THE CONDUCTION-ELECTRON CONTRIBUTION TO THE ELECTRIC-FIELD GRADIENTS AT NUCLEAR SITES IN METALS

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THE CONDUCTION-ELECTRON CONTRIBUTION TO THE ELECTRIC-FIELD GRADIENTS AT NUCLEAR SITES IN METALS (*)

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Résumé. — Il est démontré qu'il existe une forte corrélation entre la grandeur et le comportement en fonction de la température du gradient quadrupolaire électrostatique produit par les électrons de conductibilité à la position du noyau dans des échantillons métalliques, eq_{ce}, et la densité d'états électroniques au niveau de Fermi. En outre, divers mécanismes qui pourraient conduire à la corrélation universelle entre eq_{ce} et le gradient quadrupolaire de la maille sont décrits.

Abstract. — It is shown that the magnitude and temperature behaviour of the conduction-electron contribution to the electric-field gradients at nuclear sites in metals, eq_{ce}, are strongly correlated with the density of states at the Fermi surface. Furthermore, various mechanisms which may lead to the observed universal correlation between eq_{ce} and the lattice field gradient are studied.

1. **Introduction.** — The systematics of Electric-Field Gradients (EFG's) at nuclear sites in non-cubic metals is not very well understood. Traditionally this EFG is written as

$$eq = (1 - \gamma_\infty)\, eq_{lat} + eq_{ce} \qquad (1)$$

where eq_{lat} is the ionic contribution due to the array of positive ions in a non-cubic lattice, γ_∞ the Sternheimer factor which takes the shielding of eq_{lat} by the core electrons into account, and eq_{ce} the EFG arising from the conduction electrons.

In many cases it is found that the total EFG, eq, has a sign opposite to eq_{lat} and a temperature behavior which is also quite different from eq_{lat}. These differences between eq and eq_{lat} have been attributed to the presence of the EFG caused by the conduction electrons.

Recently, Raghavan, Kaufmann and Raghavan [1], determined eq_{ce} empirically by subtracting the ionic contribution, $(1 - \gamma'_\infty)\, eq_{lat}$, from measured EFG's, using Sternheimer factors, γ'_∞, calculated for free ions. The EFG, eq'_{ce}, thus obtained plotted versus $(1 - \gamma'_\infty)\, eq_{lat}$ led to the surprising correlation shown in figure 1 of ref. [1], which in crude approximation can be written as

$$eq'_{ce} \cong - K(1 - \gamma'_\infty)\, eq_{lat} \qquad (2)$$

with $K \simeq 2$.

Existing detailed calculations [2] of eq_{ce} do not predict such a correlation at all. In section 3 the various mechanisms which may lead to such a correlation will be investigated.

First, however, we will consider (section 2) the conduction-electron field gradient without the perturbation of eq_{lat}, and study its temperature dependence and its relation to the density of states at the Fermi surface.

2. **The conduction-electron field gradient.** — The EFG at a nuclear site arising from the conduction electrons is given by

$$eq_{ce} = - e \sum_{k=0}^{k_F} < \psi_k \,|\, 2\, P_2(\hat{r})\, r^{-3} \,|\, \psi_k > \qquad (3)$$

where $\psi_k(\mathbf{r})$ is the conduction-electron wavefunction. In this section the pure conduction-electron EFG eq_0, i. e. eq_{ce} without the perturbations arising from eq_{lat} (section 3), is investigated.

Recently, a study of the temperature dependence of eq_0 was reported by Jena [3, 4]. Following conventional theory, Jena expressed $\psi_k(\mathbf{r})$ in the pseudo-wave function $\varphi_k(\mathbf{r})$, orthonormalized on the core-electron wavefunctions $|\alpha\,;\mathbf{R}_n>$ of an atom at lattice site $\mathbf{R}_n$;

$$\psi_k(\mathbf{r}) = \\ = C_k\Big[\varphi_k(\mathbf{r}) - \sum_{\mathbf{R}_n} e^{i\mathbf{k}.\mathbf{R}_n} \sum_\alpha |\,\alpha\,;\mathbf{R}_n><\alpha\,|\,\varphi_k>\Big], \qquad (4)$$

where C_k is a normalization constant. Regarding the pseudo potential as a perturbation the pseudo wavefunction can be written as

$$\varphi_k(\mathbf{r}) = \varphi_k^{(0)}(\mathbf{r}) + \varphi_k^{(1)}(\mathbf{r}) + \text{etc.}$$

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which inserted in eq. (3) yields ;

$$eq_0 = eq_0^{(0)} + eq_0^{(1)} + \text{etc.}\,.$$

The first and higher order terms in the expansion of $\varphi_{\mathbf{k}}(\mathbf{r})$ are temperature dependent ;

$$\varphi_{\mathbf{k}}^{(1)}(\mathbf{r}, T) = \sum_{\mathbf{g}}{}' a_{\mathbf{g}} \mid \mathbf{k} + \mathbf{g} > \mathrm{e}^{-W(\mathbf{g},T)}, \qquad (5)$$

where $\mathbf{g}$ is a reciprocal lattice vector $W(\mathbf{g}, T)$ the Debye-Waller factor which is related to the mean square displacement of a *host* atom, $< x_{\mathrm{T}}^2 >$, via $W(\mathbf{g}, T) = g^2 < x_{\mathrm{T}} >/2$. Using

$$\exp\{ - W(\mathbf{g}, T)\} \cong 1 - g^2 < x_{\mathrm{T}}^2 >/2$$

one readily sees that the temperature dependence of eq_0 can be represented by

$$eq_0 = eq_0^{(0)} + eq_0^{(1)}(1 - a < x_{\mathrm{T}}^2 >)\,. \qquad (6)$$

The temperature dependence of eq_0 in tin [4], for example, is found to change by 40 % with temperature, and it is not obvious from Jena's work that the temperature dependence in the first-order term of eq_0 is able to produce such a large temperature variation. Therefore $eq_0^{(0)}$ has to be scrutinized.

The zero-order term of $\varphi_{\mathbf{k}}(\mathbf{r})$ is a plane wave, which can be expanded in a series of spherical Bessel functions, $j_l(z)$, and spherical harmonics, $Y_{lm}(z)$:

$$\varphi_{\mathbf{k}}^{(0)}(\mathbf{r}) \sim \sum_{l,m} \imath^l j_l(kr)\, Y_{lm}^*(\hat{k})\, Y_{lm}(\hat{r})\,.$$

Inserting this series expansion in eq. (4) one readily sees that the zero-order conduction-electron wavefunction can formally be written as

$$\psi_{\mathbf{k}}^{(0)}(\mathbf{r}) = \sum_{l,m} \xi_1(kr)\, Y_{lm}^*(\mathbf{k})\, Y_{lm}(\hat{r})\,, \qquad (7)$$

which inserted in eq. (3) leads to

$$eq_0^{(0)} = - 2\,\mathrm{e} \sum_{\substack{l,m \\ l'=l,l\pm 2}} < Y_{lm} \mid 2\,\mathrm{P}_2 \mid Y_{l'm} > \times$$

$$\times \sum_{\mathbf{k}=0}^{\mathbf{k}_{\mathrm{F}}} < \xi_l \mid r^{-3} \mid \xi_{l'} > Y_{lm}(\hat{k})\, Y_{l'm}(\hat{k})\,. \qquad (8)$$

Consider the states with $\mid \mathbf{k} \mid < k_0$, where k_0 is the radius of the maximum sphere which can be inscribed within the Fermi surface. For these states one can sum or integrate over *all* directions of the wave vector $\mathbf{k}$, so that the $l' = l \pm 2$ terms in eq. (8) will disappear, because of the orthogonality properties of $Y_{lm}(\hat{k})$. Since

$$\sum_m < Y_{lm} \mid 2\,\mathrm{P}_2 \mid Y_{lm} > = 0\,,$$

one readily sees that also the $l = l'$ terms in eq. (8) yield a zero contribution for $\mid \mathbf{k} \mid < k_0$. Hence, only the occupied states outside the sphere with radius k_0 contribute to $eq_0^{(0)}$ so that in fair approximation :

$$eq_0^{(0)} = - e\eta(E_{\mathrm{F}}) \sum_{l,l'=l,l\pm 2} < \xi_l(E_{\mathrm{F}}) \mid r^{-3} \mid \xi_{l'}(E_{\mathrm{F}}) > A_{ll'}\,, \qquad (9)$$

where E_{F} is the Fermi energy, $\eta(E)$ the density of states F on the shape of the Fermi surface. In the case of a spherical Fermi surface, $k_0 = k_{\mathrm{F}}$ and $A_{ll'} = 0$.

Hence, when the $A_{ll'}$ or the density of states at the Fermi surface are small, $eq_0^{(0)}$ is negligible with respect to $eq_0^{(1)}$ to which all occupied states contribute, so that eq. (6) simplifies to

$$eq_0 \cong eq_0^{(1)}(1 - a < x_{\mathrm{T}}^2 >)\,, \qquad (10)$$

and the temperature dependence in the first-order term in $\varphi_{\mathbf{k}}(\mathbf{r})$ has become the temperature dependence in zero order in eq_0.

For large values of $\eta(E_{\mathrm{F}})$, however, eq_0 is no longer negligible, and eq. (9) indicates that in that cases a linear correlation between eq_0 and $\eta(E_{\mathrm{F}})$ exists. In this case also a more complicated temperature behaviour of the EFG at a nuclear site as predicted by eq. (6) is expected, since electrons are excited to states above the Fermi level when temperature is increased. This changes the l character of electrons in the vicinity of the Fermi level, and in turn changes the EFG at the nuclear site (see section 4).

3. **The perturbation of eq_{ce} by eq_{lat}.** — In an attempt to explain the correlation observed by Raghavan *et al.* [1] the perturbation of eq_{ce} by the potential V_2,

$$V_2(\mathbf{r}) = - er^2\, 2\,\mathrm{P}_2(\hat{r})\, eq_{\mathrm{lat}} \qquad (11)$$

is studied next. In first-order perturbation theory eq_{ce} can be expressed as

$$eq_{\mathrm{ce}} = eq_0 + eq_1 + eq_2 + eq_3\,, \qquad (12)$$

where eq_0 is the *pure* conduction-electron EFG dealt with in section 2 and eq_1, eq_2, and eq_3 are associated with perturbation by V_2 of the conduction-electron energies, the conduction-electron wave-functions and the core-electron wavefunctions, respectively.

Due to the perturbation of the energy states by V_2 conduction electrons in the vicinity of the Fermi surface may occupy states with different l character. Such a repopulation at the Fermi surface results in a change of the EFG and the nuclear site which is represented by eq_1. Watson, Gossard and Yafet [5] showed that $eq_1 = - c\eta(E_{\mathrm{F}})\, eq_{\mathrm{lat}}$ and calculated values of $c\eta(E_{\mathrm{F}})$ which are of the same order of magnitude as $K(1 - \gamma_\infty)$. This result seems promising in order to explain eq. (2). However, the eq_1 calculated with the aid of eq. (12) in ref. [5] represents the EFG of conduction-electrons above the unperturbed Fermi surface and does not correct fot the fact that these electrons also produce an

EFG in their unperturbed states which is of the same order of magnitude [6]. Hence, the actual value of eq_1 is expected to be at least one order of magnitude smaller than the values given by Watson *et al.* [5], so that eq_1 becomes too small to be responsible for a correlation such as given by eq. (2).

The eq_2 term arises from the perturbation of the conduction-electron wavefunction by V_2. According to Watson *et al.* [5] eq_2 is smaller than

$$| \gamma_{nl} | \, eq_{\text{lat}} \, z/2 \, (2\,l + 1) \,,$$

where $\gamma_{n,l}$ is the shielding factor of the (n, l) valence shell in a neutral atom and z is the number of conduction electrons per site. Hence, eq_2 is positively correlated to eq_{lat} as opposed to the negative correlation empirically found (see Eq.(2)).

Besides the terms eq_1 and eq_2 already discussed by Watson *et al.* [5] we consider here a new term, eq_3, which arises from the fact that the conduction-electron wavefunctions are affected by the perturbation of those of the core electrons because they have to be orthogonal to each other. The core-electron wavefunctions are perturbed by the lattice EFG and by the quadrupole field of the nucleus, so that

$$| \alpha > = | \alpha^{(0)} > + | \alpha' > .$$

The perturbation $| \alpha' >$ gives rise to the shielding factor γ_α ;

$$- \gamma_\alpha = - 2\, e < \alpha^{(0)} | \, 2\, \mathrm{P}_2(\hat{r})\, r^{-3} \, | \alpha' > \qquad (13)$$

The Sternheimer factor is given by $\gamma_\infty = \sum_\alpha \gamma_\alpha$.

One readily sees from eq. (3) using eq. (13) that

$$eq_3 = - \gamma_\beta \, eq_{\text{lat}} \sum_{\mathbf{k}} C_{\mathbf{k}}^2 < \beta | \varphi > < \varphi | \beta > \qquad (14)$$

where β denotes the (n, l) quantum numbers of the most outer core shell. The contributions to eq_3 from the inner core shells are neglected. Furthermore, we have for sake of simplicity neglected the effect of $| \alpha' >$ on the orthogonalization coefficients $< \alpha | \varphi >$. Since in good approximation $- \gamma_\beta \simeq - \gamma_\infty \simeq 1 - \gamma_\infty$, eq_3 is proportional to $(1 - \gamma_\infty)\, eq_{\text{lat}}$ in accordance with the empirical correlation, eq. (2). However, the correlation coefficient

$$K = - \sum_{\mathbf{k}} C_{\mathbf{k}}^2 < \beta | \varphi > < \beta | \varphi >$$

is found to be of the order of $- 0.1$ in disagreement with the value $K \cong + 2$ obtained empirically.

If eq_3 is added to the lattice EFG, the Sternheimer factor if effectively increased by about 10 %.

4. **Discussion.** — It has been known [5] for some time that in certain cases a linear correlation between the EFG at the nuclear site and the density of states at the Fermi level, $\eta(E_F)$, exists, Watson, Gossard and Yafet [5] attributed this effect to the term eq_1 in eq. (12). In section 3 it was shown, however, that in ref. [5] eq_1 is overestimated, and thus does not dominate the other terms in eq. (12). In section 2 it was found that instead the *pure* conduction-electron contribution, eq_0, is strongly related to $\eta(E_F)$.

Furthermore, we showed in section 2 that for small values of $\eta(E_F)$ the temperature behaviour of eq_0 is given by eq. (10). To elucidate the physics which leads to this result, we describe the conduction electrons by simple plane waves, $e^{i\mathbf{k}.\mathbf{r}} = | \mathbf{k} >$, which are scattered by the lattice atoms. The plane waves $| \mathbf{k} >$ don't produce an EFG since $< \mathbf{k} | \, 2\, \mathrm{P}_2\, r^{-3} \, | \mathbf{k} > = 0$. The EFG at the impurity site arises from the mixing of the plane waves $| \mathbf{k} >$ with the Bragg reflected waves $| \mathbf{k} + \mathbf{g} >$ which yields an EFG at the nuclear site of $- e < \mathbf{k} | \, 2\, \mathrm{P}_2\, r^{-3} \, | \mathbf{k} + \mathbf{g} >$. As well known the thermal motion of the host atoms reduces the amplitude of the Bragg reflected waves. This effect leads to the temperature dependence given by eq. (10), where $< x_T^2 >$ is thus the mean-square displacement of the host atoms. The consequence of this result is that the EFG at an impurity site should have the same temperature behaviour as that of the EFG at the host sites. This effect has indeed been observed for various impurities in a number of hosts [7].

The fact that the plane waves $| \mathbf{k} >$ have to be orthogonal to the core wavefunctions yields the term $eq_0^{(0)}$ in eq. (6), which is linear in $\eta(E_F)$ as shown by eq. (9). In the case where $\eta(E_F)$ is large, $eq_0^{(0)}$ as well as $eq_0^{(1)}$ in eq. (6) will be affected by the change in occupation of the levels in the vicinity of the Fermi surface as function of temperature. The resulting increase in p or d character may increase eq_0 and in part compensate for the decrease in eq_0 arising from the temperature motion of the host atoms discussed above. When an impurity is introduced in the lattice, $\eta(E_F)$ in the local surroundings of the impurity may change and thus affect the temperature behaviour of the EFG at the impurity nucleus, as has been observed for various impurities in Ti and Be hosts [8, 9].

A direct comparison of theory with experimental values of EFG's is very difficult as long as the origin of the empirical *universal* correlation found by Raghavan, Kaufmann, and Raghavan [1] is not understood. In order to explain this *universal* correlation the perturbation of the conduction-electron contribution to the EFG at a nuclear site, eq_{ce}, by the lattice EFG, eq_{lat}, was studied in section 3. The terms eq_1 and eq_2 in eq. (12) are proportional to eq_{lat}, and eq_3 is proportional to $(1 - \gamma_\infty)\, eq_{\text{lat}}$. However, none of these terms can be responsible for the empirically found correlation (eq. (2)) since either the sign of their correlation with eq_{lat} is wrong or their order of magnitude is too small.

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