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Nuclear Quadrupole Interaction in Pure Metals

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Calculations of the ionic part of the electric field gradient at the nuclei of certain metals are combined with available experimental data to obtain information about the electronic structures of the metals, or estimates of nuclear quadrupole moments. The metals considered are Be, Sc, Re, La, Mg, Co, Zn, and Cd, which have the hexagonal close-packed structure, and indium, which has a centered tetragonal structure. Some comparison is made with other information about the shapes of the Fermi surfaces and a pertinent experiment on Zn is suggested.

I. INTRODUCTION

In an earlier paper,[1] the field gradient at Be^9 nuclei in metallic beryllium was calculated to derive the Be^9 nuclear quadrupole moment from the measured value of the quadrupole coupling constant. It was shown that the major part of the field gradient arose from the charges on the ions at the lattice sites, the conduction electrons serving to enhance the field gradient by only 8%. This behavior of the conduction electrons is quite different from the electrons which take part in the bonds in covalent compounds.

In the present paper, we shall report the results of our calculations for the lattice part of the field gradient in other metals with hexagonal close-packed structure about which experimental evidence is available regarding the nuclear quadrupole coupling constant. In addition, the quadrupole coupling constant in metallic indium, which has face centered tetragonal structure, is also available from pure quadrupole resonance measurements. We have computed the contribution to the field gradient in indium metal from the In^{3+} ions in the lattice. To obtain the total field gradient at the nuclei in these metals one needs the contribution from the conduction electrons. This requires a calculation of the wave functions of the conduction electrons, which is rather complicated because of the presence of large numbers of core states. Our program here is thus simpler: we shall calculate the ionic part of the field gradient in each of the metals and, wherever possible, compare this to the total field gradient as derived from known values of the coupling constant e^2qQ, and the nuclear quadrupole moments Q. Knowing the ionic contribution gives an estimate of the field gradient produced by the conduction electrons, and thus gives information about the departure of the electron charge distribution from spherical symmetry. Where Q is not known, some estimate of it can be made from a knowledge of the lattice part of the field gradient and a rough estimate of the electronic contribution to the field gradient. Another useful result of this work is to emphasize the utility of the method of Nijboer and de Wette[2] for calculating quadrupolar (and other) lattice sums. Its rapid convergence and simple form make it suitable even for desk calculation.

II. CALCULATION OF THE IONIC SUMS: THE NIJBOER AND DeWETTE METHOD

In order to find the ionic field gradient, i.e., the sum

$$q_{\text{lattice}}=\sum\nolimits_i{}'(3z_i^2-r_i^2)/r_i^5, \tag{1}$$

over all lattice points at distances $\mathbf{r}_i=(x_i,y_i,z_i)$ from the origin, in a hexagonal close-packed metal one might be tempted only to scale the value of q found for Be according to the cube of the ratio of the lattice spacings of Be and the other metal, ignoring any differences in the c/a ratio. Earlier calculation by Campbell *et al.*[3] of the field gradients in hcp metals indicated, however, a strong dependence of q on the c/a ratio. They used the Ewald-Kornfeld method[4] and gave equations for the crystalline potential as a linear function of (c/a). The value we obtained[1] for the lattice sum in Be differed by a small but appreciable amount (about 1.5%) from that given in reference 3, so we have calculated q for several values of c/a corresponding to axial ratios observed in some metals, using the method of Nijboer and de Wette.[2] We have verified the strong linear dependence found by Campbell *et al.*, but our values differ slightly from theirs (less than 2% in all cases). Our results appear in Fig. 1; on this scale the difference between our results and those of Campbell *et al.* is not perceptible. We deduce the following linear relation:

$$q_{\text{lattice}}=[0.0065-4.3584(c/a-1.633)]/a^3,$$

as compared to Campbell *et al.*'s relation:

$$q_{\text{lattice}}=[0.0068-4.4288(c/a-1.633)]/a^3.$$

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[1] M. Pomerantz and T. P. Das, Phys. Rev. **119**, 70 (1960).

[2] B. R. A. Nijboer and F. W. de Wette, Physica **24**, 1105 (1958) and references therein.

[3] L. L. Campell, J. M. Keller, and E. Koenigsberg, Phys. Rev. **84**, 1256 (1951).

[4] H. Kornfeld, Z. Physik **22**, 27 (1924).

We shall now make some remarks on the details of the application of the Nijboer and de Wette method to the calculation of electric field gradients. The reader who is more interested in the results than in the method may skip to Sec. III without loss of continuity.

In reference 4, p. 1110, the following expressions appear in Eq. (15):

$$\textstyle\sum_{\lambda}{}' \sum_j q_j r_{\lambda j}^{-l-1} Y_{lm}(\theta_{\lambda j},\phi_{\lambda j}) \equiv \mathcal{S}_{lm}'(0|0,\tfrac{1}{2}),$$

where $r_{\lambda j}=r_\lambda+r_j$, r_λ is the distance from the origin to another unit cell designated by λ, r_j is the distance from the origin of the unit cell to the jth atom in the basis, which has charge q_j. $\theta_{\lambda j}$ and $\phi_{\lambda j}$ are likewise the polar angles of the radius to the lattice points at $r_{\lambda j}$ with respect to some axes. For $l=2$, $m=0$ this sum has the form of one half the field gradient produced by all the point charges in the lattice, excluding the unit cell at the origin (as indicated by the prime on the summation over the cell index λ).

To improve the convergence of this slowly convergent sum (1), Nijboer and de Wette manipulated it into the form of a rapidly converging sum and a slowly converging sum. The slowly convergent sum is Fourier transformed and appears as a rapidly converging sum in reciprocal space. The form they finally obtained is

$$\begin{aligned}\mathcal{S}_{lm}'(0|0,\tfrac{1}{2})=\frac{1}{\Gamma(l+\frac{1}{2})}\Big[&\sum_{\lambda}{}'\sum_j q_j\Gamma(l+\tfrac{1}{2},\pi r_{\lambda j}^2)\\ &\times Y_{lm}(\theta_{\lambda j},\phi_{\lambda j})/r_{\lambda j}^{l+1}-q_1\delta_{l0}-\sum_j{}' q_j\gamma(l+\tfrac{1}{2},\pi r_j^2)\\ &\times Y_{lm}(\theta_j,\phi_j)+\frac{i^l\pi^{l-\frac{1}{2}}}{v_a}\sum_j{}' G(h_\lambda)h_\lambda^{l-2}\\ &\times\exp(-\pi h_\lambda^2)Y_{lm}(\theta_{h\lambda},\phi_{h\lambda})\Big],\end{aligned}\qquad(2)$$

where $G(h)=\sum_j q_j \exp(2\pi i\mathbf{h}\cdot\mathbf{r}_j)$ is the structure factor, $\Gamma(n,x)$ is the incomplete gamma function, defined by

$$\Gamma(n,x)=\int_x^\infty e^{-t}t^{n-1}dt,$$

$$\gamma(n,x)=\Gamma(n)-\Gamma(n,x)=\int_0^x e^{-t}t^{n-1}dt.$$

$\mathbf{h}_\lambda$ are the reciprocal lattice vectors defined by

$$\mathbf{h}_\lambda=\lambda_1\mathbf{b}_1+\lambda_2\mathbf{b}_2+\lambda_3\mathbf{b}_3,\quad(\lambda_i\text{ integral}),$$
$$\mathbf{b}_i=\mathbf{a}_j\times\mathbf{a}_k/\mathbf{a}_i\cdot[\mathbf{a}_j\times\mathbf{a}_k]=\mathbf{a}_j\times\mathbf{a}_k/v_a,$$

and

$$\mathbf{r}_\lambda=\lambda_1\mathbf{a}_1+\lambda_2\mathbf{a}_2+\lambda_3\mathbf{a}_3.$$

The field gradient includes the contribution from the lattice points within the unit cell at the origin, excluding the point at the origin; these must be added to $\mathcal{S}_{lm}'$ to obtain the field gradient:

$$q_{\text{lattice}}=2\mathcal{S}_{20}'(0|0,\tfrac{1}{2})+\textstyle\sum_j{}' 2q_jY_{20}(\theta_j,\phi_j)/r_j^3.\qquad(3)$$

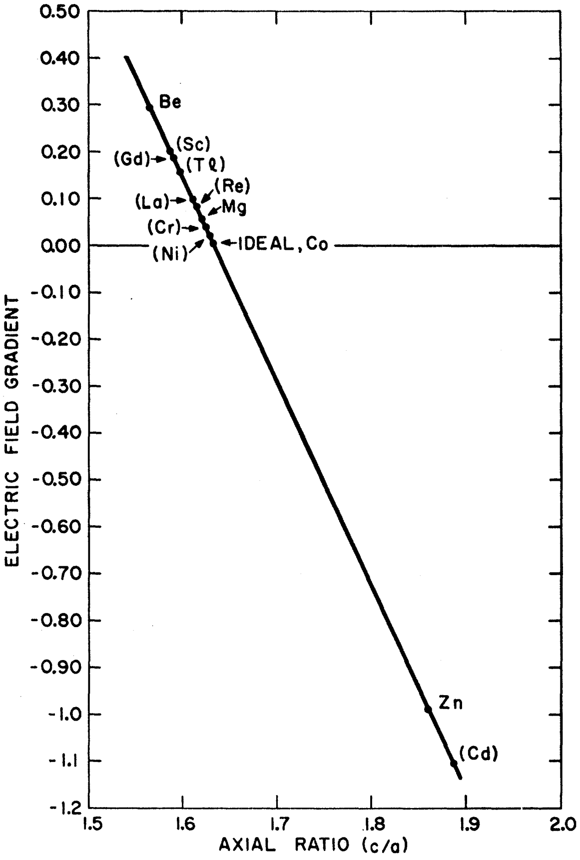

FIG. 1. Lattice contribution to the electric field gradient in hexagonal close-packed metals vs axial ratio. (The field gradient is expressed here in the dimensionless form $q_{\text{lattice}}a^3$.)

The second summation in the brackets for $\mathcal{S}_{20}'$ in (2) can be written

$$\sum_j{}'\frac{q_j\gamma(\frac{5}{2},\pi r_j^2)Y_{20}(\theta_j,\phi_j)}{r_j^3}=\sum_j{}'\frac{q_j[\Gamma(\frac{5}{2})-\Gamma(\frac{5}{2},\pi r_j^2)]Y_{20}(\theta_j,\phi_j)}{r_j^3}.\qquad(4)$$

Combining all the terms in q, the second sum in $\mathcal{S}_{20}'$ is eliminated completely, part of it being canceled by the second sum in Eq. (3), the rest being combined with the first sum on the right-hand side of (2). This sum, instead of excluding all points within the unit cell containing the origin, is now taken over all points in the lattice except the one point at the origin:

$$\begin{aligned}q_{\text{lat}}=\frac{2}{\Gamma(\frac{5}{2})}\Big[&\sum_\lambda\sum_j{}'\frac{q_j\Gamma(\frac{5}{2},\pi r_{\lambda j}^2)Y_{20}(\theta_{\lambda j},\phi_{\lambda j})}{r_{\lambda j}^3}\\ &-\frac{\pi^{\frac{3}{2}}}{v_a}\sum_\lambda G(h_\lambda)\exp(-\pi h_\lambda^2)Y_{20}(\theta_{h_\lambda},\phi_{h\lambda})\Big].\end{aligned}\qquad(5)$$

Equation (5) was the form employed in our calculations.

The values of the incomplete Γ function were from the tables by Pearson,[5] in which values are given of

$$I(u,p)=\int_0^{u\surd(p+1)} e^{-t}t^p dt \Big/ \Gamma(p+1),$$

from which we want to obtain $\Gamma(l+\frac{1}{2}, x)=\int_x^\infty e^{-t}t^{l-\frac{1}{2}}dt$. For the case of $l=2$ the relation of these is

$$\Gamma(\tfrac{5}{2},\pi r_{\lambda_j}{}^2)=\Gamma(\tfrac{5}{2})\left[1-I\left(u=\frac{\pi r_{\lambda_j}{}^2}{\sqrt{2.5}}, p=1.5\right)\right].$$

One may inquire about the relative ease and conveniences of computation by the Ewald-Kornfeld and Nijboer and de Wette methods. In fact it can be shown that the Ewald method is identical in principle to the Nijboer-de Wette method, the difference being that in the former Gaussian functions are used as convergence factors, but in the latter the incomplete Γ function is employed. The final expressions obtained by the two methods differ in form, and it seems that the Nijboer-de Wette method is somewhat simpler to use.

The following expression, given by Kornfeld,[4] can be compared to the above expression for q:

$$\begin{aligned} q(\mathbf{s})=\sum_\lambda \sum_j{}' \Big[& G(\epsilon|r_{\lambda_j}|)/r_{\lambda_j}{}^3+(2/\pi^{\frac{1}{2}})\epsilon\exp(-\epsilon^2 r_{\lambda_j}{}^2)/r_{\lambda_j}{}^2 \\ & -(\mathbf{s}\cdot\mathbf{r}_{\lambda_j})^2[3G(\epsilon|r_{\lambda_j}|)/r_{\lambda_j}{}^5+6\epsilon\exp(-\epsilon^2 r_{\lambda_j}{}^2/\pi^{\frac{1}{2}}r_{\lambda_j}{}^4 \\ & +4\epsilon^3\exp(-\epsilon^2 r_{\lambda_j}{}^2)/\pi^{\frac{1}{2}}r_{\lambda_j}{}^2] \\ & +\frac{2}{v_a}\left(\frac{\mathbf{s}\cdot\mathbf{h}_\lambda \exp(-\pi^2 h_\lambda{}^2/\epsilon^2)}{h_\lambda{}^2}-\frac{4}{3\pi^{\frac{1}{2}}}\epsilon^3\right)\Big], \end{aligned} \tag{6}$$

where ϵ is chosen to give rapid convergence, $G(x) = (2/\sqrt{\pi})\int_x^\infty \exp(-\alpha^2)d\alpha$, and $\mathbf{s}$ is a unit vector in the direction in which the field gradient is found.

It can be seen that there six sums to be computed in Eq. (6), compared to two in Eq. (5). There is the further problem of the choice of ϵ, which requires some experience. In using Eq. (5) we found that it was necessary to carry the summation at the most to the fifth nearest neighbors in order to get better than 1% convergence. It may be that with a proper choice of ϵ the Ewald-Kornfeld method can be made to converge more rapidly.

III. RESULTS

We shall now consider in order of increasing c/a those metals about whose quadrupole coupling something is known. The results and references are summarized in Table I.

Be^9: $c/a=1.5671$. (See Table I, reference a.) The first order splitting of the Be^9 nuclear magnetic resonance (NMR) spectrum in Be metal powder has been observed by Knight (see Table I, reference c), who found $e^2qQ/h=48$ kc/sec. A lattice of singly charged points produces a field gradient $q_{\mathrm{lattice}}=0.2937/a^3$. (This differs slightly from a previously reported value,[1] which was erroneous.) From these data, the value of the antishielding factor $\gamma_\infty=-0.185$ for Be^{++} (reference b in Table I) and the contribution of the conduction electrons calculated earlier,[1] we derive a value for the nuclear quadrupole moment of Be^9:

$$Q(\mathrm{Be}^9)=0.032 \text{ barn}.$$

Sc^{45}: $c/a=1.5884$. The only information about the quadrupole coupling in Sc is that no quadrupole effects were observed in the NMR of the metal. (See Table I, reference f.) If there are no first-order quadrupole effects,[6] then

$$3e^2qQ/14h<\Delta\nu,$$

where $\Delta\nu$ is the observed NMR linewidth, which is 0.0165 Mc/sec in the case of Sc.

The value of $Q(\mathrm{Sc}^{45})$ is unknown, but an estimate of it can be made if it is assumed that the major contribution to the field gradient comes from ions in the lattice, i.e.,

$$q_{\mathrm{ion}}=Zq_{\mathrm{lattice}}(1+\gamma_\infty),$$

where $Z=$ the normal valence$=3$. We then find

$$Q<0.017 \text{ barn},$$

from the absence of first-order effects.

It is possible that the first-order effects are appreciable, but unobserved. Then a less stringent requirement is set by the absence of second-order broadening of the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition. The condition,[6] for $I=\frac{7}{2}$, is

$$(125/48)(e^2qQ/14h)^2(1/\nu_L)<\Delta\nu,$$

where ν_L is the NMR (Larmor) frequency. We find

$$Q<0.63 \text{ barn},$$

from the absence of second order broadening, using $\nu_L=7$ Mc/sec (see Table I, reference f).

Tl: $c/a=1.598$. Wertheim and Pound (Table I, reference g) have measured the attenuation of the angular correlation of successive γ rays emitted from excited states of Pb^{204} in the Tl lattice. (The second γ ray is emitted from a state for which $I=4$, lifetime $t_N=0.27$ μsec, but whose quadrupole moment is unknown.) The measured value of the quadrupole coupling constant is

$$e^2qQ/h\approx 12 \text{ Mc/sec}.$$

The interpretation of quadrupole couplings measured in excited nuclear states involves a number of uncertainties, which are discussed by Heer and Novey in a survey article (Table I, reference s). These are (1) The

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[5] K. Pearson, *Tables of the Incomplete Γ-Function* (Cambridge University Press, New York, 1921) (reissued 1954).

[6] M. H. Cohen and F. Reif, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 339.

TABLE I. Results based on the lattice contribution to the electric field gradients (f.g.) in hcp metals and indium.

Elements	a (A)	c/a	$(1+\gamma_\infty)$	I	Q (barn)	$Ze^2q_{\text{lat}}Q(1+\gamma_\infty)/h$ (calc, Mc/sec)	e^2qQ/h (exp, Mc/sec)	$Ze^2q_{\text{lat}}Q(1+\gamma_\infty)/e^2qQ(\text{exp})$	Derived quantity
Be^9	2.2866[a]	1.5671[a]	0.815[b]	$\frac{3}{2}$			0.048[c]		$Q(Be^9)=0.032$ barn[d]
Sc^{45}	3.302	1.5884	~8[e]	$\frac{7}{2}$			<0.0776 (1st order)[f] <2.9 (2nd order)		$Q<1.7\times10^{-2}$ barn $Q<0.633$ barn
Pb^{204m} in Tl	3.4498	1.5983	~100[e](Pb)	4			12[g]		$Q(Pb^{204m})\lesssim0.2$ barn
Re^{185}	2.757	1.613 at 1°K	~100[e]	$\frac{5}{2}$	2.9	87	274[h]	32%	Lattice contrib. $\approx\frac{1}{3}$ total f.g.
Re^{187}	2.757	1.613 at 1°K	~100[e]	$\frac{5}{2}$	2.7	87	274[h]	32%	Lattice contrib. $\approx\frac{1}{3}$ total f.g.
La^{139}	3.75	1.616	~110[e]	$\frac{7}{2}$	0.1 ± 0.1[i]	1.1	<0.037 (no 1st order)[f] <1.54 (no 2nd order)		Electronic contribution to f.g. $\lesssim$ lattice contribution
Mg^{25}	3.203	1.622	4.2[j]	$\frac{5}{2}$	0.14[k]	0.067	0.23[l]	29%	Lattice contribution $\approx\frac{1}{3}$ total f.g.
Co^{59}	2.514	1.633	~8[e]	$\frac{7}{2}$	0.404[m]	0.136	$\gtrsim 10$[n] <3.5 (1st order) <112 (2nd order)		
Zn^{67}	2.619	1.835	10[e]	$\frac{5}{2}$	0.17[o]	5.7	<74[p]	$>8\%$	Lattice contribution $>8\%$ of total f.g
Cd^{111m} in Cd	2.973	1.886	16[q]	$\frac{5}{2}$			5.4–9.3[r]		$Q(Cd^{111m})\approx0.15$ barn
Cd^{111m} in In			16	$\frac{5}{2}$			14[s]		
In^{115}	4.588 3.244	1.0763 (fct) 1.522 (bct)	12[q]	$\frac{9}{2}$	1.161	5.6	30 (at 300°K)[t]	$\approx20\%$	Lattice contribution $\approx20\%$ of total

[a] D. R. Schwarzenberger, Phil. Mag. **4**, 1242 (1959).
[b] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).
[c] W. D. Knight, Phys. Rev. **92**, 539 (1953).
[d] Includes a +8% contribution to q by the conduction electrons [see reference 1]. The value of q_{lat} in the latter reference is slightly erroneous and is corrected here.
[e] Approximated from E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).
[f] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 52 (1960).
[g] G. K. Wertheim and R. V. Pound, Phys. Rev. **102**, 185 (1956).
[h] P. H. Keesom and C. A. Bryant, Phys. Rev. Letters **2**, 260 (1959).
[i] K. Murakawa and T. Kamei, Phys. Rev. **105**, 671 (1957).
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[k] A. Lurio, Bull. Am. Phys. Soc. **4**, 419 (1959).
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[m] D. V. Ehrenstein, H. Kopfermann, and S. Penselin, Z. Physik **159**, 230 (1960).
[n] W. A. Hardy, *Proceedings of the Conference on Magnetism and Magnetic Materials, New York, New York, 1960* [Suppl. J. Appl. Phys. **32**, 122S (1961)]. R. Street, D. S. Rodbell, and W. L. Roth, Phys. Rev. **121**, 84 (1961). Y. Kôi, A. Tsujimura, and T. Kushida, J. Phys. Soc. Japan **15**, 2100 (1960).
[o] A. Lurio, Bull. Am. Phys. Soc. **4**, 429 (1959).
[p] G. Seidel and P. H. Keesom, Phys. Rev. Letters **2**, 261 (1959); W. H. Lien and N. E. Phillips, Phys. Rev. **118**, 958 (1960); and private communication with G. Seidel.
[q] G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961).
[r] J. J. Kraushaar and R. V. Pound, Phys. Rev. **92**, 522 (1953).
[s] E. Heer and T. B. Novey, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 9, p. 217 ff.
[t] R. R. Hewitt and W. D. Knight, Phys. Rev. Letters **3**, 18 (1959).

excited nucleus results from nuclear changes and thus may be a different element, i.e., an impurity, in the original lattice. (2) Although the nucleus may have changed to that of another element, the electronic structure may not have changed to the electronic state appropriate to that element in the host lattice, representing an impurity in an excited electronic state. This is expected to have a larger effect in nonmetals than in metals, in which electronic transfer may occur within a relaxation time shorter than 10^{-12} sec, or shorter than the lifetime of the states being measured. (3) In the processes of bombardment and decay the nuclei may be displaced from lattice positions, so that they are not subjected to the field gradients present at the normal nuclear sites. In γ emission the recoil energy is $533(E^2/A)$ ev, where A is the atomic weight of the nucleus and E is the energy of the γ ray in Mev. For typical values (Table I, reference s) of $E=0.5$ Mev and $A=100$, the recoil energy is 1.33 ev, which is probably insufficient to dislocate the nucleus.

If it is assumed that none of the above objections apply to γ emission in metals,[7] and further that the entire field gradient at the Pb^{204} nucleus arises from the Tl^{3+} ions in the lattice, i.e.,

$$q=Z(\text{Tl})[1+\gamma_\infty(\text{Pb})]q_{\text{lattice}}(\text{Tl}),$$

we can estimate the nuclear quadrupole moment of the excited nuclear state

$$Q(\text{Pb}^{204m})\approx0.3 \text{ barn}.$$

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[7] B. G. Petterson, J. R. Gerholm, J. Thun, and K. Siegbahn, Phys. Rev. Letters **6**, 14 (1961).

Because the Pb atom has a $6s^26p^2$ ground-state electronic configuration there may well be a considerable electronic contribution to the field gradient in the metal, so that the value of 0.3 barn may be considered an upper limit.

Re^{185} and Re^{187}: $c/a=1.61$. A coupling constant $e^2qQ/h=274$ Mc/sec has been derived from low-temperature specific heat data (Table I, reference h). Using the known values of $Q\approx 2.8$ barn for each isotope, $Z=2$, and $\gamma_\infty \approx 100$ (Table I, reference e), we find an "ionic" contribution

$$e^22q_{\text{lattice}}(1+\gamma_\infty)Q/h=87 \text{ Mc/sec},$$

which is about 30% of the observed coupling.

La^{139}: $c/a=1.616$. The analysis for La is similar to that of Sc; the data are derived from the absence of first order satellites or second order broadening of the NMR. In contrast to Sc, some strain and annealing effects were observed in La indicating the presence of quadrupole effects in strained samples. Using the value $Q=0.3$ barn, $Z=3$, $\gamma_\infty\approx 110$ (Table I, references i and e), we find an ionic contribution to the field gradient,

$$e^2Zq_{\text{lattice}}(1+\gamma_\infty)Q/h=5.3 \text{ Mc/sec.}^9$$

In order for first-order effects to be unobservable,[6]

$$(3/14)e^2qQ/h<\Delta\nu, \quad 1.13 \text{ Mc/sec}<\Delta\nu.$$

The observed linewidth was 0.0078 Mc/sec, hence it appears that first order splittings are large and only the central line corresponding to the $\frac{1}{2}\leftrightarrow -\frac{1}{2}$ transition is seen. The absence of second order broadening requires that

$$\Delta\nu>(125/\nu_L)(e^2qQ/14h)^2=0.004 \text{ Mc/sec.}$$

This condition is satisfied for $\nu_L=4$ Mc/sec, the lowest frequency used in the experiment. The ionic field gradient thus seems large enough to give first order splitting, but not quite enough to give second-order broadening, neither of which is observed. This implies further that the electronic contribution is either less than or of the opposite sign to the lattice contribution since the total field gradient cannot be much greater than the ionic contribution.

Mg^{25}: $c/a=1.622$. Second-order quadrupole broadening of the $\frac{1}{2}\leftrightarrow -\frac{1}{2}$ transition of Mg^{25} in Mg metal was observed and interpreted by Rowland (Table I, reference l), who obtained

$$e^2qQ/h(\text{exp})=0.23 \text{ Mc/sec.}$$

From the known values of $Z=2$, $\gamma_\infty=4.2$, $Q=0.14$ barn (Table I, references j and k), we find

$$e^2Zq_{\text{lattice}}(1+\gamma_\infty)Q/h=0.067 \text{ Mc/sec.}$$

The ionic contribution thus appears to be about 30% of the measured field gradient in magnesium.

Co^{59}: $c/a=1.63$. At least five NMR lines have been observed in ferromagnetic Co (Table I, reference n). One of these is associated with the hexagonal phase, the others with the cubic phase and various fault structures. The hexagonal line lies 10 Mc/sec above the cubic line and has a width of about 0.8 Mc/sec. Its shape is not of the dispersion form shown by the cubic line, but rather is like an absorption or mixture of absorption and dispersion.

Street *et al.* (Table I, reference n) have observed a difference in the intensities of the resonances in the cubic and hexagonal phases, such that when x-ray diffraction indicates that the amounts of cubic and hexagonal materials are about equal, the resonance in the hexagonal phase is about 20% as intense as in the cubic phase. They have suggested that the difference in intensity is caused by the quadrupole interaction in the hexagonal phase that splits all except the $\frac{1}{2}\leftrightarrow -\frac{1}{2}$ transition from the main resonance, such that the remaining intensity is about $\frac{1}{5}$ of the cubic resonance, for which there is no quadrupole splitting. In order to remove all the satellites out of the linewidth of the $\frac{1}{2}\leftrightarrow -\frac{1}{2}$ transition, it is necessary that

$$(e^2qQ/14h)\gtrsim\Delta\nu,$$

which gives

$$e^2qQ/h\gtrsim 10.5 \text{ Mc/sec.}$$

The contribution to e^2qQ/h from the ionic field gradient in Co is

$$Ze^2q_{\text{lattice}}(1+\gamma_\infty)Q/h=0.14 \text{ Mc/sec},$$

using $Z=2$, $\gamma_\infty=8$ (Table I, reference e), $Q=0.4$ barn (Table I, reference m). The ionic field gradient is about a factor of 100 smaller than the field gradient required to split all the satellites out of the $\frac{1}{2}\leftrightarrow -\frac{1}{2}$ transition.

Hardy (Table I, reference n) has pointed out that the method of excitation of the resonance in ferromagnets may depend on the crystalline anisotropy, and hence on the crystal structure. This may lead to differences in the intensities of the hexagonal and cubic phases, which are quite independent of any quadrupole interactions. Koi *et al.* (Table I, reference n) reported experiments which correlate the intensity changes with changes in the anisotropy of the hexagonal phase. It seems that more study of the problem is required before the cause of the unequal intensities can be unequivocally established, but the explanation on the basis of quadrupole interactions seems unlikely.

Zn^{67}: $c/a=1.83$. Phillips' data on the specific heat of Zn in the 0.5°K range have been interpreted by Seidel and Keesom (Table I, reference p) as showing a quadrupole coupling $e^2qQ/h=74$ Mc/sec. Lien and Phillips (p, Table I) have pointed out that the difference between the thermodynamic and magnetic temperature scales at these temperatures can give rise to a spurious effect of the magnitude reported in Zn, so that Seidel now feels that the quadrupole coupling is probably a good deal less than the earlier estimate (p, Table I).

The ionic contribution is found to be

$$e^2Zq_{\text{lattice}}(1+\gamma_\infty)Q/h=5.7\ \text{Mc/sec},$$

using $Z=2$, $\gamma_\infty=10$, $Q=0.17$ barn (e and o, Table I). This is indeed less than the upper limit set by the specific heat measurements.

Cd^{111m}: $c/a=1.886$. Using the attenuation of γ-ray correlation, Kraushaar and Pound (r, Table I) have measured a coupling constant for Cd^{111m} in Cd metal of

$$8.4\ \text{Mc/sec}\leq e^2qQ/h(\text{exp})\leq 14.1\ \text{Mc/sec}.$$

The excited nuclear state of Cd was obtained by neutron bombardment of enriched Cd^{110} in the metal. This avoids the difficulties of studying an impurity in the target material; no element other than Cd is ever present. Kraushaar and Pound gave a value of the nuclear lifetime of the measured state of $t_N=8\times10^{-8}$ sec. More recently (s, Table I) t_N was given as $t_N=12.5\times10^{-8}$ sec. Since the data are interpreted in terms of $e^2qQt_N=\text{constant}$, the coupling constant may be better given by

$$5.4\ \text{Mc/sec}\leq e^2qQ/h\leq 9.3\ \text{Mc/sec}\quad(\text{corrected}).$$

If it is assumed that the field gradient arises only from the Cd lattice, $Z=2$, $\gamma_\infty=+15$ (q, Table I), we find

$$Q(\text{Cd}^{111m}\text{ in }d_{\frac{5}{2}}+\text{state})\approx0.15\ \text{barn}.$$

This value is not unreasonable because Cd^{111} is an even proton, odd neutron nucleus and the quadrupole moment on the shell model is expected to be small.

Another angular correlation measurement has been made on Cd^{111m} that results from K capture by In^{111}. In this case the Cd nucleus is an impurity in the indium crystal. The coupling constant of Cd^{111m} in indium was measured (s, Table I) to be

$$e^2qQ/h=14\ \text{Mc/sec}.$$

If it is assumed that the electrons around the Cd nucleus take up the form appropriate to a Cd impurity in the indium lattice in a time short compared to the nuclear lifetime (complete electronic relaxation) the ionic coupling constant is

$$e^2q_{\text{lattice}}(\text{In})Z(\text{In})[1+\gamma_\infty(\text{Cd})]Q(\text{Cd})/h=0.84\ \text{Mc/sec},$$

where $Z(\text{In})=3$, $\gamma_\infty(\text{Cd})=+15$ (q, Table I), $q_{\text{lattice}}(\text{In})=0.342\times10^{22}\ \text{cm}^{-3}$ (cf. following discussion of In), $Q(\text{Cd})$ is the value derived above.

If it is assumed that there is no change in the electronic configuration around the site where the In decayed to Cd (no electronic relaxation) the field gradient at this site remains what it was in the pure indium lattice, but the quadrupole moment of In is replaced by that of Cd^{111m}. We find then that, using the measured value of the quadrupole coupling in In (t, Table I) and $Q(\text{In})=1.2$ barn, the quadrupole coupling of Cd^{111m} in In under the assumption of no electronic relaxation is

$$e^2q(\text{In})Q(\text{Cd}^{111m})/h=4\ \text{Mc/sec}.$$

Although the coupling obtained under the assumption of no electronic relaxation is closer to the observed value than that obtained using only the ionic contribution and complete relaxation, in view of the work of Petterson *et al.*[7] it is more likely that complete relaxation occurs, and that most of the field gradient arises from electrons localized about the Cd site.

In: We have calculated q_{lattice} for the indium lattice. Indium may be regarded as a body-centered tetragonal lattice with $a=3.244$ A, $c/a=1.522$, or as face-centered tetragonal with $a=4.588$ A, $c/a=1.0763$. c/a is strongly temperature dependent and we have used only the value corresponding to room temperature. We find $q_{\text{lattice}}=0.342\times10^{22}\ \text{cm}^{-3}$, which, when combined with $\gamma_\infty=+10$ (q, Table I), $Q=1.2$ barn, $Z=3$ gives an ionic coupling constant

$$e^2qQ/h(\text{ionic})=5.6\ \text{Mc/sec}.$$

Hewitt and Knight (t, Table I) have measured the coupling constant in indium metal by pure quadrupole resonance. At room temperature they find a coupling constant

$$e^2qQ/h(\text{exp})=30\ \text{Mc/sec}.$$

The ionic contribution to the quadrupole coupling constant is thus about 20% of the measured value.

CONCLUSIONS

A primary objective of this work was to obtain information about the electronic distribution in metals from the electronic contributions to the nuclear quadrupole couplings. In general, one expects that the more the conduction electrons resemble free electrons, the smaller will be the electric field gradient produced by them. This follows because completely free electrons cannot produce an orientation-dependent interaction.[1] The electronic contribution to the electric field gradient is a measure of the non-spherical electronic distribution in real space, which reflects a non-spherical momentum distribution in reciprocal space. Recently, experimental studies of the de Haas-van Alphen effect, cyclotron resonance in metals, magneto-acoustic attenuation, and magnetoresistance have often been interpreted on a free-electron model.[8] We shall try here to correlate the results for the electronic quadrupole coupling with the Fermi surface deduced from other kinds of measurements.

In beryllium the electronic contribution to the field gradient seems small. We found[1] that the matrix elements of the potential at certain points of high symmetry in the Brillouin zone were small, indicating that the admixture of orthogonal plane wave states

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[8] See *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1961).

was small. McClure, seeking an explanation of the axial ratios of hexagonal metals,[9] found that Herring and Hill's[10] wave functions for Be also closely resemble plane waves, implying a nearly spherical Fermi surface.

In magnesium, a significant electronic contribution seems to be necessary to explain the observed interaction. The electronic field gradient $q_{\mathrm{el}} \geqq q_{\mathrm{tot}} - q_{\mathrm{ion}} = 1.07/a^3$. There has been some success in interpreting the de Haas–van Alphen oscillations in Mg on a modified free electron model, but the magnetoresistance requires a Fermi surface markedly different from the nearly spherical (free electron) shape (cf. p. 80, reference 8). Thus it may be that the crystalline potential in Mg perturbs the electronic states such that the free electron approximation fails. This implies that a considerable electronic field gradient may result, which would be consistent with our result.

The only other case for which precise experimental data are available is that of rhenium, the element of the lanthanide series that possesses a $(5d)^5(6s)^2$ atomic configuration. The electronic field gradient is of the order of $q_{\mathrm{el}} \geqq q - q_{\mathrm{ion}} = 40.4/a^3$. The applicability of the free electron approximation to such a metal is doubtful, as pointed out by Cohen (cf. p. 325, reference 8) because there may be overlap of the *d*-state cores and *s-d* hybridization. Thus it is not surprising that we find a sizable electronic contribution to the electric field gradient.

An interesting experiment that would check on the point of view we have taken would be a study of the NMR or pure quadrupole resonance of enriched Zn^{67}. A modified free electron model has had considerable success in explaining de Haas–van Alphen and cyclotron resonance experiments. It is assumed from this success that the main effects of the anisotropy of the zinc crystal (which is manifested in c/a greatly different from ideal and anisotropic elastic properties[11]) is to move the Brillouin zone faces without much alteration of the spherical Fermi surface. It has been suggested, however, that spin-orbit coupling splits certain states in the hcp lattice,[12] which perturbs the energy states in zinc more than in Be or Mg. A measurement of the quadrupole interaction in Zn will elucidate whether the Fermi surface in this metal is indeed very anisotropic or rather spherical.

Note added in proof. Our values for the lattice field gradients in HCP metals and indium agree with those recently published by F. W. de Wette [Phys. Rev. **123**, 103 (1961)], who used a similar summation method. His paper does not emphasize the detailed interpretation of the field gradient data. W. W. Simmons and C. P. Slichter [Phys. Rev. **121**, 1580 (1961)] also calculated the lattice field gradient in indium metal and got a value in agreement with that reported here.

J. F. Cornwell [Proc. Roy. Soc. (London) **261**, 551 (1961)] reported an extensive calculation of the electronic energy surfaces in Be metal. Starting with Herring and Hill's[10] values of the energy levels calculated at points of high symmetry in the Brillouin zone, he found the form of the constant energy surfaces throughout reciprocal space, using an interpolation method. Up to values of the electronic energy of the order of one half the Fermi energy the surfaces are roughly spherical. For higher energies, particularly those near the Fermi surface, the shapes of the equienergy surfaces are not at all spherical. If this is indeed the case there may be a considerable electronic contribution to the electric field gradient. This effect of the higher energy electrons is reduced somewhat because the density of electronic states tends to decrease near the Fermi energy.

It should also be mentioned that there is some doubt about the quantitative accuracy of the energy levels calculated by Herring and Hill, although they are the best values known at present. In the years since this calculation was performed there has been considerable improvement in the treatment of the exchange and correlation energies in metals. A more precise calculation of the energy levels is now possible, from which the energy surfaces could be interpolated.

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