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# Symmetry-Dependent Effective Force-Constant Changes around Impurities in Ionic Crystals*

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The lattice relaxation and effective force-constant changes for even symmetry modes around substitutional impurities in ionic crystals are studied in terms of a simple classical ionic-crystal model for the potential energy. It is shown that Coulomb and second-neighbor repulsive interactions can make large contributions to the effective force-constant changes. These contributions are symmetry dependent, and may even yield, for example, $A_{1g}$ and $E_g$ effective force-constant changes which have opposite signs, contrary to what has been frequently assumed in the literature. Illustrative results are presented for the Raman scattering of substitutional $Ag^+$ ions in sodium chloride.

## I. INTRODUCTION

To obtain quantitative agreement with experimental data on substitutional impurities in ionic crystals, it is generally necessary to include changes in force constants as well as in mass in the theoretical treatment. Furthermore, although the major force-constant changes are localized around the defect, it is often not sufficient to restrict these changes to first neighbors only; the work of several authors on the substitutional $H^-$ ion ($U$ center) in the alkali halides[1–4] provides a good illustration of this point. For example, the model of Gethins, Timusk, and Woll[2] for the $U$ center permits changes in the force constants between the impurity ion and its first neighbors, and in those linking ions in the first and fourth shells, since these should be most strongly affected by the relaxation about the defect. Although perhaps surprising at first, it is easy to show that small lattice relaxations can produce large force-constant changes.

In this paper, we will be concerned primarily not with changes in the force constants between pairs of ions, but rather with changes in the effective force constants for even symmetrized displacements about the defect. While the force constants connecting pairs of ions are, of course, symmetry independent, the effective force constants for symmetrized motion are linear combinations of the pairwise interactions, and these effective force constants generally depend upon the symmetry mode in question, even in the perfect lattice.

Whether only the first-neighbor shell is included in the defect space or a more extended model is used, it is tempting, and in some cases justified, to assume that the force-constant changes for the ions in any particular shell are dominated by changes in the repulsive interactions of these ions with their first neighbors.[2-4] This assumption leads directly to certain conclusions, of which the one we shall be most concerned with is that the effective force-constant changes for $A_{1g}$ and $E_g$ motion about the defect are the same, as are those for $T_{2g}$ and $T_{1g}$ displacements. As has been shown by Montgomery, Klein, Ganguly, and Wood,[5] this conclusion is not consistent with the Raman scattering results for silver in sodium chloride ($\mathrm{NaCl:Ag^+}$).

In this paper we will use a simple classical ionic-crystal approximation for the potential energy[6] to investigate the first- and fourth-shell relaxation and effective force-constant changes for even symmetrized displacements about substitutional impurity ions in sodium-chloride–type crystals. It will be demonstrated that substantial differences can indeed occur between the force-constant changes for $A_{1g}$ and $E_g$ and for $T_{2g}$ and $T_{1g}$ displacements, and that these differences can have a marked effect on the Raman scattering. The relative importance of the Coulomb and short-range contributions for the various modes will be exhibited, as will the sensitivity of the force-constant changes to the lattice relaxation and to variations in the potential energy parameters.

Section II summarizes the definitions of the symmetrized displacements and the potential energy model, and briefly describes the method used to calculate the relaxation and force-constant changes. Section III presents illustrative results results for $\mathrm{NaCl:Ag^+}$. Section IV recapitulates some of the conclusions reached, and indicates some directions that might be taken to obtain better agreement with experiment.

## II. THEORY

Symmetrized displacements of the equivalent ions in a shell $n$ about a defect or impurity are linear combinations of individual ionic displacements which transform according to the irreducible representations of the point group.

$$Q_n(\Gamma p) = u \sum_j \vec{e}_{nj}(\Gamma p) . \tag{1}$$

Here, $\Gamma$ and $p$ label the irreducible representations and their components, respectively, and $j$ runs over the ions in the shell.[7] The vectors $\vec{e}_{nj}(\Gamma p)$ can be chosen such that

$$Q_n(\Gamma p)\cdot Q_n(\Gamma' p') \equiv u^2 \sum_j \vec{e}_{nj}(\Gamma p)\cdot \vec{e}_{nj}(\Gamma' p') = u^2 \delta_{\Gamma\Gamma'}\delta_{pp'} . \tag{2}$$

Table I shows the allowed irreducible representations for (100), (110), and (111) shells in octahedral symmetry, and Table II gives the vectors $\vec{e}_{nj}(\Gamma p)$ for the even modes of (100) shells.

In the presence of an isolated defect or impurity, the surrounding ions relax to new equilibrium positions, and the force constants for ionic motion change. The force constants for symmetrized displacements about the defect can be related to those connecting pairs of ions[4,5] through the definition (1). In terms of individual ionic displacements $\vec{u}_{nj}$ from equilibrium, the potential energy in the harmonic approximation is

$$V = V_{\mathrm{eq}} + \frac{1}{2} \sum_{nj,n'j'} \vec{u}_{nj}\cdot \underline{B}(nj,\, n'j')\cdot \vec{u}_{n'j'} . \tag{3}$$

The corresponding expression involving symmetrized displacements is

$$V = V_{\mathrm{eq}} + \frac{1}{2} \sum_{\Gamma p,nn'} Q_n(\Gamma p) K_{nn'}(\Gamma) Q_{n'}(\Gamma p) . \tag{4}$$

From Eqs. (1), (3), and (4), the force constants $K_{nn'}(\Gamma)$ for the various symmetry modes are linear combinations of the interionic force constants $\underline{B}(nj,\, n'j')$:

$$K_{nn'}(\Gamma) = \sum_{jj'} \vec{e}_{nj}(\Gamma p)\cdot \underline{B}(nj,\, n'j')\cdot \vec{e}_{n'j'}(\Gamma p) . \tag{5}$$

Substituting from Table II in Eq. (5), we find that the force constants for the allowed even modes of (100)-type shells are

$$K_{nn'}(A_{1g}) = B_{xx}(n1,\, n'1) + 4B_{xy}(n1,\, n'2) - B_{xx}(n1,\, n'4) , \tag{6a}$$

$$K_{nn'}(E_g) = B_{xx}(n1,\, n'1) - 2B_{xy}(n1,\, n'2) - B_{xx}(n1,\, n'4) , \tag{6b}$$

$$K_{nn'}(T_{2g}) = B_{yy}(n1,\, n'1) + 2B_{yx}(n1,\, n'2) - B_{yy}(n1,\, n'4) , \tag{6c}$$

TABLE I. Allowed symmetry modes for (100), (110), and (111) shells in cubic crystals.

| | |
|---|---|
| (100) | $A_{1g}+E_g+T_{2g}+T_{1g}+T_{2u}+2T_{1u}$ |
| (110) | $A_{1g}+A_{2g}+2E_g+2T_{2g}+2T_{1g}+A_{1u}+E_u+2T_{2u}+3T_{1u}$ |
| (111) | $A_{1g}+E_g+2T_{2g}+T_{1g}+A_{1u}+E_u+T_{2u}+2T_{1u}$ |

$$K_{nn'}(T_{1g})=B_{yy}(n1,\,n'1)-2B_{yx}(n1,\,n'2)-B_{yy}(n1,\,n'4)\,. \tag{6d}$$

In the sodium chloride structure, these expressions apply for the defect space of first- and fourth-nearest neighbors used by Gethins, Timusk, and Woll,[2] as well as for the smaller defect space of first neighbors only.[8] No two of these are the same unless only first-neighbor interactions are kept,[9] and even in this case the $A_{1g}$, $E_g$ force constants are different from those for the $T_{2g}$, $T_{1g}$ modes. For $n=n'=1$, the second-neighbor interactions may give rise to large differences between the force-constant changes for the $A_{1g}$ and $E_g$ and the $T_{2g}$ and $T_{1g}$ modes, which would not occur if only changes in the interactions between ions in the defect space and their nearest neighbors were important.

We have used a simple iterative-derivative procedure to calculate the relaxation and the force constants for symmetrized displacements about an isolated defect or impurity. First, the potential energy is expanded in a Taylor series in symmetrized displacements $\Delta Q_n(\Gamma p)$ about the perfect-lattice positions,

$$V=V_0+\sum_{\Gamma p}\biggl(\sum_n A_n(\Gamma)\Delta Q_n(\Gamma p)+\frac{1}{2}\sum_{n,n'}k_{nn'}(\Gamma)\Delta Q_n(\Gamma p)\Delta Q_{n'}(\Gamma p)+\cdots\biggr)\,. \tag{7}$$

At equilibrium, the first derivatives must vanish,

$$0=\left(\frac{\partial V}{\partial\Delta Q_n(\Gamma p)}\right)_{\text{eq}}=A_n(\Gamma)+\sum_{n'}k_{nn'}(\Gamma)\Delta Q_{n'}^{\text{eq}}(\Gamma p)+\cdots\,. \tag{8}$$

We assume for the moment that the coefficients $A_n(\Gamma)$ and $k_{nn'}(\Gamma)$ are known and neglect the anharmonic terms not shown explicitly in the series. The matrix equations (8) can then readily be solved for the equilibrium displacements $\Delta Q_n^{\text{eq}}(\Gamma p)$. In terms of displacements $Q_n(\Gamma p)$ about these equilibrium positions, the potential energy can be written as in Eq. (4), with $K_{nn'}(\Gamma)=k_{nn'}(\Gamma)$, and

$$V_{\text{eq}}=V_0+\sum_{\Gamma p}\biggl(\sum_n A_n(\Gamma)\Delta Q_n^{\text{eq}}(\Gamma p)-\frac{1}{2}\sum_{n,n'}k_{nn'}(\Gamma)\Delta Q_n^{\text{eq}}(\Gamma p)\Delta Q_{n'}^{\text{eq}}(\Gamma p)\biggr)\,. \tag{9}$$

If there is substantial relaxation around the defect, the harmonic approximation may not be very accurate for an expansion about the perfect-lattice positions. The procedure just outlined is therefore repeated until satisfactory results are obtained. In each iteration, the potential energy is expanded in a Taylor series of the form (7), but with the symmetrized displacements $\Delta Q_n(\Gamma p)$ referred to the last calculated values for the equilibrium positions, and with coefficients $A_n(\Gamma)$ and $k_{nn'}(\Gamma)$ evaluated at these positions. New equilibrium displacements are then found by setting the first derivatives equal to zero as in Eq. (8). Pathological cases can be imagined for which this iterative procedure would not work, but none have so far been encountered in practice.

Equations (7)–(9) are formally the same as the basic equations of the method of lattice statics,[10–14] but written for a symmetry mode basis in real space rather than for wave vectors $q$ in the first Brillouin zone. One difference between our approach and the method of lattice statics is that by solving Eqs. (7)–(9) iteratively, we obtain an expansion for the potential energy which is correct to second order in displacements about the relaxed equilibrium ionic positions, rather than to second order in displacements about the perfect-lattice positions. The method of lattice statics does permit the calculation of the ($A_{1g}$) relaxation of all neighbors of the defect. To do so, however, requires repeated numerical integration over the Brillouin zone. For the purpose of demonstrating how differences may arise between the effective force-constant changes for the various symmetry modes, and how these differences may affect the Raman scattering results, it is more straightforward and computationally simpler to apply Eqs. (7)–(9) directly to the motion of a few shells of neighbors whose effective force-constant changes are expected to be large.

The coefficients $A_n(\Gamma)$ and $k_{nn'}(\Gamma)$ are determined by numerical differentiation of an approximate expression for the potential energy of the crystal as a function of arbitrary ionic displacements about the defect. For the calculations reported in this paper, only first- and fourth-nearest-neighbor shells are allowed to move, and Coulomb and first- and second-neighbor short-range interactions are in-

TABLE II. Vector ionic displacements $\vec{e}_j(\Gamma p)=N\vec{\sigma}_j(\Gamma p)$ for the even modes of (100) shells in cubic crystals. The $N$'s are normalization constants, $j=1$–6 labels the ions at (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), (00$\bar{1}$), respectively, and $\hat{x}$, $\hat{y}$, $\hat{z}$ denote unit vectors along the Cartesian axes.

| $\Gamma p$ | $N$ | $\vec{\sigma}_1$ | $\vec{\sigma}_2$ | $\vec{\sigma}_3$ | $\vec{\sigma}_4$ | $\vec{\sigma}_5$ | $\vec{\sigma}_6$ |
|---|---|---|---|---|---|---|---|
| $A_{1g}$ | $1/\sqrt{6}$ | $\hat{x}$ | $\hat{y}$ | $\hat{z}$ | $-\hat{x}$ | $-\hat{y}$ | $-\hat{z}$ |
| $E_g\epsilon$ | $1/2\sqrt{3}$ | $-\hat{x}$ | $-\hat{y}$ | $2\hat{z}$ | $\hat{x}$ | $\hat{y}$ | $-2\hat{z}$ |
| $E_g\theta$ | $\frac{1}{2}$ | $\hat{x}$ | $-\hat{y}$ | 0 | $-\hat{x}$ | $\hat{y}$ | 0 |
| $T_{2g}x$ | $\frac{1}{2}$ | 0 | $\hat{z}$ | $\hat{y}$ | 0 | $-\hat{z}$ | $-\hat{y}$ |
| $T_{2g}y$ | $\frac{1}{2}$ | $\hat{z}$ | 0 | $\hat{x}$ | $-\hat{z}$ | 0 | $-\hat{x}$ |
| $T_{2g}z$ | $\frac{1}{2}$ | $\hat{y}$ | $\hat{x}$ | 0 | $-\hat{y}$ | $-\hat{x}$ | 0 |
| $T_{1g}x$ | $\frac{1}{2}$ | 0 | $\hat{z}$ | $-\hat{y}$ | 0 | $-\hat{z}$ | $\hat{y}$ |
| $T_{1g}y$ | $\frac{1}{2}$ | $-\hat{z}$ | 0 | $\hat{x}$ | $\hat{z}$ | 0 | $-\hat{x}$ |
| $T_{1g}z$ | $\frac{1}{2}$ | $y$ | $-\hat{x}$ | 0 | $-\hat{y}$ | $\hat{x}$ | 0 |

cluded. Polarization effects are neglected, as are Madelung energy differences which begin at fourth order in the ionic displacements. This simple model is sufficient to demonstrate the symmetry dependence of the force-constant changes and their strong dependence on the interaction parameters.

The calculations of Hardy[13] for $K^+$ in NaCl and those of Boswarva and Lidiard[6] for positive and negative ion vacancies in NaCl support the conclusions of Gethins, Timusk, and Woll[2] that the central-ion–first-shell and first-shell–fourth-shell separations generally change most when the defect is introduced. The next largest changes in nearest-neighbor interionic distances are in the (100)–(110) and (200)–(300) bonds; the differences between these changes if only (100) and (200) relaxation is allowed, or if (110) and (300) relaxation is also permitted, are less than the change in the (100)–(200) separation by more than a factor of 2, and less than the first-shell relaxation by more than a factor of 4. Polarization effects for even modes are most important when the charge of the defect differs from that of the ion it replaces, but even with impurities of the same charge, the relaxation and accompanying strain fields can give rise to nonnegligible polarizations. Hence the results we obtain by restricting ourselves to first- and fourth-neighbor motion while neglecting polarization will be of qualitative rather than quantitative significance.

In the simple classical ionic-crystal model we have adopted, the potential energy can be written in the form[6]

$$V - V_0 = W_2 + \Delta W_2 + W_3 , \tag{10}$$

$$W_2 = \frac{1}{2} \sum_{jk}{}'' [\phi_R(r_j - r_k) - \phi_R(r_{j0} - r_{k0}) + \phi_C(r_j - r_k) - \phi_C(r_j - r_{k0}) - \phi_C(r_{j0} - r_k) + \phi_C(r_{j0} - r_{k0})] , \tag{11}$$

$$\Delta W_2 = \sum_{j}{}' \{\phi_{RI}(r_j) - \phi_{RI}(r_{j0}) - (1-\gamma)[\phi_C(r_j) - \phi_C(r_{j0})]\} , \tag{12}$$

$$W_3 = \sum_{j\nu}{}'' [\phi_R(r_j - r_{\nu 0}) - \phi_R(r_{j0} - r_{\nu 0})] . \tag{13}$$

Here, $j$ and $k$ label ions allowed to move, while $\nu$ labels ions held fixed at their perfect-lattice positions. The central site is not included in either singly or doubly primed sums, and in the latter, terms involving equal indices are also forbidden. $\phi_R$ and $\phi_C$ denote the short-range and Coulomb interactions, respectively, between ions of the host lattice. $\phi_{RI}$ describes the short-range interactions of the impurity with its neighbors, and $\gamma$ is the ratio of the impurity charge to that of the ion it replaces; for a vacancy, $\gamma = 0$. However, we will consider only those cases where $\gamma \simeq 1$, since otherwise polarization effects might become quite important. $W_2 + \Delta W_2$ sums the interactions of the displaced ions with each other and with the impurity, and $W_3$ gives the energy of interaction with the other, undisplaced ions in the crystal.

The short-range forces between first and second neighbors are taken to be the sum of Born–Mayer and van der Waals interactions.[15,16] For first-neighbor positive and negative ions separated by a distance $r$, the van der Waals energy is

$$\phi_{\mathrm{vdW}}(r) = c_{+-}/r^6 + d_{+-}/r^6 , \tag{14}$$

and the Born–Mayer interaction is

$$\phi_{\mathrm{BM}}(r) = a_{+-}\, b\, e^{-[r-(r_+ + r_-)]/\rho} , \tag{15}$$

with the Pauling coefficient $a_{+-}$ determined from the valences $Z_+$, $Z_-$ and the numbers of outer-shell electrons $n_+$, $n_-$ by

$$a_{+-} = 1 + Z_+/n_+ + Z_-/n_- . \tag{16}$$

Corresponding equations hold for the ++ and -- second-neighbor interactions.

## III. RESULTS

For an illustrative example, we will consider a positive impurity in an alkali-halide crystal, silver in sodium chloride. Potential energy parameters for the host lattice have been found by Tosi and Fumi,[16] and Mayer[17] gives values for the Born–Mayer and van der Waals coefficients in silver chloride. These latter results provide a useful reference point for the $Ag^+$-$Cl^-$ interaction parameters in NaCl, but it will be recognized that the forces between a silver impurity ion and its nearest neighbors in sodium chloride may differ markedly from those between silver and chlorine ions in silver chloride. Also, Mayer's work is now quite dated, and more recent work by Loje and Schuele[18] on the thermodynamic properties of AgCl would yield somewhat different values for some of the parameters; as we will demonstrate, rather small changes in the potential energy parameters can have a large impact on the relaxation and force-constant changes around the impurity.

### A. Relaxation and Force-Constant Changes

Mayer wrote his expression for the Born–Mayer interaction between positive and negative nearest neighbors in the form

$$\phi_{\mathrm{BM}}(r) = a_{+-}\, b_M b_+ b_-\, e^{-r/\rho} . \tag{17}$$

Comparing this to Eq. (15), we can write

$$r_+ = \rho \ln(b_M b_+ b_-/b) - r_- . \tag{18}$$

In what follows, we will show how the first- and fourth-shell relaxation and even-mode force constants vary with the $\rho$ for the impurity-host lattice interactions when Eq. (18) is used to determine $r_+(\mathrm{Ag}^+)$, with all of the other parameters held fixed at the values listed in Table III. The sodium chloride parameters are taken from the first set of data in Table I of Tose and Fumi[16] and those for the silver-chlorine interactions from Mayer. The van der Waals coefficients for the second-neighbor silver-sodium interactions were chosen to be the averages of the $\mathrm{Ag}^+$-$\mathrm{Ag}^+$ and $\mathrm{Na}^+$-$\mathrm{Na}^+$ values. While this may not be a very good approximation, the $\mathrm{Ag}^+$-$\mathrm{Na}^+$ van der Waals interactions make only a small contribution to the energy.

Figure 1 shows the first- and fourth-neighbor relaxation around $\mathrm{Ag}^+$ in NaCl as a function of $\rho$, along with the force-constant changes for the allowed even modes of these shells. The figure makes several points. First, the first shell-first shell (11) force-constant changes for the various modes are quite different. Those for the $T_{2g}$ and $T_{1g}$ displacements have different signs over most of the range shown, while the much steeper changes for the $A_{1g}$ and $E_g$ modes have opposite signs in the shaded region; in this connection, it should be noted that Montgomery, Klein, Ganguly, and Wood[5] (MKGW hereafter) have recently fitted the $A_{1g}$ and $E_g$ Raman spectra of NaCl : $\mathrm{Ag}^+$ with 11 force-constant changes of opposite signs. Second, the force constants are extremely sensitive to the interaction parameters, or put another way, to the equilibrium displacements around the impurity. From $\rho = 0.247$, which is Mayer's value for AgCl, to $\rho = 0.270$, the first-shell relaxation goes from $-4.15\%$ to $+0.71\%$ of the nearest-neighbor distance. Over the same range, the 11 force constants for the $A_{1g}$, $E_g$, $T_{2g}$, and $T_{1g}$ modes vary by 23%, 71%, 9%, and 2% of their perfect lattice values, respectively. Finally, the 14 and 44 $A_{1g}$ force-constant changes can be rather large, and, in contrast to the results for $n = n' = 1$, are virtually equal to those for $E_g$ motion in the model used.

TABLE III. Born–Mayer and van der Waals parameters for the illustrative NaCl : $\mathrm{Ag}^+$ calculations. Units are angstroms for all lengths, $10^{-12}$ erg for $b$ and $b_M$, and $10^{-60}$ erg cm$^6$, $10^{-76}$ erg cm$^8$ for the $c$, $d$ van der Waals coefficients. $b_+$ and $b_-$ are dimensionless.

| | | | |
|---|---|---|---|
| $b$ | 0.338 | $c_{+-}$(Na–Cl) | 11.2 |
| $b_M$ | 1.0 | $c_{++}$(Na–Na) | 1.68 |
| $b_+$ | 187.8 | $c_{--}$(Cl–Cl) | 116. |
| $b_-$ | 77.4 | $d_{+-}$(Na–Cl) | 13.9 |
| | | $d_{++}$(Na–Na) | 0.8 |
| $r_+(\mathrm{Na}^+)$ | 1.170 | $d_{--}$(Cl–Cl) | 233. |
| $r_-(\mathrm{Cl}^-)$ | 1.585 | | |
| | | $c_{+-}$(Ag–Cl) | 89. |
| | | $c_{++}$(Ag–Na) | 34.34 |
| $\rho$(NaCl) | 0.317 | $d_{+-}$(Ag–Cl) | 150. |
| | | $d_{++}$(Ag–Na) | 45.9 |

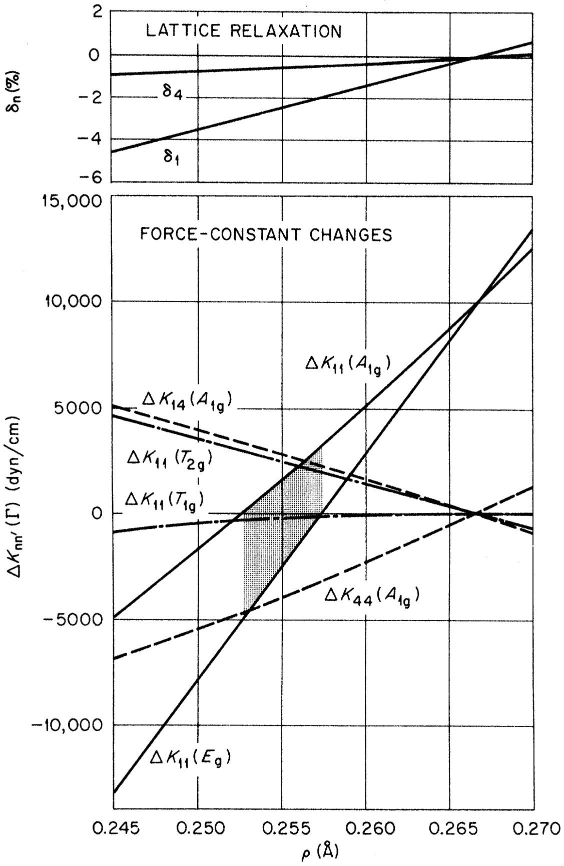

FIG. 1. First- and fourth-shell relaxation and force-constant changes around NaCl : $\mathrm{Ag}^+$ as functions of $\rho$. For the $T_{2g}$ and $T_{1g}$ modes, $\Delta K_{14}$ and $\Delta K_{44}$ are not shown because they are almost zero over the whole range of $\rho$, while for the $E_g$ modes, $\Delta K_{14}$ and $\Delta K_{44}$ lie virtually on top of the $A_{1g}$ results. In the shaded region, $\Delta K_{11}(A_{1g})$ and $\Delta K_{11}(E_g)$ have opposite signs.

Figure 2 shows the breakdown between Coulomb and short-range contributions to the first-shell force-constant changes for $A_{1g}$, $E_g$, and $T_{1g}$ displacements. The Coulomb contributions are negligible for the $E_g$ modes, but they are large for $A_{1g}$ displacements, and are responsible for most of the difference between $\Delta K_{11}(A_{1g})$ and $\Delta K_{11}(E_g)$. As previously noted, these would be equal if only changes in first-nearest-neighbor interactions were included. For the $T_{1g}$ modes, the very small total change in $\Delta K_{11}$ results from the near cancellation of the Coulomb and short-range contributions. For the $T_{2g}$ modes not included in Fig. 2, the short-range forces dominate the force-constant changes, contributing more than 80% to $\Delta K_{11}(T_{2g})$.

### B. Raman Scattering

Raman scattering and infrared absorption are powerful tools for the study of impurities in insulators, and can provide a great deal of informa-

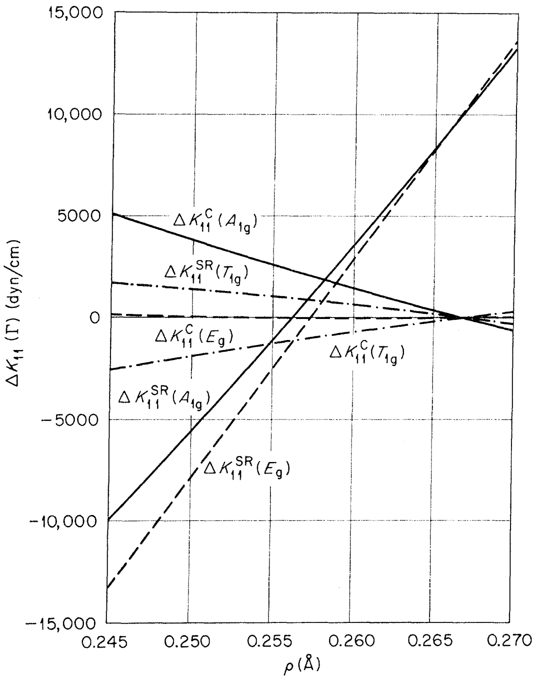

FIG. 2. Coulomb and short-range contributions to $\Delta K_{11}$ for $A_{1g}$, $E_g$, and $T_{1g}$ displacements.

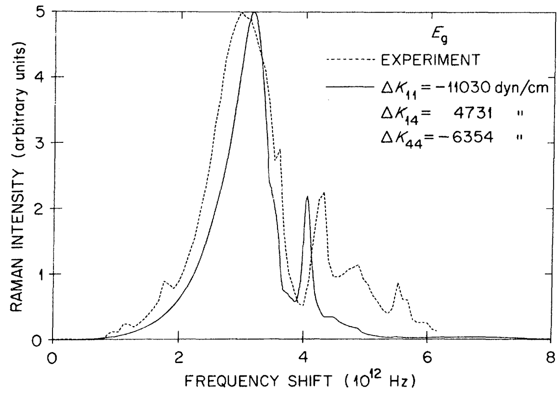

FIG. 3. $E_g$ Raman scattering for $\rho = 0.247$, Mayer's value for AgCl.

tion about the interactions of the defect with its neighbors. Gethins, Timusk, and Woll[2] have employed a simple model for substitutional impurities in sodium-chloride–type crystals which allows 11, 14, and 44 force-constant changes, subject to the constraint $\Delta K_{14}(\Gamma) = -\Delta K_{44}(\Gamma)$; the latter would follow from Eqs. (6a)–(6d) if only first-neighbor interactions were retained. This model has been successfully applied to Raman and infrared results for NaCl : Ag$^+$ by MKGW. Figure 1, in which $\Delta K_{44}(A_{1g}) \sim -1.4\Delta K_{14}(A_{1g})$, and calculations discussed later in which the silver charge is allowed to vary, indicate that the approximation $\Delta K_{14}(\Gamma) = -\Delta K_{44}(\Gamma)$ may not be very good in some cases, but parametrization of the two independent force-constant changes of the model may neutralize this problem. Since we determine the 14 and 44 force-constant changes from the potential energy coefficients, we will not make this approximation.

Figure 3 compares the observed Raman scattering for the $E_g$ modes of NaCl : Ag$^+$, taken roughly from MKGW, to results calculated with the force-constant changes for $\rho = 0.247$, Mayer's value for AgCl, with $r_+(\text{Ag}^+) = 1.0503$ from Eq. (18) and the remainder of the potential energy parameters taken from Table III. The perfect-lattice Green's functions which enter the Raman calculations are the same as in MKGW. Given the simplicity of the model for the potential energy, and the *a priori* way in which the parameters were chosen, the agreement is reasonably good. For the $A_{1g}$ modes, however, the fit obtained with the $A_{1g}$ force-constant changes for $\rho = 0.247$ is rather poor, as shown in Fig. 4.

Figure 5 is a comparison of two calculated curves for the $E_g$ Raman modes. One is that found with the $E_g$ force-constant changes for $\rho = 0.247$, already shown in Fig. 3, while the other was calculated with the $A_{1g}$ force-constant changes for $\rho = 0.247$. The point reinforced here is that the same force-constant changes cannot generally be used for both the $E_g$ and $A_{1g}$ displacements, which is equivalent to saying that second-neighbor interactions cannot be neglected. Figure 1 showed that the 11 force-constant changes for the $A_{1g}$ and $E_g$ modes were quite different; Fig. 5 demonstrates that these differences have a considerable impact on the Raman scattering.

Although we have made no concerted attempt to vary the potential energy parameters to fit the Raman data, one very simple line of approach was taken. If our results for the force-constant changes in Figs. 1, 3, and 4 are compared to those

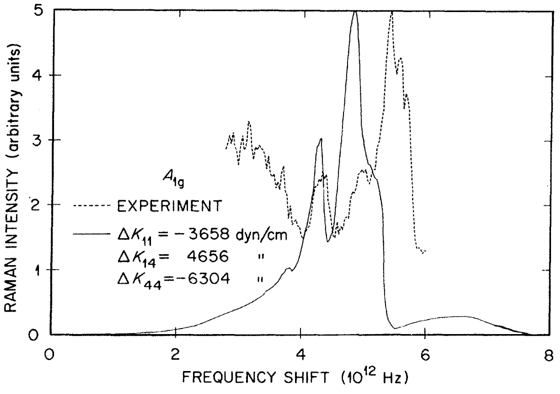

FIG. 4. $A_{1g}$ Raman scattering for $\rho = 0.247$.

of MKGW, a major difference observed is that our values for $\Delta K_{14}$ and $\Delta K_{44}$ for $A_{1g}$ and $E_g$ displacements are much larger than those of MKGW at comparable values of $\Delta K_{11}$. One reason for the large values that we find is that the fourth-shell relaxation is much smaller than that of the first neighbors of the impurity, and this gives rise to large changes in the repulsive interactions between first- and fourth-shell ions. Decreasing the charge on the silver impurity ions is an easy way to reduce the difference between the first- and fourth-shell relaxation, and thereby reduce $\Delta K_{14}$ and $\Delta K_{44}$. We therefore varied $Z(\mathrm{Ag}^+)$, keeping $\rho$ fixed at Mayer's value, in an effort to improve the fit to the $E_g$ Raman modes.

Qualitatively, decreasing $Z(\mathrm{Ag}^+)$ had the desired effect on the $E_g$ force-constant changes, reducing the magnitude of $\Delta K_{14}$ and $\Delta K_{44}$ by fairly large amounts while producing much smaller percentage changes in $\Delta K_{11}$. Quantitatively, a fit to the $E_g$ Raman scattering was obtained that is comparable to that of MKGW, as shown in Fig. 6; for these results, the silver charge was $Z(\mathrm{Ag}^+) = 0.94$. For the $A_{1g}$ modes, however, $\Delta K_{11}$ grew in magnitude as the silver charge decreased, and no improvement occurred in the agreement with the Raman data. Still, the partial success achieved by varying $Z(\mathrm{Ag}^+)$ leaves some hope that a reasonably good fit to all of the Raman data might be obtained by systematic variation of a few parameters in the potential energy model, particularly if it were extended to include additional shells and electrical and mechanical polarization effects in a satisfactory manner.

## IV. CONCLUSION

Proceeding from a simple model for the potential energy around substitutional defects in ionic crystals, we have confirmed the conclusion reached by MKGW in fitting the Raman data for NaCl : Ag$^+$, namely, that the effective force-constant changes for even symmetrized displacements around an impurity are not always dominated by the repulsive interactions between nearest neighbors. Coulomb forces and second-neighbor short-range interactions can make sizeable contributions to $\Delta K_{11}(\Gamma)$, causing $\Delta K_{11}(A_{1g})$ and $\Delta K_{11}(E_g)$ to differ by amounts large enough to significantly affect the Raman scattering. The force-constant changes are quite sensitive to variations in the parameters which characterize the impurity-host lattice interactions, and surprisingly large values can be found for $\Delta K_{14}$ and $\Delta K_{44}$ for $A_{1g}$ and $E_g$ displacements. These results for even symmetry modes, obtained with polarization neglected, are complementary to the conclusions of Bilz, Strauch, and Fritz,[1] who showed for the $U$ center that the electronic polarizability of the defect can have a significant effect on the different effective force constants obtained for modes of both even and odd parity, although it contributes directly only to the latter since the polarization of the central ion is necessarily zero for even modes.

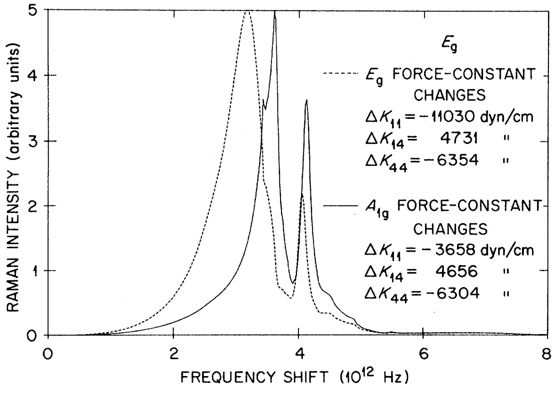

FIG. 5. $E_g$ Raman scattering calculated with $E_g$ and $A_{1g}$ force-constant changes for $\rho = 0.247$.

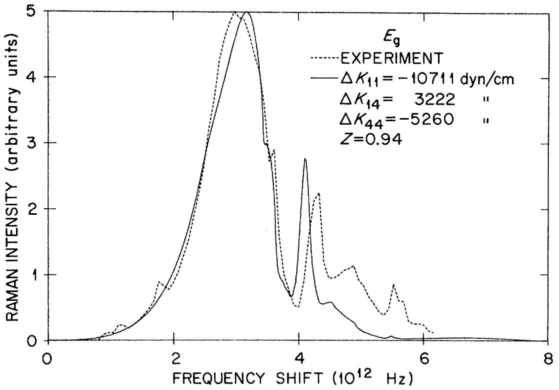

FIG. 6. $E_g$ Raman scattering for $\rho = 0.247$, $Z(\mathrm{Ag}^+) = 0.94$.

Our illustrative example of silver in sodium chloride is probably not the best test of the simple model assumed for the potential energy; for that purpose, a substitutional alkali or halogen ion in an alkali halide would have been a better choice and perhaps of even greater interest. However, in order to make our approach apply quantitatively to a variety of impurities, several improvements in the calculations will be required. Already mentioned in this connection is the inclusion of polarization effects, and strain effects can be approximately handled in much the same way.[6] The size of the 14 and 44 force-constant changes suggests that second-shell relaxation and force-constant changes may sometimes be important. The host-lattice interaction parameters may change around the defect. While such modifications would make the computational job more difficult, they are worth pursuing since they may allow more information to be extracted from infrared and Raman data.

## ACKNOWLEDGMENTS

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# Molecular-Orbital Theory of the Excited-State Exchange Interaction

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An approximate molecular-orbital exchange theory is derived in which the various contributions to the exchange interaction are expressed explicitly as functions of the covalency amplitudes, overlaps, single-ion Coulomb and exchange integrals and charge-transfer excitation energies. The relative sizes of contributions of the same type to the different pairwise interactions between electrons occupying specific orbitals on neighboring sites can be evaluated fairly reliably from such a theory. Fixing over-all scale factors for the kinetic and potential exchange to produce agreement with ground-state exchange constants then has the effect of incorporating higher-order relaxation and correlation effects into the theory and making it relatively insensitive to some of the approximations which enter into its derivation. Application of the theory to the ground-state exchange constants of $MnF_2$, $KMnF_3$, $NiF_2$, and $KNiF_3$ not only determines the required scale factors, which prove to agree adequately with simple *a priori* estimates, but also produces interesting information on the relative sizes of different components of the covalent bonding: $p_\sigma$, $p_\pi$, and $s_\sigma$. Properties derived from the exchange interactions of the excited ${}^4E(I)$ multiplet in $MnF_2$ are then deduced from the theory and compared to the experimental results. The agreement is fair to excellent for all quantities studied: two dispersion constants and two exciton-magnon coupling constants.

## INTRODUCTION

In recent years, experimental data has become available concerning the exchange interactions of optically excited transition-metal ions.[1,2] These interactions affect the observable optical properties of insulating transition-metal compounds. A theory of such excited-state exchange interactions is needed to provide a systematic framework for understanding such data. In addition, one would hope to obtain a deeper insight into the exchange interaction *per se* through making full use of information on the excited as well as on the ground multiplet of a given ion in a constant crystal environment. The present work represents one approach to deriving such a theory. It was originally motivated by a desire to explain experimental observations on the properties of the exciton-magnon sidebands associated with the lower ${}^4E$ excited multiplet in $MnF_2$.[1] This has proved to be a very appropriate test case and will be treated in detail in the present paper.

The exchange interaction can be regarded as arising out of the pairwise interaction of electrons on nearby cation sites. Simply expressing the over-all exchange interaction in terms of these pairwise interactions permits one to derive exchange constants for the various excited multiplets as well