

From formula (23) we have

$$C_{2h} = 1.0 \times 10^8 \text{ ohm}^{-1} \text{ cm}^{-1}, \quad (24)$$

$$C_{2e} = 1.4 \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}. \quad (25)$$

The experimental values of C_{2h} obtained by Fritzsche¹ for *p*-type germanium are, independently of N , about $4.2 \text{ ohm}^{-1} \text{ cm}^{-1}$. For *n*-type germanium the plot in the paper⁶ gives (for the sample “-20”) $C_{2e} \cong 6 \text{ ohm}^{-1} \text{ cm}^{-1}$. Thus in both cases the theoretical values are too high. Certainly the extensive extrapolation consisting of the use of the formulas for μ at low temperatures results in large errors in the theoretical values. However, the fact that the experimental values of C_2 are much smaller than those given by formula (23) assures, on one hand, the fulfillment of the necessary conditions for the possibility of the proposed mechanism, and, on the other hand, is consistent with the weak carrier-phonon

interaction in germanium. This weak interaction yields the high mobilities observed. Therefore the limiting process for the conduction is the excitation of carriers from the ground states to the energies higher than ϵ_2 . This process requires a separate consideration.

Formula (23) can have an immediate application, and not only that of giving the upper limit of the conductivity in the case of semiconductor with strong carrier-phonon interaction. Unfortunately, up to the present time, we have no experimental results on any such material.

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Electric Field Gradients in Point-Ion and Uniform-Background Lattices*

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The lattice contribution to the field gradient in ionic crystals and metals is a quantity which has a well-defined value. However, for an actual evaluation, the field gradient is usually broken up into a number of conditionally convergent series with poor convergence. Rapidly convergent expressions for these series, and consequently, for the field gradient can be obtained by applying the method of *plane-wise summation*. This method is applied to the field gradient in ionic crystals with tetragonal and hexagonal symmetry and to the field gradient in tetragonal and hexagonal close-packed metal structures. As an example, an expression for the field gradient at the position of the anion is derived for ionic crystals with the CdI_2 structure. This expression is numerically evaluated for CoBr_2 , FeBr_2 , MgBr_2 , MnBr_2 , CaI_2 , CdI_2 , CoI_2 , FeI_2 , GeI_2 , MgI_2 , and MnI_2 . Rather extensive numerical results are also presented for both close-packed metal structures, including values for the field gradient in Li, Be, Zn, In, and Rh.

I. INTRODUCTION

IN the theory of nuclear quadrupole resonance, one is interested in the total electric-field gradient (FG) at the position of the nucleus. The FG may be considered to consist of two contributions, FG_{cell} and $\text{FG}_{\text{lattice}}$. FG_e is due to the electrons inside the central cell surrounding the nucleus, and FG_l is due to all the electrons and nuclei making up the rest of the lattice. Evaluation of FG_e requires a detailed knowledge of the electronic wave functions inside the central cell, but for an evaluation of FG_l of comparable accuracy, a precise knowledge of the electronic wave functions is much less essential. As a first approximation, the crystal may be considered as an electrostatic assembly of point charges (the ion cores), which, in the case of metals, are embedded in a uniform sea of negative

charge (the conduction electrons). Such models have been used for the evaluation of FG_l in ionic crystals¹ as well as in metals.^{2,3} The advantage of such a model is that the evaluation of FG_l is reduced to a purely electrostatic problem, namely, to that of the evaluation of lattice sums of the type

$$S = \sum_{\lambda}' \frac{2P_2(\cos\theta_{\lambda})}{r_{\lambda}^3} \quad (1)$$

(notation explained in Sec. II). In this paper, we will restrict ourselves exclusively to this problem.

At this point, we would like to remark that, although the expression for FG_l contains lattice sums like (1) which are conditionally convergent (i.e., their values

¹ R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

² M. Pomerantz and T. P. Das, Phys. Rev. **119**, 70 (1960).

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³ W. W. Simmons, thesis, University of Illinois, 1960 (unpublished); W. W. Simmons and C. P. Slichter, Phys. Rev. **121**, 1580 (1961).

depend on the shape of the crystal), the value of FG_l itself does not depend on the shape of the crystal (it would be a very awkward situation if it did!). This simply follows from the fact that, in all crystals, the unit cell is electrically neutral. Hence, if we were to expand the charge distribution in the unit cell (having a center of inversion) in terms of multipole moments, the quadrupole moments would be the first nonvanishing moments. This means that the contribution of a cell to FG_l falls off as r^{-5} with distance.

For the actual evaluation of FG_l , it is convenient to consider separately, in the case of ionic crystals, the contributions to FG_l resulting from the different sublattices, and in the case of metals, the contributions due to the negative background and the positive point-charge lattice. In doing so, one regards FG_l , which has a perfectly well-defined value, as the sum of a number of conditionally convergent series of the type (1). However, no ambiguity will arise from these conditionally convergent series if all the various sums or integrals are evaluated for crystals of identical shape; adding these contributions in the end will give the desired (unambiguous) result.

The series S is slowly convergent, consequently, the form (1) is unfavorable for direct numerical computations (cf. reference 1). In studying the same lattice sum in a different context some years ago, Nijboer and the author⁴ introduced a method for bringing the series into a rapidly converging form. In this paper, we will apply that method to the evaluation of FG_{lattice} for ionic crystals with tetragonal and hexagonal unit cells and for close packed tetragonal (tcp) and hexagonal (hcp) metal structures.

In Sec. II, we introduce the FG and discuss the applicability of our method to different crystal structures. In Sec. III we treat the case of ionic crystals, developing the summation method as we go along. As an illustration, we derive a formula for FG_l at the position of an anion in CdI_2 -type crystals. In Sec. IV, we consider the close-packed metal structures. In Sec. V, we present some numerical results. We have calculated FG_l for the CdI_2 -type crystals and the close-packed metal structures as a function of $\alpha=c/a$ in the range $\alpha=0.5$ – 2.5 . This includes the values of FG_l for the ionic crystals and the metals listed in the abstract. Finally, in Sec. VI, we propose a possible test for the importance of the FG_l contribution to quadrupole resonance effects in certain crystals.

II. THE FIELD GRADIENT (FG)

The potential at a point \mathbf{r} due to a charge distribution of density $\rho(\mathbf{r})$ is

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}') d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (2)$$

⁴ B. R. A. Nijboer and F. W. de Wette, *Physica* 24, 422 (1958); F. W. de Wette, thesis, University of Utrecht, 1959 (unpublished).

In the theory of nuclear quadrupole resonance, one is interested in the electric-field gradients at the position of the nucleus. With respect to its principal axes, the field-gradient tensor is in general determined by two quantities.⁵ A symmetry axis of the crystal is always a principal axis of the field gradient. We restrict our considerations to such lattices, where the c axis is an n fold symmetry axis with $n > 2$. (In the tcp and hcp structures, n is 4 and 3, respectively.) Consequently, the field-gradient tensor is symmetric around the c axis, which means that the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ vanishes on the axis. (The z axis is chosen along the c axis.) The field-gradient tensor is then completely determined by the quantity which is normally called the field gradient, namely

$$eq = \left(\frac{\partial^2}{\partial z^2} V(\mathbf{r}) \right)_{\mathbf{r}=0} = V_{zz}(0). \quad (3)$$

It follows immediately from (2) and (3) that

$$eq = \int \rho(\mathbf{r}) \frac{3z^2 - r^2}{r^5} d^3\mathbf{r} = \int \rho(\mathbf{r}) \frac{2P_2(\cos\theta)}{r^3} d^3\mathbf{r}, \quad (4)$$

where $P_2(\cos\theta)$ is the Legendre polynomial of second order [$\mathbf{r} = \mathbf{r}(r, \theta, \phi)$].

We will briefly indicate in which cases the present method or a generalization of it can be used. Let the unit cell of the lattice be given by the basic vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 , and let us ask for FG_l in the \mathbf{a}_3 direction. The present method can be applied in all cases where \mathbf{a}_3 is perpendicular to both \mathbf{a}_1 and \mathbf{a}_2 . Thus, FG_l can be evaluated along the c axis of all crystals with monoclinic or higher symmetry. If the c axis is a symmetry axis with lower than three-fold symmetry, a second FG_l is required to determine completely the field-gradient tensor (with respect to its principal axes). This additional FG_l (say along \mathbf{a}_1) can also be determined by the present method if \mathbf{a}_1 is also perpendicular to \mathbf{a}_2 , which is the case for all crystals with orthorhombic or higher symmetry.

There exist many crystals for which a unit cell, satisfying these conditions, cannot be defined. In the Appendix, we quote a rapidly converging expression for the field gradient which is valid under the most general conditions. That expression can thus be used for the evaluation of the field gradient in such cases.

III. FG_l IN IONIC CRYSTALS

We consider an ionic crystal with a tetragonal or hexagonal unit cell, containing γ different point charges e_j ($j=0, \dots, \gamma-1$). The lattice translation vector \mathbf{r}_λ and the base vector \mathbf{r}_j can be expressed in terms of the basic

⁵ Cf. M. H. Cohen and F. Reif, *Solid-State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. V, p. 321.

vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 , as

$$\mathbf{r}_\lambda = \lambda_1 \mathbf{a}_1 + \lambda_2 \mathbf{a}_2 + \lambda_3 \mathbf{a}_3, \quad \lambda_1, \lambda_2, \lambda_3 = 0, \pm 1, \pm 2, \text{ etc.}$$

$$\mathbf{r}_j = j_1 \mathbf{a}_1 + j_2 \mathbf{a}_2 + j_3 \mathbf{a}_3, \quad 0 \leq j_1, j_2, j_3 < 1.$$

The position of the point charge j in the cell λ is given by $\mathbf{r}_{\lambda,j} = \mathbf{r}_\lambda + \mathbf{r}_j$. The lattice can be considered to consist of γ different sublattices j , each containing one kind of point charge ϵ_j . All of these sublattices have the same structure.

If we choose the origin O in the lattice point at which we want to evaluate FG_L , then the charge density in that lattice is (omitting the point charge at O):

$$\rho(\mathbf{r}) = \sum_{\lambda'} \sum_j \epsilon_j \delta(\mathbf{r} - \mathbf{r}_{\lambda,j}) + \sum_{j'} \epsilon_{j'} \delta(\mathbf{r} - \mathbf{r}_{j'}). \quad (5)$$

The charge neutrality of the unit cell is expressed by $\sum_j \epsilon_j = 0$. Substitution of (5) into (4) gives

$$eq = \sum_{\lambda'} \sum_j \epsilon_j \frac{2P_2(\cos\theta_{\lambda,j})}{r_{\lambda,j}^3} + \sum_{j'} \epsilon_{j'} \frac{2P_2(\cos\theta_{j'})}{r_{j'}^3}. \quad (6)$$

Because of the charge neutrality of the unit cell, the value of FG_L does not depend on the shape of the crystal. In terms of the summations occurring in (6), this means that the series in λ is absolutely convergent, provided the summation over j has been carried out first. However, such an order of summation is not practical for an actual evaluation of the series. Instead, it is preferable to break the series up into γ different series over the γ sublattices, i.e., to interchange the order of λ and the j summation. Then

$$eq = \epsilon_0 \sum_{\lambda'} \frac{2P_2(\cos\theta_{\lambda})}{r_{\lambda}^3} + \sum_{j'} \epsilon_{j'} \sum_{\lambda} \frac{2P_2(\cos\theta_{\lambda,j'})}{r_{\lambda,j'}^3} \\ \equiv \epsilon_0 S_0 + \sum_j \epsilon_j S_j. \quad (7)$$

Now, each of the subsums S_j is conditionally convergent⁶; its value depends on the order of summation. However, we may choose the order of the λ summation in a way which is most advantageous for the evaluation of the subsums, provided that the same summation order is used to evaluate all subsums. This ensures a result that is independent of the shape of the crystal.

Keeping in mind the symmetry of the tetragonal and hexagonal lattices, we now ask which summation order is most advantageous for evaluation of the subsums. It has been shown in reference 4 that the procedure of *plane-wise summation* leads to a rapidly converging expression for the sum, and that such a summation procedure has definite advantages over the usual procedure of *spherical summation*. Having chosen the z axis along the crystal c axis (the \mathbf{a}_3 direction), plane-wise summation means that we first carry out a summation over λ_1

and λ_2 in the plane $\lambda_3 = 0$, then in the planes $\lambda_3 = \pm 1$ (planes adjacent to the origin), then in the planes $\lambda_3 = \pm 2$, etc. In short, the λ_1, λ_2 summation should be carried out before the λ_3 summation. This summation order is equivalent to considering a *slab-shaped* crystal, the faces of which are perpendicular to the z axis. Once this summation order has been established, one may consider the slab to be infinitely thick, i.e., consider an infinite (slab-shaped) crystal. In contrast to this, in the method of spherical summation, one adds contributions of lattice points according to their distance from the origin. In this way one considers an infinite spherical crystal.

We will now evaluate the subsums in (7). In reference 4 we derived, with the method of plane-wise summation, the following expression for S_0 in the case of a tetragonal lattice [reference 4, Eq. (23)]

$$S_0^{\text{tet}} = \frac{1}{a^3} \left\{ -9.0336217 + 8\pi^2 \sum'_{\mu_1, \mu_2} \frac{h_{\mu_1, \mu_2}}{\exp(2\pi h_{\mu_1, \mu_2} \alpha) - 1} \right\}. \quad (8)$$

a is the lattice distance in the x, y planes, $\alpha = c/a$. The number -9.0336217 represents the contribution of all the lattice points situated in the plane which contains the origin. The contribution of all the other lattice points in the physical lattice is represented by the two-dimensional series \sum'_{μ_1, μ_2} . This series is a summation over a square lattice with lattice vector $\mathbf{h}_{\mu_1, \mu_2}$ of length $h_{\mu_1, \mu_2} = (\mu_1^2 + \mu_2^2)^{1/2}$ and with lattice distance 1 ($\mu_1, \mu_2 = 0, \pm 1, \pm 2, \dots$). The prime on the summation sign indicates that the term $\mu_1 = \mu_2 = 0$ is excluded from the summation. This lattice is the reciprocal of the two-dimensional lattices which form the x, y planes of the physical lattice. The way in which the series \sum'_{μ_1, μ_2} was derived will become clear when we derive a similar expression for S_j .

The equivalent expression for a hexagonal lattice is⁷ [reference 4, Eq. (25)]

$$S_0^{\text{hex}} = \frac{1}{a^3} \left\{ -11.0341754 + \frac{16\pi^2}{\sqrt{3}} \sum'_{\mu_1, \mu_2} \frac{h_{\mu_1, \mu_2}}{\exp(2\pi h_{\mu_1, \mu_2} \alpha) - 1} \right\}. \quad (9)$$

The terms in (9) have a meaning similar to those in (8). In particular, \sum'_{μ_1, μ_2} is a summation over a plane hexagonal lattice with lattice distance $2/\sqrt{3}$.

We now have to derive similar expressions for the sums

$$S_j = \frac{1}{a^3} \sum_{\lambda} \frac{2P_2(\cos\theta_{\lambda,j})}{\rho_{\lambda,j}^3}, \quad (10)$$

where $\rho_{\lambda,j} = r_{\lambda,j}/a$ is the dimensionless lattice vector. As we said previously, we want to evaluate this conditionally convergent sum S_j by plane-wise summation. This implies that the λ_1, λ_2 summation must be carried out before the λ_3 summation. Such ordering clearly

⁶ This conditionally convergent series appears in a number of problems. For example, in the calculation of the Lorentz field in dipole lattices (see reference 4), in the calculation of the normal modes of an oscillator lattice [U. Fano, Phys. Rev. **118**, 451 (1960)], and in the spin-wave theory of ferromagnetism [M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955)].

⁷ The factor $2/\sqrt{3}$ in front of the sum has been erroneously omitted in the original expression (25) of reference 4.

does not improve the convergence properties of the summand of (10), but it enables us to perform a trick to improve the convergence. This trick consists of taking the two-dimensional Fourier transform (FT_2) of the two-dimensional λ_1, λ_2 series. To this end we write this series as an integral

$$S_j = \frac{1}{a^3} \sum_{\lambda_3} \sum_{\lambda_1, \lambda_2} \frac{2P_2(\cos\theta_{\lambda,j})}{\rho_{\lambda,j}^3} \\ = \frac{1}{a^3} \sum_{\lambda_3} \int \left[\sum_{\lambda_1, \lambda_2} \delta(\sigma - \sigma_{\lambda_1, \lambda_2} - \sigma_{j_1, j_2}) \right] \\ \times \frac{2P_2[(\lambda_3 + j_3)\alpha / \{\sigma^2 + (\lambda_3 + j_3)^2\alpha^2\}^{\frac{1}{2}}]}{\{\sigma^2 + (\lambda_3 + j_3)^2\alpha^2\}^{\frac{3}{2}}} d^2\sigma. \quad (11)$$

In Fig. 1, we have indicated how the lattice vector $\sigma_{\lambda,j}$ is decomposed into two vectors, one parallel and the other perpendicular to the z axis.

We now use Parseval's formula. It states that the integral over ordinary space of the product of two real functions is equal to the integral over Fourier space of the product of their Fourier transforms. One can show that⁸

$$FT_2 \left\{ \sum_{\lambda_1, \lambda_2} \delta(\sigma - \sigma_{\lambda_1, \lambda_2} - \sigma_{j_1, j_2}) \right\} \\ = O_a^{-1} \sum_{\mu_1, \mu_2} \exp[-2\pi i(j_1\mu_1 + j_2\mu_2)] \delta(\mathbf{h} - \mathbf{h}_{\mu_1, \mu_2}), \quad (12)$$

where O_a is the unit area in the untransformed two-dimensional lattice, in this case expressed for a situation where the lattice distance is 1. Furthermore,

$$FT_2 \left\{ \frac{2P_2[(\lambda_3 + j_3)\alpha / \{\sigma^2 + (\lambda_3 + j_3)^2\alpha^2\}^{\frac{1}{2}}]}{\{\sigma^2 + (\lambda_3 + j_3)^2\alpha^2\}^{\frac{3}{2}}} \right\} \\ = 4\pi^2 h \exp(-2\pi h\alpha |(\lambda_3 + j_3)|). \quad (13)$$

$$S_j = \frac{4\pi^2}{O_a a^3} \sum'_{\mu_1, \mu_2} \exp\{-2\pi i(j_1\mu_1 + j_2\mu_2)\} \frac{h_{\mu_1, \mu_2} [\exp\{-2\pi h_{\mu_1, \mu_2}\alpha(1 - j_3)\} + \exp\{-2\pi h_{\mu_1, \mu_2}\alpha j_3\}]}{1 - \exp\{-2\pi h_{\mu_1, \mu_2}\alpha\}}. \quad (14)$$

For the tetragonal lattice $O_a = 1$ and \sum'_{μ_1, μ_2} is a summation over a square lattice with lattice distance 1. For the hexagonal lattice $O_a = \frac{1}{2}\sqrt{3}$ and \sum'_{μ_1, μ_2} is a summation over a plane hexagonal lattice with lattice distance $2/\sqrt{3}$. In both cases, the form of the summand clearly guarantees the rapid convergence of \sum'_{μ_1, μ_2} . In many cases, the factor $\exp\{-2\pi i(j_1\mu_1 + j_2\mu_2)\}$ has the effect of a multiplying constant when contributions of a certain shell of neighbors are added together. Furthermore, since the summand of \sum'_{μ_1, μ_2} contains only the length of the lattice vector h_{μ_1, μ_2} , each shell of neighbors can in such cases be represented by only one term. The convergence rate of a sum of such term depends only slightly upon the value of α for the region of interest and we find that between five and ten terms generally

⁸ Cf. B. R. A. Nijboer and F. W. de Wette, *Physica* **23**, 309 (1957).

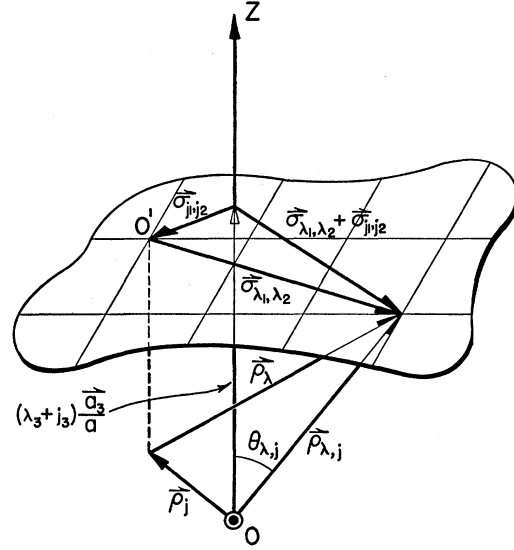


FIG. 1. Decomposition of the lattice vector $\sigma_{\lambda,j}$ in lattices with monoclinic or higher symmetry. The z axis is parallel to the crystal c axis.

Applying Parseval's formula to (11), using (12) and (13), we find

$$S_j = 4\pi^2 O_a^{-1} a^{-3} \sum_{\lambda_3} \sum'_{\mu_1, \mu_2} h_{\mu_1, \mu_2} \\ \times \exp[-2\pi i(j_1\mu_1 + j_2\mu_2) - 2\pi h_{\mu_1, \mu_2}\alpha |(\lambda_3 + j_3)|].$$

We have omitted the term $\mu_1 = \mu_2 = 0$ since it vanishes. This series is absolutely convergent in λ_3 , as well as in μ_1 and μ_2 . Consequently, the summation order may now be reversed. This gives rise to a geometrical series in λ_3 which can be summed directly. One finds

provide sufficient accuracy. Finally, the total value of eq is found by adding the appropriate sums together according to (7).

Example : CdI_2 Structure

We are interested in FG_l at the position of an I^- ion. The CdI_2 structure has a hexagonal unit cell with I^- ions in the positions $j_1 = j_2 = j_3 = 0$ and $j_1 = j_2 = \frac{1}{3}$, $j_3 = \frac{2}{3}$, and a Cd^{++} ion at the position $j_1 = j_2 = \frac{2}{3}$, $j_3 = \frac{1}{3}$. So, besides $S^{\text{hex}}_{0,0,0}$ which is given by (9), we have to evaluate $S^{\text{hex}}_{\frac{1}{3}, \frac{1}{3}, \frac{2}{3}}$ and $S^{\text{hex}}_{\frac{2}{3}, \frac{2}{3}, \frac{1}{3}}$. One readily derives from (14)

$$S^{\text{hex}}_{\frac{1}{3}, \frac{1}{3}, \frac{2}{3}} = \frac{1}{a^3} \frac{8\pi^2}{\sqrt{3}} \sum'_{\mu_1, \mu_2} \exp\{-\frac{2}{3}\pi i(\mu_1 + \mu_2)\} \\ \times \frac{h_{\mu_1, \mu_2}}{\sinh(\pi h_{\mu_1, \mu_2}\alpha)}, \quad (15)$$

and

$$S_{2/3,2/3,3/4}^{\text{hex}} = \frac{1}{a^3} \frac{8\pi^2}{\sqrt{3}} \sum'_{\mu_1, \mu_2} \exp\{-\frac{4}{3}\pi i(\mu_1 + \mu_2)\} \times \frac{h_{\mu_1, \mu_2} \cosh(\frac{1}{2}\pi h_{\mu_1, \mu_2} \alpha)}{\sinh(\pi h_{\mu_1, \mu_2} \alpha)}. \quad (16)$$

The field gradient at the position of an I^- ion is, according to (7), given by

$$eq_{\text{anion}} = e\{2S_{2/3,2/3,3/4}^{\text{hex}} - S_{0,0,0}^{\text{hex}} - S_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}^{\text{hex}}\}. \quad (17)$$

This expression is valid for all ionic crystals with the CdI_2 structure. In Sec. V, we will evaluate the sums for some relevant values of α and present the corresponding values of q_{anion} .

IV. FG_I IN THE UNIFORM-BACKGROUND LATTICE

The uniform-background lattice is a simple model for a metal. The conduction electrons are considered to be free, giving rise to a uniform charge distribution, and the ionic cores are considered as point charges. The charge density in such a lattice is

$$\rho(\mathbf{r}) = \rho_e + Ze \sum_{\lambda} \delta(\mathbf{r} - \mathbf{r}_{\lambda}), \quad (18)$$

where ρ_e is the background density and Ze is the net charge of the ionic cores. Charge neutrality of the elementary cell requires that $\rho_e = -Ze/v$, where v is the volume of the elementary cell (i.e., the volume allotted to one ion).

With regard to the simplifications implied in (18) as compared to the real charge density in a metal, we may remark that this free-electron-point-ion model seems to lead to results for FG_I which, at least in some cases, are not drastically different from those of a more precise treatment. This seems to follow from Pomerantz and Das' calculation for beryllium.² However, the total FG may be drastically different from the value contributed by the lattice, if the charge distribution (conduction electrons and core electrons) in the central cell is not almost spherically symmetric, as is the case when conduction electrons in p states are present (see reference 3). In such cases, the main contribution to the FG will be due to these charges inside the central cell and FG_I is probably only a small correction to this. If the present method is used to evaluate this correction in such cases, it should be remembered that one must compensate for the uniform electron density inside the central cell which is included in (18).

Insertion of (18) into (4) gives for FG_I in the uniform background lattice

$$eq = -\frac{Ze}{v} \int \frac{2P_2(\cos\theta)}{r^3} d^3r + Ze \sum_{\lambda} \frac{2P_2(\cos\theta_{\lambda})}{r_{\lambda}^3}. \quad (19)$$

As in the case of ionic crystals, eq is independent of both the shape and the size of the crystal because of the

charge neutrality. However, this is not true for either the integral (as is sometimes asserted) or the sum when considered separately. Again, we may choose the shape of our hypothetical specimen in a way which is most favorable for the evaluation of the sum, but in doing so we must be sure to evaluate the integral for an integration region of identical shape.

Since we have chosen to evaluate the sum by plane-wise summation, we must evaluate the integral for a slab-shaped region of integration. A straightforward integration gives

$$\int_{\text{slab-shaped region}} \frac{2P_2(\cos\theta)}{r^3} d^3r = -(8/3)\pi. \quad (20)$$

In deriving this result, use has been made of the fact that the integral vanishes for a spherical region, when the integration over the angles is carried out first. The result (20) is independent of the thickness of the sample and, hence, is correct for a slab of infinite thickness.

Tetragonal Close-Packed Lattice

The tetragonal close-packed (tcp) lattice can be considered either as a face-centered tetragonal (fct) or as a body-centered tetragonal (bct) lattice. We will use the bct unit cell which contains two particles. It has three mutually perpendicular basic vectors; $a_1 = a_2 = a_{\text{bet}}$, $c = a_3 = a_{\text{bet}} a_{\text{bet}}$. The volume/ion is $v_{\text{bet}} = \frac{1}{2} a_{\text{bet}}^3$. Sometimes the lattice distances for a tcp lattice are given in terms of a fct unit cell. One has $a_{\text{fet}} = \sqrt{2} a_{\text{bet}}$ and $\alpha_{\text{fet}} = \alpha_{\text{bet}}/\sqrt{2}$. This should be kept in mind when applying the formulas derived below. Here, we use the bct unit cell and we will henceforth drop the subscript bct.

Substituting (20) and the expression for v_{bet} into (19), we have for FG_I

$$eq_{\text{tcp}} = \frac{Ze}{a^3} \left\{ \frac{16\pi}{3\alpha} + a^3 \sum_{\lambda} \frac{2P_2(\cos\theta_{\lambda})}{r_{\lambda}^3} \right\}. \quad (21)$$

The bct lattice can be considered to consist of two interpenetrating simple tetragonal (st) lattices, and the series in (21) may consequently be considered as the sum of two subsums $S_{0,0,0}$ and $S_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$. Both sums are taken over a st lattice, $S_{0,0,0}$ with respect to the origin and $S_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ with respect to the center of the unit cell (the point $j_1 = j_2 = j_3 = \frac{1}{2}$) of such a lattice. The expression for $S_{0,0,0}$, obtained by plane-wise summation, has been given in (8), while the corresponding expression for $S_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ is obtained from (14) by substituting $O_a = 1$ and $j_1 = j_2 = j_3 = \frac{1}{2}$. Note that the factor $\exp\{-2\pi i \times (j_1\mu_1 + j_2\mu_2)\}$ assumes the simple form $(-1)^{\mu_1 + \mu_2}$. One finds

$$S_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}^{\text{tet}} = \frac{4\pi^2}{a^3} \sum'_{\mu_1, \mu_2} \frac{(-1)^{\mu_1 + \mu_2} h_{\mu_1, \mu_2}}{\sinh(\pi h_{\mu_1, \mu_2} \alpha)}. \quad (22)$$

If we add (8) and (22), the final expression for eq_{tcp} is found to be

$$eq_{\text{tcp}} = \frac{Ze}{a^3} \left\{ \frac{16\pi}{3} - 9.0336217 + 4\pi^2 \sum'_{\mu_1, \mu_2} \frac{h_{\mu_1, \mu_2} [\exp(-\pi h_{\mu_1, \mu_2} \alpha) + (-1)^{\mu_1 + \mu_2}]}{\sinh(\pi h_{\mu_1, \mu_2} \alpha)} \right\}, \quad (23)$$

where \sum'_{μ_1, μ_2} is a summation over a square lattice with lattice distance 1.

Hexagonal Close-Packed Lattice

We choose the unit cell as usual with \mathbf{a}_1 and \mathbf{a}_2 ($a_1 = a_2 = a$) perpendicular to the c axis and \mathbf{a}_3 parallel

to it ($a_3 = \alpha a$). The unit cell contains two ions and hence $v = \frac{1}{2}\sqrt{3}\alpha a^3$. The derivation is completely analogous to that for the tcp lattice. The series appearing in (19) is now considered as the sum of the two subsums $S^{\text{hex}}_{0,0,0}(9)$ and $S^{\text{hex}}_{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}}(15)$. Adding these expressions and the first term of (19), the final result for eq_{hcp} is found to be

$$eq_{\text{hcp}} = \frac{Ze}{a^3} \left\{ \frac{32\pi}{3\sqrt{3}\alpha} - 11.0341754 + \frac{8\pi^2}{\sqrt{3}} \sum'_{\mu_1, \mu_2} \frac{h_{\mu_1, \mu_2} \{ \exp[-\pi h_{\mu_1, \mu_2} \alpha] + \exp[-\frac{2}{3}\pi i(\mu_1 + \mu_2)] \}}{\sinh(\pi h_{\mu_1, \mu_2} \alpha)} \right\}, \quad (24)$$

where \sum'_{μ_1, μ_2} is a summation over a plane hexagonal lattice with lattice distance $2/\sqrt{3}$. The factor $\exp[-\frac{2}{3}\pi i(\mu_1 + \mu_2)]$, when summed for a given shell of neighbors, has the effect of a multiplying constant (cf. Table I).

V. NUMERICAL RESULTS

For carrying out the numerical evaluations of the various sums, it is useful to write them in a somewhat different form. The expressions (8) and (9) have the general form

$$S_{0,0,0} = \frac{1}{a^3} \left\{ -B + C \sum_i \frac{n_i h_i \exp(-h_i \pi \alpha)}{\sinh(h_i \pi \alpha)} \right\}. \quad (25)$$

The summation \sum_i is another way of writing the two-dimensional sum \sum'_{μ_1, μ_2} . It indicates a summation over the successive shells of neighbors in the two-dimensional lattice: i counts the shells, n_i is the number of particles in the shell i , and h_i is their distance to the origin.

Similarly, (15) and (16) can be written as

$$S^{\text{hex}}_{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}} = \frac{1}{a^3} C_{\text{hex}} \sum_i \frac{n_i h_i c_i}{\sinh(h_i \pi \alpha)}, \quad (26)$$

and

$$S^{\text{hex}}_{2/3, 2/3, 3/4} = \frac{1}{a^3} C_{\text{hex}} \sum_i \frac{n_i h_i c_i \cosh(\frac{1}{2} h_i \pi \alpha)}{\sinh(h_i \pi \alpha)}. \quad (27)$$

In these expressions, c_i is the multiplying constant resulting from the factors $\exp\{-\frac{2}{3}\pi i(\mu_1 + \mu_2)\}$ and $\exp\{-\frac{4}{3}\pi i(\mu_1 + \mu_2)\}$ which appear in the summands of (15) and (16), respectively. Both factors give rise to the same set of factors c_i .

The expression (22) is of the same general form as (26). That is

$$S^{\text{tetr}}_{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}} = \frac{1}{a^3} C_{\text{tetr}} \sum_i \frac{n_i h_i c_i}{\sinh(h_i \pi \alpha)}. \quad (28)$$

However, n_i and h_i are now values for the square lattice, while c_i results from the factor $(-1)^{\mu_1 + \mu_2}$ in (22).

The field gradient at an anion in a CdI_2 -type crystal is given in (17) by

$$q_{\text{anion}} = 2S^{\text{hex}}_{2/3, 2/3, 3/4} - S^{\text{hex}}_{0,0,0} - S^{\text{hex}}_{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}}. \quad (29)$$

For the field gradients in the close-packed metal structures we have [see (23)]

$$\frac{1}{Z} q_{\text{tcp}} = \frac{A_{\text{tcp}}}{a^3 \alpha} + S^{\text{tetr}}_{0,0,0} + S^{\text{tetr}}_{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}}, \quad (30)$$

and [cf. (24)]

$$\frac{1}{Z} q_{\text{hcp}} = \frac{A_{\text{hcp}}}{a^3 \alpha} + S^{\text{hex}}_{0,0,0} + S^{\text{hex}}_{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}}. \quad (31)$$

The constants A , B , and C have the following values for the tetragonal and hexagonal lattices⁹:

$$\begin{aligned} A_{\text{tcp}} &= (16/3)\pi, & A_{\text{hcp}} &= (32/3\sqrt{3})\pi, \\ B_{\text{tetr}} &= 9.0336217, & B_{\text{hex}} &= 11.0341754, \\ C_{\text{tetr}} &= 4\pi^2, & C_{\text{hex}} &= 8\pi^2/\sqrt{3}. \end{aligned} \quad (32)$$

TABLE I. Values of n_i , h_i^2 , and c_i .

| i | Square lattice | | Tcp c_i | Plane hexagonal lattice | | Hcp c_i |
|-----|----------------|---------|--------------|-------------------------|----------|----------------|
| | n_i | h_i^2 | | n_i | $3h_i^2$ | |
| 1 | 4 | 1 | -1 | 6 | 4 | $-\frac{1}{2}$ |
| 2 | 4 | 2 | +1 | 6 | 12 | +1 |
| 3 | 4 | 4 | +1 | 6 | 16 | $-\frac{1}{2}$ |
| 4 | 8 | 5 | -1 | 12 | 28 | $-\frac{1}{2}$ |
| 5 | 4 | 8 | +1 | 6 | 36 | +1 |
| 6 | 4 | 9 | -1 | 6 | 48 | +1 |
| 7 | 8 | 10 | +1 | 12 | 52 | $-\frac{1}{2}$ |
| 8 | 8 | 13 | -1 | 6 | 64 | $-\frac{1}{2}$ |
| 9 | 4 | 16 | +1 | 12 | 76 | $-\frac{1}{2}$ |
| 10 | 8 | 17 | -1 | 12 | 84 | +1 |
| 11 | 4 | 18 | +1 | 6 | 100 | $-\frac{1}{2}$ |
| 12 | 8 | 20 | +1 | 6 | 108 | +1 |

⁹ The values for A are characteristic for the tcp and hcp lattices only, but the values for B and C are valid for all lattices with tetragonal and hexagonal unit cells.

TABLE II. $a^3 S^{\text{tet}}_{0,0,0}(\alpha)$, $a^3 S^{\text{tet}}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}(\alpha)$, and $a^3 Z^{-1} q_{\text{top}}(\alpha)$.

| α | $a^3 S^{\text{tet}}_{0,0,0}$ (25) | $a^3 S^{\text{tet}}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ (28) | $a^3 Z^{-1} q_{\text{top}}$ (30) |
|----------------|--------------------------------------|--|-------------------------------------|
| 0.50 | 13.32 | -21 | 20 |
| 0.60 | 1.284 | -20 | 9 |
| 0.70 | -4.03193 | -16.2 | 3.4 |
| 0.80 | -6.535081 | -13.23 | 1.15 |
| 0.90 | -7.761424 | -10.59 | 0.26 |
| 0.92 | -7.920210 | -10.11 | 0.17 |
| 0.94 | -8.058727 | -9.65 | 0.11 |
| 0.96 | -8.179644 | -9.21 | 0.06 |
| 0.98 | -8.285266 | -8.788 | 0.024 |
| 1.00 (bcc) | -8.377581 | -8.378 | 0.000 |
| 1.02 | -8.458309 | -7.983 | -0.015 |
| 1.04 | -8.528940 | -7.604 | -0.022 |
| 1.06 | -8.590767 | -7.239 | -0.023 |
| 1.08 | -8.644910 | -6.889 | -0.020 |
| 1.10 | -8.692344 | -6.554 | -0.014 |
| 1.12 | -8.733916 | -6.232 | -0.006 |
| 1.1336 | | | 0.000 |
| 1.14 | -8.770362 | -5.924 | 0.003 |
| 1.16 | -8.802327 | -5.629 | 0.012 |
| 1.18 | -8.830368 | -5.347 | 0.022 |
| 1.20 | -8.854976 | -5.077 | 0.030 |
| 1.22 | -8.876576 | -4.819 | 0.038 |
| 1.24 | -8.895541 | -4.5730 | 0.0436 |
| 1.26 | -8.912196 | -4.3379 | 0.0476 |
| 1.28 | -8.926826 | -4.1136 | 0.0495 |
| 1.30 | -8.939680 | -3.8997 | 0.0492 |
| 1.32 | -8.950976 | -3.6958 | 0.0465 |
| 1.34 | -8.960904 | -3.5016 | 0.0413 |
| 1.36 | -8.969632 | -3.3167 | 0.0336 |
| 1.38 | -8.977306 | -3.1407 | 0.0234 |
| 1.40 | -8.984054 | -2.9733 | 0.0106 |
| 1.414214 (fcc) | -8.988350 | -2.85934 | 0.00000 |
| 1.42 | -8.989989 | -2.81410 | -0.00469 |
| 1.44 | -8.995210 | -2.66278 | -0.02246 |
| 1.46 | -8.999803 | -2.51900 | -0.04266 |
| 1.48 | -9.003845 | -2.38244 | -0.06523 |
| 1.50 | -9.007401 | -2.25279 | -0.09009 |
| 1.52 | -9.010530 | -2.12975 | -0.11715 |
| 1.5210 (In) | -9.010677 | -2.12376 | -0.11855 |
| 1.5245 | -9.011181 | -2.10294 | -0.12353 |
| 1.54 | -9.013285 | -2.01301 | -0.14632 |
| 1.56 | -9.015710 | -1.90229 | -0.17751 |
| 1.58 | -9.017844 | -1.79731 | -0.21062 |
| 1.60 | -9.019724 | -1.69781 | -0.24556 |
| 1.70 | -9.026244 | -1.273788 | -0.44406 |
| 1.80 | -9.029701 | -0.9520161 | -0.673294 |
| 1.90 | -9.031536 | -0.7092246 | -0.922255 |
| 2.00 | -9.032512 | -0.5269000 | -1.181831 |
| 2.25 | -9.033392 | -0.2482920 | -1.834946 |
| 2.50 | -9.033574 | -0.1158417 | -2.447351 |

In Table I, we list the values of n_i and h_i^2 for the first twelve shells of neighbors of both the square lattice (with lattice distance 1) and the plane hexagonal lattice (with lattice distance $2/\sqrt{3}$). We also list the values of c_i for these shells, as they result from the factors $\exp\{-2\pi i(j_1\mu_1 + j_2\mu_2)\}$.

The numerical evaluations of the expressions (25) through (31) for various values of α have been carried out on the IBM 650. This avoids a time consuming numerical evaluation of the exponential function. An added advantage is, of course, the relative ease with which future calculations for different values of α can be performed. This might be useful, for example, in studying the influence of the temperature dependence of α on quadrupole resonance phenomena.

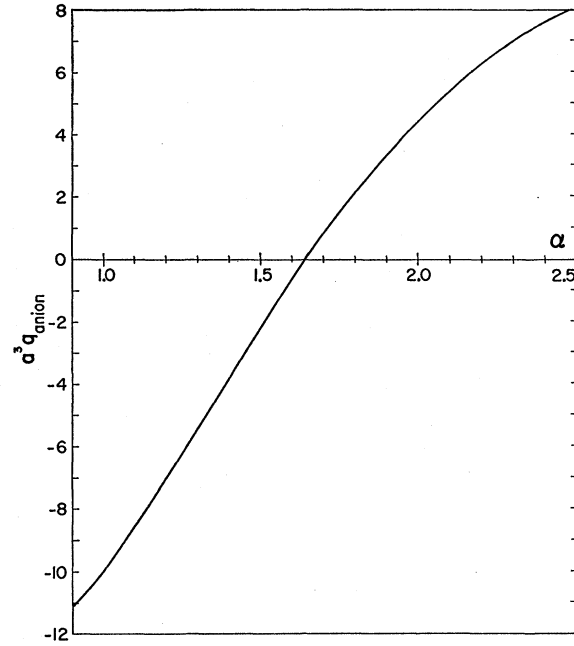


FIG. 2. The field gradient FG_l at the position of an anion in a CdI_2 -type crystal. $a^3 q_{\text{anion}}(\alpha)$ in the range $\alpha=0.9$ –2.5.

We have chosen to program the numerical evaluation of the expressions (25) through (28) rather than that of the original expressions (8), (9), (15), (16), and (22), since modifying the latter expressions into the former and compiling the information in Table I saves greatly on both programming and machine time. However, this was possible only because the factors c_i could be determined easily in these cases. In situations where this is not the case, it is probably advantageous to program the original expressions.

In Tables II and III are listed the results of numerical calculations accurate to the last significant figure shown. For the small α values, the accuracy is limited by the limited number of neighbor shells that have been taken into account. For the larger α values, the eight-place accuracy per machine word of the IBM 650 was the limiting factor. Higher accuracy can, of course, always be obtained by specifying the accuracy in the program.

In Fig. 2, we have plotted $a^3 q_{\text{anion}}(\alpha)$; and in Fig. 3, we have plotted $a^3 q_{\text{top}}(\alpha)$ and $a^3 q_{\text{hcp}}(\alpha)$. Since the overall plot in Fig. 3 does not bring out the details in the α region of interest, we have enlarged the central region in Fig. 4.

For the tcp structure, there are two α values which provide a check on expression (23) for eq_{top} . For $\alpha=\sqrt{2}$, we obtain the fcc lattice; and for $\alpha=1$ the bcc lattice. In both cases, FG_l should be zero because of the cubic symmetry. This is indeed what we find to within the stated accuracy of the calculations. Moreover, there is a third zero point of $a^3 q_{\text{top}}(\alpha)$ at about $\alpha=1.1336$. This point is not a result of symmetry but is due simply to the shape of the curve. For the hcp structure, a similar

TABLE III. $a^3S^{\text{hex}}_{0,0,0}(\alpha)$, $a^3S^{\text{hex}}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}(\alpha)$, $a^3S^{\text{hex}}_{2/3,2/3,3/4}(\alpha)$, $a^3q_{\text{anion}}(\alpha)$, and $a^3Z^{-1}q_{\text{hcp}}(\alpha)$.

| α (crystal of interest) | $a^3S^{\text{hex}}_{0,0,0}$ (25) | $a^3S^{\text{hex}}_{\frac{1}{2},\frac{1}{2},\frac{1}{2}}$ (26) | $a^3S^{\text{hex}}_{2/3,2/3,3/4}$ (27) | a^3q_{anion} (29) | $a^3Z^{-1}q_{\text{hcp}}$ (31) |
|----------------------------------|-------------------------------------|---|---|-------------------------------|-----------------------------------|
| 0.50 | 9.436 | -27 | | | 20 |
| 0.60 | -1.97127 | -21.5 | | | 8.7 |
| 0.70 | -6.855355 | -16.59 | | | 4.18 |
| 0.80 | -9.064619 | -12.56 | | | 2.56 |
| 0.90 | -10.09474 | -9.359 | -15 | -11 | 2.04 |
| 1.00 | -10.58314 | -6.8794 | -13 | -10 | 1.8846 |
| 1.10 | -10.81684 | -4.9994 | -12 | -8.5 | 1.7721 |
| 1.20 | -10.92924 | -3.59976 | -10.7 | -7.0 | 1.59366 |
| 1.30 | -10.98346 | -2.57286 | -9.47 | -5.39 | 1.32614 |
| 1.40 | -11.00964 | -1.828139 | -8.29 | -3.75 | 0.98164 |
| 1.50 | -11.02231 | -1.292983 | -7.23 | -2.15 | 0.58284 |
| 1.55 | -11.02592 | -1.085850 | -6.743 | -1.375 | 0.37029 |
| 1.554(CaI ₂) | -11.02615 | -1.070751 | -6.705 | -1.314 | 0.35303 |
| 1.5679(Be) | -11.02692 | -1.019855 | -6.574 | -1.102 | 0.29278 |
| 1.57 | -11.02703 | -1.012374 | -6.555 | -1.070 | 0.28365 |
| 1.59 | -11.02800 | -0.9437548 | -6.370 | -0.770 | 0.19629 |
| 1.61 | -11.02883 | -0.8796845 | -6.190 | -0.473 | 0.10837 |
| 1.613(CdI ₂) | -11.02895 | -0.8704482 | -6.164 | -0.429 | 0.09515 |
| 1.6148(Rh) | -11.02902 | -0.8649522 | -6.148 | -0.402 | 0.08720 |
| 1.620(MnBr ₂) | -11.02921 | -0.8492640 | -6.102 | -0.326 | 0.06424 |
| 1.63 | -11.02956 | -0.8198733 | -6.015 | -0.180 | 0.02002 |
| 1.6322(Co) | -11.02963 | -0.8135424 | -5.996 | -0.148 | 0.01028 |
| 1.632993(Ideal ^h hcp) | -11.02965 | -0.8112719 | -5.989 | -0.137 | 0.00676 |
| 1.634(Na) | -11.02969 | -0.8083978 | -5.980 | -0.122 | 0.00230 |
| 1.6345 | -11.02970 | -0.8069747 | -5.976 | -0.115 | 0.00009 |
| 1.6357(β -Sr) | -11.02974 | -0.8035686 | -5.965 | -0.098 | -0.00523 |
| 1.637(Li) | -11.02978 | -0.7998946 | -5.954 | -0.079 | -0.01099 |
| 1.639(MnI ₂) | -11.02985 | -0.7942746 | -5.937 | -0.050 | -0.01986 |
| 1.64 | -11.02988 | -0.7914790 | -5.928 | -0.035 | -0.02429 |
| 1.643(MgBr ₂) | -11.02997 | -0.7831501 | -5.902 | 0.007 | -0.03759 |
| 1.644(GeI ₂) | -11.03000 | -0.7803929 | -5.894 | 0.021 | -0.04203 |
| 1.650(FeBr ₂) | -11.03018 | -0.7640486 | -5.843 | 0.107 | -0.06866 |
| 1.66 | -11.03046 | -0.7375502 | -5.758 | 0.250 | -0.11307 |
| 1.662(MgI ₂) | -11.03051 | -0.7323597 | -5.742 | 0.278 | -0.12196 |
| 1.663(CoBr ₂) | -11.03054 | -0.7297780 | -5.733 | 0.292 | -0.12641 |
| 1.671(FeI ₂) | -11.03074 | -0.7094423 | -5.667 | 0.406 | -0.16197 |
| 1.679(CoI ₂) | -11.03094 | -0.6896629 | -5.601 | 0.518 | -0.19755 |
| 1.68 | -11.03096 | -0.6872288 | -5.593 | 0.532 | -0.20200 |
| 1.70 | -11.03140 | -0.6402814 | -5.431 | 0.809 | -0.29097 |
| 1.72 | -11.03177 | -0.5964883 | -5.273 | 1.081 | -0.37989 |
| 1.74 | -11.03210 | -0.5556439 | -5.119 | 1.349 | -0.46866 |
| 1.76 | -11.03238 | -0.5175546 | -4.969 | 1.612 | -0.55721 |
| 1.78 | -11.03262 | -0.4820399 | -4.8225 | 1.8695 | -0.64545 |
| 1.80 | -11.03283 | -0.4489296 | -4.6796 | 2.1223 | -0.73332 |
| 1.82 | -11.03301 | -0.4180648 | -4.5404 | 2.3702 | -0.82075 |
| 1.84 | -11.03317 | -0.3892966 | -4.4047 | 2.6129 | -0.90769 |
| 1.8563(Zn) | -11.03328 | -0.3673040 | -4.2967 | 2.8071 | -0.97814 |
| 1.86 | -11.03330 | -0.3624853 | -4.2725 | 2.8507 | -0.99407 |
| 1.88 | -11.03342 | -0.3375006 | -4.1437 | 3.0834 | -1.07986 |
| 1.90 | -11.03352 | -0.3142203 | -4.0183 | 3.3110 | -1.16501 |
| 2.00 | -11.03386 | -0.2196367 | -3.4397 | 4.3741 | -1.57990 |
| 2.25 | -11.03412 | -0.08935290 | -2.30446 | 6.51455 | -2.52472 |
| 2.50 | -11.03417 | -0.03622118 | -1.522901 | 8.024585 | -3.33151 |

check on the formulas does not exist. There exists no symmetry argument which shows $a^3q_{\text{hcp}}(\alpha)$ to be zero at $\alpha=1.63299$ (the value for the ideal hcp structure), and it is not. But a^3q_{hcp} is zero for α very close to this value: we find $a^3q_{\text{hcp}}=0.00009$ for $\alpha=1.6345$.

The results of the present calculations are in good agreement with values calculated by other means. For indium (tcp structure), Simmons and Slichter³ computed, by a direct machine calculation of expression (19), the value $eq=(-0.349)Zea^{-3}$. Our result for the same $\alpha=1.5245$ is $eq=(-0.34940)Zea^{-3}$. For beryllium (hcp structure), Pomerantz and Das² report the value $q=0.2953a^{-3}$, with an accuracy of 0.1%. For the same $\alpha=1.5671$, we find $q=0.29626a^{-3}$.

In Table IV, we list some of the ionic crystals with the CdI₂ structure together with the corresponding values for α and a^3q_{anion} . Similarly, in Table V, we list some of the metals with close-packed structures together with the corresponding values of α and $a^3Z^{-1}q$.

VI. CONCLUDING REMARKS

A rather striking characteristic of the numerical calculations is the rapid variation of both $q_{\text{anion}}(\alpha)$ and $q_{\text{hcp}}(\alpha)$ with small changes of α . Bersohn¹ has observed this sensitivity of FG_I on lattice distances and has discussed how it affects quadrupole resonance phenomena.

In this connection, we would like to draw attention to the zero points of FG_I in the various structures

TABLE IV. Values of a^3q_{anion} for various ionic crystals with the CdI_2 structure.

| Crystal | α^a | a^3q_{anion} |
|-----------------|-------------------|-----------------------|
| CoBr_2 | 1.66 ₃ | 0.292 |
| FeBr_2 | 1.65 ₀ | 0.107 |
| MgBr_2 | 1.64 ₃ | 0.007 |
| MnBr_2 | 1.62 ₀ | -0.326 |
| CaI_2 | 1.55 ₄ | -1.314 |
| CdI_2 | 1.61 ₃ | -0.429 |
| CoI_2 | 1.67 ₉ | 0.518 |
| FeI_2 | 1.67 ₁ | 0.406 |
| GeI_2 | 1.64 ₄ | 0.021 |
| MgI_2 | 1.66 ₂ | 0.278 |
| MnI_2 | 1.63 ₉ | -0.050 |

^a Values taken from R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948).

studied here. It is well known that the zero points of $q_{\text{top}}(\alpha)$ for $\alpha=1$ (bcc lattice) and $\alpha=\sqrt{2}$ (fcc lattice) are the result of the cubic symmetry. This symmetry causes *all* contributions to the total FG to vanish. Not only FG_i but also the contributions due to electrons in covalent bonds and to overlap deformation (squeezing) are zero. In contrast to this, the zero points of $q_{\text{anion}}(\alpha)$ and $q_{\text{hcp}}(\alpha)$ are not a result of the hexagonal symmetry. That is, possible contributions to FG resulting from covalent bonding or overlap deformation will not necessarily vanish at these zero points. This situation may, for some crystals, allow a separation of quadrupole-resonance effects caused by FG_i from those resulting from other causes. For instance, from Table IV, it is

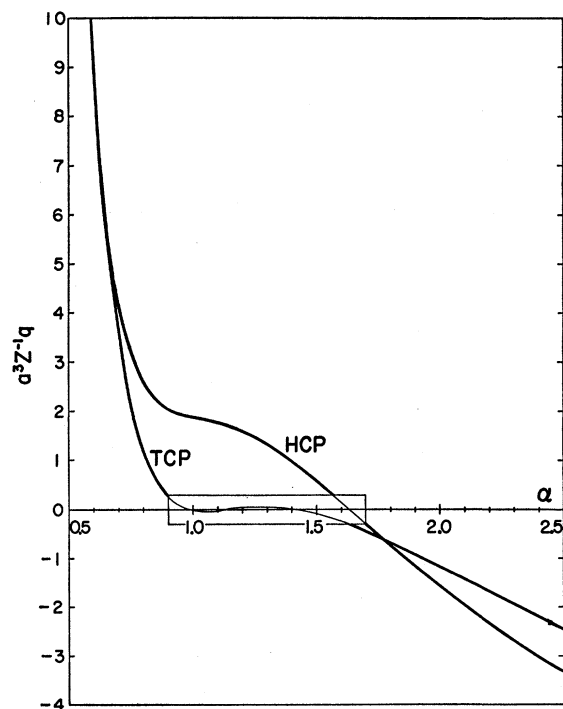


FIG. 3. The field gradient FG_i in close-packed metal structures. $a^3Z^{-1}q_{\text{top}}(\alpha)$ and $a^3Z^{-1}q_{\text{hcp}}(\alpha)$ in the range $\alpha=0.5$ –2.5. The part of the graph inside the rectangle is enlarged in Fig. 4.

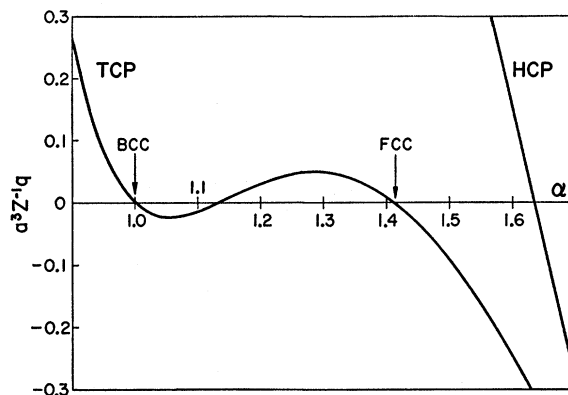


FIG. 4. The field gradient FG_i in close-packed metal structures. $a^3Z^{-1}q_{\text{top}}(\alpha)$ and $a^3Z^{-1}q_{\text{hcp}}(\alpha)$ in the range $\alpha=0.9$ –1.7. This is the enlarged central section of Fig. 3.

seen that q_{anion} for MgBr_2 is practically zero. If one could vary α in the neighborhood of the zero point, for instance by compression of a single crystal of MgBr_2 or by temperature variation of a powder sample, then a resulting strong variation of the observed quadrupole-coupling constant in the neighborhood of zero would indicate that q_{anion} is mainly responsible for the quadrupole-resonance effect. A sensitive dependence of the coupling constant on the lattice parameters should also be expected if overlap deformation played a role. In either of these cases, the conclusion seems justified that the binding of the crystal is predominantly of ionic character. On the other hand, if covalent bonding played a role of importance, one would expect much larger quadrupole-coupling constants which are much less susceptible to changes in the lattice parameters.

A similar situation with respect to the zero point of FG_i exists for the hcp-metal structures. Again, an α variation might make a distinction between metallic- and covalent-bonding effects feasible.

It is well to notice, in connection with these remarks, that some of the x-ray data used are rather old and possibly not quite reliable. Furthermore, we have not made any quantitative estimate of the influence of lattice vibrations on these effects.

TABLE V. Values of $a^3Z^{-1}q$ for various metals with close-packed structures.

| Element | Structure | α | $a^3Z^{-1}q$ |
|---------------------------------|-----------|---------------------|--------------|
| Indium | tcp | 1.5210 ^a | -0.11855 |
| Beryllium | hcp | 1.5679 ^a | 0.29278 |
| Rhenium | hcp | 1.6148 ^a | 0.08720 |
| α -cobalt ^b | hcp | 1.6322 ^c | 0.01028 |
| Sodium (5°K) | hcp | 1.634 ^c | 0.00230 |
| β -strontium ^b | hcp | 1.6357 ^c | 0.00523 |
| Lithium (78°K) | hcp | 1.637 ^c | -0.01099 |
| Zinc | hcp | 1.8563 ^a | -0.97814 |

^a Values taken from R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948). The value for indium holds for the body-centered unit cell.

^b Nuclear quadrupole moment unknown.

^c Values taken from W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (Pergamon Press, New York, 1958).

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APPENDIX

Expression for the Field Gradient in an Arbitrary Ionic Lattice

In the foregoing, we have presented a method for the calculation of field gradients in point-charge lattices. The unit cell of the crystal has to satisfy certain symmetry conditions in order for the method to be applicable. These conditions were outlined in Sec. II.

However, there exist many crystals for which a unit cell satisfying these conditions cannot be defined. In such cases, another rapidly converging expression may be used for numerical calculations of the field gradient. This expression is valid for the component of the field gradient in an arbitrary direction in any lattice point of an arbitrary ionic crystal.

Let us choose the z axis in the direction in which we want to know the field gradient. The field gradient is then quite generally given by [see (3) and (6)]

$$V_{zz}(0) = \sum_{\lambda} \sum_{\substack{j=0 \\ \text{excluded}}} \epsilon_j \frac{2P_2(\cos\theta_{\lambda,j})}{r_{\lambda,j}^3}. \quad (\text{A.1})$$

By a method which has been described previously,^{8,10} we can derive the following rapidly converging ex-

¹⁰ F. W. de Wette and B. R. A. Nijboer, *Physica* **24**, 1105 (1958).

pression for $V_{zz}(0)$,

$$V_{zz}(0) = -\frac{8}{3} \pi^{-\frac{1}{2}} \left\{ \sum_{\lambda} \sum_{\substack{j=0 \\ \text{excluded}}} \epsilon_j \frac{\Gamma(\frac{5}{2}, \pi r_{\lambda,j}^2) P_2(\cos\theta_{\lambda,j})}{r_{\lambda,j}^3} - \frac{\pi^{\frac{3}{2}}}{v_a} \sum_{\mu}' G(\mathbf{h}_{\mu}) \exp(-\pi h_{\mu}^2) P_2(\cos\vartheta_{\mu}) \right\}. \quad (\text{A.2})$$

$V_{zz}(0)$ is expressed here as the sum of two lattice sums. These contain the rapidly converging functions $\Gamma(\frac{5}{2}, \pi r^2)$ and $\exp(-\pi h^2)$, respectively. The first sum is a summation over the original ionic lattice. The second sum is a summation over the reciprocal of the basic Bravais lattice of the crystal. The vector \mathbf{h}_{μ} ($h_{\mu}, \vartheta_{\mu}, \varphi_{\mu}$) is the reciprocal lattice vector and μ stands for the three indices μ_1, μ_2, μ_3 . $G(\mathbf{h})$ is the structure factor of the unit cell of the ionic lattice

$$G(\mathbf{h}) \equiv \sum_j \epsilon_j e^{2\pi i \mathbf{h} \cdot \mathbf{r}_j}. \quad (\text{A.3})$$

Finally, $\Gamma(\frac{5}{2}, \pi r^2)$ is an incomplete gamma function, defined by

$$\Gamma(\frac{5}{2}, x) = \frac{3}{4} \pi^{\frac{1}{2}} \text{Erfc}(x^{\frac{1}{2}}) + (\frac{3}{2} + x) x^{\frac{1}{2}} \exp(-x) = -\frac{3}{2} \int_{x^{\frac{1}{2}}}^{\infty} \exp(-t^2) dt + (\frac{3}{2} + x) x^{\frac{1}{2}} \exp(-x). \quad (\text{A.4})$$

The expression (A.2) can, of course, be used to obtain values for the field gradient in all the crystals, which in this paper have been treated by plane-wise summation. But (A.2) involves more computational work, since one has to evaluate $P_2(\cos\theta_{\lambda,j})$ for all lattice points, and $P_2(\cos\vartheta_{\mu})$ and $G(\mathbf{h}_{\mu})$ for all reciprocal lattice points which are taken into account in the calculation.