

Universal Correlation of Electronic and Ionic Field Gradients in Noncubic Metals

R. S. Raghavan and E. N. Kaufmann
Bell Laboratories, Murray Hill, New Jersey 07974

and

P. Raghavan*
Rutgers University, New Brunswick, New Jersey 08903
(Received 24 March 1975)

From available quadrupole coupling constants in noncubic metals, measured with the sign, we have extracted in each case the component eq' commonly attributed to specific conduction-electron field gradients. These data reveal for the first time a systematic and universal dependence of eq' on the lattice gradient *as well as* the Sternheimer antishielding factor $1-\gamma_\infty$. This is unexpected from the point of view of current theoretical models of the electric field gradients in metals.

The electric field gradient (EFG) at a nuclear site in a metal has traditionally been considered in the theoretical framework of the equation¹

$$eq = eq_{\text{latt}}(1 - \gamma_\infty) + eq_{\text{loc}}(1 - R). \quad (1)$$

The first term represents the ionic contribution, arising from the array of positive ions in a noncubic lattice and amplified by the Sternheimer antishielding factor γ_∞ of the interacting atom. The second contribution is from the conduction electrons whose dominant effect is considered to be local. Hence, this term is corrected for the interactions with the core of the interacting atom by the shielding factor $1-R$, which is of the order of unity. The first term in (1) can be calculated in a straightforward manner^{2,3} while attempts to calculate the second term have generally been far from successful. The purpose of this Letter is to present experimental systematics of the extraionic component $eq' = eq - eq_{\text{latt}}(1 - \gamma_\infty)$ and confront it with the properties of its theoretical counterpart, $eq_{\text{loc}}(1 - R)$. These systematics reveal for the first time a well-defined and universal correlation of eq' with $eq_{\text{latt}}(1 - \gamma_\infty)$, the two contributions opposing each other. This is unexpected since the theoretical framework of (1) as well as detailed calculations for the second term in (1)^{4,5} do not predict such a universality, nor do they indicate a dependence of the conduction-electron component on the antishielding factor $1 - \gamma_\infty$. The present result thus indicates the need for significant rethinking in the methods of calculating EFG's in metals. In particular, it poses the question: "Is the influence of the distorted core of the interacting atom on the spatial distribution of the conduction electrons in a metal adequately accounted for by the parameter

$1 - R$?"

Separation of the component eq' from a measured coupling constant e^2qQ crucially requires the knowledge of the sign of e^2qQ . Determination of these signs involves more specialized types of experiments than needed to measure the magnitudes alone. Recently a number of different techniques have been devised for this purpose and a sizable number of e^2qQ values are now available with signs. Of these, we have selected all those measured in pure noncubic metals or at foreign atoms present as dilute impurities. As far as possible we have been guided in the selection by our interest in conduction-electron effects in metals. A variety of experimental methods have been employed to obtain these data though Mössbauer and nuclear-spin-precession methods predominate.⁶ Since the nuclear quadrupole moment Q is known in each case with reasonable accuracy, one has a set of experimental values for eq . The ionic gradient was calculated according to the methods of Refs. 2 and 3 assuming a charge number Z of the most stable valence of the *host atom* and the crystal parameters of the *host lattice* and taking mostly from Feiock and Johnson⁷ the values of γ_∞ for the *probe atom* at which the coupling constant is measured. Algebraic subtraction of this calculated ionic gradient from the experimental eq yields eq' in each case. Figure 1 shows a plot of eq' versus $eq_{\text{latt}}(1 - \gamma_\infty)$, both being in units of 10^{17} volts per square centimeter.

Figure 1 shows a striking correlation between eq' and $eq_{\text{latt}}(1 - \gamma_\infty)$. The solid curve emphasizes the remarkable organization of the data. It is not theoretically derived. The observed correlation cannot be merely an artifact of the way in which eq' was extracted since eq and $eq_{\text{latt}}(1$

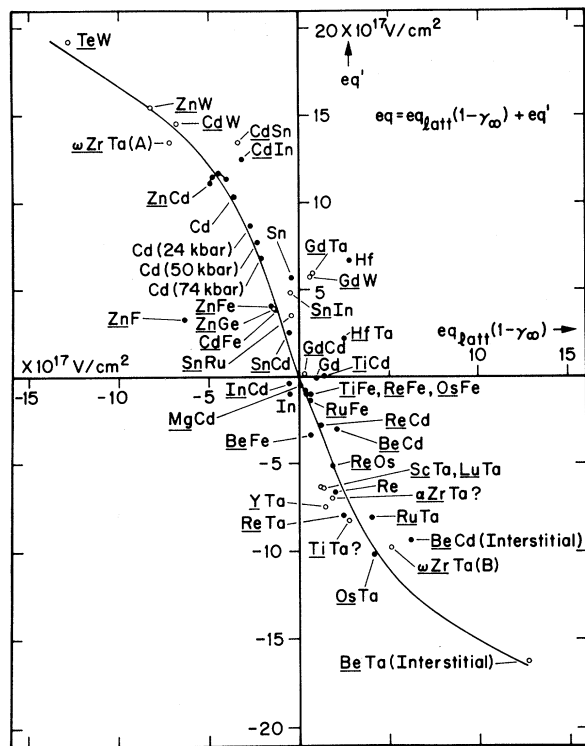


FIG. 1. Correlation of ionic and extraionic field-gradients in metals. Most values refer to room temperature. A typical temperature dependence is shown in the case of ZnCd by an arc of data points. Underlined symbols refer to the host metal. A and B refer to two inequivalent substitutional sites in ω -Zr. Filled circles indicate data from e^2qQ values of known signs. For open circles, e^2qQ signs are unknown. Locations of these points are predicted.

$-\gamma_\infty$) were in most cases of comparable magnitudes and with very few exceptions of opposite signs. It should be recalled that these data have been drawn from a variety of dilute-alloy systems prepared in many different ways. There are certainly secondary effects such as local strains, mismatch of sizes of the impurity and host ions, impurity electronic-screening effects, etc., operating in most cases. Also, the choice of the charge number Z for the computation of the ionic gradient is probably appropriate in some cases but less certain in others. Thus it is surprising that the correlation is as smooth as it is. The correlation is observed to apply to most of the systems studied, apparently not distinguishing any group of hosts or impurities in particular, and treats elemental and binary cases on the same footing. Even for a given host-impurity combination, the data for a substitutional

and a regular-interstitial site fit in with the same basic trend. Since the twenty-odd data points are distributed over most of the noncubic metals and the impurities include the light, medium, and heavy metals (γ_∞ varying between -10 and -60), there appears to be good reason to believe that the correlation discovered here is a universal one.

Encouraged by this, we have attempted to predict the signs of several other coupling constants whose magnitudes only are known. These points are represented in Fig. 1 by open circles.⁸ In each of these cases, eq' was computed with the two possible signs for e^2qQ and it was found that one of these always resulted in the corresponding point being located at or near the universal curve. In most cases this choice of sign also is the one most likely as seen by comparison with known signs in related system(s). This brings about a dozen additional data points into the systematics. The weights of these points are admittedly tentative at this stage, but they do indicate a broad measure of support for the universality of the phenomenon. Confirmation of these signs is clearly quite important.

There are however a few glaring exceptions to the trend of the data of Fig. 1. In contrast to the rest of the cases which occur exclusively in the II and IV quadrants of Fig. 1 [eq' opposed to $eq_{latt}(1 - \gamma_\infty)$] these points tend to be located in the I and III quadrants. These are Hf, HfTa, TiCd, In, and InCd. It seems likely that in these "anomalous" cases, other sources of EFG which "normally" play only a secondary role are of sufficient importance to create strong cancellation effects. The EFG's in Ti provide an intriguing case in point. The field gradient for $Ti^{57}Fe$ is negative whereas for $Ti^{111}Cd$ it is positive, providing the only known case where for the same host the sign of eq' is different for two different impurities. For this reason, the predicted points for $Ti^{181}Ta$ and for α -Zr¹⁸¹Ta, which is isoelectronic and isostructural with Ti (and also Hf), are tagged with question marks since there is no guidance available to decide the signs. The case of $Zn^{19}F$, although the sign is known, is still far outside the main correlation, which could conceivably be connected with the fact that this is the only case where the impurity ion is considered to be negatively charged.

Leaving aside these cases for the present, we can summarize the general properties of EFG's in metals as inferred from Fig. 1:

- (1) The major part of the extraionic gradient

eq' is correlated to the ionic gradient $eq_{\text{latt}}(1 - \gamma_\infty)$. For a given host lattice, eq' for two different impurities scales with the $1 - \gamma_\infty$ factor of the impurity; for the same impurity atom measured in different host lattices, eq' scales with eq_{latt} computed for the host.

(2) eq' is of the opposite sign to $eq_{\text{latt}}(1 - \gamma_\infty)$.

(3) For moderate values of $eq_{\text{latt}}(1 - \gamma_\infty)$, eq' is proportional to it; $eq' \approx -K eq_{\text{latt}}(1 - \gamma_\infty)$, where K is a positive constant with $|K| \approx 3$. For larger ionic gradients $|K|$ tends to be progressively less than 3 indicating some sort of saturation of the extraionic gradient.

(4) Superimposed on this main correlation there are secondary term(s) specific to the particular impurity and/or host combination producing individual deviations from the mean correlation.

Empirically, one can thus write for the EFG at a nuclear site in a noncubic metal

$$eq = eq_{\text{latt}}(1 - \gamma_\infty)(1 - K) + \langle eq \rangle, \quad (2)$$

where K is a positive constant of the order of 3 and $\langle eq \rangle$ accounts for item (4) above.

Comparison of these systematics for eq' with that expected for its theoretical counterpart $eq_{\text{loc}}(1 - R)$ reveals significant difficulties. The major theoretical efforts^{1,4,5,9} which in recent years have gone into estimating the effect of this "local" contribution have all been approximate, the degree and type of approximation being largely a matter of taste. Thus, while Refs. 4, 5, and 9 have taken the pseudopotential approach to consider individual cases (which does not transparently predict any correlative trend), Ref. 1 emphasizes effects of the repopulation of the levels near the Fermi surface [which results in an "overshielding" contribution proportional to eq_{latt} but not to $eq_{\text{latt}}(1 - \gamma_\infty)$]. These authors also briefly consider possible spatial distortions of conduction electrons which could lead to a term proportional to $1 - \gamma_\infty$ but not of the opposite sign. In none of these theories is there any hint that the *major* portion of the extraionic gradient should be universally correlated to $eq_{\text{latt}}(1 - \gamma_\infty)$ and of the opposite sign to it. Dependence on this *product* is the key to the universality. The quantity $eq_{\text{latt}}(1 - \gamma_\infty)$ can be essentially pictured as the nonsphericity of the atomic core of the interacting nucleus which results both from the lattice gradient and from the deformability of the core. The implication then is that this nonsphericity systematically and proportionately influences the conduction-electron distribution and creates

thereby a large EFG of the opposite sign. The role of the distorted core in producing the EFG in metals would thus seem to be considerably more far reaching than that pictured in current theory.

One possible reason for this gulf between theory and experiment could be the artificial way in which the two components are separately evaluated as pictured in Eq. (1). The question of the interactions of the distorted core in metals is dealt with in the same way as in nonmetallic lattices by inserting the factors γ_∞ and R which are evaluated for *free ions*. The present result strongly suggests that this is very likely not adequate for ions in a metal where the distortion of the core could influence the spatial distribution of the conduction electrons. A theory where all the charges—ionic, conduction electron, and core electron—are treated simultaneously and self-consistently might well be essential. Difficult as this task may be the experimental systematics presented here provide room for optimism that it should be possible to develop a formulation which can predict the EFG at a nuclear site in metals in general.

It is a pleasure to thank Y. Yafet for valuable discussions and W. L. Brown for his interest and encouragement.

*Work supported in part by the National Science Foundation. Resident Visitor at Bell Laboratories, Murray Hill, N. J. 07974.

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Direct Nonvertical Interband and Intraband Transitions in Al

E. Petri

Sektion Physik, Universität München, München, Federal Republic of Germany

and

A. Otto

Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany

(Received 3 March 1975)

Electron-energy-loss spectra of epitaxial Al foils of $\{110\}$ orientation show previously unobserved structures between 1.5 and 10 eV for the momentum transfer \vec{k} in directions $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$. For $\vec{k} \parallel \langle 100 \rangle$, this structure may be consistently interpreted within the essential features of the nearly-free-electron-band structure. Interband transitions show a marked influence on the plasmon dispersion for small k ; only for $k > 0.75 \text{ \AA}^{-1}$ may it be discussed within the jellium model.

Important information on the electronic structure of crystalline solids is contained in the dielectric response function $R = [\vec{k} \vec{\epsilon}(\omega \vec{k}) \vec{k}]^{-1}$, where $\vec{\epsilon}(\omega \vec{k})$ is the macroscopic dielectric tensor for the macroscopic fields of phase $\exp[i(\vec{k} \cdot \vec{x} - \omega t)]$. The electron-energy-loss cross section with electrons of some 10 keV kinetic energy is given by¹

$$(e/\pi \hbar v)^2 (1/k^2) \text{Im}R.$$

For a free degenerate electron gas $\text{Im}R$ contains a strong plasmon peak for values lower than the classical plasmon cutoff $k_c \sim \omega_p/V_F^2$ and weak structures at lower energies due to single-particle excitations.³ These structures have as yet only been observed by Raman scattering from degenerate semiconductor plasmas.⁴ For a nearly-free-electron metal like aluminum, one should expect an influence of the crystalline background of the atomic cores both on the spectrum of the single-particle excitations and on the dispersion of the plasmons.

Here we report electron-energy-loss spectra from Al films of $\{110\}$ orientation, which were epitaxially grown by vapor deposition on polished $\{110\}$ faces of rock salt.⁵ The experimental procedure has been described elsewhere.⁶ Energy-loss spectra were monitored for \vec{k} in the $\langle 100 \rangle$ (see Fig. 1), $\langle 110 \rangle$, and $\langle 111 \rangle$ directions. For $\vec{k} \approx 0$ one observes the surface plasmon at the Al-aluminum-oxide interface at about 6.5 eV.⁷ It

disappears for k not far from zero, because its theoretical cross section decreases as k^{-3} .⁸ For $k > 0.3 \text{ \AA}^{-1}$, new structures appear whose dispersion and shape are different for the different crystalline directions. For $\vec{k} \parallel \langle 100 \rangle$, two separate peaks become apparent in the spectra. The dispersion of these structures is plotted in Fig. 2.

We assign them to direct nonvertical interband and intraband transitions, which correspond to the low-energy single-particle excitations in a free-electron gas, mentioned above. The structures for $\vec{k} \parallel \langle 100 \rangle$ may be explained qualitatively in the following way: The pseudopotential U_{200} splits the free-electron parabolic band at the Brillouin-zone boundaries of class $\{100\}$ into parallel bands of $2U_{200} = 1.5 \text{ eV}$ distance. Optical (vertical) interband transitions between these parallel bands (so-called parallel-band transitions⁹) occur mainly near the W points and the X - W - X direction in the extended-zone scheme.¹⁰ This transition at 1.5 eV is found experimentally in $\epsilon_2(\omega, 0)$, superimposed on the Drude-type susceptibility of free electrons.^{11,12} For $\vec{k} \parallel \langle 100 \rangle$, \vec{k} is parallel to X - W - X on four $\{100\}$ zone boundaries and parallel to X - Γ - X on two $\{100\}$ zone boundaries. Therefore, the main effect may be explained by help of these two orientations. A quantitative analysis has to consider transitions throughout the Brillouin zone and \vec{k} -dependent