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Temperature-dependent field gradients in Zn and Cd: First-principles analysis of electronic and lattice contributions†

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An *ab initio* investigation has been carried out for the influence of isotropic, anisotropic, and anharmonic phonons on the ionic and electronic contributions to the field gradients in zinc and cadmium. In addition to explaining the trend of experimental temperature-dependence data in these metals, it is shown that the different phonons influence the ionic and electronic contributions very differently. In particular, it is found that the isotropic components of the phonon spectra lead to no variation in the lattice contribution to the field gradient but produce substantial changes in the electronic contribution. These latter changes represent the leading contribution to the temperature dependence of the total field gradient. The net lattice contribution, composed of opposing contributions from the anisotropic and anharmonic components of phonon spectra is of the same order and sign as the electronic contribution, although somewhat smaller in magnitude. The relationship of our results to those from earlier work is discussed.

I. INTRODUCTION

There have been considerable advances[1] recently, in the understanding of the origin of field gradients q in metallic systems. In particular, in the four hcp metals, beryllium, magnesium, zinc, and cadmium, good agreement with experimental data[2] has been obtained[3] with respect to the magnitude of the field gradient, the sign also being in agreement for cadmium, where it is experimentally available.[4] Recently, attention has been focused on the origin of the temperature dependence of q in metals, experimental data[5] on which are available by several different techniques.

It has been recognized for some time[6] that the influence of phonons has to be considered in attempting to understand the temperature dependence of q, the lattice contribution, q_{latt}, having been the earliest one explored in this respect. The temperature dependence of the electronic contribution q_{el} has only recently been analyzed[7-10] through two main approaches. In one, the electronic contribution to the temperature dependence has been taken into account through a consideration of the dielectric screening of the lattice potential by the conduction electrons through a parametric enhancement factor for the field gradient.[9] The second approach[8,10] discusses the influence of electron-phonon interactions on the band structure and wave functions for conduction electrons as in an earlier treatment[11] of the Knight shift and proposes a parametric dependence of q_{el} on T to explain the observed temperature variation.[2]

In the present work, we carry out an *ab initio* treatment of the temperature dependence of the ionic and electronic contributions to q in zinc and cadmium, explicitly including the effects of the isotropic, anisotropic, and anharmonic components of the phonon spectra. Such a nonparametric treatment was necessary because, while the anisotropic Knight-shift and field gradient involve similar operators, they show[2,11,12] opposite direction tions of variation with temperature. The present approach provides clear insights into the relationship between the temperature variations of q_{latt} and q_{el} as well as the relative importance of the different features of the phonon spectra and gives a satiafactory explanation of experimental data in the two metals.

In Sec. II, we shall consider the contribution to the temperature dependence from the influence of phonons on the component of the field gradient due to the ions in the lattice. In Sec. III, the corresponding contribution from the electronic component shall be considered. In Sec. IV, the contributions from the lattice and electronic components of the field gradient to the temperature dependence are combined and compared with experiment. The relative importance of the various contributions will be analyzed and the relationship of our results to those from previous work will be discussed. Section V summarizes the main conclusions from our results and discusses further theoretical improvements that should be examined in the future to bridge the remaining differences between theory and experiment in the two metals we have studied.

II. THEORY OF TEMPERATURE DEPENDENCE OF THE LATTICE CONTRIBUTION TO THE FIELD GRADIENT

The temperature dependence of the net field gradient in metals is expected to be composed of contributions from the charges in the lattice and conduction electrons as perturbed by phonons. Thus,

$$q(T)=q_{\text{latt}}(T)+q_{\text{el}}(T). \tag{1}$$

In the quantitative evaluation of $q_{\text{latt}}(T)$ and $q_{\text{el}}(T)$, both at any one temperature, as well as their variations with temperature, one has to incorporate the influence of antishielding effects.[13,14] For the lattice contribution

$$q_{\text{latt}}(T)=q_{\text{latt}}^{\text{bare}}(T)(1-\gamma_\infty), \tag{2}$$

where $(1-\gamma_\infty)$ is the antishielding factor calculated for the ion core in the presence of external charge, and $q_{\text{latt}}^{\text{bare}}(T)$ represents the field gradient at the nuclear site in question due to the ionic charges in the lattice without a consideration of the influence of the core electrons surrounding the nucleus. The antishielding effect in $q_{\text{el}}(T)$ is somewhat more complicated but a method for treating this effect quantitatively has been recently developed.[15] We shall discuss this question in more detail in the next section. The present section is concerned with the lattice contributions.

The instantaneous value of q_{latt} is given by:[14]

$$q_{\text{latt}}(T)=\sum_{n\neq 0}\xi_n e\left(\frac{3(Z_n-Z_0)^2-(|\vec{R}_n-\vec{R}_0|)^2}{(|\vec{R}_n-\vec{R}_0|)^5}\right)(1-\gamma_\infty) \tag{3}$$

where $\xi_n e$ are the charges on the ions, $(1-\gamma_\infty)$ is the antishielding factor[13,14] and $\vec{R}_0$, Z_0, $\vec{R}_n$, and Z_n refer respectively to the instantaneous values of the radius vectors and z coordinates for the central and nth ions. To obtain the temperature variation of q_{latt}, one has to carry out a Taylor expansion in the changes δX_n, δY_n and δZ_n in the lattice coordinates due to the influence of phonons. Thus,

$$q_{\text{latt}}(T)=q_{\text{latt}}(0)+\sum_n\sum_{i=1}^{3}\left(\frac{\partial}{\partial X_{ni}}q_{\text{latt}}\right)_0\langle\delta X_{ni}\rangle +\frac{1}{2}\sum_n\sum_{i,j=1}^{3}\left(\frac{\partial^2}{\partial X_{ni}\partial X_{nj}}q_{\text{latt}}\right)_0\langle\delta X_{ni}\delta X_{nj}\rangle+\cdots, \tag{4}$$

where $X_{ni}X_{nj}$ represent respectively the x, y, and z components of the position vector $\vec{R}$ for $i,j=1$, 2, and 3 and the averages are taken over the phonon spectrum. In Eq. (4), the subscript zero outside the curly brackets in the expressions for the derivatives indicates that they are evaluated for the equilibrium position of the lattice points. For harmonic vibrations,

$$\langle\delta X_{ni}\rangle=0$$

and

$$\langle\delta X_{ni}\delta X_{nj}\rangle=\langle\delta X_i^2\rangle\delta_{ij}, \tag{5}$$

where the subscript n has been dropped on the right-hand side of Eq. (5) to indicate that the averages are independent of n. Thus,

$$q_{\text{latt}}(T)=q_{\text{latt}}(0)+\frac{1}{2}\sum_n\sum_{i=1}^{3}\left\{\frac{\partial^2}{\partial X_{ni}^2}q_{\text{latt}}\right\}_0\langle\delta X_i^2\rangle \tag{6}$$

where $q_{\text{latt}}(0)$ is obtained by evaluating the summations in Eq. (3) at 0 °K. Now in the isotropic approximation

$$\langle\delta X_1^2\rangle=\langle\delta X_2^2\rangle=\langle\delta X_3^2\rangle, \tag{7}$$

and the temperature variation arising from the second term in Eq. (6) can be written in the form

$$\begin{aligned}\delta q_{\text{latt}}^{\text{iso}}&=q_{\text{latt}}^{\text{iso}}(T)-q_{\text{latt}}(0)\\&=\frac{1}{2}\sum_n\nabla_n^2\left(\sum_{n\neq 0}\xi_n e\frac{(4\pi/5)^{1/2}Y_2^0(\Omega_{\vec{R}_{n'}-\vec{R}_0})}{|\vec{R}_{n'}-\vec{R}_0|^3}\right)_0\\&\quad\times\langle\delta X_3^2\rangle(1-\gamma_\infty).\end{aligned} \tag{8}$$

It is a well-known result in electrostatics[16] that $\nabla^2(Y_l^m/r^{l+1})=0$ and so the lattice contribution to the temperature variation of the field gradient vanishes in the isotropic approximation. When one account of the anisotropy of the phonons in an axially symmetric system,[17] Eq. (7) is replaced by:

$$\langle\delta X_1^2\rangle=\langle\delta X_2^2\rangle=\epsilon(T)\langle\delta X_3^2\rangle, \tag{9}$$

where $\epsilon(T)$ is the temperature-dependent phonon anisotropy factor different from unity. Using Eqs. (6) and (9), we obtain for the temperature-variation of the field gradient in an axially symmetric lattice,

$$\begin{aligned}\delta q_{\text{latt}}^{\text{aniso}}(T)&=(1-\gamma_\infty)(q_{\text{latt}}(T)-q_{\text{latt}}(0))\\&=(1-\gamma_\infty)\sum_{n\neq 0}\xi_n e(1-\epsilon(T))\langle\delta X_3^2\rangle\left(\frac{9}{|\vec{R}_n-\vec{R}_0|^5}-\frac{90(Z_n-Z_0)^2}{|\vec{R}_n-\vec{R}_0|^7}+\frac{105(Z_n-Z_0)^4}{|\vec{R}_n-\vec{R}_0|^9}\right).\end{aligned} \tag{10}$$

Note that for $\epsilon(T)=1$, corresponding to the isotropic phonon approximation [Eq. (7)], one gets $\delta q_{\text{latt}}^{\text{iso}}(T)=0$ as was found from Eq. (8).

The anharmonic aspect of the phonons is reflected by the thermal expansion of the lattice with increase in temperature. The thermal expansion leads to increases in both c and a of the hcp lattice which lead to both an increase in volume of the lattice as well as a change in the c/a ratio. Thus, the contributions of the anharmonicity of the phonons to the temperature dependence of the field gradient can be obtained by calculating q_{latt} [Eq. (3)] using the lattice parameters at different temperatures. The field gradient is more sensitive to the change in the c/a ratio rather than the volume since the former strongly influences the noncubicity of the environment around the nucleus. The contribution $\delta_{\mathrm{latt}}^{\mathrm{anharm}}(T)$ to the temperature variation of q_{latt} due to the lattice expansion can be obtained from the available expression[18] for the dependence of q_{latt} on the c/a ratio, namely,

$$q_{\mathrm{latt}}^{\mathrm{anharm}}(T)=\frac{2}{[a(T)]^3}\left[0.0065-4.4584\times\left(\frac{c(T)}{a(T)}-1.6330\right)\right]. \tag{11}$$

The anharmonic phonon effect on the lattice contribution has been examined for cadmium in the literature.[19] We have evaluated $q_{\mathrm{latt}}(T)$ for zinc and cadmium in the temperature ranges, 0 to 490 °K and 0 to 462 °K respectively using available structural data[20] on $c(T)$ and $a(T)$. Our results for the anharmonic phonon-lattice contribution

$$\delta q_{\mathrm{latt}}^{\mathrm{anharm}}(T)=q_{\mathrm{latt}}^{\mathrm{anharm}}(T)-q_{\mathrm{latt}}^{\mathrm{anharm}}(0) \tag{12}$$

as well as $\delta_{\mathrm{latt}}^{\mathrm{aniso}}(T)$ for both metals shall be presented and discussed in Sec. IV.

III. THEORY OF TEMPERATURE DEPENDENCE OF CONDUCTION-ELECTRON CONTRIBUTION TO THE FIELD GRADIENT

We consider next the temperature variation of the electronic contribution to the field gradient. For this purpose, one needs the change in the expectation value of the field-gradient operator over the electronic wave functions due to the influence of the phonons in the lattice. This expectation value changes[11] both because of the fluctuation in the position of the nuclear site where the field gradient is being evaluated, as well as due to the changes in the electronic wave functions, as a consequence of the electron-phonon interactions. One would again have to consider both the harmonic and anharmonic components of the phonon spectra, the latter being comprised of both isotropic and anisotropic components. The most important point to notice is that the isotropic phonon contribution to the change in the conduction electron part of the field gradient is not expected to vanish, in contrast to the case of the lattice contribution. In the latter case, as discussed earlier in Sec. II, the vanishing of $\delta q_{\mathrm{latt}}^{\mathrm{iso}}(T)$ was a consequence of the specific form of the lattice field-gradient term $[Y_2^0(\Omega_{\vec{R}_\mu}-_{\vec{R}_0})/|\vec{R}_\mu-\vec{R}_0|^3]$ for which the Laplacian in Eq. (8) vanished. The dependence of the electronic contribution on the lattice coordinates is not expected to have this form and therefore does not lead to a vanishing temperature dependence. In fact, as we shall see from the results in Sec. IV, the electronic contribution to the temperature dependence from the influence of the isotropic phonons is the leading one among all the contributions.

The conduction-electron contribution to the field gradient at the nuclear site $\vec{R}_0$, apart from antishielding effects, is given by[3,14]

$$q_{\mathrm{el}}=-e\sum_{\vec{k},i}\left\langle\psi_{\vec{k},i}\left|\frac{3\cos^2\theta_{\vec{r},\vec{R}_0}-1}{|\vec{r}-\vec{R}_0|^3}\right|\psi_{\vec{k},i}\right\rangle, \tag{13}$$

where the summation is carried out over all occupied bands i and the region in $\vec{k}$ space in the first Brillouin zone below the Fermi surface, $\theta_{\vec{r},\vec{R}_0}$ represents the angle made by the radius vector $\vec{r}-\vec{R}_0$ with the c axis. The temperature dependence of q_{el} arises from both the change in $\vec{R}_0$ and of the conduction electron wave functions $\psi_{\vec{k},i}$ due to the influence of the phonons. The temperature-dependence of the wave functions $\psi_{\vec{k},i}$ is incorporated through the use of a temperature-dependent pseudopotential,[11] which is used to obtain the temperature dependent pseudowave functions

$$\eta_{\vec{k},i}=\sum_{\vec{K}}c_{i,\vec{k}+\vec{K}}\chi_{i,\vec{k}+\vec{K}}, \tag{14}$$

the $\chi_{i,\vec{k}+\vec{k}}$ being normalized plane waves of wave vector $\vec{k}+\vec{K}$ from band i. The true wavefunction $\psi_{\vec{k}}$ is then obtained by orthogonalizing $\eta_{\vec{k},i}$ to the atomic cores[21]:

$$\psi_{\vec{k},i}=(1-P)\eta_{\vec{k},i}=\sum_{\vec{K}}c_{i,\vec{k}+\vec{K}}A_{i,\vec{k}}\phi_{\vec{k}+\vec{K}}(r), \tag{15}$$

i representing the band index, $\vec{k}$ the wave-vector in the reduced zone scheme, $\vec{K}$ being reciprocal lattice vectors and $\phi_{\vec{k}}$ being orthogonalized plane wave (OPW) functions given by:

$$\phi_{\vec{k}}=\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}}-\frac{1}{\sqrt{\Omega}}\sum_{nlm}\int e^{i\vec{k}\cdot\vec{r}\,'}\psi_{nlm}^*(\vec{r}\,')\,d^3r'\,\psi_{nlm}(\vec{r}), \tag{16}$$

where $\psi_{nlm}(\vec{r})=P_{nl}(r)/rY_l^m(\theta,\phi)$ are the wave functions for the core state in the metal and Ω is the volume of the Wigner-Seitz cell. The $A_{i\vec{k}}$ are constants which normalize the OPW functions and are given by

$$A_{i,\vec{k}}=\left(\sum_{\vec{K}}|c_{i,\vec{k}+\vec{K}}|^2-\sum_{\vec{K},\vec{k}\,',t}c_{i,\vec{k}+\vec{K}'}^*c_{i,\vec{k}+\vec{K}}b_{t,\vec{k}+\vec{K}'}^*(T)b_{t,\vec{k}+\vec{K}}(T)\right)^{-1/2} \tag{17}$$

with $b_{t,\vec{k}+\vec{K}}(T)$ given by:

$$b_{t,\vec{k}+\vec{K}}(T)=\frac{4\pi}{\sqrt{\Omega}}\,i^{l}\,Y_{l}^{m*}(\Omega_{\vec{k}+\vec{K}})\cos(\tfrac{1}{2}\vec{K}\cdot\vec{\rho})e^{-K^{2}D(T)}\times\int_{0}^{\infty}j_{l}(|\vec{k}+\vec{K}|r)P_{nl}(r)r\,dr\,, \tag{18}$$

where t represents the quantum numbers nlm of the core states and $\vec{\rho}$ is radius vector joining the two atoms in each unit cell of the hcp lattice. The function $D(T)$ arising from the influence of the phonons on the structure-factor brings the temperature dependence into the wave functions and can be evaluated[11] in terms of the experimental dispersion curves for the phonons from neutron scattering data. For the present we shall use the Debye approximation, in which case[11]

$$D(T)=\frac{3\hbar^{2}}{Mk_{B}\Theta_{D}}\left[\left(\frac{T}{\Theta_{D}}\right)^{2}\int_{0}^{\Theta/T}\frac{x\,dx}{e^{x}-1}+\frac{1}{4}\right], \tag{19}$$

Θ_D being the Debye temperature.

The pseudopotential matrix elements over the plane-wave basis functions $\chi_{\vec{k}+\vec{K}}$

$$\chi_{\vec{k}+\vec{K}}=\frac{1}{\sqrt{\Omega}}\,e^{i(\vec{k}+\vec{K})\cdot\vec{r}} \tag{20}$$

including their temperature dependence, are given by[11,22]

$$\langle\chi_{\vec{k}+\vec{K}'}|V_{p}(E)|\chi_{\vec{k}+\vec{K}}\rangle_{T}=\Big(U(|\vec{K}-\vec{K}'|)+\sum_{t}(E-E_{F}+V(t))\,b^{*}_{t,\vec{k}+\vec{K}'}(0)b_{t,\vec{k}+\vec{K}}(0)\Big)e^{-|\vec{K}-\vec{K}'|^{2}D(T)} \tag{21}$$

the quantities involved in the large parentheses in Eq. (21) having the meaning explained in Ref. 22. The pseudopotential matrix elements in Eq. (21) are energy dependent, which is important in our present work since the conduction-electron field gradient in Eq. (13) involves the entire occupied k space below the Fermi surface instead of only the region near the Fermi surface as in other properties such as the Knight shift. Temperature dependence is introduced into the pseudopotential through the structure factors in Eq. (21). The coefficients $c_{i,\vec{k}+\vec{K}}$ in Eq. (14) are obtained at various temperatures by minimizing the energy variationally using the pseudofunctions[21] $\eta_{\vec{k}i}$ [Eq. (14)] leading[22] to the linear equations

$$\sum_{\vec{K}'}c_{i,\vec{k}+\vec{K}'}[(H_{p})_{\vec{k}+\vec{K},\vec{k}+\vec{K}'}-ES_{\vec{k}+\vec{K},\vec{k}+\vec{K}'}] \tag{22}$$

with

$$(H_{p})_{\vec{k}+\vec{K},\vec{k}+\vec{K}'}=\langle\chi_{\vec{k}+\vec{K}}|-\nabla^{2}+V_{p}(E)|\chi_{\vec{k}+\vec{K}'}\rangle \tag{23}$$

and

$$S_{\vec{k}+\vec{K},\vec{k}+\vec{K}'}=\delta_{\vec{K}\vec{K}'}-\sum_{t}b^{*}_{t,\vec{k}+\vec{K}}(0)b_{t,\vec{k}+\vec{K}'}(0), \tag{24}$$

The solution of the linear equations for $c_{i,\vec{k}+\vec{K}}$ leads to the secular equation:

$$\det|(H_{p})_{\vec{k}+\vec{K},\vec{k}+\vec{K}'}-ES_{\vec{k}+\vec{K},\vec{k}+\vec{K}'}|=0\,. \tag{25}$$

The process of solving the secular equations self-consistently with respect to E_F which occurs in the expression for the pseudopotential matrix element has been described earlier.[22] The pseudopotential parameters $U(|\vec{K}-\vec{K}'|)$ and $v(t)$ for zinc and cadmium were taken from the work of Stark and Falicov[23] who had derived them from the study of Fermi-surface properties of the two metals.

Once the $c_{i,\vec{k}+\vec{K}}$ are obtained, we have the conduction electron wave functions $\psi_{\vec{k},i}$ [Eq. (15)] at various points in the occupied Fermi-volume which are needed to carry out the expectation values in Eq. (13) for the electronic contribution to the field gradient. On evaluating these expectation values, one gets three types of terms.[15,22] The first is the pure plane-wave–plane-wave type terms, the second is hybrid terms involving both plane-wave and core-wave functions, and the third involving purely core-state terms. The expectation value of the field gradient also involves structure factors which give additional temperature dependence besides that arising from the $c_{i,\vec{k}+\vec{K}}$. This is the temperature variation arising from the fluctuation in position of the nuclear site referred to earlier. The plane-wave–plane-wave terms in the expectation value, Eq. (13), for the conduction electron contribution are given by

$$q_{\mathrm{pw\text{-}pw}}=\frac{2}{\Omega}\left(\frac{64\pi^{3}}{45}\right)^{1/2}\sum_{i,\vec{k}}|A_{i\vec{k}}|^{2}\sum_{\vec{K}\vec{K}'}c^{*}_{i,\vec{k}+\vec{K}}c_{i,\vec{k}+\vec{K}'}\,S_{0}(\vec{K}-\vec{K}')e^{-|\vec{K}'-\vec{K}|^{2}D(T)}Y_{2}^{0}(\Omega_{\vec{K}-\vec{K}'}) \tag{26}$$

TABLE I. Choices of antishielding parameters for various contributions to the field gradient in zinc and cadmium.

Nature of contribution \ Metal	Zn	Cd
Local (R)	0.0	0.0
Hybrid ($\gamma_{\rm eff}$ hybrid)	0.0	0.0
Distant electronic[a] ($\gamma_{\rm eff\ pw-pw}$)	−9.0	−20.0
Lattice contribution (γ_∞)	−13.97	−32.26

[a] This number is about $\frac{2}{3}\gamma_\infty$ and was chosen from the results of the *ab initio* antishielding calculation in Ref. 15.

where the $A_{i\vec{k}}$ and $c_{i,\vec{k}+\vec{K}}$ arise from the wave functions [Eq. (15)] and are themselves temperature dependent. The summations in i and k in Eq. (26) refer respectively to each of the occupied bands and corresponding occupied regions of $\vec{k}$ space in the first Brillouin zone for each of these bands. One gets corresponding expressions for the tight-binding and hybrid terms.

In evaluating the temperature-dependent electronic contribution quantitatively, one has to incorporate appropriate antishielding effects. The extent of antishielding of the field gradient due to different components of the conduction electron density depends[15,22] on the extent of their penetration of the core region of the ion containing the nucleus at which the field gradient is being evaluated. A first-principle procedure has recently been developed[15] for quantitative evaluation of the antishielding effect associated with the conduction electrons. Using this procedure, it has been found that we have to antishield (shield) the "local" contribution to the field gradient from the conduction electrons, that is, terms involving the tight-binding component of the wave functions, by $(1-R)$, an atomic-like antishielding factor, such as that associated with the shielding of the field gradient due to the valence electrons in an atom, which is nearly unity. The "external" contributions purely from the plane-wave components of the charge density such as the plane-wave–wave term in Eq. (26) has to be antishielded by a factor $(1-\gamma_{\rm eff})$, where $\gamma_{\rm eff} \approx \frac{2}{3}\gamma_\infty$. It should be noted that this antishielding has an important effect on the variation of the conduction electron contribution to the field gradient, making the plane-wave–plane-wave component account for about one-half of the change with temperature of that due to the conduction electrons. The hybrid terms are expected to experience a small antishielding effect[15], much smaller than γ_∞ and closer to R. We have taken $\gamma_{\rm eff} \approx 0$ for these terms. For easy reference, the antishielding parameters we have used for the various contributions to the field gradients are listed in Table I for both metals.

For studying the influence of the anisotropy of the phonon spectra on the electronic contribution to the field-gradient one has to take into account[11] the dependence of the Debye-Waller factor in the pseudopotential matrix elements on the direction of $\vec{K}$. The corresponding Debye-Waller factor would be substantially more complicated to evaluate than that for the isotropic case [Eq. (19)]. From our experience with the results for the lattice contributions discussed in Sec. II, the influence of phonon anisotropy on $\delta q_{\rm el}$ is not expected to be insignificant. However, there is a difference between $\delta q_{\rm latt}$ and $\delta q_{\rm el}$ in this respect. While $(\delta q_{\rm latt})_{\rm iso}$ vanished, $(\delta q_{\rm el})_{\rm iso}$ will be seen in Sec. IV to make the most important contribution to the net δq. Therefore, $(\delta q_{\rm el})_{\rm aniso}$ is expected to be relatively less important in effect on the net $\delta q_{\rm el}$ than would have been the case for $\delta q_{\rm latt}$.

Finally, the influence of the anharmonic phonon spectra can, as in the case of the lattice contribution to the field gradient, be incorporated by including the changes[20] in the lattice parameters c and a in the electronic field gradient calculation. We have done this and find that the influence of lattice expansion leads to changes, $(\delta q_{\rm el})_{\rm anharm}$, in the conduction electron contribution, of less than 5% of the isotropic-phonon contribution $(\delta q_{\rm el})_{\rm iso}$.

IV. RESULTS AND DISCUSSION

Our results for the various contributions to the temperature variation of the field gradient are presented for zinc and cadmium in Fig. 1 and 2, respectively. The lattice parameters at a number of temperatures in the ranges studied for zinc and cadmium and Debye temperatures used are given in Tables II and III. In both metals, the electronic contribution, $\delta q_{\rm el}(T)$, is seen to be larger in size than the lattice contribution but the latter also makes a significant contribution to the net temperature dependence of the field gradient.

Considering the electronic contribution first, it arises mainly from the isotropic phonon effect and is seen to lead to a decrease in the field gradient

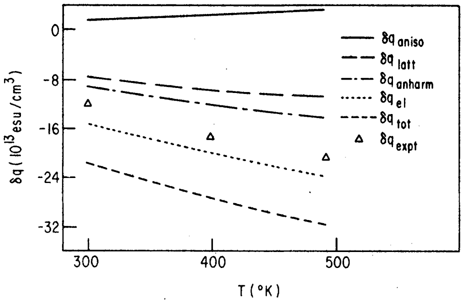

FIG. 1. Temperature dependence of the field gradient in zinc. Our calculated anharmonic and anisotropic lattice contributions are labeled δq_{anharm} and δq_{aniso} respectively, with δq_{latt}, δq_{el} and δq_{tot} being the net lattice net electronic, and total changes in q, respectively. The experimental values δq_{expt} are obtained from H. Bertschat, R. Recknagel and B. Spellmeyer in Ref. 2.

TABLE II. Lattice parameter data for cadmium in the temperature range studied, distances are in atomic units.

T(°K)	$C(T)$	$A(T)$	Θ_D
0[a]	10.443	5.610	
75[b]	10.461	5.599	209°[c]
200[b]	10.539	5.609	
298[a]	10.594	5.618	
462[a]	10.677	5.639	

[a] Taken from Reference 11.

[b] Reference 20.

[c] Reference 20, Sec. IV, p. 115.

from the positive value of q_{el} at 0 °K in both metals. This change is in the same direction as experiment and is opposite in sign to the change in the anisotropic Knight shift found in cadmium.[11,12] This is interesting since, apart from antishielding effects for the field gradient, the latter as well as the anisotropic Knight shift (K_{aniso}) both involve the expectation value of the same operator Y_2^0/r^3. However, K_{aniso} involves[11] only the region of $\vec{k}$-space near the Fermi surface while q_{el} involves the entire Fermi volume, deriving its major contribution (about 95% in cadmium) from the first and second bands at all temperatures. Both q_{el} and K_{aniso} depend on the differences between the p_z and the sum of the p_x and p_y characters of the p-components of the conduction electron-wave functions. The results of our calculation for (δq_{el}) and the earlier ones[11] on temperature variation of K_{aniso} are a consequence of the fact that the changes in the character of the conduction-electron wave functions with temperature for the first and second bands are very different from the changes at the Fermi surface. One other feature of the electronic contributions δq_{el} is the comparable contributions from the local and the plane-wave–plane-wave components of the conduction electron charge density, after proper antishielding effects (as discussed in Sec. II) are utilized for the field gradient due to the latter.

The lattice contribution δq_{latt} in both metals is seen from Figs. 1 and 2 to be dominated by the anharmonic contribution $(\delta q_{\text{latt}})_{\text{anharm}}$ which is in the same direction as experiment and δq_{el}. The anisotropic lattice contribution $(\delta q_{\text{latt}})_{\text{aniso}}$ is substantially smaller than $(\delta q_{\text{latt}})_{\text{anharm}}$ and of opposite sign. The ratio of the net δq_{latt} to δq_{el} is seen to range from 0.40 to 0.33 in zinc and 0.68 to 0.21 in cadmium over the temperature ranges covered. The fact that δq_{latt} is a significant fraction of δq_{el} in both metals indicates that the former has to be included in attempting to explain the experimental temperature dependence. Further, the fact that the ratio $\delta q_{\text{latt}}/\delta q_{\text{el}}$ is temperature dependent also indicates the necessity for combining δq_{latt} with δq_{el} in attempting to explain the experimental curvatures[2] of the plots of δq_{el} against T.

This point ragarding the ratio of $\delta q_{\text{el}}(T)$ and $\delta q_{\text{latt}}(T)$ is worth remarking further on. The fact

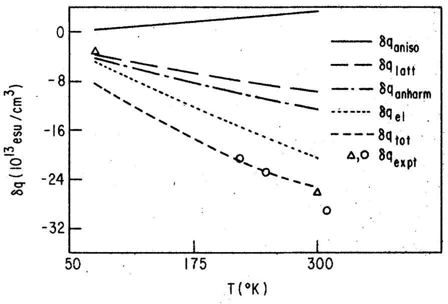

FIG. 2. Temperature variation of the field gradient in cadmium. The calculated anharmonic and anisotropic lattice contributions are labeled δq_{anharm} and δq_{aniso} respectively, with δq_{latt}, δq_{el} and δq_{tot} being the net lattice, net electronic, and total changes in q, respectively. Δ represents data obtained from R S Raghavan and P Raghavan in Ref. 2, and O represents data obtained from J Bleck *et al.* also from Ref. 2.

TABLE III. Lattice parameter data for zinc in the temperature range studied, distances are in atomic units.

T(°K)	$C(T)$	$A(T)$	Θ_D
300[a]	9.330	5.027	
400[a]	9.389	5.034	310°[b]
490[a]	9.441	5.041	
560[a]	9.479	5.048	

[a] Reference 20.

[b] Reference 26.

that $\delta q_{\mathrm{el}}(T)$ and $\delta q_{\mathrm{1att}}(T)$ do not bear the same factor of proportionality to each other at different temperatures means also that

$$\frac{q_{\mathrm{el}}(T)}{q_{\mathrm{1att}}(T)}=\frac{q_{\mathrm{el}}(0)+\delta q_{\mathrm{el}}(T)}{q_{\mathrm{1att}}(0)+\delta q_{\mathrm{1att}}(T)}$$

would also be expected to be temperature dependent, although not as strongly as $\delta q_{\mathrm{el}}/\delta q_{\mathrm{1att}}$ because $\delta q_{\mathrm{el}}(T)/q_{\mathrm{el}}(0)$ and $\delta q_{\mathrm{1att}}(T)/q_{\mathrm{1att}}(0)$ are small (about 5 and 4%, respectively, in cadmium) over the temperature range over which experimental data[2] are available. This expected departure of $q_{\mathrm{el}}(T)/q_{\mathrm{1att}}(T)$ from a constant should not be construed as a manifestation of departures from the empirical universal correlation[24] found for this ratio for different metallic systems, in principle, at the same temperature. Instead, the departure of this ratio from a constant value for the same metal at different temperatures is more a reflection of the fact, found from the results of the present work, that the major contributions to the temperature variation of $q_{\mathrm{el}}(T)$ and $q_{\mathrm{1att}}(T)$ arise from different aspects of the phonons, the isotropic and anharmonic components, respectively. From Figs. 1 and 2, our calculated $\delta q(T)$, obtained by combining the net $\delta q_{\mathrm{1att}}(T)$ and $\delta q_{\mathrm{el}}(T)$, are in reasonable agreement with experiment and in general (especially for zinc) somewhat larger than the latter. Since the present work does not involve any adustable parameters, we can properly look for sources that could bridge the remaining differences between our theoretical results and experiment. Two possibilities are the use of more accurate wave functions for the conduction electrons and the influence of band effects associated with the d electrons which have been presently handled[11,22,23] as core states. One effect that could contribute to the temperature dependence is the additional influence of the phonons on the pseudopotential matrix elements in Eq. (21) through any changes in $U(|\vec{K}-\vec{K}'|)$ and $v(t)$ which have not been included. The phonon effect which has been included in the pseudopotential is the major one arising from the temperature dependence of the structure factors in Eq. (21).

We consider next the relationship of our work to earlier theoretical approaches to the origin of the temperature dependence of the field gradient. In a recent parametric approach to the temperature dependence[8] of q_{el}, it had been assumed that the effects of electron-phonon interactions would be to produce a decrease in q_{el} with temperature. Our *ab initio* claculation of $\delta q_{\mathrm{el}}(T)$ shows that the assumed direction of change in this earlier work was correct. However, it was important to demonstrate this, in view of the fact that, as pointed out earlier, the anisotropic Knight shift, which involves the same operator $[Y_2^0(\theta,\phi)]/r^3$ as the field gradient, shows an increase[11,12] with temperature. Our analysis has shown that the field gradient which involves contributions from the entire $\vec{k}$ space, in contrast to only the Fermi surface region which influences the Knight shift, does in fact lead to a decrease with temperature for $\delta q_{\mathrm{el}}(T)$. Further, for a quantitative analysis of the temperature dependence of q_{el}, we have shown that it is necessary to apply proper antishielding factors[15] to the local and distant contributions to the field gradient which make these two contributions comparable. If the sizable antishielding effect for the distant contribution had not been incorporated, the latter would have been much smaller than the local contribution and the net $\delta q_{\mathrm{el}}(T)$ would have been seriously underestimated.

The other two recent theoretical approaches to the field gradient relate the temperature dependence of q_{el} to the temperature dependence of q_{1att}. In the earlier of these,[7] δq_{el} was taken to have the form

$$\delta q_{\mathrm{el}}=q''\langle\delta Z^2\rangle \qquad (27)$$

with $\langle\delta Z^2\rangle$ obtained from the Debye approximation and q'' being adjusted to fit experimental data. From our Eq. (10) it appears that Eq. (27) is equivalent to assuming that δq_{el} is proportional to $(\delta q_{\mathrm{1att}})_{\mathrm{harm}}$. Our work has shown that $(\delta q_{\mathrm{1att}})_{\mathrm{harm}}$ derives its major contribution from anisotropic phonon effects while δq_{el} derives its main contribution from isotropic phonon effects. It is therefore difficult to ascribe a physical meaning to the assumed proportionality between electronic and lattice contributions to the changes in field gradient.

The authors of the other parametric-type investigation[9] for δq_{el} do not consider the electronic wave functions explicitly. Instead, the conduction electrons are regarded as providing a dielectric screening of the lattice potential, whose second derivative (q_{1att} in the absence of screening) is enhanced by an empirical factor to obtain $\delta q_{\mathrm{el}}(T)$. The screening of the lattice potential is essential for their work since they employ an isotropic phonon approximation and the unscreened $q_{\mathrm{1att}}(T)$ would have led to a vanishing result [in view of our Eq. (8)]. The empirical enhancement factor needed by these authors is unusually large, namely $\gamma_{\mathrm{eff}}\simeq 6\gamma_\infty$. Since the maximum enhancement factor due to antishielding effects can never exceed γ_∞, other factors have to be considered to explain this large enhancement effect. We feel that the major source of this enhancement effect is the need to incorporate the influence of the Pauli repulsion effect of the core electrons at the site containing the nucleus of interest. This effect on the conduction electrons is included in the orthogonalization procedure [Eqs. (15)-(17)] used in constructing the OPW wave functions employed in the present work, and leads to substantial enhancement of the conduction electron density near the nucleus. Another possible contribution to the empirical enhancement factor is the necessity in quantitative investigations to use a dielectric constant appropriate for Block electrons, a rather difficult task.

V. CONCLUSION

Summarizing, we have shown that a first-principles calculation of q_{el} and q_{latt} at 0 °K, incorporating antishielding effects appropriately, does provide a proper quantitative explanation of the nuclear quadrupole coupling energies in zinc and cadmium. Further, our work has also demonstrated that an *ab initio* calculation of the various contributions from the lattice and conduction electrons to the temperature dependence of the field gradient through a proper consideration of antishielding effects and lattice-phonon spectra does give reasonably good agreement with experiment[2] for the pure metals zinc and cadmium and clarifies the roles of different phonon contributions to the field gradients in these metals. In attempting to further the improvement between theoretical and experimental results for the temperature dependence of the field gradients, additional refinements in the calculations would be desirable in the future. Among these are first, the examination of the contribution to the field gradients from bands associated with the *d* electrons which have been handled here, and in earlier band-structure studies[23] as core electrons, secondly, the temperature dependence of the pseudopotential form factors and a more detailed analysis of phonon effects through use of experimental phonon-dispersion curves (including their anisotrophy) to obtain the Debye-Waller factor. Finally, we note that the relative importance of the various mechanism responsible for the temperature variation of the field gradient in other systems[10,25] may not be the same as in the two metals considered here and one should include the contributions of all these mechanisms in attempting to understand the temperature dependence of the field gradient in any metallic system.

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