

Nuclear-Quadrupole Effects in Alkali-Halide Solid Solutions*

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While point-multiple models provide approximate agreement with observed field gradients in alkali-halide solid solutions, there are still quantitative discrepancies. In an attempt to understand the source of disagreement, we have analyzed the influence of the finite extent of the ions, taking into account contributions due to the electronic orbitals both on the solvent nuclei where the field gradients are measured and on adjacent ions. These electronic contributions are comparable to that from the point-multipole model for ions neighboring the solute and are, in the proper direction to improve agreement with experiment for the positive-ion nuclei, but their inclusion worsens agreement with experiment for negative-ion nuclei. Possible implications of these results concerning the overlapping-ion model for the solid solutions are discussed.

I. INTRODUCTION

RECENTLY there has been considerable interest in theoretical and experimental studies concerning microscopic properties of solid solutions of ionic crystals.¹⁻¹⁵ In contrast to defects with a net charge such as vacancies or interstitial ions which polarize the lattice over a large region, an impurity ion in dilute solid solution alters the perfect crystal structure in a region close to itself, and allows one to treat localized properties quantitatively without requiring a detailed investigation of an extensive region of the crystal.

Theoretical investigations of this type have been carried out in the past in dilute alkali-halide solid solutions using the semiempirical Born-Mayer model. These investigations yielded displacements of ions surrounding the impurity and also the electric dipole moments induced in the displaced ions, thus permitting the investigation of a localized microscopic effect, namely the field gradients (FG) at the nuclei of displaced ions. For example, pure NaCl is a cubic lattice with the Na²³ and Cl^{35,37} nuclei occupying sites of zero FG. However, if a solid solution is formed by substitution of, for example, a Br⁻ ion, the displacements of the ionic charges and the

induced moments on the ions destroy the cubic symmetry at lattice sites in the neighborhood of the impurity and yield a measurable FG. A number of experimental results are now available^{8-11,16} for the interaction of this FG with the nuclear quadrupole moment from NMR experiments at a variety of sites around the impurity and in a number of solid solutions. Das and Dick^{1,2} have calculated the FG using a point charge-point dipole model and obtained results in order-of-magnitude agreement with experiment. Fukai^{3,4} has also analyzed this problem using a somewhat different model involving elastic displacements and excluding induced dipole effects.

Additional contributions to the FG from the lattice distortion around the solute ion could arise if we consider the ions not as point charges but as having a finite size. One such contribution would arise from the deformation of the charge density from cubic symmetry by the differing overlap from the various neighbors of the ion under study. This overlap distortion is due to the Pauli exclusion principle which must be taken into account when the ion cores overlap each other. The situation here is similar to that which arises in consideration of the chemical shifts of alkali and halide ions in different crystals, which is a consequence of the differential overlap of an ion in going from one crystal to another (for example, a Br⁻ ion in NaBr and KBr). For the FG in solid solutions, we are interested in the tensor character of the differential overlap caused by nonsimilar neighboring ions in a distorted crystal. Thus, while a cubic deformation is adequate for producing a finite paramagnetic shielding of the nuclei, a deformation less than cubic, namely, axial or rhombic, is necessary for finite FG.

The motivation of our study here as well as for the chemical shift is to determine whether the simple model of an ideal ionic crystal distorted only by considerations of overlap is capable of describing microscopic proper-

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¹ T. P. Das and B. G. Dick, *Phys. Rev.* **127**, 1063 (1962).

² B. G. Dick, *Phys. Rev.* **145**, 609 (1966).

³ Y. Fukai, *J. Phys. Soc. Japan* **18**, 1413 (1963).

⁴ Y. Fukai, *J. Phys. Soc. Japan* **18**, 1580 (1963).

⁵ Y. Fukai, *J. Phys. Soc. Japan* **19**, 175 (1964).

⁶ J. L. Marsh, Jr., and P. A. Casabella, *Phys. Rev.* **150**, 546 (1966).

⁷ W. D. Wilson, *Bull. Am. Phys. Soc.* **13**, 500 (1968).

⁸ R. E. Slusher and E. L. Hahn, *Phys. Rev.* **166**, 332 (1968).

⁹ Mitsuo Satoh, Paul R. Spencer, and Charles P. Slichter, *J. Phys. Soc. Japan* **22**, 666 (1967).

¹⁰ L. O. Andersson, and Lars Ödberg, *Arkiv. Fysik* **35**, 85 (1966).

¹¹ L. O. Andersson, *Helv. Phys. Acta* **40**, 364 (1967).

¹² Robert J. Quigley and T. P. Das, *Phys. Rev.* **164**, 1185 (1967).

¹³ R. W. Astrue and H. O. Hooper, *Phys. Rev.* **164**, 1206 (1967).

¹⁴ H. O. Hooper and P. J. Bray, *J. Appl. Phys.* **37**, 1633 (1966).

¹⁵ Thomas B. Douglas, *J. Chem. Phys.* **45**, 4571 (1966).

¹⁶ L. O. Andersson, *Helv. Phys. Acta* **41**, 414 (1968).

ties which emphasize certain limited regions of phase space. This model has been successful in calculation of the cohesive energy by Löwdin,¹⁷ which lends encouragement to this study. However, a macroscopic property, such as energy, takes into account all regions of phase space and may be seriously wrong in a limited region.

We would like to investigate whether the agreement with experiment for the chemical shifts¹⁸⁻²¹ of positive ions and lack of consistent agreement for negative ions is also common to FG calculations in alkali-halide solid solutions. Our general approach to determining the electronic structure of the ionic crystal is to proceed one step at a time learning what we can from each step. After determining the effect of including overlap in the wave function, we will consider other effects such as charge transfer covalency, in which some atomic states are admixed into the pure ionic state, and electrostatic polarization, which amounts to admixture of excited states of the ions. In this paper we shall also consider the FG at sites other than the nearest neighbor and compare the relative importance of the point-charge-point-dipole model and the electronic overlap model, as we move to nuclei further from the impurity ion. Such a study can lead to information concerning under what conditions each mechanism contributes strongly to the FG.

The influence of overlap effects on nuclear quadrupole interactions has been studied earlier for the KCl molecule²² and in two instances in ionic crystals. Of the latter, one is in uniaxially strained sodium halides by Marsh and Casabella,⁶ the other is on some alkali- and silver-halide solid solutions by Fukai.⁵ In Fukai's analysis, FG at ions farily distant from the impurity ion were considered, using a continuum elastic model for displacements. In our analysis, we shall, on the other hand, confine ourselves to the FG at ions in the immediate neighborhood of the impurity ion, the displacements of and around which, are obtained by a minimization of crystal energy. In addition, both Marsh and Casabella and Fukai considered only the "local" term arising out of the noncubic overlap distortion of the ion containing the nucleus in question. We shall follow broadly the procedure utilized in the work on quadrupole interaction on KCl molecule and the chemical shifts in alkali halides to study the relative contributions of the "local," "nonlocal," and distant terms to the FG in solid solutions.

Formulation of the expression for the overlap contribution to the FG is given in Sec. II. In Sec. III, we present the results and comparison of the relative contribution arising from the point-charge-point-dipole

model and the electron overlap distortion model at the various lattice sites. Further, we discuss implications concerning the Sternheimer antishielding factor in solids brought out by a comparison between theory and experiment. Section IV contains a summary of the FG results and of the validity of the overlapping-ion model in light of these results and earlier work on the chemical shift.

II. THEORY

In this section, we shall concern ourselves with the formalism necessary to calculate the electronic-overlap contribution to the FG which couples to the quadrupole moment of the nucleus n , imbedded in ion i . As an example of how the overlap can contribute to the FG, let us consider the 001 site in NaCl with a K^+ impurity ion at 000. The charge density of the 001 Cl^- ion is not spherically symmetric, but is distorted from the overlap of its electron shell with the neighboring Na^+ and K^+ shells. The distortion is due to the Pauli exclusion principle, which demands that the wave functions of the electrons of the same spin on different ions rearrange themselves so as not to occupy the same states when they overlap. However, there still would be no FG if the overlap distortion was cubically symmetric. The neighbors of the Cl^- ion are not equidistant, since they are displaced unevenly from their cubic lattice sites by the presence of the K^+ impurity. Thus, since different neighbors produce varying distortions, a nonvanishing FG arises at the Cl^- nucleus. The 001 ion has to be treated as a special case since not only is there an overlap contribution to the FG from the unequal displacement of neighbors, but FG can also arise from overlap owing to unlike neighbors. In our example, the 001 Cl^- has six nearest neighbors of which five are Na^+ and one is the K^+ impurity, and again owing to the tensor character of the FG operator, we will obtain a nonvanishing result. We shall refer to both of these effects as due to differential overlap.

It is illustrative to compare the situation in the solid solutions to the ionic diatomic molecules, for example, NaCl. If we were investigating the FG at the Cl^- nucleus, we see immediately that the Cl^- is at a site in the molecule of less than cubic symmetry. Hence, there would be a net FG which would not depend too sensitively on small changes in the internuclear separation. In the solid solution, a net FG is made possibly only by change from the cubic symmetry which is already present in the undistorted crystal. The destruction of cubic symmetry is accomplished when the ions displace from these perfect crystal positions due to effects of the mismatch in size between solute and solvent ions. Thus, we must have an accurate knowledge of the displacements on all sides of the ion under study. This consideration makes it mandatory that we concentrate only on the near neighbors of the impurity ion, where we know the displacement of at least the nearest neighbors of the ion under study. Since, from Dick, we know the displace-

¹⁷ Per-Olov Löwdin, *Advan. Phys.* **5**, 1 (1956).

¹⁸ Dennis Ikenberry and T. P. Das, *Phys. Rev.* **138**, A822 (1965).

¹⁹ Dennis Ikenberry and T. P. Das, *J. Chem. Phys.* **43**, 2199 (1965); **45**, 1361 (1966).

²⁰ D. W. Hafemeister and W. H. Flygare, *J. Chem. Phys.* **44**, 3584 (1966).

²¹ Yukio Yamagata, *J. Phys. Soc. Japan* **19**, 10 (1964).

²² T. P. Das and M. Karplus, *J. Chem. Phys.* **42**, 2885 (1965).

ments of the five nearest shells of ions, we know the displacements of the nearest neighbors to the 001 and 101 ions. Further, if we consider the 003 ion displacement to be small, we can consider that we know the displacements of nearest neighbors (nn) of the 002 site. There are experimental results available at all these sites as well as the point-charge-point-dipole calculations. Recently, Douglas¹⁵ has calculated the displacements of ions in the first ten shells surrounding the impurity for a large number of alkali-halide solid solutions. We could have used these displacements, but in order to be consistent, we wanted to use the same displacements of the ions as were used for the point charge FG calculations, and hence we have used Dick's.

To determine FG at nucleus n imbedded in ion i , we take the expectation value of the FG operator centered at n as defined by

$$(-\nabla E)_{ij} = \partial^2 V / \partial x_i \partial x_j = V_{ij}, \quad (1)$$

where i and j stand for the Cartesian axes x , y , and z . We will be interested in the FG in the z direction

$$V_{zz} = \sum_i (-) e_i^{\pm} \frac{(3 \cos^2 \theta_i - 1)}{r_i^3}, \quad (2)$$

where $e^+ = 1$ represents a positive charge and $e^- = -1$ stands for a negative charge, and θ_i and r_i have their origin at the nucleus n under investigation. In the principal-axis system (x', y', z'), the off-diagonal components of the FG tensor are 0.

$$V_{x'y'} = V_{y'z'} = V_{x'z'} = 0.$$

As is the usual convention, we choose the principal axis according to the convention

$$|V_{z'z'}| \geq |V_{y'y'}| \geq |V_{x'x'}|.$$

Laplace's equation demands that

$$V_{x'x'} + V_{y'y'} + V_{z'z'} = 0,$$

and we may specify all the information about the FG from the direction of the principal axes and the two quantities q and η defined as follows:

$$q = V_{z'z'}, \quad \eta = |V_{y'y'} - V_{x'x'}| / |V_{z'z'}|.$$

When we have axial symmetry such as at the 001 site, η is zero. The contribution to q from point charges is found by carrying out the sum in Eq. (2) over negative and positive ions. Usually, one can correctly approximate the inner core electrons of neighboring ions as point charges centered at the nucleus; in effect one core electron cancels one proton. For the outer orbitals, we must take the expectation value of $V_{z'z'}$:

$$q^{e1} = \langle \Psi_0 | (+) \sum_i \frac{(3 \cos^2 \theta_i - 1)}{r_i^3} | \Psi_0 \rangle. \quad (3)$$

Our model for the crystal is specified by the wave function Ψ that we use in (3). The most straightforward way to include overlap distortion due to the Pauli principle is to use an orthogonal basis set for the crystal orbitals comprising Ψ . That is, Ψ is a many-electron wave function and for purposes of quantitative calculation, we have to expand it out in terms of one-electron wave functions. Since for the alkali-halide solid solution we have a diamagnetic system with doubly occupied states, Ψ_0 can be expressed in the form of a single determinant in the Hartree-Fock approximation as in (4):

$$\Psi_0 = (2n!)^{1/2} |\psi_{1\uparrow}^{(1)} \psi_{1\downarrow}^{(2)} \dots \psi_{n\downarrow}^{(2n)}| \quad (4)$$

where ψ_n are the one-electron wave functions. Substituting (4) into (3), we obtain the FG in terms of one-electron functions:

$$q^{e1} = \sum_i \langle \psi_i | \frac{(3 \cos^2 \theta_i - 1)}{r_i^3} | \psi_i \rangle. \quad (5)$$

In energy-band language, this would correspond to a tight-binding approximation and the ψ_i to Wannier functions. Since the valence bands are completely filled in our model of the alkali halides, it can be shown²³ that (4) is equivalent to the Heitler-London wave function, where the ψ_i correspond to localized atomic orbitals.

Now if we choose a set of orthogonalized atomic orbitals (OAO) for the one-electron wave functions ψ_i , we have automatically used a model in which the distortion to the fictitious ideal crystal is caused solely by the overlap of the ions. The Pauli exclusion principle is automatically taken into account once we use a determinantal function, and the final results are equivalent no matter what orthogonalization scheme we use. It is just a matter of convenience which choice we take and, in fact, we could have used nonorthogonal orbitals. There are two choices commonly made for the OAO's. The first choice is the symmetric orthogonalization procedure which Löwdin used in cohesive energy calculations. In this formalism, the orbitals are all treated on an equivalent footing, and hence preserve the symmetry of the crystal, which is important for properties such as the cohesive energy. Formally, they are

$$\psi_\mu = \sum_\alpha \varphi_\alpha (1+S)_{\alpha\mu}^{-1/2}$$

or for our case

$$\psi_{0i} = \varphi_{0i} - \frac{1}{2} \sum_\alpha \sum_j S_{0\alpha}{}^{ij} \varphi_{\alpha j} + \frac{3}{8} \sum_\alpha \sum_j \sum_\beta \sum_k S_{0\alpha}{}^{ij} S_{\alpha\beta}{}^{0k} \varphi_{\beta k}, \quad (6)$$

where $S_{0\alpha}{}^{ij} = \langle \varphi_{0i} | \varphi_{\alpha j} \rangle$, α and β denote the ion sites, and i and j the orbitals. A second procedure would be Schmidt orthogonalization, which turns out to reduce the algebra involved in most calculations on a local

²³ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Co., New York, 1940).

microscopic level. Here the orbital on the nearest neighbor to the ion 0 which is under investigation is not perturbed, but is simply the atomic function for an ion, $\varphi_{\alpha j}$. The wave function φ_{0i} is then orthogonalized to the $\varphi_{\alpha j}$.

$$\begin{aligned} \psi_{\alpha} &= \varphi_{\alpha j}, \\ \psi_{0i} &= (\varphi_{0i} - \sum_{\alpha} \sum_j S_{0\alpha}{}^{ij} \varphi_{\alpha j}) / (1 - \sum_{\alpha} \sum_j |S_{0\alpha}{}^{ij}|^2)^{1/2}, \end{aligned} \quad (7)$$

where 0 represents the ion under study, α the site of the neighboring ions, and i and j the orbitals of these ions.

Of course, the orbitals on ion 0 are now not orthogonal to each other and we must repeat the process to completely orthogonalize these functions. The equivalence of (6) and (7) would only be valid up to terms linear in S if we did not carry out the further iterations. For our localized property, it is sufficient to obtain results correct to second order in overlap, which means we need only one extra cycle of orthogonalization.

Upon substituting $\psi_{\alpha i}$ from (7) into the expression for q^{e1} in (5), we obtain the following expression which we have divided into three types of terms:

$$\begin{aligned} q_{(001)}{}^{e1} &= \sum_i \sum_j \sum_{\alpha} ((1 - |S_{0\alpha}{}^{ij}|^2)^{-1/2})^2 \left\langle \varphi_{0i} \left| \frac{3 \cos^2 \theta_i - 1}{r_i^3} \right| \varphi_{0i} \right\rangle && \text{(local)} \\ &+ (1 - \gamma_{\infty}) \left[\left\langle \varphi_{\alpha i} \left| \frac{3 \cos^2 \theta_i - 1}{r_i^3} \right| \varphi_{\alpha i} \right\rangle - \frac{e_i^+}{R^3} \right] + |S_{0\alpha}{}^{ij}|^2 \left\langle \varphi_{\alpha i} \left| \frac{3 \cos^2 \theta_i - 1}{r_i^3} \right| \varphi_{\alpha i} \right\rangle && \text{(distant)} \\ &- (1 - \gamma_{\infty}') (2) S_{0\alpha}{}^{ij} \left\langle \varphi_{0i} \left| \frac{3 \cos^2 \theta_i - 1}{r_i^3} \right| \varphi_{\alpha j} \right\rangle \Big\}. && \text{(nonlocal)} \end{aligned} \quad (8)$$

Similar expressions hold for other components using the appropriate operator V_{ij} . The designation local, nonlocal, and distant signifies whether respectively two, one, or zero wave functions φ_0 are involved in the one-electron matrix elements $\langle \varphi | (3 \cos^2 \theta_i - 1) / r_i^3 | \varphi \rangle$. The local terms that contribute to q^{e1} will be second order in overlap and come from the normalization constant $(1 - |S_{0\alpha}{}^{ij}|^2)^{-1/2}$. The distant integrals are of two types. The first distant contribution on the right-hand side of (8) is a result of the diffuseness of the negative-ion electron distribution of the neighboring ions compared to the point-charge-like contribution of the corresponding positive nuclear charge, represented by the terms e_i^+ / R^3 . The second contribution to q^{e1} from distant integrals in (8) is from the Pauli principle manifested through overlap. The nonlocal term might be described as arising from orthogonalization effects. Both Fukai and Marsh and Casabella used a local approximation and discarded integrals in which one or both orbitals are on an ion other than the ion at which the FG is being calculated. Whereas we have found that in chemical shift calculation this is justified, it is not at all obvious that this will be the case here, since these integrals must be modified by the Sternheimer antishielding effect. It arises from the deformation of the electronic orbitals of the ion within which the nucleus is imbedded and this deformation is produced by the FG due to the external charge distribution. In effect, it amplifies the FG due to the external charge by one or two orders of magnitude.^{24,25} The distant terms with most of their charge density completely external to ion 0, in a first approxi-

mation can be likened to a point charge placed at the internuclear distance. In this case, the field gradient q is enhanced one or two orders of magnitude by the antishielding effect, and we multiply the distant terms by $1 - \gamma_{\infty}$, where γ_{∞} is the antishielding factor due to a point charge far removed from the ion. The nonlocal term has its charge neither wholly internal or external to the charge density of ion 0, since it is a product $\varphi_{0i} \varphi_{\alpha i}$. In Sec. III, we will discuss how we handle the antishielding for the nonlocal term for each of the crystals considered. For the local term $1 - \gamma(r) \simeq 1$, since here most all of the charge density is within the atom and the antishielding factor is approximately zero inside the ion.

As an example, we will present the expression for q^{e1} for a 001 ion, with respect to the impurity as shown in the figure. The FG at the 001 site is the difference of FG due to the influence of the ions along the z axis and those perpendicular to it, and would add to zero in the perfect crystal.

We have chosen the determinant to be made up of the OAO's in (9):

$$\begin{aligned} \psi_{0x} &= N_{0x} (\varphi_{0x} - S_{03}{}^{\sigma\sigma} \varphi_{3x} - S_{04}{}^{\sigma\sigma} \varphi_{4x} - S_{05}{}^{\sigma\sigma} \varphi_{5x} - S_{06}{}^{\sigma\sigma} \varphi_{6x}), \\ \psi_{0y} &= N_{0y} (\varphi_{0y} - S_{01}{}^{\sigma\sigma} \varphi_{1y} - S_{02}{}^{\sigma\sigma} \varphi_{2y} - S_{01}{}^{\sigma\sigma} \varphi_{1s} - S_{02}{}^{\sigma\sigma} \varphi_{2s}), \\ \psi_{0z} &= N_{0z} [\varphi_{0z} - S_{05}{}^{\sigma\sigma} \varphi_{5z} - S_{06}{}^{\sigma\sigma} \varphi_{6z} - S_{05}{}^{\sigma\sigma} \varphi_{5s} - S_{06}{}^{\sigma\sigma} \varphi_{6s} \\ &\quad + (S_{06}{}^{\sigma\sigma} S_{06}{}^{\sigma\sigma} + S_{05}{}^{\sigma\sigma} S_{05}{}^{\sigma\sigma}) \varphi_{0s}], \\ \psi_{1x} &= \varphi_{1x}, \quad \psi_{1z} = \varphi_{1z}, \quad \psi_{1s} = \varphi_{1s}, \\ \psi_{1y} &= N_{1y} (\varphi_{1y} - S_{01}{}^{\sigma\sigma} \varphi_{0s}), \\ \psi_{2y} &= N_{2y} (\varphi_{2y} - S_{02}{}^{\sigma\sigma} \varphi_{0s}), \\ \psi_{5z} &= N_{5z} (\varphi_{5z} - S_{05}{}^{\sigma\sigma} \varphi_{0s}), \\ \psi_{6z} &= N_{6z} (\varphi_{6z} - S_{06}{}^{\sigma\sigma} \varphi_{0s}), \\ \psi_{3z} &= N_{3z} (\varphi_{3z} - S_{03}{}^{\sigma\sigma} \varphi_{0s}), \quad \psi_{4z} = N_{4z} (\varphi_{4z} - S_{04}{}^{\sigma\sigma} \varphi_{0s}), \end{aligned} \quad (9)$$

²⁴ R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

²⁵ E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

where the normalization factors are defined as $N_{\beta i} = (1 - \sum_{\alpha, j} |S_{\beta\alpha}^{ij}|^2)^{-1/2}$. $\varphi_{\alpha i}$ are the ion p_x , p_y , p_z or s -wave functions on center α directed as shown in Fig. 1, and $S_{0i}^{\sigma\sigma} = \langle \varphi_{0z} | \varphi_{iz} \rangle$ when the z axes are aligned along the line connecting 0 and i . Here we have neglected π - π -type overlaps since they are usually about one-quarter of the $\sigma\sigma$ overlap, and we only have a nonzero contribution proportional to overlap squared. We checked this by considering the contribution of $|S_{0i}^{\pi\pi}|^2 \times \langle r_0^{-3} \rangle_p$ to the local term and indeed found it to be negligible. We do not have any cross terms like $S_{0i}^{\sigma\sigma} S_{0i}^{\pi\pi}$, which arose in the chemical shift calculations.

However, we must include the distant integrals of both σ and π type that do not involve overlap. Here a partial cancellation takes place between σ -type integrals like $\langle \varphi_{6z} | V_{zz} | \varphi_{6z} \rangle$ and π -type integrals like $\langle \varphi_{6x} | V_{zz} | \varphi_{6x} \rangle$. This can be seen by considering the product wave functions

$$\begin{aligned} \varphi_{6z} \varphi_{6z} &= [\varphi_{6z}(\mathbf{r}) Y_1^0]^2 \\ &= \varphi_6^2(\mathbf{r}) \{ (4\pi)^{-1/2} [Y_0^0 + (2/\sqrt{5}) Y_2^0] \}, \\ \varphi_{6x} \varphi_{6x} &= [\varphi_{6x}(\mathbf{r}) Y_1^1]^2 \\ &= \varphi_6^2(\mathbf{r}) \{ (4\pi)^{-1/2} [Y_0^0 - (1/\sqrt{5}) Y_2^0] \}. \end{aligned}$$

Since there are twice as many π -type integrals as σ type, the $l=2$ terms effectively cancel except for modification due to normalization. The fact that these terms are amplified by $1 - \gamma_\infty$, and that the Y_0^0 contribution is

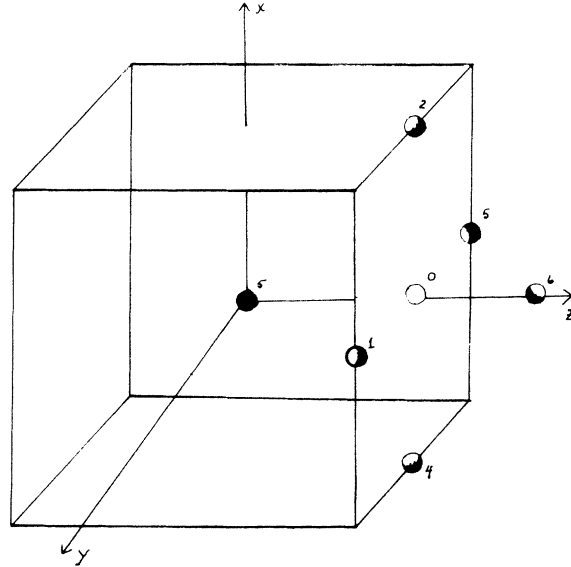


FIG. 1. Labeling the nearest neighbors of ion 0 containing the nucleus where the FG is calculated for the 001 site. (Ref. 5) is the impurity.

mostly cancelled by the positive nuclear charge, makes this point very important.

Taking into account the above considerations, and substituting the determinantal wave function made up of the OAO's in (9), and after some simplification, we obtain (10) for $q^{\sigma 1}$:

$$\begin{aligned} q^{\sigma 1} &= (8/5) \{ |S_{05}^{\sigma\sigma}|^2 + |S_{05}^{\sigma s}|^2 + |S_{06}^{\sigma\sigma}|^2 + |S_{06}^{\sigma s}|^2 - 2|S_{01}^{\sigma\sigma}|^2 - 2|S_{01}^{\sigma s}|^2 \} \langle 1/r_0^3 \rangle_p & \text{(local)} \\ &+ 2(1 - \gamma_\infty) \{ 4N_{1y}^2 \langle \varphi_{1y} | \varphi_{1y} \rangle + 4/R_1^3 + N_{5z}^2 \langle \varphi_{5z} | \varphi_{5z} \rangle - 2/R_5^3 + N_{6z}^2 \langle \varphi_{6z} | \varphi_{6z} \rangle - 2/R_6^3 \\ &+ 4 \langle \varphi_{1x} | \varphi_{1x} \rangle + 4 \langle \varphi_{1z} | \varphi_{1z} \rangle + 8/R_1^3 + 2 \langle \varphi_{5x} | \varphi_{5x} \rangle - 4/R_5^3 + 2 \langle \varphi_{6x} | \varphi_{6x} \rangle - 4/R_6^3 \\ &+ 4N_{0y}^2 [|S_{01}^{\sigma\sigma}|^2 \langle \varphi_{1y} | \varphi_{1y} \rangle + |S_{01}^{\sigma s}|^2 \langle \varphi_{1s} | \varphi_{1s} \rangle + 2S_{01}^{\sigma\sigma} S_{01}^{\sigma s} \langle \varphi_{1s} | \varphi_{1y} \rangle] \\ &+ N_{0z}^2 [|S_{05}^{\sigma\sigma}|^2 \langle \varphi_{5z} | \varphi_{5z} \rangle + |S_{05}^{\sigma s}|^2 \langle \varphi_{5s} | \varphi_{5s} \rangle + |S_{06}^{\sigma\sigma}|^2 \langle \varphi_{6z} | \varphi_{6z} \rangle + |S_{06}^{\sigma s}|^2 \langle \varphi_{6s} | \varphi_{6s} \rangle \\ &+ 2S_{05}^{\sigma\sigma} S_{05}^{\sigma s} \langle \varphi_{5s} | \varphi_{5z} \rangle + 2S_{06}^{\sigma\sigma} S_{06}^{\sigma s} \langle \varphi_{6s} | \varphi_{6z} \rangle \} & \text{(distant)} \\ &- 4(1 - \gamma_\infty) \{ N_{0y}^2 (4S_{01}^{\sigma\sigma} \langle \varphi_{0y} | \varphi_{1y} \rangle + 4S_{01}^{\sigma s} \langle \varphi_{0y} | \varphi_{1s} \rangle) \\ &+ N_{0z}^2 [S_{05}^{\sigma\sigma} \langle \varphi_{0z} | \varphi_{5z} \rangle + S_{05}^{\sigma s} \langle \varphi_{0z} | \varphi_{5s} \rangle + S_{06}^{\sigma\sigma} \langle \varphi_{0z} | \varphi_{6z} \rangle + S_{06}^{\sigma s} \langle \varphi_{0z} | \varphi_{6s} \rangle] \\ &+ 4N_{1y}^2 S_{01}^{\sigma\sigma} \langle \varphi_{1y} | \varphi_{6s} \rangle + N_{5z}^2 S_{05}^{\sigma\sigma} \langle \varphi_{5z} | \varphi_{0s} \rangle + N_{6z}^2 S_{06}^{\sigma\sigma} \langle \varphi_{6z} | \varphi_{0s} \rangle \}. & \text{(nonlocal) (10)} \end{aligned}$$

The operator $(3 \cos^2 \theta_i - 1)/r_i^3$ is represented by $\|$ in all the above expectation values. We have used Clementi's²⁶ ion wave functions for the $\varphi_{\alpha i}$'s, and have evaluated the necessary two-center integrals using Löwdin's α -function¹⁷ technique. For calculation in which we use a local approximation and neglect non-local and distant terms, the only two-center integrals involved are overlap integrals, and such integrals may be expressed as $A e^{-R/\rho}$, where A and ρ are constants, and R is the distance between centers. Hafemeister and Flygare²⁷ have made a tabulation of the overlap inte-

grals in this form, and for convenience we have used their results when using the local approximation requiring only overlaps.

III. RESULTS

We have applied the theory of Sec. II to the solid solutions NaCl:Br, NaCl:K, and KBr:Na, for which Dick has calculated the ion displacements and the ionic contribution to the FG. We have used (10) for a complete study of ions at the 001 site and further calculated results for these and several other solid solutions for ions located at the 001, 101, and 002 lattice sites using

and D. W. Hafemeister has kindly communicated the correct results.

²⁶ Enrico Clementi, IBM J. Res. Devel. 9, 2 (1965).

²⁷ D. W. Hafemeister and W. H. Flygare, J. Chem. Phys. 43, 795 (1965). The values of A for NaCl are incorrect in this reference,

a local approximation for the electronic contribution. These latter results will allow us to compare the contributions of q^{ionic} and q^{el} for more distant ions than the nearest neighbor of the impurity, since we shall show, from analysis of the (001) ion, that the local approximation is valid for a qualitative understanding. Comparison of our findings with experiment will enable us to comment on the validity of the simple overlapping-ion model.

We relate the calculated FG to experimental results for the quadrupole coupling constant e^2qQ/h , which involves the product of the FG, q , and the nuclear quadrupole moment Q , and hence the FG derived from experiment is known to the same accuracy as Q . Currently, there are two main techniques for studying the coupling constant e^2qQ/h . One involves measurement by resonant NMR technique, the shift of the ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) nuclear resonance lines in high magnetic field caused by quadrupole interactions (and the splitting of higher m lines wherever possible). This shift in resonance frequency is different for nuclei at different distances from the impurity. (From measurements of the NMR patterns in single crystals as a function of rotation, one can make assignments of FG tensors to respective nuclei.) The second method uses sensitive NMR double-resonance techniques to measure the value of e^2qQ/h in essentially zero field. The quadrupole resonance is measured in terms of a change in the prepared magnetic order of an abundant spin system with a long relaxation time, to which the rare nuclei are dipolar coupled. A small rf field is swept over a frequency range and when on resonance, causes quadrupole transition of the rare spins, which in turn influence the states of the abundant spin system. The double-resonance technique is more sensitive than the high-field experiment, and allows determination of smaller quadrupolar frequencies. However, it has the disadvantage compared to high field work that it may sometimes lead to difficulties in the assignment of resonance lines to particular displaced ions. Thus, two or more displaced ions involving different nuclei could have nearly the same e^2qQ/h , and thus have the same effect on the abundant spin species, and hence would not be resolved. In high field, the resonances of two different nuclei would be widely separated by virtue of their varying magnetogyric ratios, and so their quadrupole effects can be resolved.

In fact, we believe such a situation exists for the results of Na^{23} at the 001 site in $\text{NaCl}:\text{Br}$ solid solution. It has been pointed out that Andersson's¹⁶ high-field experimental result for Na^{23} at the 001 site in $\text{NaCl}:\text{Br}$ solid solutions is not consistent with results obtained by Slusher and Hahn using the sensitive double-resonance technique. Slusher and Hahn were not able to associate the resonance lines that they obtained for $\text{NaCl}:\text{Br}$ with particular nuclei or sites, but it appeared from their results that there was no line with the proper resonant structure that would correspond to Anderson's results for Na^{23} at 001, i.e., $e^2qQ/h = 0.654 \pm 0.02$ Mc/sec. There

is now enough information available to remove this discrepancy. Satoh, Spencer, and Slichter,⁹ using the high-field technique, have independently measured for Cl^{35} at the 110 site in $\text{NaCl}:\text{Br}$, $e^2qQ/h = 0.650$ Mc/sec. This turns out to be nearly identical to Anderson's result for Na^{23} at the 001 site, $e^2qQ/h = 0.654 \pm 0.02$ Mc/sec. Slusher and Hahn attempted to obtain e^2qQ/h for Na^{27} and Cl^{35} surrounding the Br^- impurity in $\text{NaCl}:\text{Br}$ by observing the effect of these two nuclei on the resonance of the abundant Na^{23} spin system in zero field. They observed a line at $e^2qQ/h = 0.657$ Mc/sec., but concluded it could not be positively identified as either a 001 Na^{23} or a 110 Cl^{35} because of the shape of its resonance spectrum, which did not resemble the situation in $\text{NaCl}:\text{K}$ where the resonances were well understood. However, from Anderson and Satoh *et al.*, we see that these two resonances lie very close together, and hence may not be resolvable by the double-resonance technique, and in fact may cause the peculiar structure which Slusher and Hahn observed for this case. In the high-field NMR experiments, these two resonances are well separated since the magnetogyric ratios of Na^{23} and Cl^{35} nuclei are rather different, leading to a quite different Larmor precession in the magnetic field. This is the only result for a positive ion which is a nearest neighbor to the solute ion that has both been measured experimentally, and for which the ion displacements have been calculated by Dick. Thus, a correct interpretation of this experimental datum is crucial to our study.

We shall begin consideration of the theoretical results by analyzing the FG at the 001 site using the full expression (10), which keeps all local, nonlocal, and distant terms that are second order in two-centeredness. That is, an overlap integral is one order, and an integral like $\langle \varphi_{\alpha i} | V_{zz} | \varphi_{0i} \rangle$ is also one order, while $\langle \varphi_{\alpha i} | V_{zz} | \varphi_{\alpha i} \rangle$ is second order, and $\langle \varphi_0 | V_{zz} | \varphi_0 \rangle$ is zero order. Here we have assumed that V_{zz} is centered at site 0. The pertinent integrals are tabulated in Table I for the 001 site in $\text{NaCl}:\text{K}$ solid solution as an example of how the various terms contribute. For easy reference, we have also included the γ_∞ values for all the ions which we will consider. For γ_∞ we have used the theoretical values calculated by Sternheimer,²⁴ who used a differential equation approach, and by Wikner and Das,²⁵ who used a variational theory. Results obtained by these two methods are in reasonable agreement, and include all the ions under study here. Some results for a few ions are available using different approaches or further refinements, and values of γ_∞ vary somewhat by including such effects. For example, Watson and Freeman²⁸ calculated $\gamma_\infty(\text{Cl}^-)$ self-consistently, including exchange effects, and obtained a result 50% larger than Wikner and Das. However, in order to be consistent in considering results of different ions, we wanted values of γ_∞ for all ions calculated using essentially the same ap-

²⁸ R. E. Watson and A. J. Freeman, *Phys. Rev.* **131**, 250 (1963).

TABLE I. List of the two-center integrals and antishielding factors necessary for evaluation of the FG at 001 Cl³⁵ in NaCl:K.

$R_{05}^a = 5.59a_0$		Local overlap integrals $R_{05} = 5.14a_0$		$R_{01} = 5.39a_0$	
$S_{Cl^-,K^+}^{σσ}$	-0.087206	S_{Cl^-,Na^+}	-0.043013	S_{Cl^-,Na^+}	-0.036009
$S_{Cl^-,K^+}^{σσ}$	0.074847	S_{Cl^-,Na^+}	0.052908	S_{Cl^-,Na^+}	0.043845
Distant integrals					
$\langle \varphi_{6z} V_{zz} \varphi_{6s} \rangle^b$	-0.004732	$\langle \varphi_{5z} V_{zz} \varphi_{5s} \rangle$	-0.003831	$\langle \varphi_{1y} V_{zz} \varphi_{1s} \rangle$	+0.001584
$\langle \varphi_{6z} V_{zz} \varphi_{6z} \rangle$	0.013570	$\langle \varphi_{5z} V_{zz} \varphi_{5z} \rangle$	0.015824	$\langle \varphi_{1y} V_{zz} \varphi_{1y} \rangle$	-0.006818
$\langle \varphi_{6z} V_{zz} \varphi_{6z} \rangle$	0.010385	$\langle \varphi_{5z} V_{zz} \varphi_{5z} \rangle$	0.014180	$\frac{1}{2}[\langle \varphi_{1x} V_{zz} \varphi_{1x} \rangle + \langle \varphi_{1y} V_{zz} \varphi_{1y} \rangle]$	-0.006170
$\langle \varphi_{6s} V_{zz} \varphi_{6s} \rangle$	0.011449	$\langle \varphi_{5s} V_{zz} \varphi_{5s} \rangle$	0.014728	$\langle \varphi_{1s} V_{zz} \varphi_{1s} \rangle$	-0.006386
Nonlocal integrals					
$\langle \varphi_{0z} V_{zz} \varphi_{6z} \rangle$	-0.004040	$\langle \varphi_{0z} V_{zz} \varphi_{5z} \rangle$	-0.002065	$\langle \varphi_{0y} V_{zz} \varphi_{1y} \rangle$	0.000741
$\langle \varphi_{0s} V_{zz} \varphi_{6z} \rangle$	-0.002090	$\langle \varphi_{0s} V_{zz} \varphi_{5z} \rangle$	-0.000938	$\langle \varphi_{0s} V_{zz} \varphi_{1y} \rangle$	0.000315
$\langle \varphi_{0z} V_{zz} \varphi_{6s} \rangle$	0.001839	$\langle \varphi_{0z} V_{zz} \varphi_{5s} \rangle$	0.001171	$\langle \varphi_{0y} V_{zz} \varphi_{1s} \rangle$	-0.000413
Antishielding factors					
Nucleus				$(1-\gamma_\infty)^c$	
Na ²³				5.53	
K ³⁹				13.8	
Cl ³⁵				50.3	
Br ⁷⁹				100	
I ¹²⁷				180	

^a $R_{0\alpha}$ represents the internuclear distance from Na²³ under study to the n ion defined in the figure.

^b V_{zz} is the FG operator defined in Eq. (2) and is centered at 0.

^c Quadrupole antishielding factors are from T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956), and Ref. 25.

proximation. The results of the theoretical and experimental FG are presented in Table II for the three cases NaCl:Br, NaCl:K, and KBr:Na. q^{e1} is calculated using Eq. (10), and q^{ionic} is taken from Dick. We have presented the results in units of 10^{12} esu/cm³.

Let us first consider the case NaCl:Br, where we are studying the FG at the 001 Na²³ nucleus. From Table II, we can see that the local term is definitely larger than either the nonlocal or distant. As was discussed in Sec. II, the local term arises solely from the distortion of the orbitals of ion i , in which the nucleus under study is imbedded due to overlap with its neighbors. In the particular case under study here, 001 Na²³, the distant contributions come not from overlap distortion, but from the failure of the diffuse outer negative-ion orbitals of the neighboring Br⁻ and Cl⁻ ion to cancel the effect from the corresponding compact nuclear charge. It was pointed out in Sec. II that there is some uncertainty in including the Sternheimer antishielding effect for the nonlocal integral, $I_{nonlocal} = \langle \varphi_{0i} | V_{zz} | \varphi_{\alpha i} \rangle$, since the

charge distribution $\varphi_{0i}\varphi_{\alpha i}$ is neither completely internal or external to the ion 0. To obtain an estimate of this effect, we plotted the value of $I(r)_{nonlocal}$ versus r and compared this with a plot of $1-\gamma(r)$ calculated by Foley, Sternheimer, and Tycko²⁹ from a point-ion model using the Foley-Sternheimer procedure. Of course, the use of a point-charge model is not a rigorous representation for solids, but it allows us to estimate the factor by which we must multiply γ_∞ for the nonlocal integrals. For the case of the FG at positive ion nuclei, we find that most all of the contribution to $I_{nonlocal}$ is in the region $0 < r < 2a_0$ and in this region $1-\gamma(r) \cong 1$ which, therefore, we have used for positive ions. For the negative ions, the situation is quite different, with a significant contribution coming from the larger region $0 < r < 5a_0$, and an appropriate value for $1-\gamma_\infty'$ for negative ion appears to be $1-\frac{1}{2}\gamma_\infty$.

From Table I we see that the total electronic contribution, 33×10^{12} esu/cm³, is of the same order as that arising from the ionic model, 19×10^{12} esu/cm³. The

TABLE II. Field gradients at the 001 site.

Solid solution	Ion ^a under study	q_{ionic}^b	q_{e1}			q_{e1}^{non}	q	q_{expt}^c
			local	nonlocal	distant			
NaCl:Br	Na ²³	19	52	-8	-11	10^{-3}	52	90
NaCl:K	Cl ³⁵	-246	337	-180	73	-20	-36	410
KBr:Na	Br ⁷⁹	264	-457	223	-84	60	6	567

^a Field gradient at the 001 site in units of 10^{12} esu/cm³.

^b From Ref. 2 using TKS polarizabilities and the shell model.

^c The Na²³ and Br⁷⁹ results are from Andersson and Cl³⁵ is from Slusher and Hahn.

²⁹ H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).

ionic result is quoted from Dick for the case using electronic polarizabilities of Tessman, Kahn, and Shockley³⁰ (TKS) and the shell model, and we will use this case throughout to be consistent in comparing with Dick's results. This was the choice that Dick believed should be the most realistic and yield the most reliable ionic results. The experimental result of Andersson is 90×10^{12} esu/cm³, and hence we see that the electronic contribution substantially improves agreement between theory and experiment. As for the remaining discrepancy, it should be mentioned that the magnitude of both q^{ionic} and the ion displacements are quite sensitive to the choice of electronic polarizabilities used. For example, Dick's value of q^{ionic} is 51×10^{12} esu/cm³, calculated using Sternheimer³¹ polarizabilities without consideration of the shell model, is quite different from the results above using TKS polarizabilities. A recalculation of q^{el} using displacements calculated from use of Sternheimer polarizabilities yields $q^{\text{el}} = 41 \times 10^{12}$ esu/cm³. A combination of $q^{\text{el}} + q^{\text{ionic}} = q$, for this case, gives $q = 92 \times 10^{12}$ esu/cm³, in excellent agreement with $q^{\text{expt}} = 90 \times 10^{12}$ esu/cm³. Ordinarily, q^{ionic} does not vary nearly as radically as for this case of the 001 site for NaCl:Br, and the question of what polarizabilities to use is not as important.

A quantitative treatment of $\gamma(r)$ in the solid solution might alter the above results somewhat, but not the general conclusion that q^{el} is of the same order of magnitude as q^{ionic} and additive with it. This is mainly due to the fact that the main contribution to q^{el} is from the local term where $\gamma(r) \sim 0$.

In contrast to the rather consistent picture presented above for the positive ions, Na⁺ in NaCl:Br, the negative ions at the 001 site present quite a different story. Again, the local term is larger than the nonlocal or distant, but the nonlocal is quite significant. In this case, the distant term arises from Pauli distortion overlap, and the diffuseness contribution is quite small as we would suspect, since the neighboring ions are the more compact positive ions. We have also considered the contribution of next nearest neighbors (nnn), since the overlap between these two diffuse negative ions is almost as large as the nearest-neighbor (nn) positive-ion-negative-ion overlap, despite the greater distance. As can be seen from Table II, the contribution of the nnn ions is an order of magnitude smaller than that due to nn. This is understandable since q^{el} is due to the differential overlap and the relative displacements of the nnn ions are not as large as those of the nn ones which lie along the 001 direction.

For the nn negative ions, q^{el} is of opposite sign to q^{ionic} calculated from the point-charge model. The latter results are already smaller than the experimental result by a factor of 2 for the cases of a 001 negative ion in

TABLE III. Field gradients at the 001, 101, and 002 sites using the local approximation.

Solid solution	Site observed	Nucleus ^a observed	q^{ionic} ^b	q^{el} (local)	q^{expt} ^c
NaCl:Br	001	Na ²³	19	52	90
KBr:Na	001	Br ⁷⁹	264	-457	564
NaCl:K	001	Cl ³⁵	-246	337	410
KI:Rb	001	I ¹²⁷	-140	351	314
KBr:Cl	001	K ³⁹	-20	-102	...
NaCl:Br	101	Cl ³⁵	176	1.9	123
KBr:Na	101	K ³⁹	-49	9	...
NaCl:K	101	Na ²³	36	2.6	99
KI:Rb	101	K ³⁹	16	-0.3	...
KBr:Cl	101	Br ⁷⁹	172	2.6	99
NaCl:Br	002	Cl ⁻	186	23	...
KBr:Na	002	K ⁺	58	-100	...
NaCl:K	002	Na ⁺	-40	63	...
KI:Rb	002	K ⁺	-18	50	...
KBr:Cl	002	Br ⁻	-206	-78	41

^a FG is in units of 10^{12} esu/cm³.

^b q^{ionic} is from Ref. 2 with TKS polarizabilities and the shell model.

^c Experimental results for NaCl:K are from Slusher and Hahn, NaCl:Br (101) is from Satoh *et al.* and the remaining values are from Andersson.

NaCl:K and KBr:Na. Thus, the electronic contribution drastically worsens agreement with experiment, and no matter what values one takes for the electronic polarizability, agreement with experiment is very poor.³²

q^{el} is larger than q^{ionic} for the three cases we have studied above, and before commenting on the results, it would be interesting to compare the relative contributions at points more distant from the impurity. As can be seen from Table II, the local term is the largest contributor to q^{el} in all three cases, and hence we can get a qualitative understanding of more distant ions by considering the local term only. Further, this is within the spirit of our calculation; since the displacement of the ions more distant to the impurity ion are less accurately known, we may not obtain as quantitative a result as for the 001 site. In Table III, we present several results for 101 and 002 ions in solid solution, where Dick has calculated the displacements. For comparison, we have also included the results for the 001 site using the local approximation. It should be pointed out that in general, the local approximation seems to give a larger q^{el} than does full application of Eq. (10).

For the 101 site, q^{el} is almost negligible compared both to q^{expt} and to q^{ionic} . This is what is expected when we consider that q^{el} is due to differential overlap that is exponential in character, while in comparison, the point-charge-point-dipole nature of q^{ionic} is more of a long-range effect. While the main contribution of q^{el} of an ion comes from the differential overlap with its nn, the contribution to q^{ionic} comes from other neighbors

³² The point-multipole results of Das and Dick, and Dick, should be of opposite sign to the quoted results. Equation (4) in Ref. 1 is correct, but Eq. (5) should be reversed in sign if the conventions for the dipole moment in Eq. (3) of that paper are used. The sign of the FG did not matter in Ref. 1 since the sign of the experimental result that was being compared is unknown. However, the signs of the calculated field gradients, both ionic and electronic, are very important in this paper, since we combine our electronic results and Dick's for comparison with experiment.

³⁰ J. R. Tessman, A. K. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

³¹ R. M. Sternheimer, Phys. Rev. **90**, 951 (1954); **107**, 1565 (1957).

other than just the nearest. It appears like any improvements with experiment for this site will have to come from q^{ionic} .

For the 002 site, the displacement of the nn 003 ion is unknown, and we shall assume its displacement to be zero. Of course in actual fact, it does have some displacement, and this tends to make our results somewhat less reliable than for 001 and 101. From Table II, we see that q^{el} is comparable to q^{ionic} . The larger ratio of $q^{\text{el}}/q^{\text{ionic}}$ for the 002 site than for 101 is due to the tensor nature of the FG operator. The nn along the z direction have large displacement relative to those perpendicular to the z direction, and we have a sizeable contribution to q^{el} . In general, it appears like $q^{\text{el}}/q^{\text{ionic}}$ decreased in going from 001 to 002 to 101, or in going from ions whose nn have large relative displacements to those ions whose nn have small displacement relative to each other. From an analysis of Dick's results for 001, 101, 111, 002, and 102, it appears that q^{ionic} remains the same order of magnitude in going from 001 to 102 and hence for more distant ions than 002, q^{ionic} will most likely dominate over q^{el} . However, for 001, both q^{el} and q^{ionic} must be taken into account.

Let us now compare theory and experiment for the 101 and 002 ions. For the one positive ion at a 101 site where experimental data is available, Na^{23} (101) in NaCl , q^{el} is smaller than the value determined by Slusher and Hahn by about a factor of three. When we consider the fact that the 001 $\text{NaCl}:\text{Br}$ result was also smaller than Andersson's result using the "best" point-multipole model, it appears that in general an increase in $1-\gamma_{\infty}$ in the crystal compared to the free ion would improve agreement between theory and experiment. In contrast, for the 001 negative ions, a reduction of $1-\gamma_{\infty}$ in the crystal would improve agreement. A severe reduction in γ_{∞} would have the effect of reducing q^{ionic} and the nonlocal and distant terms of q^{el} , while leaving the local contribution to q^{el} unchanged. The over-all effect on q would be to sharply increase its value much more in line with experiment. Consideration of Br^- at the 101 site in $\text{KBr}:\text{Cl}$ shows that $q^{\text{el}} \ll q^{\text{ionic}}$, and again a reduction of $1-\gamma_{\infty}$ would decrease q^{ionic} , bringing theory closer to experiment. A calculation of $1-\gamma(r)$ in the crystal rather than for the free ion would be most helpful in the interpretation of our results.

For the 002 site, no experimental results are available for comparison for positive ions, but there is one negative-ion result available from Andersson, namely $\text{KBr}:\text{Cl}$. From Table III, we find that q^{el} is 33% of q^{ionic} , and again worsens agreement with experiment this time, adding to an already too large q^{ionic} , however.

Interpretation of the results of this section would be greatly facilitated if we knew the sign of the experimental coupling constant, for this would tell us whether the electronic contribution was of proper sign to improve agreement with experiment. If it was, this might argue for a significant reduction of γ_{∞} for a negative ion in a crystal, since the local term in q^{el} , which is not multi-

plied by any antishielding factor, is nearly in agreement with experiment. If the point-charge result and the non-local and distant terms were reduced by an order of magnitude, the final result for q would be in fair agreement with experiment.

There is some reason to believe that this is what actually happens. The ion charge distribution is contracted in the solid in comparison to the free ion where γ_{∞} have been calculated. The more compact distribution would lead to a smaller value of γ_{∞} , as was shown by Burns. However, it does not necessarily follow that γ_{∞} must be decreased for both positive and negative ions if charge transfer covalency is present. With some charge transferred away from the negative ion, its charge distribution would become even more compact than in the free ion; but the opposite would occur for the positive ion, which now gains some charge and becomes more neutral. It should also be stressed, as was done by Fukai, that if charge transfer covalency is present, q^{el} for negative ion would be quite different. Then, we would have to mix some atomic states into the pure ionic model, and in effect this would leave a hole in the p shell of the negative ion leading to an appreciable contribution to q^{el} . At the present time, we do not know how much charge transfer covalency is present, since we do not have the appropriate wave functions in the crystal.

One method of determining the answer to this question is to calculate the total energy using a Hartree-Fock formalism with a basis set that included the atomic configuration for the crystal as well as the ionic. The atomic character could be represented by a variational parameter, which would be determined by minimizing the total energy with respect to the charge-transfer covalency parameter.

Another improvement would be to allow for electrostatic polarization of the ions by including both some excited states of the ion and the possibility of radial deformation. That is, first include in the total energy calculation some excited states with a variational parameter to be determined by energy minimization, for example, for NaCl crystal, some $\text{Na}^+(2s^2, 2p^5 3s)$ and $\text{Cl}^-(3s^2 3p^5 4s)$ states. Next, allow in a similar manner for radial deformation, in particular, contraction for the negative ions which would give us an answer to whether $1-\gamma_{\infty}$ is less in the crystal than for the free ion, as our results have suggested.

Finally, we should really determine the ion displacements by a first-principle calculation that obviated use of the semiempirical Born-Mayer potential. Although it is true that this potential may be adequate for energy calculation, to be self-consistent, we should determine the ion displacements from the same model we use in calculation the FG. With these improvements, and a calculation of $1-\gamma(r)$ in the crystal, we would indeed gain a great deal of insight concerning the charge distribution of ionic crystal by comparison between experimental and theoretical FG.

The net results of these improvements would be to have done a Hartree-Fock self-consistent-field calculation in which not only are the electronic orbitals allowed to vary, but also the ions are allowed to relax from their undistorted positions. It is evident that such a calculation would be an order of magnitude more elaborate than the analogous treatment of molecules. Recently, Matcha³³ has carried out variational Hartree-Fock wave-function calculations for alkali-halide molecules and has determined quite successfully the FG at the nuclei of these molecules. It would be interesting to carry out a detailed comparison between Matcha's calculations and those involving separated overlapping ions in the molecule, as were also used in the present problem. Such a comparison would throw some light on the role of antishielding effects which have to be introduced explicitly in the distinct-ion model, but which occur indirectly through the polarization of atomic orbitals that occur in the molecular-orbital Hartree-Fock theory using linear combinations of atomic orbitals. However, the bearing of such a comparison in molecules on the relationship between overlap and Hartree-Fock calculations in solid solutions is somewhat tenuous, because of the sensitive dependence of the FG on internuclear distance, which is quite different for molecules and ionic crystals.

IV. SUMMARY

We have calculated the electronic contribution to the FG of ions surrounding the impurities in alkali-halide solid solutions using a model which differs from the extreme ionic model by inclusion of Pauli overlap distortion. In general, we have found the magnitude of the electronic contribution to be larger than that from a point-ion calculation that also takes into account the polarizability of the ions, for the nn to the solute and of comparable order for 002 sites. For neighbors at the 101 site, for which the relative displacements of the surrounding ions are less, it appears that the electronic portion of the FG is quite small compared to experiment and point-charge results. For the one case where the FG at a positive ion was available from experiment, for a nn ion, the electronic FG combined with the point-charge result to improve agreement with experiments and tended to indicate the validity of our model for the positive ions. For the negative ions, where more experimental data was available, the situation was just the reverse, with the electronic contributions tending to severely worsen agreement between experiment and the point-charge results calculated by Dick. The situation here is quite similar to the results found for the

³³ R. L. Matcha, *J. Chem. Phys.* **47**, 4595 (1967); **47**, 5294 (1967); **48**, 335 (1968).

chemical shift of alkali and halogen ions in going from one crystal to another. The chemical shift of the positive ions calculated from the simple model of overlapping ions was consistent with the experimental results, while the negative-ion calculations were not. Although there were approximations made in the calculations of both the FG and the chemical shift, it would appear from the general nature of the results that we must use a more realistic model for the ionic crystal if we wish to find agreement with experiment for such properties that depend very sensitively on the wave function chosen. As was discussed in Sec. III, one obvious improvement would be to allow for charge transfer covalency in which some atomic character is admitted in the pure ionic wave function. This would leave a hole in the previously filled p shell of the halogen ions, and would lead to additional contributions to the FG and the chemical shift, since both properties depend sensitively on the amount of non- s character in the wave functions. Furthermore, charge-transfer covalency would have little effect on the positive-ion results since alkali ions add on s character. Unfortunately, at present, such wave functions are not available with which we could make a first-principle calculations, since we do not know how much charge-transfer covalency is present in the crystal. Even when such wave functions are available, in order to compare theoretical FG with experiment, it appears from this study that we really should calculate Sternheimer antishielding factors, not for a free ion, but for an ion in the solid state. Our results would be in tolerable agreement, without involving charge-transfer covalency if γ_∞ was increased for positive ions and decreased substantially for negative ions. While there are important differences in our analysis as compared to those of Fukai and Casabella and Marsh, and refer to different situations, all three investigations agree in terms of the necessity for reduction in the antishielding factors for negative-ion nuclei. As was mentioned in Sec. III, the answer to this question would be clearer if a method could be developed to determine the sign of the experimental result for e^2qQ/h in these systems.

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