
TDPAC				*Christiansen <i>et al.</i> , 1976	(T)		
TDPAC				*DaJornada <i>et al.</i> , 1978	(P)		
TDPAC				*Devare and Devare, 1976	(T)	t	
In	$\pm 3.27(31)$		TDPAC	Haas and Shirley, 1973			
			TDPAC	*Soares <i>et al.</i> , 1973		ff	
Sb	Sn	$\pm 5.78(48)$	TDPAC	*Krien <i>et al.</i> , 1974a			
			ME	Collins, 1976	(T)		
	Te	$ \nu_Q $		ME	Alekseevskii <i>et al.</i> , 1963	Neg. QI sign det.	
				TDPAD	Ivanov <i>et al.</i> , 1974		xx
				TDPAC	Krien <i>et al.</i> , 1975a		i
				TDPAC	Haas and Shirley, 1973		z
	Ge	$ \nu_Q $		TDPAD	Bartsch <i>et al.</i> , 1974a		xx
				TDPAD	Bartsch <i>et al.</i> , 1975		
				TDPAD	Raghavan and Raghavan, 1978a		
				TDPAC	Haas, 1977		xx
TDPAC				Haas and Shirley, 1973		e	
TDPAC				*Haas and Shirley, 1973		f	
Te	Ru	$\pm 14.2(31)$	TDPAC	Lis and Naumann, 1977b	(T)		
			TDPAC	Krien <i>et al.</i> , 1974a		ff	
	Cd	$\pm 4.07(62)$		NQR	*Hewitt and Williams, 1963	(T)	gg
				NQR	*O'Sullivan and Schirber, 1964b	(T, P)	
	Pb	$\pm 4.4(5)$		SH	Collan <i>et al.</i> , 1970		
				TDPAC	Haas and Shirley, 1973		z
				TDPAC	Lis and Naumann, 1977a	(T), Parent ac: ¹¹¹ In	f
				TDPAC	Kulesa and Tung, 1978	Parent ac: ¹¹¹ Ag	f
	Sn	$\pm 8.1(14)$		TDPAC	Rots <i>et al.</i> , 1978	Interst. site	ff
				ME	*Boolchand <i>et al.</i> , 1970	EFG at 4.2 K	l
I	$\pm 78.4(10)$		ME	*Boolchand <i>et al.</i> , 1973			
			ME	Violet and Booth, 1966	(T)		
			ME	*Boolchand, 1978		yy	
			ME	*Langouche <i>et al.</i> , 1974			
			ME	Pasternak and Bukspan, 1967			
			TIPAC	Makaryunas and Makaryunene, 1968			
	Cs	ν_Q		TIPAC	Ooms <i>et al.</i> , 1978a		
				TDPAC	Haas and Shirley, 1973		
				TDPAC	Ooms <i>et al.</i> , 1978b		
				TDPAC	Ooms <i>et al.</i> , 1977		
Sm	$\pm 2.1(5)$		TDPAC	Kulesa and Tung, 1978	Neg. QI sign det.	xx	
W	$\pm 6.46(40)$		IMPAC	*Rösch <i>et al.</i> , 1975		u	
			IMPAC	*Rösch, 1975			
			IMPAC	*Rösch <i>et al.</i> , 1975		ww	
			IMPAC	*Rösch, 1975			
Os	$\pm 6.7(7)$		IMPAC	*Rösch <i>et al.</i> , 1975		v	
			IMPAC	*Rösch, 1975			
La	$\pm 1.47(21)$		NMR	*Narath, 1969	EFG at 4 K	hh	
			NMR	Torgeson and Barnes, 1964			
			NQR	Poteet <i>et al.</i> , 1970			
			TDPAC	Klemme <i>et al.</i> , 1973			
Gd	Sc	$\pm 2.05(10)$	TDPAC	Colley <i>et al.</i> , 1976	(T)	o	
			TDPAC	*Boström <i>et al.</i> , 1970		f	
	Cd	$\pm 1.37(21)$		TDPAC	*Boström <i>et al.</i> , 1971		
				TDPAC	*Fechner <i>et al.</i> , 1973		
				TDPAC	*Forker and Hammesfahr, 1973b		
				TDPAC	*Lis <i>et al.</i> , 1977	(T)	
	Te	$ \nu_Q $		TIPAC	Cruse <i>et al.</i> , 1970		
				IMPAC	*Rösch <i>et al.</i> , 1975		u
	Sm	$\pm 2.63(35)$		IMPAC	*Rösch, 1975		
				ME	*Bauminger <i>et al.</i> , 1975	EFG at 4 K	ii
ME				Fink, 1967			
Gd	$\pm 2.81(28)$		ME	Göring, 1972			

TABLE IV. (Continued)

Host	Probe	EFG [10^{17} V/cm ²]	Method	References	Remarks	Footnote
	Ta	+6.58(54)	IMPAC	Spehl and Wirtz, 1971		g
	W	+6.84(32)	TDPAC	Forker <i>et al.</i> , 1974		ww
	Os	±13.2(16)	IMPAC	*Rösch <i>et al.</i> , 1975		
			IMPAC	*Rösch, 1975		
			IMPAC	Klepper <i>et al.</i> , 1973		v
	Ir	+19.5(50)	IMPAC	*Rösch <i>et al.</i> , 1975		
			IMPAC	*Rösch, 1975		
			TIPAC	Forker <i>et al.</i> , 1978		
	Au	+14.4(7)	ME	Perscheid and Forker, 1978	EFG at 4.2 K	vv
			ME	Perscheid <i>et al.</i> , 1976	EFG at 4.2 K	h
			TDPAC	*Fechner <i>et al.</i> , 1973		f
Tb	Cd	±1.46(22)	TDPAC	*Forker and Hammesfahr, 1973b		
			TDPAC	*Lis <i>et al.</i> , 1977	(T)	
			TDPAC	*Lounasmaa and Roach, 1962	EFG at 1 K	kk
	Tb	+13.5(-)	SH	Bleaney and Hill, 1961		
			SH	VanKempen <i>et al.</i> , 1964		
			SH	Sano <i>et al.</i> , 1975		
Dy	Ta	±6.02(37)	NMR	Sano <i>et al.</i> , 1975		
			TDPAC	Forker <i>et al.</i> , 1974		g
			TDPAC	*Forker and Hammesfahr, 1973a		f
	Cd	±1.56(24)	TDPAC	*Forker and Hammesfahr, 1973b		
			TDPAC	*Lis <i>et al.</i> , 1977	(T)	
			TDPAC	*Ofer <i>et al.</i> , 1965		ll
	Dy	±34.8(27)	ME	Sano <i>et al.</i> , 1975		
			NMR	Sano <i>et al.</i> , 1975		
			NMR	Sano <i>et al.</i> , 1975		
Ho	Ta	±6.58(41)	TDPAC	Forker <i>et al.</i> , 1974		g
			TDPAC	*Fechner <i>et al.</i> , 1973		f
			TDPAC	*Forker and Hammesfahr, 1973b		
	Cd	±1.44(23)	TDPAC	*Lis <i>et al.</i> , 1977	(T)	
			TDPAC	*VanKempen <i>et al.</i> , 1964	EFG at 1 K	mm
			TDPAC	Brunhardt <i>et al.</i> , 1965		
	Ho	+2.53(47)	SH	Lounasmaa, 1962		
			SH	*Forker <i>et al.</i> , 1974		g
			SH	Rasera <i>et al.</i> , 1978b	(T)	
Er	Ta	±6.73(42)	TDPAC	*Fechner <i>et al.</i> , 1973		f
			TDPAC	*Forker and Hammesfahr, 1973b		
			TDPAC	*Lis <i>et al.</i> , 1977	(T)	
	Cd	±1.13(17)	TDPAC	*Kienle, 1964	(T)	
			TDPAC	*Reese and Barnes, 1967	(T)	nn
			TDPAC	Sano <i>et al.</i> , 1975		
Tm	Ta	±7.60(48)	NMR	Sano <i>et al.</i> , 1975		
			TDPAC	Forker <i>et al.</i> , 1974		g
			TDPAC	*Uhrich and Barnes, 1967	(T), EFG at 120 K	oo
	Tm	±6.9(-)	ME	Kalvius <i>et al.</i> , 1963	(T)	
			ME	*Chuhuran-Long <i>et al.</i> , 1973	(T)	pp
			ME	Li-Scholz and Rasera, 1969		
	Yb	±5.12(88)	TDPAC	Rasera and Li-Scholz, 1970		
			TDPAC	Qaim, 1969		d
			TDPAC	*Brewer and Kaindl, 1978	EFG at 5 mK	rr
Lu	Fe	±1.51(20)	NO	Lounasmaa, 1964		
			NO	*Butz and Kalvius, 1974	(T)	g
			NO	Butz <i>et al.</i> , 1976	(P)	
	Lu	+1.08(4)	SH	Qaim, 1969		d
			SH	*Kaindl <i>et al.</i> , 1973	EFG at 3 mK	ss
			SH	Boelchand <i>et al.</i> , 1969		
	Ta	±4.99(30)	ME	Gerdau <i>et al.</i> , 1968		
			ME	Snyder <i>et al.</i> , 1968		
			ME	Klepper <i>et al.</i> , 1973		
Hf	Fe	±1.66(20)	IMPAC	*Kaindl and Salomon, 1972		cc
			IMPAC	Berthier <i>et al.</i> , 1971		
			IMPAC	Gerdau <i>et al.</i> , 1969		
	Ta	+4.7(7)	TDPAC	Rasera <i>et al.</i> , 1978a	Zr alloys	
			TDPAC	Sommerfeldt <i>et al.</i> , 1965		
			TDPAC	Buttler, 1970	(T)	
			TDPAC	Lieder <i>et al.</i> , 1971	(T)	
			TDPAC	Salomon <i>et al.</i> , 1964	(T)	
			TDPAC	Unterricker, 1974	(T)	
			TDPAC	DaJornada <i>et al.</i> , 1974	(P)	
			TDPAC	Ernst <i>et al.</i> , 1977	(P)	
			TDPAC	*Wortmann and Williamson, 1975		d
			TDPAC	Qaim, 1969		
			TDPAC	Raghavan <i>et al.</i> , 1976		f
			TDPAC	*Kaindl <i>et al.</i> , 1972		cc

TABLE IV. (Continued)

Host	Probe	EFG [10 ¹⁷ V/cm ²]	Method	References	Remarks	Footnote
			ME	*Kaindl and Salomon, 1972		
			TDPAC	Netz and Bodenstedt, 1973	(T)	
			TDPAC	Butz and Potzel, 1975	(T, P)	
	Re	-4.7(11)	NAR	*Buttet and Bailey, 1970	EFG at 4.2 K	tt
			SH	Gregers-Hansen <i>et al.</i> , 1971		
			SH	Keesom and Bryant, 1959		
			SH	Rockwood <i>et al.</i> , 1969		
			SH	Smith and Keesom, 1970		
			NO	Ernst <i>et al.</i> , 1978		
			TDPAC	Haas and Shirley, 1973		
	Os	-2.9(6)	ME	Wagner <i>et al.</i> , 1972	EFG at 4.2 K	uu
	Hg	-2.82(45)	NO	Herzog <i>et al.</i> , 1978	EFG at 0.05 K	qq
Os	Fe	-0.75(3)	ME	Wortmann and Williamson, 1975		d
	Ta	-6.0(7)	ME	*Kaindl and Salomon, 1972		cc
			TDPAC	Netz, 1973		
	Os	±3.3(5)	IPAC	Grodzins and Chow, 1966	EFG at 4.2 K	uu
	Ir	±3.3(9)	ME	*Atzmony <i>et al.</i> , 1967	EFG at 4.2 K	vv
			ME	*Wagner and Zahn, 1970		
Hg	Cd	±6.38(98)	TDPAC	Haas and Shirley, 1973	EFG at 77 K	f
	Hg	±11.1(14)	TDPAC	*Vianden and Krien, 1977	EFG at 77 K	i
			TDPAC	Edelstein and Pound, 1975		
			TDPAC	Haas and Shirley, 1973		
			TIPAC	Pound and Wertheim, 1956		
	Pb	±18(-)	TDPAC	Haas and Shirley, 1973	EFG at 77 K	z
Tl	Fe	±1.75(16)	ME	Qaim, 1969		d
	Ge	ν_Q	TDPAD	Raghavan and Raghavan, 1977		xx
	Cd	±0.45(8)	TDPAC	Haas and Shirley, 1973		f
	Pb	±1.8(-)	TDPAC	*Haas and Shirley, 1973		z
			TDPAC	*Lieder <i>et al.</i> , 1967		
			TDPAC	*Wertheim and Pound, 1956		
	Po	ν_Q	TDPAD	Feilitzsch <i>et al.</i> , 1974	(T)	xx
Bi	Ge	ν_Q	TDPAD	Raghavan and Raghavan, 1977	(T)	xx
	Cd	±17.4(26)	TDPAC	Haas and Shirley, 1973	Parent ac. alloyed	f
		±4.3(3)	TDPAC	Heubes <i>et al.</i> , 1977	Parent ac. implanted	f
	Pb	±2.4(-)	TDPAC	Haas and Shirley, 1973		z
	Bi	±5.32(19)	NQR	*Bastow and Whitfield, 1976	(T)	x
			NQR	Williams and Hewitt, 1966		
			SH	Phillips, 1960		
			SH	Collan <i>et al.</i> , 1970		

The nuclear quadrupole moments in the following list are taken from Shirley's "Table of Nuclear Moments" [Shirley and Lederer, 1977], unless another reference is given. The abbreviation w.a. indicates that a weighted average of the available values was taken. (Units are in barns.)

- a ⁹Be(g.st., $\frac{3}{2}^-$) = +0.053(3).
 b ¹²B(g.st., 1^+) = ±0.0171(16).
 c ¹⁹F(ex.st: 197 keV, $\frac{5}{2}^+$) = ±0.12(2).
 d ⁵⁷Fe(ex.st: 14 keV, $\frac{3}{2}^+$) = +0.192(5) w.a.
 e ⁸⁹Ru(ex.st: 90 keV, $\frac{3}{2}^+$) = +0.23(5), Kistner and Lumpkin, 1976.
 f ¹¹¹Cd(ex.st: 247 keV, $\frac{5}{2}^+$) = +0.72(11).
 g ¹⁸¹Ta(ex.st: 482 keV, $\frac{5}{2}^+$) = +2.51(15), Netz and Bodenstedt, 1973
 h ¹⁹⁷Au(g.st., $\frac{3}{2}^+$) = +0.594(10).
 i ¹⁹⁷Hg(ex.st: 134 keV, $\frac{5}{2}^-$) = ±0.47(6), Vianden and Krien, 1977.
 j ¹¹⁵In(g.st., $\frac{5}{2}^+$) = +0.861(-).
 k ²⁵Mg(g.st., $\frac{5}{2}^+$) = +0.22(-).
 l ¹²⁵Te(ex.st: 35 keV, $\frac{3}{2}^+$) = -0.225(30) w.a.
 m ¹²⁹I(ex.st: 28 keV, $\frac{5}{2}^+$) = -0.685(-).
 n ⁴⁵Sc(g.st., $\frac{7}{2}^-$) = -0.218(10) w.a.
 o ⁴⁴Sc(ex.st: 68 keV, 1^+) = -0.21(2).
 p ^{47,49}Ti(g.st., $\frac{5}{2}^+$, $\frac{7}{2}^+$) = +0.27(-) average value.
 q ⁵⁵Mn(g.st., $\frac{5}{2}^-$) = +0.40(2).
 r ⁵⁹Co(g.st., $\frac{7}{2}^+$) = +0.42(3).
 s ⁶⁷Zn(g.st., $\frac{5}{2}^-$) = +0.150(15).
 t ¹¹¹In(ex.st: 659 keV, $\frac{3}{2}^+$) = -0.62(4) w.a.
 u ¹⁵²Sm(ex.st: 122 keV, 2^+) = -1.65(-).
 v ¹⁸⁰Os(ex.st: 155 keV, 2^+) = -1.45(11) w.a.
 w ⁶⁹Ga(g.st., $\frac{3}{2}^-$) = +0.168(-).
 x ²⁰⁹Bi(g.st., $\frac{9}{2}^-$) = -0.38(1) w.a.
 y ⁷⁵As(g.st., $\frac{3}{2}^-$) = +0.29(-).
 z ²⁰⁸Pb(ex.st: 1274 keV, 4^+) = ±0.3(-).
 aa ⁹²Mo(ex.st: 2761 keV, 8^+) = ±0.35(2), Baba *et al.*, 1974.
 bb ⁹⁹Tc(g.st., $\frac{9}{2}^+$) = ±0.34(34).
 cc ¹⁸¹Ta(g.st., $\frac{7}{2}^+$) = +3.9(4), Lindgren, 1965.
 dd ⁶⁷Zn(ex.st: 605 keV, $\frac{9}{2}^+$) = (+)0.61(-), Vetterling and Pound, 1977.
 ee ¹¹³Sn(ex.st: 731 keV, $\frac{11}{2}^-$) = ±0.46(10).
 ff ¹¹⁹Sn(ex.st: 24 keV, $\frac{3}{2}^+$) = -0.065(5).
 gg ¹²¹Sb(g.st., $\frac{5}{2}^+$) = -0.26(10).
 hh ¹³⁹La(g.st., $\frac{7}{2}^+$) = +0.22(3).
 ii ¹⁵⁵Gd(g.st., $\frac{3}{2}^-$) = +1.59(16).
 jj ⁹¹Zr(g.st., $\frac{5}{2}^+$) = -0.21(2), Büttgenbach *et al.*, 1978.
 kk ¹⁵⁹Tb(g.st., $\frac{3}{2}^+$) = +1.34(11).
 ll ¹⁶¹Dy(ex.st: 26 keV, $\frac{5}{2}^-$) = +2.45(18) w.a.
 mm ¹⁶⁵Ho(g.st., $\frac{7}{2}^-$) = +2.73(6).
 nn ¹⁶⁶Er(ex.st: 81 keV, 2^+) = -1.9(4).
 oo ¹⁶⁹Tm(ex.st: 8 keV, $\frac{3}{2}^+$) = -1.3(1).
 pp ¹⁷²Yb(ex.st: 79 keV, 2^+) = ±2.16(37).
 qq ¹⁹⁷Hg(ex.st: 299 keV, $\frac{13}{2}^+$) = +1.61(13).
 rr ¹⁷⁷Lu(g.st., $\frac{7}{2}^+$) = +5.51(6).
 ss ¹⁸⁰Hf(ex.st: 1142 keV, 8^+) = +4.4(5).
 tt ¹⁸⁷Re(g.st., $\frac{5}{2}^+$) = +2.24(50).
 uu ¹⁸⁶Os(ex.st: 137 keV, 2^+) = -1.71(19).
 vv ¹⁹³Ir(g.st., $\frac{3}{2}^+$) = +0.70(18).
 ww ¹⁸²W(ex.st: 100 keV, 2^+) = -2.05(-), Rösch, 1975.
 xx Corresponding QI frequencies can be found in Vianden, 1978.
 yy ¹²⁹I(g.st., $\frac{7}{2}^+$) = -0.553(-).

carding nonsingular terms and factoring out of the integral smooth functions of q evaluated at $q = 2k_F$, the resulting one-dimensional transforms of the singular factors can be replaced by using the results of Lighthill (1962),

$$\begin{aligned} \int_{-\infty}^{\infty} x \ln |x| e^{ixr} dx &= -\frac{\pi i}{r^2} \\ \int_{-\infty}^{\infty} x^2 \ln |x| e^{ixr} dx &= \frac{2\pi}{r^3} \\ \int_{-\infty}^{\infty} x^2 \ln^2 |x| e^{ixr} dx &= \frac{-4\pi}{r^3} (\ln r + \gamma - 3/2), \end{aligned} \quad (\text{A2})$$

where $\gamma = 0.5772156649\dots$ is Euler's constant. The asymptotic result for $V(r)$ becomes

$$V(r) \rightarrow A \frac{\cos y}{y^3} - DA^2 \frac{\sin y [\ln y + \gamma']}{y^4}, \quad (\text{A3})$$

where

$$A = \frac{2m_e e^2 k_F^2 V_C(2k_F)}{\pi^2 \hbar^2 \epsilon^2 (2k_F)}; \quad D = \frac{\pi \epsilon (2k_F)}{k_F^3 V_C(2k_F)}$$

$$\gamma' = \ln 2 + \gamma - 3/2; \quad \text{and } y = 2k_F r.$$

The first term of Eq. (A3) corresponds to Eq. (5.18) in the text.

To obtain the asymptotic form for the radial part of the EFG, some authors (Sholl, 1967) have differentiated Eq. (5.18) directly, obtaining

$$V''(r) \rightarrow A(2k_F)^2 \left[\frac{-\cos y}{y^3} + \frac{7\sin y}{y^4} + \frac{15\cos y}{y^5} \right]. \quad (\text{A4})$$

Only the leading term is correct and corresponds to Eq. (5.16) in the text. It is clear that if Eq. (A3) were differentiated, the second term would contribute additional terms of the same or lower order in y as the second two terms in Eq. (A4). We shall not display that result since the order of differentiation after taking the asymptotic limit is incorrect. The correct result is obtained by finding the asymptotic form of Eq. (5.14) directly, using the method outlined above. The full result is

$$\begin{aligned} V''(r) \rightarrow A(2k_F)^2 & \left\{ \frac{-\cos y}{y^3} + \frac{3\sin y}{y^4} + \frac{3\cos y}{y^5} \right. \\ & + DA \left[\frac{\sin y \ln y}{y^4} + \frac{\gamma' \sin y}{y^4} + \frac{3\cos y \ln y}{y^5} \right. \\ & \left. \left. + \frac{3\gamma' \cos y}{y^5} - \frac{3\sin y \ln y}{y^6} - \frac{3\gamma' \sin y}{y^6} \right] \right\}. \end{aligned} \quad (\text{A5})$$

Although the highest-order terms here would be augmented further if third- and higher-order terms in the expansion of $1/\epsilon(q)$ were retained, the terms above which go as $\ln y/y^4$ and $1/y^4$ would be appropriate to correct asymptotic lattice sums for near-neighbor distances where $k_F r \gg 1$ is not strictly satisfied.

APPENDIX B. ELECTRIC FIELD GRADIENTS IN NONCUBIC METALS

Electric field gradients in noncubic metals are given in Table IV. Values of the principal component of the EFG at room temperature are listed in units of 10^{17} V/cm^2 . In cases where no measurement near 293 K was available, the temperature for which the EFG was derived is given in the remarks column. The abbreviations T and P in this column indicate that the temperature or pressure dependence of the EFG was determined. All other abbreviations used are explained in the glossary of symbols. The letters in the last column refer to footnotes at the end of the table, where the values of the nuclear quadrupole moments used in the derivation of the EFG can be found. Where multiple references for a given system occur, asterisks indicate those sources used to compute the quoted EFG value.

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