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Lattice Distortions and Field Gradients in Alkali Halide Solid Solutions*

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Earlier work by the author and Das is extended to apply to new experimental results. The extensions over previous work include: detailed treatment of 56 neighboring ions as compared with the earlier 24, the use of the shell model, and inclusion of the crystal beyond the 56 neighbors in a continuum approximation. Comparison with experiment indicates that calculations of field gradients using a shell model are good only to within a factor of about 2. Possible reasons for the discrepancy are discussed.

INTRODUCTION

RECENT experimental results of Slusher and Hahn,[1] Andersson and Forslind,[2,3] and Ohlsen and Melich[4] in alkali-halide solid solutions have made it desirable to extend and apply to additional mixed-crystals calculations made earlier by Das and the author.[5–7] The treatment of lattice deformations near monovalent substitutional impurities in alkali halides described in this paper differs from that in DDI in the following particulars:

1. The shell model[8] has been employed here.
2. The number of ions near to the impurity treated individually has been extended from the 24 (0,0,1)-, (1,0,1)-, and (0,0,2)-type ions to make a total of 56 ions treated individually.
3. The rest of the crystal beyond these 56 ions has been included in a continuum approximation in the energy minimization which yields their displacements and dipoles.
4. Van der Waals interactions have not been included. This choice is based on the results of DDI and DDII where it was found that field-gradient tensor components were less sensitive to inclusion of van der Waals forces than to uncertainties in other parameters, notably electronic polarizabilities; that the use of Born-Mayer repulsion parameters without van der Waals interactions led to heats of solution in better correspondence with experiment than the use of Huggins-Mayer repulsion parameters with van der Waals included; and that van der Waals interactions are difficult to include with any confidence of accuracy.

The additional ions of type (1,1,1) and (1,0,2) have been introduced because we wish to compare the newly available experimental data on field gradients at sites as distant as (1,0,2) from the impurity with our calculations and the original set of ions used in DDI is too restricted in extent to expect it to yield very accurate predicted field gradients at these more distant sites.

The results of this work point out the limitations of commonly used ionic-crystal models for the purpose of calculating effects as subtle as electric field gradients near defects in ionic crystals. In view of the success of these models in accounting for many properties of perfect crystals such limitations in their application to crystals with defects are, perhaps, somewhat unexpected. In order to expose deficiencies of a model rather than deficiencies of a calculational scheme it is necessary to employ the model with as few additional approximations as seem feasible. This paper gives an account of such an effort.

In Sec. I the energy expressions to be minimized in finding ion displacements and electronic dipoles are given, and in Sec. II expressions for field-gradient tensor components at various sites are written in terms of these displacements and dipoles. The modifications of the calculation which are necessary in order to incorporate the shell model are derived in Sec. III. The results of the calculations are presented in Sec. IV and compared with experiment in Sec. V.

I. DISPLACEMENTS AND DIPOLES

Except for the modifications mentioned in the Introduction, the calculation is the same as that described in DDI to which the reader is referred for further details. As will be shown below, introduction of the shell model involves only a slight modification of the calculation, and so we will ignore this feature for the moment. Figure 1 shows one example of each of the ion types to be included explicitly along with the direction of its displacement. The displacements of A-, B-, C-, D-, and E-type ions are assumed to be radial and are given, in units of the perfect crystal nearest-neighbor distance a by ξ_i, $i=A, \cdots, E$. In addition to the ion displacements shown in Fig. 1, each of these ions is allowed to polarize. The dipole vectors are chosen to be radially directed and in units ea are denoted μ_i, $i=A, \cdots, E$.

To evaluate the displacement and dipole parameters the change in crystal energy ΔE which arises from

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[1] R. E. Slusher and E. L. Hahn, Phys. Rev. Letters 12, 246 (1964).

[2] L. O. Andersson and E. Forslind, J. Chem. Phys. 38, 2303 (1963).

[3] L. O. Andersson and E. Forslind, Arkiv Fysik 28, 49 (1964).

[4] W. D. Ohlsen and M. Melich, Phys. Rev. 144, 240 (1966).

[5] B. G. Dick and T. P. Das, Phys. Rev. 127, 1053 (1962), hereafter referred to as DDI.

[6] T. P. Das and B. G. Dick, Phys. Rev. 127, 1063 (1962), hereafter referred to as DDII.

[7] B. G. Dick and T. P. Das, J. Appl. Phys. 33, 2815 (1962).

[8] B. G. Dick, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., London, 1965), p. 159.

introducing a single subsitutional impurity is minimized with respect to these parameters. We may break up ΔE into four parts:

$$\Delta E=\Delta E_r+\Delta E_e+\Delta E_s+\Delta E_c\,,$$

where ΔE_r comes from nearest-neighbor repulsive interactions, ΔE_e is electrostatic energy, ΔE_s is the self-energy of the electronic dipoles, and ΔE_c is a continuum estimate of the elastic and electrostatic energy of that part of the crystal outside the region of the 56 $A, \cdots, E$ ions. This region will be referred to as the "outer crystal." We assume that the Born-Mayer repulsive-interaction constants between the impurity and its nearest neighbors alone differ from the pure crystal, all other interactions being the same function of ion separation as before.

If the repulsive energy of an anion-cation pair in the host is given by $A\exp(-r/\rho)$ and that of the impurity ion with an A ion is $B\exp(-r/\sigma)$, then to second order in the displacement parameters

$$\begin{aligned}\Delta E_r={}&6(Be^{-a/\sigma}-Ae^{-a/\rho})+6[(a/\rho)Ae^{-a/\rho}-(a/\sigma)Be^{-a/\sigma}]\xi_{\mathrm{A}}+6\left[\left(\frac{a^2}{2\rho^2}-\frac{2a}{\rho}\right)Ae^{-a/\rho}+\frac{a^2}{2\sigma^2}Be^{-a/\sigma}\right]\xi_{\mathrm{A}}{}^2\\&+Ae^{-a/\rho}\left\{6\left(\frac{a^2}{\rho^2}-\frac{2a}{\rho}\right)(2\xi_B{}^2+\xi_C{}^2)+12\sqrt{2}(a/\rho)\xi_{\mathrm{A}}\xi_B-6(a^2/\rho^2)\xi_{\mathrm{A}}\xi_C+8\left(\frac{a^2}{\rho^2}-\frac{2a}{\rho}\right)\xi_D{}^2\right.\\&\left.+8(\sqrt{6})(a/\rho)\xi_D\xi_B+(2a/5^{1/2}\rho)\xi_C\xi_E+\frac{1}{(10)^{1/2}}\left(\frac{a}{\rho}-\frac{2a^2}{\rho^2}\right)\xi_B\xi_E+\left(\frac{a^2}{\rho^2}-2\frac{a}{\rho}\right)\xi_E{}^2\right\}.\end{aligned}\tag{1}$$

In application of Eq. (1) we will explicitly assume that the repulsive interaction between the impurity ion and its nearest neighbors is the same function of ion separation as that deduced for the pure crystal composed of these ions.

The electrostatic energy, further described in DDI, is

$$\begin{aligned}\frac{a\Delta E_e}{3e^2}={}&\left(\frac{3}{(2)^{1/2}}+\frac{1}{4}\right)M_{\mathrm{A}}{}^2+\left(\frac{3}{4}+\frac{7}{3(6)^{1/2}}+\frac{5}{(2)^{1/2}}+\frac{1}{4(2)^{1/2}}\right)M_B{}^2+\left(\frac{1}{32}+\frac{3}{8(2)^{1/2}}\right)M_C{}^2+\left(\frac{2}{3}+\frac{5}{12(2)^{1/2}}+\frac{1}{9(3)^{1/2}}\right)M_D{}^2\\&+\frac{4}{5}\left(\frac{3}{4}+\frac{9}{64}+\frac{1}{4(5)^{1/2}}+\frac{7}{4(8)^{1/2}}+\frac{4}{3(12)^{1/2}}+\frac{33}{4(2)^{1/2}}+\frac{19}{12(18)^{1/2}}+\frac{13}{3(6)^{1/2}}+\frac{17}{7(14)^{1/2}}+\frac{3}{2(10)^{1/2}}\right)M_E{}^2\\&-2\left(2(2)^{1/2}+\frac{52}{25(10)^{1/2}}+\frac{4(2)^{1/2}}{3(3)^{1/2}}\right)M_{\mathrm{A}}M_B+4\left(1-\frac{1}{27}-\frac{12}{25(5)^{1/2}}\right)M_{\mathrm{A}}M_C+\frac{2}{(3)^{1/2}}\left(\frac{1}{(2)^{1/2}}+\frac{1}{(6)^{1/2}}\right)M_{\mathrm{A}}M_D\\&+\frac{8}{(5)^{1/2}}\left(\frac{1}{8}-\frac{33}{32(2)^{1/2}}+\frac{5}{6(6)^{1/2}}+\frac{43}{100(10)^{1/2}}\right)M_{\mathrm{A}}M_E+2\left(1+\frac{2}{3(3)^{1/2}}+\frac{13}{25(5)^{1/2}}\right)M_BM_C\\&-\frac{8}{3(6)^{1/2}}\left(6+\frac{14}{27}+\frac{108}{25(5)^{1/2}}\right)M_BM_D+\frac{8}{(10)^{1/2}}\left(-3+\frac{4}{3(3)^{1/2}}+\frac{51}{25(5)^{1/2}}+\frac{124}{121(11)^{1/2}}+\frac{5}{9}+\frac{81}{169(13)^{1/2}}\right)M_BM_E\\&-\frac{8}{3(3)^{1/2}}\left(\frac{2}{(3)^{1/2}}+\frac{102}{121(11)^{1/2}}\right)M_CM_D+\frac{8}{(5)^{1/2}}\left(\frac{14}{25(5)^{1/2}}+\frac{50}{169(13)^{1/2}}+2+\frac{20}{81}+\frac{74}{289(17)^{1/2}}\right)M_CM_E\\&+\frac{8}{(15)^{1/2}}\left(\frac{3}{(2)^{1/2}}+\frac{31}{25(10)^{1/2}}+\frac{5}{3(6)^{1/2}}+\frac{51}{49(14)^{1/2}}\right)M_DM_E\,,\end{aligned}\tag{2}$$

where

$$\begin{aligned}M_A&=q\xi_A+\mu_A\,,\\M_B&=-q\xi_B+\mu_B\,,\\M_C&=-q\xi_C+\mu_C\,,\\M_D&=q\xi_D+\mu_D\,,\\M_E&=q\xi_E+\mu_E\end{aligned}\tag{3}$$

are the total dipoles associated with the various ions. Here $q=+1$ for an anion and -1 for a cation impurity.

The dipole self-energies are given by

$$\frac{a\Delta E_s}{3e^2}=a^3\left(\frac{\mu_{\mathrm{A}}{}^2}{\alpha_{\mathrm{A}}}+\frac{2\mu_B{}^2}{\alpha_B}+\frac{\mu_C{}^2}{\alpha_B}+\frac{4}{3}\frac{\mu_D{}^2}{\alpha_{\mathrm{A}}}+\frac{4\mu_E{}^2}{\alpha_{\mathrm{A}}}\right),\tag{4}$$

where α_i is the electronic polarizability of ion i and we have used the facts: $\alpha_C=\alpha_B$, $\alpha_E=\alpha_D=\alpha_A$.

The continuum estimate ΔE_i is handled exactly as in DDI except that the electrostatic hexadecapole is taken to be that due to all the $A, \cdots, E$ ionic dipoles and the forces giving rise to the elastic strain are chosen to be those due to the C and E ions. The radius of the hole in the continuum is taken as $3a$. Then following the treatment in DDI:

$$\Delta E_c=K_e\left[\xi_A+(2)^{1/2}\xi_B-8\xi_C-\frac{8}{(3)^{1/2}}\xi_D+\frac{20}{(5)^{1/2}}\xi_E\right]^2 +K_e\left[\frac{6}{(5)^{1/2}}\xi_E+\xi_C\right]^2 \tag{5}$$

with

$$K_e=\frac{e^2}{a}\frac{1400}{3^{10}}\frac{(1-\epsilon)(10\epsilon^2-\epsilon+9)}{(5\epsilon+4)^2} \tag{6}$$

$$K_s=8C_{44}aA^2e^{-2a/\rho}/27\pi C_{11}{}^2\rho^4. \tag{7}$$

In DDI this outer crystal part of the energy was considered for the cases studied there but, being small, was not minimized along with the other energy terms. This procedure has been questioned by Fukai.[9] As will be seen below, it makes little difference in the present calculated field-gradient components whether these terms are included or not.

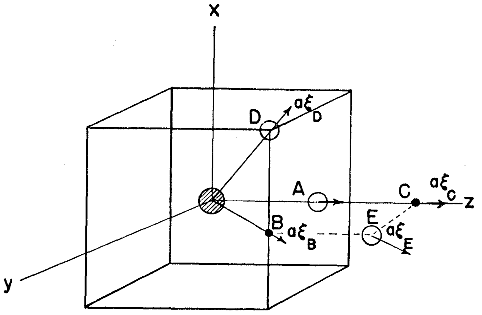

FIG. 1. Labeling of axes and neighbors in the vicinity of an impurity ion. The case shown is that of a cation impurity. The shaded, open and filled circles are impurity, host anions, and cations, respectively.

II. FIELD GRADIENTS

Once the displacements and electronic dipoles at lattice sites have been found by minimizing ΔE the field-gradient components at various lattice sites due to the total dipoles at other sites may be calculated. This has been done as described in DDII (Sec. II and Appendix). Field-gradient components at (0,0,1) and (1,0,1) sites are calculated including the contributions of all A-, B-, C-, D-, and E-type ions. All the nearest neighbors of (0,0,1) and (1,0,1) sites are included among these contributors. This is not true for (1,0,2), (1,1,1), and (0,0,2) sites which have nearest neighbors which are not among the A- through E-type ions. In these cases field-gradient components have been calculated by including contributions from all A- through E-type ions and, in addition, from dipoles at the missing nearest-neighbor sites calculated from the continuum approximation as described in the Appendix of DDII. The resulting expressions for the field-gradient components (in units $3e/a^3$) are:

(0,0,1) site

$$\begin{aligned} &E_{xx}=E_{yy}=-\tfrac{1}{2}E_{zz}=0.5929M_A-1.1666M_B+1.0124M_C+0.3384M_D+0.01041M_E, \\ &E_{xy}=E_{yz}=E_{zx}=0; \end{aligned} \tag{8}$$

(1,0,1) site

$$\begin{aligned} &E_{zz}=E_{xx}=-\tfrac{1}{2}E_{yy}=0.1213M_A+0.2171M_B+0.1787M_C-1.1034M_D+0.8948M_E, \\ &E_{xz}=2.3212M_A+0.7401M_B-0.4704M_C+0.1164M_D-0.9496M_E, \\ &E_{xy}=E_{yz}=0; \end{aligned} \tag{9}$$

(1,0,2) site

$$\begin{aligned} &E_{xx}=-0.2792M_A+0.6492M_B-0.04319M_C-0.008125M_D+0.01408M_E-0.05417M', \\ &E_{yy}=0.1071M_A+0.4138M_B-0.03897M_C-0.4626M_D-0.2812M_E+0.8891M', \\ &E_{zz}=0.1721M_A-1.0630M_B+0.08216M_C+0.4707M_D+0.2672M_E-0.03473M', \\ &E_{zx}=-0.1372M_A+0.9455M_B+1.0295M_C+0.2780M_D+0.2792M_E-0.1200M', \\ &E_{xy}=E_{yz}=0; \end{aligned} \tag{10}$$

(1,1,1) site

$$\begin{aligned} &E_{xx}=E_{yy}=E_{zz}=0, \\ &E_{xy}=E_{yz}=E_{zx}=0.4254M_A+1.6003M_B+0.04019M_C+0.1110M_D-0.3900M_E-0.1326M'; \end{aligned} \tag{11}$$

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[9] Y. Fukai, J. Phys. Soc. Japan **18**, 1413 (1963).

(0,0,2) site

$$E_{xx}=E_{yy}=-\tfrac{1}{2}E_{zz}=0.8803M_A-0.6106M_B-0.03705M_C-0.2247M_D+0.5901M_E+0.1111M', \quad (12)$$

$$E_{xy}=E_{yz}=E_{zx}=0.$$

Here,

$$M'=q\left(\frac{a}{\rho}\right)^2\frac{Ae^{-a/\rho}}{C_{11}\pi a^3}\left(\frac{6}{\sqrt{5}}\xi_E+\xi_C\right), \quad (13)$$

and terms containing M' arise from the dipoles estimated in the continuum approximation. The axes are those of Fig. 1; all of the field-gradient tensors are symmetric.

III. SHELL MODEL

The calculations described in Sec. I yield the ion center-of-mass displacements ξ_i, and electronic dipoles μ_i by using a simple Born-Mayer approach to the crystal. The ion-repulsion contribution to ΔE, as it appears in Eq. (1), is based on the assumption that the distance to be used in calculating the repulsive potential energy between ions is the separation of the centers of mass of the ions. In the shell model[8] (in its simplest form) the ions are separated into massive cores of charge X and massless shells of charge Y with $X+Y=Z$, the ion charge. In addition, the core and shell are connected by an isotropic restoring spring of spring constant k to give the ion a finite polarizability $Y^2e^2k^{-1}$. In using this model the repulsion is taken to act between shells instead of cores (centers of mass) in contrast with the calculation of Sec. I.

Since the shell model has proved to be a significant improvement over the simple Born-Mayer model when applied to problems involving lattice polarization, it will be useful to modify the calculation of Sec. I so as to incorporate the features of the shell model. This turns out to be very simple and to involve only an alteration of the polarizabilities and a reinterpretation of the ξ_i.

Consider a single deformed-shell-model ion displaced from a lattice site (Fig. 2). The dipole moment of this ion with respect to the lattice site is

$$M=Xd_c+Yd_s=Z\xi+\mu, \quad (14)$$

where the second equality shows how we have previously written this dipole moment as the sum of an ionic ($Z\xi$) and electronic part (μ). There is a certain amount of arbitrariness in this partitioning depending on how we choose to interpret ξ. Consider two cases:

$$\xi=d_c,\quad \text{case } 1, \qquad \xi'=d_s,\quad \text{case } 2, \quad (15)$$

where we distinguish the cases by the prime on ξ in case 2. The cases differ in the origin chosen to calculate the electronic dipole. In case 1, μ is core centered; in case 2 the electronic dipole, which we will call μ' in this case, is shell centered. In both cases the total dipole is the same:

$$M=Z\xi+\mu=Z\xi'+\mu'. \quad (16)$$

Using (15) it is easy to see that

$$\mu=Y(d_s-d_c), \qquad \mu'=X(d_c-d_s), \quad (17)$$

and hence that

$$\mu'=[(Y-Z)/Y]\mu \quad (18)$$

remembering that $X+Y=Z$.

Now, using the case-2 choice of notation, we can write ΔE for the shell model. In ΔE_r Eq. (1) the displacement parameters which should appear are the *shell*-displacement parameters, that is to say ξ_i', since the repulsion is between the shells and not the cores. We can write this altered form of Eq. (1) for convenience as

$$\Delta E_r=R_1\xi_1'+\sum_{i,j}R_{ij}\xi_i'\xi_j', \quad (19)$$

where the R_1 and R_{ij} are given as the coefficients of ξ_1, ξ_i,ξ_j in Eq. (1) and we have ignored the additive constant term. It is to be emphasized that this alteration of ΔE_r is the feature which introduces the shell model into our calculation. The electrostatic energy ΔE_e depends only on total dipoles and may be written

$$\Delta E_e=\sum_{ij}C_{ij}M_iM_j=\sum_{ij}C_{ij}(Z_i\xi_i'+\mu_i')(Z_j\xi_j'+\mu_j'). \quad (20)$$

The electronic dipole self-energy ΔE_s of Eq. (4) involves the electronic polarizabilities α_A, α_B. These polarizabilities are determined theoretically or semiempirically considering the nucleus of the ion to be fixed and so the dipoles which must be used in ΔE_s when employing Eq. (4) must be core-centered dipoles. We can write this as

$$\Delta E_s=\textstyle\sum_i n_i(\mu_i^2/\alpha_i), \quad (21)$$

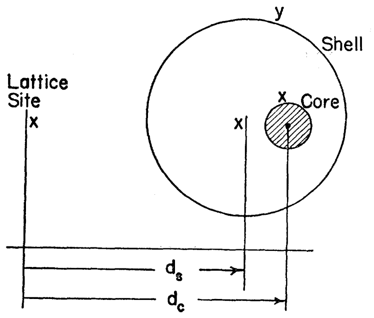

FIG. 2. Notation for the specification of a displaced and electronically polarized shell-model ion. The core is connected to the shell by an isotropic spring (not shown) tending to bring core and shell centers into coincidence.

where the n_i are numerical factors such as those occurring in Eq. (4) which have to do with the number of ions of type A, type B, etc. By using Eq. (18) we may express ΔE_s in terms of μ_i':

$$\Delta E_s = \sum_i n_i(\mu_i'^2/\alpha_i'), \tag{22}$$

$$\alpha_i' = \alpha_i((Y_i - Z_i)/Y_i)^2. \tag{23}$$

If we now combine Eqs. (19), (20), and (22) to get an expression for ΔE, we find that, except for the occurrence of α_i' in place of α_i, ΔE is the same function of ξ_i', μ_i', as we had in Sec. I for ξ_i, μ_i. In this way, we can see that the shell model may be incorporated into the calculation described in Sec. I very simply: Replace the electronic polarizabilities α_i by modified ion polarizabilities given by (23) and regard the ξ_i and μ_i of the calculation as ξ_i' and μ_i', i.e., the positions of shell centers rather than core centers and shell-centered rather than core-centered dipoles.

An alternative, equivalent, and less convenient scheme would be to write ΔE in terms of unprimed variables. In Eq. (19) use the easily proved relation

$$\xi_i' = \xi_i + \mu_i/Y_i; \tag{24}$$

in Eq. (20) one may merely remove the primes because of Eq. (16); and these combined with Eq. (21) give ΔE in terms of unprimed quantities. In this case, minimization of ΔE would yield core positions ξ_i and core-centered electronic dipoles μ_i. The value of the M_i is the same in either case.

We are interested primarily in calculating measurable field-gradient components. As can be seen in Eq. (8) through (13), except for the terms in M' the field gradients depend only on the total dipoles M_i and not on ξ_i or μ_i separately. As explained in DDII the continuum estimates of dipoles which are involved in the M' terms are related to elastic displacements of the crystal beyond the E ions produced by the displacement of the outermost ions (in this case taken to be E and C ions). For this purpose it is clearly more physical to use the shell center displacements ξ_C' and ξ_E' in Eq. (13) than to use core displacements ξ_C and ξ_E. It is therefore preferable from the point of view of simplicity and physical plausibility to introduce the shell model into our calculation by simply modifying the polarizabilities and interpreting the ξ_i', μ_i' appropriately rather than by altering the variables in ΔE_r. To carry out this program we must have values of the shell-charge parameters Y_i.

Equation (23) shows that $\alpha_+' > \alpha_+$ and $\alpha_-' < \alpha_-$ since the shell charges Y_i are negative and greater than unity in magnitude. This bears out a conjecture made in DDII. It was observed in both DDI and DDII that the Sternheimer polarizabilities employed in those calculations led, in general, to better agreement with experiment than use of Tessman, Kahn, and Shockley (TKS) polarizabilities. Sternheimer polarizabilities are greater for negative and smaller for positive ions than the TKS polarizabilities. In DDII it was conjectured that the effect of introducing the shell model would be to reduce negative ion and increase positive ion polarizabilities as compared with supposed free-ion values, and we see this conjecture confirmed in Eq. (23).

In the sections which follow we will drop the primes on ξ_i and μ_i understanding, always, that primes are implicitly present whenever a shell-model calculation is involved.

IV. RESULTS OF CALCULATIONS

In order to deduce ξ_i and μ_i we need to solve the 10 simultaneous linear equations

$$\partial\Delta E/\partial\xi_i = \partial\Delta E/\partial\mu_i = 0, \quad i = A, \cdots, E. \tag{25}$$

The coefficients are determined in terms of the Born-Mayer parameters A, ρ, B, σ, the equilibrium nearest-neighbor distance of the host crystal a, the modified polarizabilities α_+', α_-', the elastic constants C_{11} and C_{44}, and the static dielectric constant ϵ of the host crystal. The Born-Mayer constants and lattice parameters from the tabulation of Born and Huang,[10] the elastic constants of Spangenberg and Haussühl,[11] and the dielectric constants of Höjendahl[12] have been used. The modified polarizabilities are not so directly available and involve a certain amount of arbitrariness. For the ion polarizabilities before modification one might choose either the TKS[13] semiempirical polarizabilities or the theoretically calculated free-ion polarizabilities of Sternheimer.[14] One would guess that the TKS polarizabilities would be the most appropriate choice to modify since they are ostensibly polarizabilities in the crystal environment unlike the Sternheimer polarizabilities. To modify the chosen polarizabilities one must still make a choice for the shell-charge parameters Y_i.

Havinga[15] has observed that shell charges smaller than those originally proposed by Dick and Overhauser[16] may be justified by physical arguments and give better agreement of dielectric theory with experiment. Inelastic neutron scattering experiments support this.[17] Benson[18] has recently pointed out that the original Dick and Overhauser estimates of the shell charges are a factor of 2 too large because of an error of interpretation of the tabulated data of Cuthbertson and

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[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 26.

[11] K. Spangenberg and S. Haussühl, Z. Krist. **109**, 4 (1957).

[12] K. Höjendahl, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **16**, No. 2 (1938).

[13] J. R. Tessman, A. K. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[14] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **107**, 1565 (1957).

[15] E. E. Havinga, Phys. Rev. **119**, 1193 (1960).

[16] B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

[17] A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. **131**, 1025 (1963); R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, *ibid.* **131**, 1030 (1963).

[18] G. C. Benson (private communication).

TABLE I. Polarizabilities and shell charges.[a]

	α_i TKS	α_i Sternheimer	Y_i	α_i' TKS-shell	α_i' Sternheimer-shell
Li^+	0.03	0.0316	-1.12	0.107	0.113
Na^+	0.41	0.145	-2.40	0.82	0.291
K^+	1.33	1.26	-4.35	2.01	1.91
Rb^+	1.98	2.73	-4.95	2.86	3.94
F^-	0.652	3.20	-2.40	0.222	1.09
Cl^-	2.97	5.65	-4.35	1.76	3.35
Br^-	4.17		-4.95	2.65	
I^-	6.44		-5.65 (-2.76)	2.62	

[a] Polarizabilities in units 10^{-24} cm^3. The Y_i shown are the corrected Dick-Overhauser estimates. The -2.76 value for I^- is that deduced by Woods, Cochran, and Brockhouse (Ref. 20). This experimental value has been used in calculating the $\alpha_i' = [(Y_i - Z_i)/Y_i]^2 \alpha_i$ for I^-.

Cuthbertson.[19] Correcting this error brings the Dick-Overhauser estimates near to the Havinga estimates. Lacking enough inelastic-neutron-scattering experiments to give a complete set of Y_i, these revised estimates furnish the only such complete set, and we have (except for I^-) accordingly used them here. TKS and Sternheimer polarizabilities along with their shell-model modifications are shown in Table I.[20]

Table II shows displacements and electronic dipoles as calculated from Eq. (25). The results for four different choices for polarizabilities are shown in Table II: TKS, Sternheimer, and their shell-model modified forms. Table III shows the principal field-gradient components calculated using ξ_i, μ_i from Table II in Eqs. (3), (8)–(13). Also in Table III is information on the orientation of the principal-axis systems. The conventions of Cohen and Reif[21] are followed according to which the principal axes x', y', and z' are chosen so that z' lies along the direction of maximum and x' lies along the direction of minimum field gradient. y' is chosen to make x', y', z' a right-handed set of orthogonal axes.

The results of Tables II and III show the sort of variations to be expected from uncertainty in choice of polarizability. Of these cases the TKS-shell case is the one we expect to be best. Two other alterations of the calculation are of interest. Fukai has suggested that (1) electronic polarizabilities are not particularly important in calculations of this kind, and (2) that the results are quite sensitive to the manner in which the outer crystal is worked into the calculation. To check these conjectures we have considered two special cases: (1) set the electronic polarizabilities of the ions equal to zero thereby completely suppressing the electronic dipole contributions; (2) set $\epsilon=1$, $C_{11}=\infty$, $C_{44}=0$. As can be seen from Eqs. (6), (7), and (13), this latter choice excludes relaxation effects of the outer crystal from playing any role. These results are shown in Tables II and III for NaCl-Br as "No Pol." and "No outer." In the "No outer" case the TKS-shell polarizabilities were used.

From these latter calculations one sees that: (1) although the larger ionic displacements are not greatly affected by putting electronic polarizabilities equal to zero, the field gradients are significantly affected; and (2) the alterations in displacements, dipoles, and field gradients produced by neglect of the outer crystal are a good deal smaller than those involved in the variations of electronic polarizabilities considered.

For (0,0,1) and (1,0,1) sites the influence of the outer crystal is slight, but this influence is greater at (1,1,1), (0,0,2), and (1,0,2) sites. This is as one would expect.

From these facts we conclude that the calculations are indeed sensitive to the inclusion and choice of polarizabilities and further that we have taken into account the detailed motion of as many ions as seems to be reasonable in consideration of the uncertainty of the polarizabilities.

We also see that among the polarizabilities tried, the Sternheimer free-ion polarizabilities give results which differ quite markedly from the other cases. This extreme case, in previous work (DDI, DDII), seemed to give calculations in best accord with experiment. As we shall see below, this feature no longer survives in these more elaborate calculations.

There are several other points worth noting:

The orientation of the z' principal-field-gradient axis at (1,0,1) sites is seen to be either (1,0,1) or (1, 0, -1). A slight change in parameters can push this axis to one or the other of these orientations because $E_{z'z'}$ and $E_{y'y'}$ turn out to be nearly equal in magnitude. Thus, because of this sensitivity no particular significance can be attached to the discrimination which the calculations purport to give between these cases.

Another difficulty is to be seen in the NaCl-K, (0,0,1) site, Sternheimer case where the calculated field-gradient components are significantly smaller than for other choices of polarizabilities. What has happened here is that the terms in Eq. (8) for E_{ij} are both positive and negative and turn out nearly to cancel among themselves. Thus the resulting E_{ij} are small differences between inaccurate larger numbers and such unusually small field gradients are not to be regarded as being reliably given by this calculation.

V. COMPARISON WITH EXPERIMENT AND DISCUSSION

Electric-field gradients at lattice sites near substitutional impurities have been measured by observing first- and second-order shifted satellite lines in nuclear magnetic resonance or loss of central line signal by a number

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[19] C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (London) **A84**, 13 (1910).

[20] A. B. D. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

[21] M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

TABLE II. Displacements and electronic dipoles.[a]

	$\xi_A\times10^2$	$\xi_B\times10^2$	$\xi_C\times10^2$	$\xi_D\times10^2$	$\xi_E\times10^2$	$\mu_A\times10^2$	$\mu_B\times10^2$	$\mu_C\times10^2$	$\mu_D\times10^2$	$\mu_E\times10^2$
NaCl-Br										
TKS shell	2.589	0.6869	0.5337	0.3401	0.0987	−0.0664	−0.3037	0.3513	0.0635	0.0169
Sternheimer shell	2.909	0.8300	0.2928	0.6643	−0.0804	0.0064	−0.7035	0.9444	0.0397	−0.0032
TKS	2.816	0.7954	0.3474	0.5785	−0.0309	−0.0023	−0.5954	0.7737	0.0496	−0.0010
Sternheimer	3.622	0.9136	0.3178	1.065	−0.1177	0.0263	−1.481	2.086	0.0297	−0.0106
No Pol.	2.328	0.6210	0.5637	0.0939	0.2222	0	0	0	0	0
No outer	2.716	0.8542	0.6573	0.2825	0.3442	−0.0517	−0.2747	0.3066	0.0618	0.00813
KBr-Na										
TKS shell	−4.577	−1.207	−1.486	−0.2816	−0.5642	−0.3119	−0.3135	0.3204	0.1541	0.0759
TKS	−4.557	−1.108	−1.704	−0.2039	−0.5575	−0.5784	−0.1903	0.1771	0.1873	0.1467
NaCl-K										
TKS shell	4.924	1.517	1.347	0.3184	0.6679	0.3073	0.2192	−0.2225	−0.1831	−0.0647
Sternheimer shell	4.924	1.293	1.845	0.2080	0.6360	0.7912	0.0676	−0.0590	−0.2374	−0.1931
TKS	4.919	1.363	1.706	0.2346	0.6490	0.6544	0.0995	−0.0905	−0.2369	−0.1543
Sternheimer	5.064	0.6162	2.986	0.0946	0.4569	1.913	0.0210	−0.0107	−0.0600	−0.5622
KI-Rb										
TKS shell	1.755	0.4579	0.5827	0.0906	0.2251	0.1070	0.0978	−0.0996	−0.0438	−0.0273
TKS	1.783	0.3180	0.7478	0.0610	0.2046	0.3180	0.0561	−0.0485	−0.0721	−0.0841
KBr-Cl										
TKS shell	−2.203	−0.5906	−0.6615	−0.1663	−0.2599	0.0970	0.2062	−0.2216	−0.0649	−0.0226
TKS	−2.332	−0.6169	−0.6128	−0.2518	−0.2276	0.0413	0.3623	−0.4232	−0.0579	−0.0073

[a] Displacements and electronic dipoles calculated from Eq. (25). For the shell cases one is to understand the entries in the table as primed quantities: ion-shell displacements ξ_i', and shell-centered dipoles μ_i'. For the other cases the entries are core displacements ξ_i and core-centered dipoles μ_i.

TABLE III. Calculated principal field-gradient components and principal axes.[a]

	(0,0,1)				(1,0,1)				(1,1,1)			
			Shell				Shell				Shell	
	TKS	Sternheimer	TKS	Sternheimer	TKS	Sternheimer	TKS	Sternheimer	TKS	Sternheimer	TKS	Sternheimer
NaCl-Br	−5.088	−9.200	−3.367	−5.708	−3.887 (a)	−4.654 (a)	−3.510 (a)	−4.009 (a)	−1.228	−2.634	−0.7528	−1.400
	2.544	4.600	1.684	2.854	3.103	3.252	3.143	3.085	0.614	1.312	0.3764	0.700
	2.544	4.600	1.684	2.854	0.784	1.402	0.367	0.924	0.614	1.312	0.3764	0.700
		No Pol.	No outer			No Pol.	No outer			No Pol.	No outer	
		−2.026	−3.442			3.330 (b)	−3.408 (a)			−0.2496	−1.016	
		1.013	1.721			−3.146	3.345			0.1248	0.508	
		1.013	1.721			−0.184	0.060			0.1248	0.508	
KBr-Na	−1.990		−2.644		3.428 (b)		3.566 (b)		−0.7212		−0.8630	
	0.995		1.322		−3.326		−3.508		0.3606		0.4315	
	0.995		1.322		−0.102		−0.057		0.3606		0.4315	
NaCl-K	3.578	−0.4362	4.914	3.089	−5.804 (b)	−5.008 (b)	−6.083 (b)	−5.707 (b)	1.450	0.656	1.726	1.349
	−1.789	0.2181	−2.457	−1.544	5.663	4.421	5.974	5.530	−0.725	−0.328	−0.863	−0.674
	−1.789	0.2181	−2.457	−1.544	0.141	0.587	0.109	0.177	−0.725	−0.328	−0.863	−0.674
KI-Rb	0.4724		0.7786		−1.054 (b)		−1.114 (b)		0.190		0.244	
	−0.2362		−0.3893		1.012		1.100		−0.095		−0.122	
	−0.2362		−0.3893		0.045		0.046		−0.095		−0.122	
KBr-Cl	1.950		1.464		1.855 (a)		−1.721 (b)		0.597		0.462	
	−0.975		−0.732		1.774		1.720		−0.298		−0.231	
	−0.975		−0.732		−0.081		0.001		−0.298		−0.231	

	(0,0,2)				(1,0,2)			
			Shell				Shell	
	TKS	Sternheimer	TKS	Sternheimer	TKS	Sternheimer	TKS	Sternheimer
NaCl-Br	−4.096	−5.542	−3.700	−4.236	1.661 (0.252, 0.968)	2.502 (0.103, 0.995)	1.429 (0.360, 0.933)	1.757 (0.216, 0.976)
	2.048	2.771	1.850	2.118	−1.300	−1.765	−1.229	−1.339
	2.048	2.771	1.850	2.118	−0.361	−0.737	−0.200	−0.418
		No Pol.	No outer			No Pol.	No outer	
		−3.4072	−4.110			1.194 (0.453, 0.891)	1.635 (0.372, 0.928)	
		1.7036	2.055			−1.174	−1.359	
		1.7036	2.055			−0.020	−0.276	
KBr-Na	−3.922		−4.176		1.616 (0.476, 0.879)		1.657 (0.442, 0.897)	
	1.961		2.088		−1.501		−1.507	
	1.961		2.088		0.115		−0.150	
NaCl-K	6.854	5.322	7.358	6.668	−2.848 (0.472, −0.882)	2.770 (−0.805, 0.593)	−2.904 (0.430, 0.903)	−2.826 (0.487, 0.873)
	−3.427	−2.661	−3.679	−3.334	2.622	−2.736	2.611	2.629
	−3.427	−2.661	−3.679	−3.334	0.226	−0.004	0.293	0.197
KI-Rb	1.180		1.310		−0.5029 (0.453, 0.892)		−0.5127 (0.453, 0.892)	
	−0.590		−0.655		0.4761		0.4750	
	−0.590		−0.655		0.0268		0.0377	
KBr-Cl	2.228		2.056		−0.8645 (0.367, 0.930)		−0.8047 (0.367, 0.908)	
	−1.114		−1.028		0.7409		0.7193	
	−1.114		−1.028		0.1236		0.0854	

[a] Principal field gradients in units of 10^{12} esu. The gradients are listed in the order $E_{z'z'}$, $E_{y'y'}$, $E_{x'x'}$ as calculated for four different choices of ion polarizabilities. For the sites (0,0,1) and (0,02) the principal axes are parallel to the crystal axes with the z axis as labeled in Fig. 1 being the z' axis. For the site (1,1,1) the z' axis in the (1,1,1) direction the other two axes being any orthogonal pair of vectors in the plane normal to this z' axis. At the (1,0,1) site the principal axes' direction numbers are either z': (1, 0, −1), y': (1,0,1), x': (0,1,0) which we call "case (a)" or z': (1,0,1), y': (1, 0, −1), x': (0,1,0) which we call "case (b)." The superscript on $E_{z'z'}$ for the (1,0,1) sites indicates whether the principal-axis system is that for case (a) or (b). At the (1,0,2) site the principal axes' z', y', x' direction cosines are in the form $(-\lambda, 0, \mu)$, $(-\mu, 0, -\lambda)$, (0,1,0). The two numbers in parentheses following $E_{z'z'}$ are λ and μ. Missing entries are absent because of the lack of Sternheimer polarizabilities for Br^- and I^-.

TABLE IV. Quadrupole moments and antishielding factors used in reducing the experimental data to field-gradient components.

Nucleus	Q^a	$(1-\gamma_\infty)^b$	$\nu_L{}^c$
Na^{23}	0.1	5.53	11.262
K^{39}	0.07	13.8	1.987
Cl^{35}	−0.079	50.3	4.172
Cl^{37}	−0.0621	50.3	3.472
Br^{79}	0.34	100	10.667
Br^{81}	0.28	100	11.498
I^{127}	−0.75	180	8.519

[a] Electrical quadrupole moment in units 10^{-24} cm². From the Varian Associates NMR Table, fifth edition.

[b] Quadrupole antishielding factors from T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956); E. G. Wikner and T. P. Das, *ibid.* **109**, 360 (1958).

[c] Magnetic resonance frequency in Mc/sec in 10 000 G. From G. E. Pake, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

of workers.[2–4,9,22,23] Slusher and Hahn[1] have observed the pure electrical quadrupole resonance itself in NaCl mixed crystals. When single crystals are used and variations of observations with rotation of the crystal with respect to external fields are employed, it is possible to identify the principal axes of the field-gradient tensor giving rise to the quadrupole effects and hence to establish the symmetry of the lattice site at which the field gradients being measured occur.

The relationship of first- and second-order splittings of nuclear magnetic resonance lines and pure quadrupole resonance frequencies with electric-field-gradient components at the ions showing these effects has been outlined in DDII. Nuclear and ionic data required to convert the experimental observations to field gradients are given in Table IV. Table V tabulates this converted experimental data and the corresponding calculated results.

It appears from Table V that the semiclassical theory which we have used gives principal field gradients to within a factor of about 2. For sites near the impurity, (0,0,1) and (1,0,1), the calculated values of $q(=E_{z'z'})$ are too small while at the more distant (0,0,2) and (1,0,2) sites the calculated values are too high. When one considers the small magnitudes of the distortions involved (they are of the same order of magnitude as the amplitude of thermal motions) the performance of the shell model in this connection is perhaps not too disappointing. On the other hand, one might hope for better results in view of the fact that the shell model, even in a simple form, predicts phonon dispersion curves with considerable success. It also appears that asymmetry parameters and direction cosines of principal axes (when these are not entirely determined by symmetry) are not reliably given by the theory.

For all sites except (1,0,2) the TKS-shell calculation of q comes nearer to the experimental value than any of the others. For the (1,0,2) site the predicted q's using unmodified TKS polarizabilities are insignificantly better than shell-TKS versions. The apparent superiority of Sternheimer polarizabilities noted in DDII does not survive in the present more elaborate calculation.

Slusher[24] reports that the resonance designated as B by Slusher and Hahn (see Table V) arises from Na^{23} nuclei at sites with 101 symmetry. This fact alters the original identification of the resonance as arising from the Na^{23} at (0,0,1) in these crystals. Since this B resonance occurred in NaCl-Br crystals, Slusher suggests the possibility of unknown cation impurities. In hopes of clarifying this situation field gradients at (1,0,1) sites in NaCl-Li and NaCl-Rb have been calculated. The unknown cation cannot be K^+ since the (1,0,1) site resonance for NaCl-K has been observed (Slusher and Hahn's resonance F) and is distinct from resonance B. The results of these calculations are that the calculated values of $q(1+\frac{1}{3}\eta^2)^{1/2}$ at a (1,0,1) site in NaCl-Li, NaCl-K, NaCl-Rb are 0.0512×10^{14}, 0.0646×10^{14}, 0.0905×10^{14} esu, respectively. These are to be compared with 0.178×10^{14} esu for NaCl-K and 0.0956×10^{14} esu for the suggested unknown cation impurity. If we take the NaCl-K case as an indication that the calculated value of $q(1+\frac{1}{3}\eta^2)^{1/2}$ should be multiplied by a factor of 2 or 3 to get an estimate of this quantity at a (1,0,1)

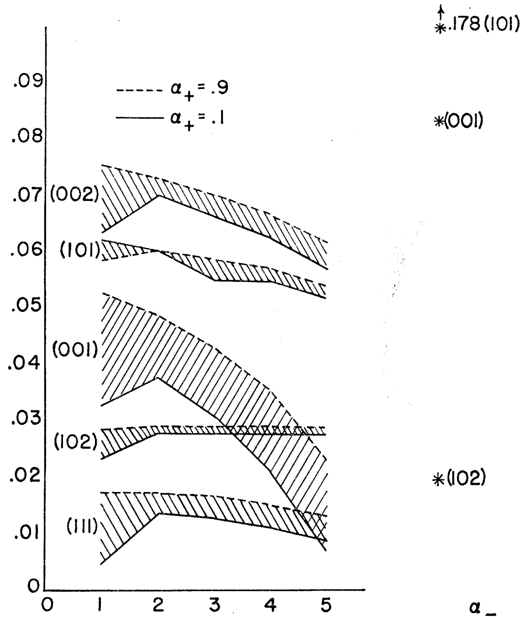

FIG. 3. Variation in calculated principal field gradients which result from variations of anion and cation electronic polarizabilities in a NaCl-K mixed crystal. The dashed lines are for $\alpha_+=0.9$; the solid lines are for $\alpha_+=0.1$. The cross hatched areas show the regions in which intermediate values of α_+ place the values q. The sites at which the q values are being calculated are shown at the left in parentheses. The experimental values of q are shown as crosses to the right. Field gradients are in units of 10^{14} esu and polarizabilities are in units of 10^{-24} cm³.

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[22] H. Kawamura, E. Otsuka, and K. Ishiwatari, J. Phys. Soc. Japan **11**, 1064 (1956).

[23] E. Otsuka and H. Kawamura, J. Phys. Soc. Japan **12**, 1071 (1957).

[24] R. Slusher and E. L. Hahn (to be published).

TABLE V. Comparison of calculations with experiment.

Crystal	Site[a]	Nucleus observed	Observed			Calculated[b]		
			$q(1+\frac{1}{3}\eta^2)^{1/2}$			$q(1+\frac{1}{3}\eta^2)^{1/2}$		
NaCl-Br	101 (unknown cation impurity?)	Na^{23}	0.0956[c] (*B*)			...		
	002	Cl^{35}, Cl^{37}	0.0226[c] (*C,E*)			0.0424		
NaCl-K	001	Cl^{35}, Cl^{37}	0.0824[c] (*G,H*)			0.0491		
	102	Cl^{35}, Cl^{37}	0.0193[c] (*D*, 220 kc/sec)			0.0314		
	101	Na^{23}	0.179[c] (*F*)			0.0646		
	002	Na^{23}	...			0.0736		
	112	Na^{23}	0.0788 (*A*)			...		
			q	η	Direction cosines of principal z' axis	q	η	Direction cosines of principal z' axis
KBr-Na	102	Br^{81}	0.0074[d] 0.0075 ±0.0004[e]	0.40[d] 0.47±0.05[e]	0.73, 0, 0.68[d] 0.707±0.06, 0, 0.707±0.06[e]	0.0167	0.821	−0.442, 0, 0.897
KBr-Cl	101	Br^{81}	0.0099 ±0.0003[e]	0.9 ±0.1[e]	0.707, 0, −0.707[e]	0.0172	0.999	0.707, 0, 0.707
KI-Rb	102	I^{127}	0.0023[d]	0.63±0.03[d]	0.752±0.003, 0, 0.659±0.003[d]	0.00513	0.854	−0.453, 0, 0.892

[a] Sites shown have been identified by rotation measurements. For the NaCl impurities: Slusher; for KBr: Ohlsen and Melich, Forslind and Andersson; for KI-Rb: Forslind and Andersson. The field gradients q are given in units of 10^{14} esu.

[b] The calculated values given are for the TKS-shell case.

[c] Slusher and Hahn (Ref. 1). The letters indicate the Slusher and Hahn designation of the resonance line. The identification of these resonances has been revised from that of Ref. 1 by Slusher (private communication).

[d] Forslind and Andersson (Refs. 2, 3).

[e] Ohlsen and Melich (Ref. 4).

site, one is led to suspect such an unknown cation impurity might be Li^+.

One might try to alter some of the more doubtful parameters such as B or α_+', α_-' so as to gain agreement with experiment in a case, such as NaCl-K, where field gradients at a number of sites have been measured. This has been tried, but such agreement does not appear to be possible within any reasonable range of these parameters. The effects on principal field gradients q from variation of α_+ and α_- are shown in Fig. 3.

It is interesting to speculate on the source of the discrepancy between this calculation and experiment. One might well expect the shell model to do better. In the calculation of phonon dispersion curves the shell model, even in its simplest form, is a significant improvement over the Born-Mayer model.[17,20] In accomplishing this the shell model is required to give an accurate picture of the electronic dipole polarization. Since we have calculated field gradients from calculated ionic and electronic dipoles and we have reason to expect these contributions to be reasonably accurate, it might be that the discrepancies lie in contributions to field gradients at nuclei other than those of these dipoles. In particular, when the nearest neighbors of an ion are not in positions of cubic symmetry with respect to this ion, the distortions of its electronic cloud involved in its overlap with its neighbors will lead to an electron distribution which will in general have a nonzero field-gradient tensor at the nucleus.

Rough estimates of this effect using the exchange-charge model[8] indicate that these additional contributions might be of an order of magnitude appropriate to explain the discrepancies. The exchange-charge model is too crude, however, to use in this connection beyond the estimation of orders of magnitude.

The relatively poor agreement between measured and calculated field gradients might be interpreted as casting doubt on the possible success of Mott-Littleton[25] type calculations of formation energies of point defects. It is possible, however, that field gradients are sensitive to features of the deformation (e.g., overlap distortions of the type just discussed) which play little role in determining displacements and energies.

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[25] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).