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Theory of nuclear quadrupole interaction in hexagonal close packed metals—cadmium and zinc*

Nimain C. Mahapatra,[†] Pratap C. Pattnaik, Michael D. Thompson, and T. P. Das
Department of Physics, State University of New York at Albany, Albany, New York 12222

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The conduction-electron contribution to the electric field gradient has been calculated for zinc and cadmium. From a study of the conduction and core electron distributions relative to each other, it is concluded that different components of the field gradient due to the conduction electrons, such as from the local and plane-wave components of the conduction-electron densities, should be shielded differently. A value of about $\gamma_\infty/2$ is estimated for the field gradient due to the plane-wave component of the density. Using the calculated field gradients in the two metals, the quadrupole moments of ^{67}Zn and ^{111}Cd are obtained as 0.50 and 0.76 b, the latter being in good agreement with the value derived earlier from ionic crystal measurements. The effect of the larger antishielding factor on the earlier calculated field gradients in beryllium and magnesium is discussed and it is concluded that the earlier good agreement between theory and experiment for these metals is not significantly affected. Finally, the bearing of the results of the present work on the empirical correlation obtained recently between the conduction-electron and lattice contributions is discussed.

I. INTRODUCTION

The subject of nuclear quadrupole interactions in metals and alloys is currently one of considerable interest.[1] One of the reasons for this is the recent success[2] in obtaining the signs and accurate values of quadrupole coupling constants e^2qQ in the excited states of a number of nuclei by perturbed-angular-correlation techniques. In addition, of course, Mössbauer measurements[3] can also provide the signs and accurate magnitudes of e^2qQ in the metastable states of a number of nuclei, these nuclei and levels often complementing those observed by perturbed-angular-correlation techniques. Conventional resonance techniques,[4] both magnetic and quadrupolar, provide measurements of only the magnitudes of e^2qQ for ground states of nuclei, but not their signs. An accurate calculation of the electric field gradient q at the nucleus, when combined with e^2qQ data, enables one to determine the nuclear quadrupole moment Q. Alternately, in those nuclei for which the atomic quadrupole coupling constants are available, the value of Q is determined by calculating q for the atom, which can be done more accurately than in the solid. The value of Q can then be used to extract q in the solid state from experimental e^2qQ data, q then serving as a property that can be utilized to test the calculated electronic structure of the metal. Electric field gradients have been obtained in the past from calculated electronic wave functions in beryllium,[5] magnesium,[6] and cadmium[7] metals, the results in the latter metal having been reported briefly. The wave functions of the conduction electrons were determined in the former two metals using calculated one-electron potentials[8,9] and employing a linear combination of orthogonalized plane waves as a basis set. For cadmium, a pseudopotential[10] was utilized to obtain pseudofunctions from which the actual wave functions were obtained by the usual procedure of orthogonalization to core states.

Recently the field gradient q in zinc has been studied,[11] following the measurement[12] of the magnitude of e^2qQ in the metal for the $\frac{9}{2}^+$ state (spin $I=\frac{9}{2}^+$) of ^{67}Zn. The aims of this calculation, which has been briefly reported before, are threefold. The first was to determine the magnitude of Q of ^{67}Zn in the $\frac{9}{2}^+$ state, the second was to obtain the sign of q so that the sign of Q could be determined in the future when the sign of e^2qQ became available, and the third aim was to compare the value of Q obtained from the data in the metal with the one obtained from ionic crystals,[6] when e^2qQ of the $\frac{9}{2}^+$ state of ^{67}Zn becomes available in these latter systems. In the calculations in both cadmium and zinc, extensions of the empirical pseudopotentials[10] were used in determining the wave functions for the conduction electrons. The original pseudopotentials had been found[13] to provide good explanations of a number of properties of the Fermi surface in these metals. In the extension used to calculate the field gradient, an implicit dependence of the pseudopotential on the wave vector $\vec{k}$ has been incorporated. In the present paper, we present a more complete description of our work[7,11] on the field gradient in the two metals and focus major attention on the question of the appropriate antishielding factors to be used for the various contributions of q from the ionic charges and conduction-electron distributions, particularly the latter. It will be shown that the proper choice of antishielding factors is of crucial importance in determining the net field gradient in the metal. This question of the appropriate antishielding factors for the various parts of q has become important at the present for two main reasons. The first is the discrepancy found recently in the values of Q of ^{111}Cd ($\frac{5}{2}^+$) derived from cadmium metal[14] and ionic cadmium compunds.[15] The second reason is the recent analysis[16] of quadrupole coupling data for ^{111}Cd and other nuclei in a number of different alloys using the former as solute where, from a knowledge of the signs and magnitudes of the quadrupole coupling constants in the alloy systems, one is able to derive the conduction-electron contributions to q, the latter appearing to depend on the antishielding factor[17] $(1-\gamma_\infty)$ of the solute ion. The bearing of our work on this question will be discussed.

Section II presents the choice of the pseudopotential and the procedure adapted to calculate the contributions to q from the conduction electrons. Section III deals with the choice of the antishielding factors for q at the nuclear site from the ionic charges in the lattice and various regions of the conduction-electron distribution, internal and external to the core-electron distribution. Section IV discusses the results of our present investigations on cadmium and zinc and the general conclusions that may be drawn from them regarding the question of the appropriate antishielding factors (including metals like beryllium and magnesium investigated earlier[5,6]) and the bearing of the present results on the interpretation[16] of data in alloys.

II. PROCEDURE FOR EVALUATION OF FIELD GRADIENT DUE TO CONDUCTION ELECTRONS

The procedure for calculation of the conduction-electron contribution to the field gradient involves two main steps, the determination of the wave function and the evaluation of the electronic field gradient from the occupied Fermi volume. The electronic wave functions were obtained by the pseudopotential procedure.[7,10,18,19] The pseudo-wave-function is given by a linear combination of plane waves, namely

$$\phi_{\vec{k}}(\vec{r}) = \sum_{\vec{K}} C_{\vec{k}+\vec{K}}\, \chi_{PW}(\vec{k}+\vec{K}) \,, \tag{1}$$

with

$$\chi_{PW}(\vec{k}+\vec{K}) = [1/(N_0\Omega_0)^{1/2}]\, e^{i(\vec{k}+\vec{K})\cdot\vec{r}} \,, \tag{2}$$

where N_0 is the number of Wigner-Seitz cells, Ω_0 the Wigner-Seitz volume, $\vec{k}$ the reduced vectors, and $\vec{K}$ the reciprocal-lattice vectors. The coefficients $C_{\vec{k}+\vec{K}}$ are obtained variationally by solving the appropriate secular equations involving the pseudo-Hamiltonian. The pseudopotentials used for both the metals were based upon the empirical ones, derived by Stark and Falicov[10] for the explanation of Fermi-surface properties, suitably adapted to apply over the entire Fermi volume as we shall now discuss.

The Stark-Falicov pseudopotentials[10] for the two metals given by

$$V_{p,\,\mathrm{SF}}(E) = U + \sum_t v_t P_t \tag{3}$$

had both local and nonlocal components corresponding to the first and second terms on the right-hand side in Eq. (3), with the U and v_t for cadmium and zinc listed by Stark and Falicov. The P_t are projection operators for the core states defined as

$$P_t = |\chi_t\rangle\langle\chi_t| \,, \tag{4}$$

with

$$|\chi_t\rangle = \frac{1}{(N_0)^{1/2}} \sum_n e^{i\vec{k}\cdot\vec{r}_n}\, \xi(\vec{r}-\vec{r}_n) \tag{5}$$

being the tight-binding wave functions for the core electrons and $\xi_t(\vec{r}-\vec{r}_n)$ the tth atomic-type core wave function for the ion located at $\vec{r}_n$.

The matrix elements of $V_{p,\,\mathrm{SF}}$ over the plane-wave wave functions in Eq. (2) are

$$\langle \chi_{PW}(\vec{k}+\vec{K}) | V_{p,\,\mathrm{SF}} | \chi_{PW}(\vec{k}+\vec{K}')\rangle = U_{\vec{K}'-\vec{K}} + \sum_t v_t \langle \chi_{PW}(\vec{k}+\vec{K}) | \chi_t\rangle\langle\chi_t | \chi_{PW}(\vec{k}+\vec{K}')\rangle \,. \tag{6}$$

In order to make the matrix elements in Eq. (6) real, the origin for the plane-wave functions is taken at the midpoint of the line joining the two atoms in the non-Bravais unit cell of the hcp lattice.

This gives

$$\langle \chi_{PW}(\vec{k}+\vec{K}) | \chi_t\rangle = \frac{4\pi}{(\Omega_0)^{1/2}}\, i^l\, Y^*_{lm}(\vec{k}+\vec{K}) \cos(\tfrac{1}{2}\vec{K}\cdot\vec{\rho}) \times \int_0^\infty j_l(|\vec{k}+\vec{K}|r) P_{nl}(r)\, r\, dr \,, \tag{7}$$

$\vec{\rho}$ representing the vector joining the two atoms in the cell. Of the nonlocal terms involving the core states, those which refer to the $3d$ states (in Zn) and the $4d$ states (in Cd) give the largest contributions. In view of this and the relative sizes of the local parameters for the d states, these terms in the pseudopotential make the leading contribution to the matrix element in Eq. (6).

Since the field gradient calculation involves the entire occupied $\vec{k}$ space, in addition to the Fermi surface, we need an energy-dependent pseudopotential applicable to the entire Fermi volume. The adaptation of the pseudopotential in (3) for this purpose was carried out as follows. The energy-dependent pseudopotential may be written in the general form[18,19]

$$V_p(E) = V_c + \sum_t (E - E_t)P_t \ , \tag{8}$$

E_t being the energies of the core states t and V_c the crystal potential. V_c can be split up into local and nonlocal parts according to the relation

$$V_c = U + \sum_t \alpha_t P_t \ , \tag{9}$$

where the parameters α_t have to be determined. This is done by substituting Eq. (9) in Eq. (8) and then comparing it with Eq. (3) at $E=E_F$. Obtaining α_t by this procedure and substituting back in Eq. (6), one obtains

$$V_p(E) = U + \sum_t (E - E_F + v_t)P_t \ . \tag{10}$$

Using the plane-wave matrix elements of the pseudopotential in Eq. (10), coefficients $C_{\vec{k}+\vec{K}}$ can be shown to satisfy the linear equations

$$\sum_{\vec{K}'} C_{\vec{k}+\vec{K}}[(H_p)_{\vec{k}+\vec{K},\vec{k}+\vec{K}'} - ES_{\vec{k}+\vec{K},\vec{k}+\vec{K}'}] = 0 \ , \tag{11}$$

with

$$(H_p)_{\vec{k}+\vec{K},\vec{k}+\vec{K}'} = \langle \chi_{\mathrm{PW}}(\vec{k}+\vec{K}) \,|\, -\nabla^2 + U + \sum_t (v_t - E_F)P_t \,|\, \chi_{\mathrm{PW}}(\vec{k}+\vec{K}')\rangle \tag{12}$$

and

$$S_{\vec{k}+\vec{K},\vec{k}+\vec{K}'} = \langle \chi_{\mathrm{PW}}(\vec{k}+\vec{K}) \,|\, I - \sum_t P_t \,|\, \chi_{\mathrm{PW}}(\vec{k}+\vec{K}')\rangle \ , \tag{13}$$

where I is the identity operator.

Equation (11) leads to the secular equation

$$\det \left| (H_p)_{\vec{k}+\vec{K},\vec{k}+\vec{K}'} - ES_{\vec{k}+\vec{K},\vec{k}+\vec{K}'} \right| = 0 \ . \tag{14}$$

The pseudo-Hamiltonian matrix elements in Eq. (12) depend on the value of the Fermi energy E_F both this and E being conveniently referred to the bottom of the energy band as origin. E_F in Eq. (10) was determined self-consistently, using the calculated energy values to obtain a histogram of states and filling them up to obtain the four electrons characteristic of the two divalent atoms per unit cell. The value of E_F obtained in this way differed very little (about 9% of E_F for zinc) from the value obtained from pseudoband calculations using the Fermi-surface pseudopotential[10] in Eq. (3). One point of procedure about the choice of the atomic wave functions used in this calculation should be mentioned here. In obtaining the pseudopotential matrix elements in Eq. (12) we used Herman-Skillman Hartree-Fock-Slater[20] core wave functions for the sake of consistency, since Stark and Falicov[10] in deriving pseudopotential parameters U and v_t had also employed these wave functions for the cores. Once the pseudofunctions $\phi_{\vec{k}}(\vec{r})$ in Eq. (1) are obtained, one can get the actual wave functions $\psi_{\vec{k}}$ by replacing $\chi_{\mathrm{PW}}(\vec{k}+\vec{K})$ in Eq. (1) with orthogonalized-plane-wave (OPW) functions $\chi_{\mathrm{OPW}}(\vec{k}+\vec{K})$:

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{K}} C_{\vec{k}+\vec{K}} A_{\vec{k}}\, \chi_{\mathrm{OPW}}(\vec{k}+\vec{K}) \ , \tag{15}$$

where

$$\chi_{\mathrm{OPW}}(\vec{k}+\vec{K}) = \chi_{\mathrm{PW}}(\vec{k}+\vec{K}) - \sum_t \langle \chi_{\mathrm{PW}}(\vec{k}+\vec{K}) \,|\, \chi_t\rangle\, \chi_t \ , \tag{16}$$

$$A_{\vec{k}} = \left(\sum_{\vec{K}} |C_{\vec{k}+\vec{K}}|^2 - \sum_{\vec{K},\vec{K}',t} C^*_{\vec{k}+\vec{K}'} C_{\vec{k}+\vec{K}} \langle \chi_t \,|\, \chi_{\mathrm{PW}}(\vec{k}+\vec{K}')\rangle \times \langle \chi_{\mathrm{PW}}(\vec{k}+\vec{K}) \,|\, \chi_t\rangle \right)^{-1/2} . \tag{17}$$

In constructing the OPW functions in Eq. (16) to obtain the actual functions $\psi_{\vec{k}}$, one has to employ Hartree-Fock wave functions, rather than the Herman-Skillman wave functions, since for the field gradient calculations, an accurate knowledge of the conduction-electron wave functions near the origin is required.[21]

Once the wave functions $\psi_{\vec{k},i}(\vec{r})$ for various bands i and reduced vectors $\vec{k}$ are obtained, q due to the conduction electrons can be calculated using the equation

$$q = - \sum_{\vec{k},i} \left\langle \psi_{\vec{k},i}(\vec{r}) \left| \frac{3\cos^2\theta - 1}{r^3} \right| \psi_{\vec{k},i}(\vec{r}) \right\rangle , \tag{18}$$

with $\vec{r}$ and θ referring to the nucleus as origin, the c axis being taken as Z direction. The negative sign on the right-hand side in Eq. (18) is a consequence of the negative charge on the electron. The summation over $\vec{k}$ in Eq. (18) involves the entire Brillouin zone and the contributions to the field gradient from all states which had energy less than or equal to the Fermi energy E_F. The scanning procedure for $\vec{k}$ in our calculation involved 189 points in $\frac{1}{24}$ of the Brillouin zone, equivalent to a total of 4536 points over the entire Brillouin zone. From earlier analyses in other hcp metals,[5,6] this number of sample points was expected to be more than adequate for the accuracy desired for the field gradient.

For the purposes of physical understanding and the proper consideration of antishielding effects, it was felt convenient to break up the electronic contribution q_{el}, the field gradient from the conduction electrons, into parts as described by Eqs. (19)–(23). Thus using Eqs. (15)–(18), one obtains

$$q_{\mathrm{el}} = q_{\mathrm{PW\text{-}PW}} + q_{\mathrm{TB\text{-}TB}} + 2q_{\mathrm{PW\text{-}TB}} + q_{\mathrm{dist.}} \,, \tag{19}$$

where

$$q_{\mathrm{PW\text{-}PW}} = \frac{2}{N_0\Omega_0}\left(\frac{64\pi^3}{45}\right)^{1/2} \sum_{i,\vec{k}} |A_{i\vec{k}}|^2 \sideset{}{'}\sum_{\vec{K},\vec{K}'} C^*_{i,\vec{k}+\vec{K}'} C_{i,\vec{k}+\vec{K}} S(\vec{K}' - \vec{K}') Y_{20}(\vec{K}' - \vec{K}) \,, \tag{20}$$

$$q_{\mathrm{TB\text{-}TB}} = \frac{2}{N_0\Omega_0}\left(\frac{1024\pi^5}{5}\right)^{1/2} \sum_{i,\vec{k}} |A_{i\vec{k}}|^2 \sum_{\vec{K},\vec{K}'} C^*_{i,\vec{k}+\vec{K}'} C_{i,\vec{k}+\vec{K}} S(\vec{K}) S(\vec{K}')$$

$$\times \sum_{\substack{n'l'm' \\ nlm}} (i)^{l'-l} Y^*_{l'm'}(\vec{k}+\vec{K}') Y_{lm}(\vec{k}+\vec{K}) G(nl, \vec{k}+\vec{K}) G(n'l', \vec{k}+\vec{K}') F(nl, n'l') \langle lm \,|\, 20 l'm' \rangle \,, \tag{21}$$

$$q_{\mathrm{PW\text{-}TB}} = \frac{-2}{N_0\Omega_0}\left(\frac{1024\pi^5}{5}\right)^{1/2} \sum_{i,\vec{k}} |A_{i\vec{k}}|^2 \sum_{\vec{K},\vec{K}'} C^*_{i,\vec{k}+\vec{K}'} C_{i,\vec{k}+\vec{K}} S(\vec{K}) S(\vec{K}')$$

$$\times \sum_{\substack{nlm \\ l'm'}} (i)^{l-l'} Y^*_{lm}(\vec{k}+\vec{K}') Y_{l'm'}(\vec{k}+\vec{K}) G(nl, \vec{k}+\vec{K}') H(nl, l', \vec{k}+\vec{K}) \langle l'm' \,|\, 20 lm \rangle \,, \tag{22}$$

$$q_{\mathrm{dist.}} = \frac{2}{N_0}\left(\frac{4\pi}{5}\right)^{1/2} \sum_{i,\vec{k}} |A_{i\vec{k}}|^2 \left(1 - \sum_{\vec{K}} C^2_{i,\vec{k}+\vec{K}}\right) \sideset{}{'}\sum_{n} \frac{Y_{20}(\vec{r}_n)}{|\vec{r}_n|^3} \,, \tag{23}$$

$$Y_{lm}(\vec{r}) = Y_{lm}(\theta_{\vec{r}}, \phi_{\vec{r}}) \,,$$

$$\langle l_1 m_1 \,|\, l_2 m_2 l_3 m_3 \rangle = \int\!\!\int Y^*_{l_1 m_1}(\theta, \phi) Y_{l_2 m_2}(\theta, \phi) \times Y_{l_3 m_3}(\theta, \phi) \sin\theta \, d\theta \, d\phi \,, \tag{24}$$

$$S(\vec{G}) = \cos(\tfrac{1}{2}\vec{\rho}\cdot\vec{G}) \,, \tag{25}$$

$$G(nl, \vec{k}+\vec{K}) = \int_0^\infty P_{nl}(r) j_l(|\vec{k}+\vec{K}|r) r \, dr \,, \tag{26}$$

$$H(nl, l', \vec{k}+\vec{K}) = \int_0^\infty P_{nl}(r) j_{l'}(|\vec{k}+\vec{K}|r) \frac{1}{r^2} \, dr \,, \tag{27}$$

$$F(nl, n'l') = \int_0^\infty P_{nl}(r) \frac{1}{r^3} P_{n'l'}(r) \, dr \,. \tag{28}$$

Equation (20) represents the contribution to q_{el} from the plane-wave (PW-PW) component of the electron density around the nucleus. If it was possible to represent the wave functions of the conduction electrons by single OPW functions, then the field gradient would vanish, since the electronic distribution would be spherical in nature. It is the presence of the lattice potential which makes the wave functions consist of linear combinations of OPW functions and hence leads to nonspherical charge density and finite field gradient. Equation (21) gives the contribution to q_{el} from the tight-binding (TB-TB) component of the wave function and Eq. (22) that from the hybrid combination (PW-TB) of the plane-wave and tight-binding components.

The expression in Eq. (23) is for the contribution from a source which is referred to as the distant term in the literature and arises from conduction-electron charge densities on ions other than that containing the nuclear site at which the field gradient is being studied. Its physical significance has also been explained in earlier literature[22] as referring to the contributions to the field gradient from the orthogonalization hole densities associated with the conduction-electron distributions at the various ionic sites. The summation over $\vec{r}_n$ in Eq. (23) is related to the ionic contribution to field gradient given by

$$q_{\mathrm{ionic}} = 2 \sideset{}{'}\sum_{n} \frac{3\cos^2\theta_n - 1}{r_n^3} = 2\left(\frac{4\pi}{5}\right)^{1/2} \sideset{}{'}\sum_{n} \frac{2Y_{20}(r_n)}{r_n^3} \,. \tag{29}$$

The primes over the summations in (23) and (29) denote that the site under consideration is excluded from the summation. The factor of 2 in Eq. (24) arises from the ionic charges at the lattice sites.

The lattice summation in Eq. (29) has been carried out[23] for divalent hcp metals earlier in the literature as a function of c/a and is given by the expression

$$q_{\mathrm{ionic}} = 2[0.0065 - 4.4584(c/a - 1.633)]/a^3 \,.$$

This expression can be used to obtain the ionic contributions to q_{ionic} in zinc and cadmium using the appropriate values of c and a. For standard temperature and pressure, we have used[24]

$$c_{\mathrm{Zn}} = 4.8618\ \text{Å}, \quad a_{\mathrm{Zn}} = 2.6596\ \text{Å},$$

$$c_{\mathrm{Cd}} = 5.5261\ \text{Å}, \quad a_{\mathrm{Cd}} = 2.9684\ \text{Å}.$$

III. ANTISHIELDING FACTORS FOR VARIOUS CONTRIBUTIONS TO THE ELECTRIC FIELD GRADIENT

In order to obtain the actual field gradient, one has to multiply the contributions to the field gradient from the conduction electrons in Eq. (19) and from the ionic charges in the lattice by appropriate shielding factors. In the past it has been the practice[5-7] to apply one antishielding or shielding factor to the entire electronic contribution (except for the distant term) to the field gradient in the metal. This one factor used has been assumed to be about the same as the antishielding factor for field gradients due to valence electrons in atoms[25] which are often rather small and indeed, in some of the earlier calculations,[6,7] the antishielding effect has been neglected for the conduction-electron contributions. We shall analyze separately the antishielding effects for the different contributions, in Eq. (19), of the field gradient from the conduction electrons and point out the need for using very different antishielding factors for these different contributions. The antishielding factor to be used for the ionic contribution to the field gradient is a relatively simpler matter, namely something of the nature of[17] γ_∞ for the ion (Zn^{2+} or Cd^{2+}) due to an external point charge. However the presence of the conduction electrons does change the core-electron wave functions on the ions and the influence of this on γ_∞ has to be considered.

We consider first this question of the proper antishielding factor in the metal for the field gradient due to the ionic charges. The core electrons on the Zn^{2+} or Cd^{2+} ions feel the charges on neighboring ions in the corresponding metals as totally external. The core electrons therefore provide antishielding effects to the field gradient at the nucleus due to the ionic charges in the lattice which are similar to those experienced by the field gradient due to a point charge totally external to the core electrons. This antishielding factor γ_∞ would appear at first sight to be that typical of free Zn^{2+} or Cd^{2+} ion. However, since the conduction electrons are present and do provide some screening of the potential experienced by the core electrons in the ion, the core electrons are expected to be somewhat more loosely bound in the metal than in the free positive ions. To test the influence of this loosening of the wave functions of the core electrons on γ_∞, we have calculated the latter for Zn^{2+} ion using the same configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ as in the free ion but with the wave functions for these electronic states taken as those in the neutral atom where two additional electrons in the $4s$ state are present. The procedure employed was the conventional one[26] involving the solutions of the differential equations for the perturbations in the one-electron wave functions due to the potential produced by the nuclear quadrupole moment. The value of γ_∞ obtained in this way[27] with the neutral Zn^0 wave functions for the core electrons was

$$(\gamma_\infty)^0_{Zn^{2+}} = -13.96$$

as compared to the value of γ_∞ for free Zn^{2+} ion with electronic wave functions corresponding to the free Zn^{2+} ion, namely

$$(\gamma_\infty)^{+2}_{Zn^{2+}} = -12.73 .$$

It is seen that the two values differ by less than 10%. Therefore no significant error is made in using values of γ_∞ corresponding to the free Zn^{2+} ion in zinc metal and free Cd^{2+} in cadmium metal. For zinc metal, since we had it available, we have used the value of $(\gamma_\infty)^0_{Zn^{2+}}$. For cadmium metal, we have used a value of γ_∞ equal to[27] -31.9 corponding to Cd^{2+} ion for the ionic contributions to the field gradient. The same antishielding factor is also appropriate for the distant conduction-electron contributions to the field gradient.

We consider next the question of appropriate shielding factors for the various conduction-electron contributions to the field gradient in Eq. (19), excluding of course the distant contribution. As remarked earlier in this section, it has been the practice in the past[14] to consider the conduction-electron field gradient to be subject to a small shielding effect appropriate for the valence electron in the atom. However there is an important point of difference between the valence-electron distribution in the atom and the conduction-electron distribution in the metal. The valence-electron distribution is usually peaked[28] a short distance outside of the maximum of the density from the outermost core electron and then vanishes exponentially. A major part of the valence-electron density therefore strongly overlaps the core density distribution and cannot perturb the core electrons as effectively as a totally external charge, which is the reason for the great difference between the shielding factor R for the valence electron[25] and γ_∞ for the external charge.[17] The conduction-electron distribution also has a peak distribution in the region of the core electrons which usually extends up to about one-half the radius of the Wigner-Seitz sphere. However, over the rest of Wigner-Seitz sphere, the conduction-electron distribution does not vanish but instead assumes[22] a near-uniform distribution described by a linear combination of plane waves. The fact that there is a linear combination of plane waves brought about by the potential (or pseudopotential) is important because a single plane wave would give an

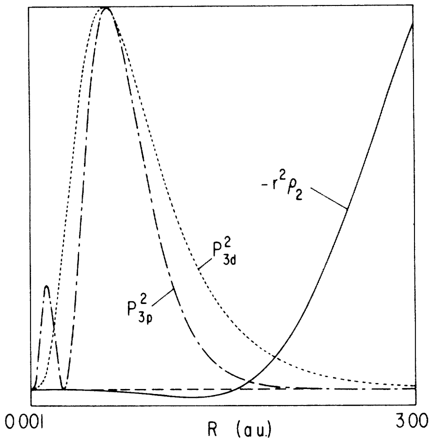

FIG. 1. Plots of core and plane-wave parts of the conduction-electron ($l = 2$ component) densities to demonstrate the relative externality of the latter. The ordinates of the various curves have been scaled for visual convenience.

isotropic density distribution and hence zero-field gradient. The crucial point is that, unlike the atomic case, the conduction-electron distribution, instead of dying down to zero away from the core region, stays finite over a volume of about $\frac{7}{8}$ of the Wigner-Seitz volume. From this latter region the antishielding factor is expected to be closer[29] to γ_∞ due to an external charge than to R for the valence electron. The reason for this expectation can be clearly emphasized by plotting the radial part $\rho_{2,\mathrm{cond}}^{\mathrm{PW-PW}}(r)$ of the $l = 2$ component of the PW-PW part of conduction-electron density as described by Eq. (30), namely

$$\rho_{\mathrm{cond}}^{\mathrm{PW-PW}}(\vec{r}) = \rho_{0,\mathrm{cond}}^{\mathrm{PW-PW}}(r)\, Y_{00}(\vec{r}) + \rho_{2,\mathrm{cond}}^{\mathrm{PW-PW}}(r) Y_{20}(\vec{r}) + \cdots, \tag{30}$$

against r and comparing it with the radial densities due to the $3p$ and $3d$ core electrons. This is done in Fig. 1, from where it is seen that while $\rho_{2,\mathrm{cond}}^{\mathrm{PW-PW}}(r)$ does penetrate into the core region, a major part of it is in fact external to the core density distribution. If there were no penetration into the core region, one would be justified in employing antishielding factor γ_∞ for the field gradient due to the PW-PW component of the conduction-electron density. From the fact that there is some penetration of $\rho_{2,\mathrm{cond}}^{\mathrm{PW-PW}}(r)$ into the core region, γ_∞ in fact appears to be an upper limit for this case. From Fig. 1 it appears that a reasonable lower limit to the antishielding factor γ for the field gradient due to the PW-PW component would be $\frac{1}{2}\gamma_\infty$, with the actual antishielding factor lying between γ_∞ and $\frac{1}{2}\gamma_\infty$; most likely somewhat closer to the lower limit[30] rather than the upper, but certainly very sizeably larger than the small value R, appropriate for valence electrons in atoms.

For the other components of the density in Eq. (19), namely the TB-TB component and the hybrid PW-TB component, the corresponding $\rho_2(r)$ closely overlap the core distribution and it would not be very erroneous to neglect shielding or antishielding effects for the field gradient due to these conduction-electron density components.

IV. RESULTS AND DISCUSSION

Tables I and II present the results of our calculation of the field gradients in the metals zinc and cadmium with the results broken up into contributions from the first four bands (the third row in the tables being the sum of the contributions from the third and fourth bands) which are either fully or partially occupied, the last row being the total from all four bands. In both of these tables, the first column gives the indices of the bands. The second, third, and fourth columns present the contributions from the sums from each band of the TB-TB and hybrid PW-TB terms in Eqs. (21) and (22), broken up according to the combinations of l and l' in the F and H integrals occurring in these equations. In other words, the various components represent the contributions to the field gradient from the combinations of the l and l' components in Ψ_k^* and Ψ_k in the TB-TB and hybrid PW-TB parts electron density $\Psi_k^*\Psi_k$. The contributions are given only for the sd, pp, and dd terms, the density terms involving l components of the wave function beyond d making very small contributions. In the fifth, sixth, and seventh columns, we have listed the PW-PW contributions from various bands using antishielding factors γ [in the net multiplying factor $(1-\gamma)$] of 0, $\frac{1}{2}\gamma_\infty$, and γ_∞, respectively, with the second choice (in the sixth column) being the most plausible as pointed out in Sec. III. The choice in the fifth column corresponds to that used in earlier calculations and the seventh column is expected to represent an overestimate. The eighth column gives the distant term given by Eq. (23) but multiplied by the antishielding factor $(1-\gamma_\infty)$. The ninth, tenth and eleventh terms represent the net conduction-electron contributions corresponding to the three choices of γ used in columns five, six, and seven for the PW-PW contributions to the field gradient.

Considering first the results for the local or TB-TB and hybrid PW-TB contributions, the sums of which for the various bands are listed in the second, third, and fourth columns, there are three main features of these results. First, the major contribution to these terms arises from the TB-TB term, the hybrid PW-TB making a small contribution of opposite sign. Thus, in zinc, the TB-TB and hybrid terms contribute, respectively,

TABLE I. List of various contributions to the field gradient from conduction electrons in Zn.[a]

Band	Local effect[b] $eq_{\mathrm{TB\text{-}TB}}+eq_{\mathrm{TB\text{-}PW}}$			Plane-wave contribution			Distant contribution	Total conduction-electron contribution[e]		
	sd	*pp*	*dd*	Unshielded	$eq_{\mathrm{PW\text{-}PW}}$ Antishielding[c] choice I	Antishielding[d] choice II	eq_{dist}	eq_{el}		
1	0.51	125.56	6.71	3.80	30.32	56.85	−3.92	132.66	159.18	185.71
2	0.45	10.96	2.42	3.59	28.65	53.71	−0.72	16.70	41.76	66.82
3	0.15	2.95	1.05	−0.70	−5.59	−10.47	−0.34	3.11	−1.78	−6.66
Total	1.11	139.47	10.18	6.69	53.38	100.09	−4.98	152.47	199.16	245.87

[a] Units of 10^{13} esu/cm^3.

[b] The sum of tight-binding and hybrid terms.

[c] Choice of antishielding factor used is $1-\frac{1}{2}\gamma_\infty=7.98$.

[d] Choice of antishielding factor used is $1-\gamma_\infty=14.96$.

[e] The three columns refer to the three choices of antishielding factors for the plane-wave contribution.

TABLE II. List of various contributions to the field gradient from conduction electrons in Cd.[a]

Band	Local effect[b] $eq_{\mathrm{TB\text{-}TB}}+eq_{\mathrm{TB\text{-}PW}}$			Plane-wave contribution			Distant contribution	Total conduction-electron contribution[e]		
	sd	*pp*	*dd*	Unshielded	$eq_{\mathrm{PW\text{-}PW}}$ Antishielding[c] choice I	Antishielding[d] choice II	eq_{dist}	eq_{el}		
1	0.18	223.03	11.83	4.04	68.48	132.92	−11.47	227.61	292.05	356.49
2	0.41	12.73	3.07	4.56	77.29	150.02	−1.82	18.95	91.68	164.41
3	0.00	0.00	0.00	−0.82	−13.90	−26.98	0.00	−0.82	−13.90	−26.98
Total	0.59	235.76	14.90	7.78	131.87	255.96	−13.29	245.74	369.83	493.92

[a] Units of 10^{13} esu/cm^3.

[b] The sum of tight-binding and hybrid terms.

[c] Choice of antishielding factor used is $1-\frac{1}{2}\gamma_\infty=16.95$.

[d] Choice of antishielding factor used is $1-\gamma_\infty=32.90$.

[e] The three columns refer to the three choices of antishielding factors for the plane-wave contribution.

102 and -2% to the net local term. Second, of the contributions from the three components *sd*, *pp*, and *dd* listed, the *pp* make the most important contribution, almost 79 and 76% for the first band and 26 and 14% for the second band of zinc and cadmium, respectively. The third feature is that the first band makes the major contribution to the local part of the field gradient, comprising 88 and 94%, respectively, of the total electronic part of the field gradient in zinc and cadmium. This feature is in some contrast with the situation in the two metals beryllium and magnesium, with c/a closer to ideal, the first and second band contributions in these metals being comparable in magnitude but opposite in sign.[14]

The first of these features for the local contribution can be understood by noticing from Eqs. (21) and (22) that $q_{\text{TB-TB}}$ involves the integral $F(nl,n'l')$ while $q_{\text{TB-PW}}$ involves $H(nl,l',|\vec{k}+\vec{G}|)$. The former, from Eq. (28) is seen to involve the product of two core radial functions P_{nl} and the latter, from Eq. (27), involves P_{nl} and $rj_{l'}(|\vec{k}+\vec{G}|r)$. The core radial function has relatively much greater amplitude near the origin and therefore makes a much larger contribution to the integral involving $1/r^3$ than the Bessel function (multiplied by r). The second feature, the greater contribution to the field gradient from the *pp* component of the local density, is also observed in molecular systems.[31] The reason for this is that the *pp* component involves wave functions with the lowest value of l and therefore the largest density near the nucleus that can contribute to the field gradient, the *ss* contribution being zero due to its spherical symmetry. The *sd* contribution involves two different l components and therefore two different types of radial functions, whose overlap with each other is less effective than for two with the same radial character as in the case of the *pp* component. The third feature, namely the largest contribution from the first band, is a little more difficult to explain, but the following explanation may be offered. The first band, being completely occupied, fills a complete Brillouin zone which departs rather strongly from cubic symmetry for zinc and cadmium. The $\vec{k}$-space anisotropy, which through the $\vec{k}$ integration leads to $\vec{r}$-space anisotropy, is expected to be more pronounced for this band than for the other bands, because while the occupied part of $\vec{k}$ space for the first band reflects the symmetry of the Brillouin zone, the higher bands which only partially fill the Brillouin zone tend to occupy a region of $\vec{k}$ space intermediate between the shape of the Brillouin zone and a Fermi sphere, the latter being the extreme case characteristic of free electrons.

Considering next the PW-PW contributions, it is seen from the columns five, six, and seven of Tables I and II that while $q_{\text{PW-PW}}$ is very small compared to the local contribution when one neglects antishielding effects, for both the choices γ_∞ and $\frac{1}{2}\gamma_\infty$, $q_{\text{PW-PW}}$ becomes comparable in importance to $q_{\text{TB-TB}}+q_{\text{TB-PW}}$. The other noticeable feature is the fact that for $q_{\text{PW-PW}}$, the first and second band contributions are of equal importance in contrast to the observed behavior in the local case in this respect. The reason for this difference in behavior in the two cases is probably due to the fact that the PW-PW contribution depends on the fractional importance of plane-wave character of the wave functions, in contrast to the importance of the core character for the local contribution. The plane-wave character is perhaps of greater importance for the second band, but this is partly neutralized by the greater anisotropy of the $\vec{k}$ space over which integration is carried out in the case of the first band, making $q_{\text{PW-PW}}$ of comparable importance from both bands.

The eighth column presents the distant contribution. Its significance has already been discussed in Sec. III and the antishielding factor used for it is γ_∞. The last three columns in the tables give the total contribution to the field gradient from the conduction electrons for the three choices 0, $\frac{1}{2}\gamma_\infty$, and γ_∞ for the antishielding factor for $q_{\text{PW-PW}}$. These three values of the net field gradients are percentagewise less different from each other than the three corresponding PW-PW contributions, since the latter are all added to a common sizeable local contribution. From an examination of the charge distribution in Fig. 1 and from preliminary calculations[30] that we have performed on the shielding for conduction electrons by a first-principle procedure, it appears that the choice of $\frac{1}{2}\gamma_\infty$ for the PW-PW contributions is a reasonable choice. Nevertheless, in choosing our confidence limit in obtaining the quadrupole moment of ^{67}Zn and ^{111}Cd from the quadrupole coupling constant in the metal from perturbed angular correlation data, we shall use a range of error of about $\pm 20\times 10^{13}$ and $\pm 30\times 10^{13}$ esu/cm^3 for zinc and cadmium, respectively, for the field gradient which correspond to about 40% of the difference between the values of $q_{\text{PW-PW}}$ with the antishielding factors of $\frac{1}{2}\gamma_\infty$ and γ_∞. These error ranges should also cover other possible sources of error such as possible inaccuracies of the conduction-electron wave functions and in the summation in $\vec{k}$ space. Thus, the conduction-electron contributions to the field gradient for the two metals can be written

$$eq_{\text{cond}}(\text{Zn}) = 199.2\times 10^{13}\ \text{esu/cm}^3\ , \qquad (31)$$
$$eq_{\text{cond}}(\text{Cd}) = 369.8\times 10^{13}\ \text{esu/cm}^3$$

at standard pressure and temperature of 760 Torr and 0 °K, respectively. Combining with the ionic contributions of

$$eq_{\text{ionic}}(\text{Zn}) = -64.4\times10^{13}\ \text{esu/cm}^3\,, \qquad eq_{\text{ionic}}(\text{Cd}) = -119.6\times10^{13}\ \text{esu/cm}^3\,, \tag{32}$$

the total field gradients, including the confidence limits we have chosen, can be written

$$eq(\text{Zn}) = (135\pm20)\times10^{13}\ \text{esu/cm}^3\,, \qquad eq(\text{Cd}) = (270\pm30)\times10^{13}\ \text{esu/cm}^3\,. \tag{33}$$

Using the experimental quadrupole coupling constants for zinc and cadmium at standard pressure and the temperature, namely,[12,32]

$$e^2qQ(^{67}\text{Zn}(\tfrac{9}{2}^+)) = 49.5\ \text{MHz}\,, \qquad e^2qQ(^{111}\text{Cd}(\tfrac{5}{2}^+)) = 137.5\ \text{MHz}\,, \tag{34}$$

the quadrupole moments obtained are

$$Q(^{67}\text{Zn}(\tfrac{9}{2}^+)) = 0.50\pm0.08\ \text{b}\,, \qquad Q(^{111}\text{Cd}(\tfrac{5}{2}^+)) = 0.76\pm0.14\ \text{b}\,. \tag{35}$$

The quadrupole moment for ^{111}Cd is in surprisingly good agreement with the value ($Q = 0.77\pm0.11$ b) obtained from ionic crystal data[15] and substantially smaller than the large value[14] of 2.17 b obtained earlier, when the antishielding effect for $q_{\text{PW-PW}}$ had been neglected. For $^{67}\text{Zn}(\frac{9}{2}^+)$, there is no value available from other sources to compare with our value in Eq. (35). There has been no perturbed angular correlation measurement in this particular level of ^{67}Zn in ionic crystals. There are Mössbauer measurements[33] in ionic compounds of zinc for a Mössbauer active level, $^{67}\text{Zn}^m(\frac{5}{2}^-)$, but unfortunately no data in the metal are available for this nuclear state. It will be interesting to have both the metal and ionic crystal environments to be able to make a similar comparison as in $^{111}\text{Cd}^m$. It should be noted that our value of Q for $^{67}\text{Zn}(\frac{9}{2}^+)$ in Eq. (35) is not as different from the earlier published value[14] as was the case for $^{111}\text{Cd}(\frac{5}{2}^+)$. The reason for this is that there was unfortunately a numerical error in the earlier calculated conduction-electron field gradient in zinc, particularly in the local contribution. The value that one actually obtains using the conduction-electron field gradient in the eighth column of Table I, in which $q_{\text{PW-PW}}$ is included without antishielding effects, comes out rather large, namely 1.3 b.

It should be pointed out that in the case of beryllium and magnesium metals, good agreement has been obtained[5,6] in the past between theoretical and experimental values of the field gradient using unshielded PW-PW contributions. The experimental values of the field gradients, for comparison with theory, were derived from the measured values of the quadrupole coupling constants e^2qQ/h in these metals for the stable ^{9}Be and ^{25}Mg nuclei obtained[34,35] by nuclear magnetic resonance techniques and dividing the measured e^2qQ/h by the available nuclear quadrupole moments[36,37] of these nuclei. The theoretical values of the field gradients in these metals should also incorporate PW-PW contributions that are antishielded in the same manner as in the cases of zinc and cadmium. However, due to the relatively small values of γ_∞ in these systems, namely[38] -3.2 and $+0.185$, respectively, in Mg^{++} and Be^{++}, one does not expect the incorporation of antishielding effects on $q_{\text{PW-PW}}$ to make them comparable in importance to the local contributions, as in zinc and cadmium, and hence have an important influence on the net field gradient in beryllium and magnesium. Thus, in the case of magnesium, if we apply an antishielding factor of $\frac{1}{2}\gamma_\infty = -1.6$, the value of the total eq is changed to 1.95×10^{13} esu/cm^3, not significantly different from the value of 2.1×10^{13} esu/cm^3 obtained earlier[5] without applying any shielding correction to $q_{\text{PW-PW}}$. The revised theoretical value of the total field gradient in magnesium,[6] as also is the case with the earlier theoretical value, is in very good agreement with the experimental value of 2.04×10^{13} esu/cm^3. For the case of beryllium, where γ_∞ is very small, namely -0.185, the antishielding of $q_{\text{PW-PW}}$ is expected to have even less significant effect on the net field gradient than in the case of magnesium and should therefore leave unaffected the good agreement between theory and experiment found in earlier work.[5]

Last, we would like to comment on the relationship between our results, and particularly the incorporation of different shielding effects for different parts of the field gradient contribution from conduction electrons, on the empirical relationship observed recently[16] between the electronic and lattice contributions to the field gradient in a number of alloys and pure metal systems. Thus, by a combination of the measured magnitudes and signs of the total quadrupole coupling constants and the lattice contributions to them from summations of the contributions from the ions in the lattice, the conduction-electron contributions were found,[16] in a number of alloy and pure metal systems, to range between -2 to -3 times the lattice contribution, antishielded by $(1-\gamma_\infty)$ of the ion containing the nucleus. The antishielding factor thus corresponds to the impurity ion in the case of an alloy and the ion in the metal for the pure metal case. From our present results in zinc and cadmium in Tables I and II, the ratios of the conduction electron and lattice contributions come out as -3.1 for both metals, in good agreement with the empirical relationship.[16] Without the antishielding effect used in this work for the PW-PW contribution, the corresponding ratios would be -2.4 and -2.1, respectively, which are also over-all in the empirically observed range.[16] The important point is that whereas in the earlier work,[14] all parts of the conduction-electron contribution were assumed not to be antishielded at all, in our present work, the PW-PW contribution is subjected to a significent shielding effect involving $\frac{1}{2}\gamma_\infty$ if not γ_∞. In the present theoretical analysis there is therefore more support for the empirical correlation.[16] In alloys, however, both the lattice and conduction-electron contributions are expected to be affected by the distortion of the lattice around the impurity ion relative to the configuration of the host lattice. This is perhaps the reason for the significant departures observed[39] from the empirical range of the ratios $q_{\text{cond}}/q_{\text{ionic}}$ in cases (with a few exceptions) where the c/a ratio is close to ideal and the host lattice has a relatively small field gradient. For host lattices with relatively large c/a as in zinc and cadmium where the departure from cubic symmetry is already quite large in the pure metal, the percentage changes in the field gradient contributions from the lattice and conduction electrons (aside from the antishielding factors) in the alloys, due to lattice distortions around the impurity ions, are expected to be relatively less important compared to the field gradients in the host lattices, than would be the case for host lattices with c/a close to ideal. The conduction electron and lattice contributions are therefore expected to follow the same empirical correlation (as is indeed observed to be the case) in the alloy systems with zinc and cadmium as hosts, as in the pure metals. Our present work shows that for the latter, the theoretical ratios for $q_{\text{cond}}/q_{\text{ionic}}$ agree well with the experimental trend.[16]

V. CONCLUSION

The field gradients due to the conduction electrons in zinc and cadmium are calculated using a pseudopotential procedure to obtain the electronic wave functions. From a careful study of the conduction electron distribution relative to that of the core electrons, the plane-wave contribution is estimated to be antishielded by a factor of about $(1-\frac{1}{2}\gamma_\infty)$. Using this choice the quadrupole moments of $^{67}\text{Zn}(\frac{9}{2}^+)$ and $^{111}\text{Cd}(\frac{5}{2}^+)$ are evaluated, the latter being in good agreement with the value obtained from ionic crystal data.[15]

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[†] Present address: Regional Engineering College, Rourkela, Orissa, India.

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