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Lattice Deformations in Alkali-Halide Solid Solutions*†

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Using the Born-Mayer model, calculations on dilute solid solutions of alkali halides have been made. The systems considered are NaCl–NaBr and KBr–NaBr. In this paper ion displacements in the vicinity of an impurity atom are calculated and the results applied to the calculation of heats of solution and lattice constant changes. Electronic and ionic polarization and van der Waals interactions are included and found to be important.

INTRODUCTION

THE Born-Mayer model of ionic crystals succeeds quite well in relating the cohesive energy, observed lattice constant, and bulk modulus to one another. It is less successful in dealing with the elastic shear moduli and the dielectric constants of these crystals. For a simple model it is remarkably successful and it has been quite naturally hoped that it would be effective in dealing with lattice defects.

Charged point defects such as vacancies or interstitials polarize the ionic lattice in a very extensive region. Uncertainties in the dielectric theory make it difficult to treat this polarization with much confidence. A monovalent substitutional impurity such as Br^- in NaCl at a Cl^- site, on the other hand, has the same charge as the ion which it replaces. Furthermore, in this case the ionic radii of Br^- and Cl^- are 1.96 and 1.81 Å, respectively. Consequently, displacements of Na^+ ions surrounding a Br^- ion impurity are expected to be small, of the order of $\sim 4\%$. Thus substitutional impurities can be very gentle disturbances to the perfection of the lattice. It is to be hoped that the Born-Mayer model will be adequate to account for the details of these defects. The work to be described here investigates this possibility. We have calculated the heat of formation of certain dilute solid solutions, the lattice constant changes associated with their formation, and the field gradients at certain lattice sites near the impurity.

Section I describes the calculation of displacements of ions near certain monovalent substitutional impurities in NaCl, NaBr, and KBr. Sections II and IV apply these results to the calculation of the heats of formation of certain dilute solid solutions and to the lattice constant changes in these solid solutions, respectively. Comparisons with experiment are made. Section III discusses the effect on these results of the elastic and dielectric deformation of the ions not treated in Sec. I. A brief summary of our conclusions appears after Sec. IV. The applications of the results of this paper to the calculation of field gradients and quadrupole splittings of nuclear magnetic resonance lines appear in a second paper.[1]

I. DISPLACEMENTS AND DIPOLES IN DILUTE SOLID SOLUTIONS

In this section the displacements of certain ions near a substitutional monovalent anion or cation impurity in rock salt structure alkali halides are calculated. The ion displacements considered are shown in Fig. 1. The D ions are only third nearest neighbors to the impurity and (unlike C ions) have no nearest neighbors with displacements in such a direction as to give a radial force on them in first order of nearest-neighbor displacements. Their displacements are therefore neglected.

Displacements ξ, η, and δ in units of the perfect crystal nearest-neighbor distance a are assumed to be radial and are calculated by minimizing the energy of interaction of the six A-, the twelve B-, and the six C-type ions with one another, and with the rest of the crystal. In addition to their displacement, the A, B, and C ions are allowed to polarize. The dipole vectors of these ions are assumed to be directed radially just

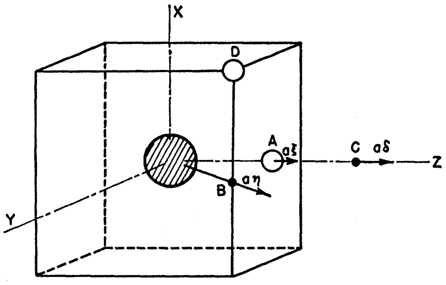

FIG. 1. Labeling of axes and neighbors in the vicinity of an impurity ion. The case shown is that of a cation impurity. The shaded circle represents the impurity; the open and filled circles are host crystal anions and cations, respectively.

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† A short account of part of this work was reported at the 1961 International Conference on "The Chemical Physics of Nonmetallic Crystals," papers from which have been published by W. A. Benjamin, Inc., New York.

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

as the displacements are and in units ea are given by μ_A, μ_B, and μ_C. For the moment the rest of the ions in crystal are considered to be undisplaced and unpolarized. This assumption will be discussed in Sec. III. The change in crystal energy ΔE which arises from introducing a single substitutional impurity may be separated into four parts: repulsive, electrostatic, electronic dipole self-energy, and van der Waals. The zero of energy is taken in this case to be the energy of the set of A, B, C ions in the host crystal. The change in zero-point energy of lattice vibrations is neglected.

The repulsive part ΔE_r^1 is calculated considering only nearest-neighbor repulsive interactions. As a trial, in one case the second-nearest-neighbor anion-anion interactions ΔE_r^2 have been included, and their effect on the displacements is shown to be small. If the repulsive energy of an anion-cation pair of the host crystal at a separation r is given by $A\exp(-r/\rho)$ and that of the impurity ion with an A ion is $B\exp(-r/\sigma)$, then to second order in ξ, η, δ

$$\begin{aligned}\Delta E_r^1={}&6(Be^{-a/\sigma}-Ae^{-a/\rho})\\&+6[(a/\rho)Ae^{-a/\rho}-(a/\sigma)Be^{-a/\sigma}]\xi\\&+6\left[\left(\frac{a^2}{2\rho^2}-\frac{2a}{\rho}\right)Ae^{-a/\rho}+\frac{a}{2\sigma^2}Be^{-a/\sigma}\right]\xi^2\\&+6\left(\frac{a^2}{\rho^2}-\frac{2a}{\rho}\right)Ae^{-a/\rho}(2\eta^2+\delta^2)\\&+12(2)^{\frac{1}{2}}Ae^{-a/\rho}\xi\eta-6(a^2/\rho^2)Ae^{-a/\rho}\xi\delta.\end{aligned}\tag{1}$$

The additional terms ΔE_r^2 to be included when second-nearest-neighbor interactions with B and C ions are taken into account in the case of an anion impurity are

$$\begin{aligned}\Delta E_r^2=12D\frac{a}{\tau}e^{-a(2)^{\frac{1}{2}}/\tau}&\left\{\left(1-\frac{C}{D}\right)\eta\right.\\&\left.+\left[\left(2+\frac{C}{2D}\right)\frac{a}{\tau}-\frac{5}{4(2)^{\frac{1}{2}}}\right]\eta^2+\left[\frac{a}{\tau}-(2)^{\frac{1}{2}}\right]\delta^2+\delta\eta\right\},\end{aligned}\tag{2}$$

where $D\exp(-r/\tau)$ and $C\exp(-r/\tau)$ are the repulsive interaction energies for host crystal anion-anion interaction and impurity anion-host anion interaction, respectively. Cation-cation interactions are neglected. The range τ of the interactions is taken to be the same for both, since the Huggins-Mayer[2] (HM) interaction is used, and HM assume the range of all the alkali and halogen ion repulsive interactions to be the same.

The electrostatic part ΔE_e is calculated as follows: At the undisplaced A, B, and C sites imagine both a fictitious positive and negative unit electronic charge to be superposed. Consider, for instance, the A ions in the case of an anion impurity. The A ions are then cations. In this case, the fictitious positive charge at the undisplaced A site restores the appropriate perfect lattice charge to that site. The remaining fictitious negative charge along with the displaced A ion may be treated as a dipole at the undisplaced A site. Thus to second order in ξ, η, δ the energy ΔE_e may be calculated by considering a set of dipoles superposed on a perfect lattice. The interaction of the dipoles with the perfect cubic lattice is zero since the field at cubic lattice sites is zero. The dipole interactions with one another give

$$\begin{aligned}\frac{a\Delta E_e}{3e^2}={}&\left(\frac{3}{(2)^{\frac{1}{2}}}+\frac{1}{4}\right)M_A^2+\left(\frac{3}{4}+\frac{7}{3(6)^{\frac{1}{2}}}+\frac{5}{(2)^{\frac{1}{2}}}+\frac{1}{4(2)^{\frac{1}{2}}}\right)M_B^2\\&+\left(\frac{1}{32}+\frac{3}{8(2)^{\frac{1}{2}}}\right)M_C^2+\left(1+\frac{2}{3(3)^{\frac{1}{2}}}+\frac{13}{25(5)^{\frac{1}{2}}}\right)M_BM_C\\&+4\left(1-\frac{1}{27}-\frac{12}{25(5)^{\frac{1}{2}}}\right)M_CM_A\\&-2\left(2(2)^{\frac{1}{2}}+\frac{52}{25(10)^{\frac{1}{2}}}+\frac{4(2)^{\frac{1}{2}}}{3(3)^{\frac{1}{2}}}\right)M_AM_B,\end{aligned}\tag{3}$$

where $M_A=\pm\xi+\mu_A$, $M_B=\pm\eta-\mu_B$, and $M_C=\pm\delta-\mu_C$, with the top sign for an anion and the bottom sign for a cation impurity. The dipole self-energies ΔE_S are given by

$$\frac{a\Delta E_S}{3e^2}=a^3\left(\frac{\mu_A^2}{\alpha_A}+\frac{2\mu_B^2}{\alpha_B}+\frac{\mu_C^2}{\alpha_C}\right),\tag{4}$$

where α_A, α_B, and α_C are the electronic polarizabilities of the A, B, C ions.

The van der Waals (VDW) term ΔE_V is calculated by considering VDW interactions between first and second nearest neighbors only. Both dipole-dipole ΔE_V^1 and dipole-quadrupole ΔE_V^2 VDW terms are included. To second order in the displacements the VDW interaction energies are given by

$$\begin{aligned}-a^6\Delta E_V^1/6={}&(i-e')+(k-g)/4+6(e'-i)\xi\\&+3(g-k)\eta/2(2)^{\frac{1}{2}}+(9e'+21i+27c/4)\xi^2\\&+(60e'+69g/8+21k/8)\eta^2\\&+(30e'+15g/4)\delta^2\\&+[3g/2(2)^{\frac{1}{2}}]\eta\delta-42e'\delta\xi+12(2)^{\frac{1}{2}}e'\xi\eta,\end{aligned}\tag{5}$$

and

$$\begin{aligned}(-a^8E_v^2/6={}&(j-f)+(l-h)+8(f-j)\xi+(h-l)\eta/(2)^{\frac{1}{2}}\\&+(20f+36j+6d)\xi^2\\&+(112f+29h/4+al/4)\eta^2\\&+(56f+7h/2)\delta^2\\&+(h/(2)^{\frac{1}{2}})\eta\delta-72f\delta\xi+16(2)^{\frac{1}{2}}f\xi\eta.\end{aligned}\tag{6}$$

Here the VDW constants are defined as follows: c, e', g, i, and k are the constants λ_{dd} for the dipole-dipole VDW interaction λ_{dd}/r^6 for the following pairs:

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[2] M. L. Huggins and J. E. Mayer, J. Chem. Phys. 1, 643 (1933).

	Cation impurity	Anion impurity
c	$(++)$	$(--)$
e'	$(+-)$	$(+-)$
g	$(--)$	$(++)$
i	$(+-^*)$	$(-+^*)$
k	$(--^*)$	$(++^*)$

$-$ and $+$ refer to the host cation and anion; $-^*$ or $+^*$ refer to the impurity cation or anion. d, f, h, j, and l are the corresponding constants λ_{dq} for the dipole-quadrupole VDW interaction λ_{dq}/r^8. The VDW constant e' is not to be confused with the electronic charge.

ξ, η, δ, and μ_A, μ_B, μ_C have been evaluated by minimizing the quadratic form

$$\Delta E=\Delta E_r+\Delta E_e+\Delta E_S+(\Delta E_V{}^1+\Delta E_V{}^2) \tag{7}$$

for the cases NaCl–Br, NaBr–Cl, KBr–Na, and NaBr–K. Here NaCl–Br designates a substitutional bromine-ion impurity in NaCl and similarly for the others. We are restricting ourselves to dilute solid solutions (concentration of solute $<1\%$). This implies that we have only isolated solute ions. In more concentrated solutions there will be a substantial chance of finding non-isolated solute ions. These are more difficult to handle and therefore will be omitted from this discussion.[3]

Choice of Constants

In order to learn the sensitivity of the calculated displacements and electronic dipoles to the assumptions of the calculation and to the choice of force constants the displacements and polarizations have been calculated in a variety of ways.

We have used both the Born-Mayer[4] (BM) and the Huggins-Mayer[2] (HM) values for the constants in the repulsive interaction. For the case of next-nearest-neighbor cation interactions only HM values are available. Since the BM values of these constants have been evaluated without including van der Waals terms in the calculation, it is inconsistent to include VDW terms in the expression for ΔE when using BM repulsive constants.

In those cases in which VDW interactions are included we have, whenever possible, used Mayer's[5] values for the VDW constants. This choice of VDW constants seems to be the most consistent one since Mayer's values have been used in evaluating the HM repulsive constants which have been used whenever VDW interactions were included. For the four impurity-host crystal systems treated, there are four VDW constants which are not given by Mayer. These are the dipole-dipole and dipole-quadrupole constants for the Br^-–Cl^- and the Na^+–K^+ interactions. For Br^-–Cl^- the VDW constants (k and l for the cases NaCl–Br and NaBr–Cl) may be evaluated from the formulas and tables of reference 5. There are insufficient data, however, in reference 5 to do the same for Na^+–K^+. In order to get an estimate for the dipole-dipole and quadrupole VDW interaction constants for this case, we make the following observation: In the case of Cl^-–Br^-, λ_{dd} and λ_{dq} when calculated by the method of reference 5 are found to be 159×10^{-60} erg-cm^6 and 361×10^{-76} erg-cm^8, respectively. We notice that the geometric mean of the constants for Cl^-–Cl^- and Br^-–Br^- are near to these values:

$$[\lambda_{dd}(Cl^-–Cl^-)\lambda_{dd}(Br^-–Br^-)]^{\frac{1}{2}}=151\times10^{-60}\text{ erg-cm}^6,$$

$$[\lambda_{dq}(Cl^-–Cl^-)\lambda_{dq}(Br^-–Br^-)]^{\frac{1}{2}}=324\times10^{-76}\text{ erg-cm}^8.$$

We use this indication to get an estimate of the VDW constants for Na^+–K^+. These geometric mean values for Na^+–K^+ are 5.4×10^{-60} erg-cm^6 and 13.9×10^{-76} erg-cm^8. Since these are only estimates and the impurity-nearest-neighbor interaction is probably the most significant of the VDW interactions, it will be important to judge the sensitivity of our results to these estimates of the VDW constants. As an alternate and rough estimate we may use the VDW constants for iso-electronic pairs of ions. For the Br^-–Cl^- pair we use Rb^+–Cl^-, giving 79×10^{-60} erg-cm^6 and 134×10^{-76} erg-cm^8 as iso-electronic estimates. For Na^+–K^+ we use the pair Na^+–Cl^-, giving 11.2×10^{-60} erg-cm^6 and 13.9×10^{-76} erg-cm^8 as iso-electronic estimates. The iso-electronic and harmonic mean estimates for the dipole quadrupole VDW constant for Na^+–K^+ differ negligibly and so are chosen to be the same. In the calculations including VDW interactions two cases have been carried through: the Mayer case $(\text{VDW})^{\text{M}}$ and the iso-electronic case $(\text{VDW})^{\text{I}}$. These differ only in the values used for k and l. In the $(\text{VDW})^{\text{M}}$ case the Mayer values for these constants are used for Br^-–Cl^- and, lacking them, the geometric mean estimates are used for the Na^+–K^+. In the $(\text{VDW})^{\text{I}}$ case the above iso-electronic estimates are used. One expects the $(\text{VDW})^{\text{M}}$ case to be the better. The $(\text{VDW})^{\text{I}}$ case is investigated solely as an indication of the sensitivity of the calculated results to variations in the choice of VDW constants.

Ionic polarizabilities have been taken alternatively from two sources. Those of Tessman, Kahn, and Shockley[6] are semi-empirical, being based on the assumption of additivity of ionic polarizabilities in crystals and measured refractive indices; and those of Sternheimer[7] are calculated polarizabilities of free ions. Tables I–III give choices for the various constants used.

In addition to the variety of force constants used, the case NaCl–Br has been worked in two additional cases. First, to investigate the importance of electronic

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[3] G. S. Durham and J. A. Hawkins, J. Chem. Phys. **19**, 149 (1951).

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

[5] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).

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

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

TABLE I. Repulsive force constants.

	$B_{\text{Na-Cl}}$ (10^{-9} erg)	$B_{\text{Na-Br}}$ (10^{-9} erg)	$\rho_{\text{Na-Cl}}$ (Å)	$\rho_{\text{Na-Br}}$ (Å)
Born-Huang	1.47	1.94	0.328	0.333
Huggins-Mayer	0.908	1.305	0.345	0.345

polarization, using BM repulsions and excluding VDW interactions, the electronic dipoles were set equal to zero ($\mu_A=\mu_B=\mu_C=0$). It is found that it is important to include these electronic polarizations. Second, the next-nearest-neighbor terms ΔE_r^2 [Eq. (2)] are included, using HM values for the repulsive constants occurring in these terms. It is found that these terms are relatively unimportant.

The results of these calculations are shown in Table IV. Figures 2 and 3 exhibit these results in graphic form for ready comparison. Included on Figs. 2 and 3 are points representing the displacements and dipoles calculated for several additional cases just mentioned. These additional cases show the importance of including the polarizability of the ions on the one hand and the insensitivity of the results to the inclusion of second nearest neighbors on the other.

Several features of these results are worthy of remark:

(1) ξ is positive for oversized impurities and negative for undersized impurities as one would expect. However, the displacements ξ are smaller by about a factor of $\frac{1}{2}$ than one would estimate by simply setting $a\xi$ equal to the difference of ionic radii between the host and the impurity ion. These estimates for ξ are 0.053, -0.0503, -0.107, and 0.117 for the four cases NaCl-Br, NaBr-Cl, KBr-Na, and NaBr-K.

(2) Among the parameters varied, the polarizabilities are the ones to which the displacements and dipoles are the most sensitive. The effect on the displacements is greater in the case of anion impurities than that of cation impurities. This is reasonable; for with an anion impurity, 18 of the 24 A, B, and C ions are anions with large electronic polarizabilities, while the converse is true with a cation impurity. The dipoles μ_A, μ_B, and μ_C are also more sensitive to the assumed polarizabilities than to the inclusion of VDW, as would be expected.

(3) The inclusion of VDW interactions has a noticeable effect on the displacements. For the anion impurities the uncertainty in the VDW constants represented by the variation from the "Mayer" to the "iso-electronic" case is of the same order as the VDW effect itself. Thus, VDW interactions can't be entirely ignored, but they are difficult to include accurately. For anion impurities inclusion of VDW terms tends to increase the magnitude of displacements, while the tendency is the opposite for negative-ion impurities. It will be noticed that for cation impurities there is essentially no difference between the $(\text{VDW})^{\text{M}}$ and $(\text{VDW})^{\text{I}}$ cases. This is as it should be since these cases differ only in the choice of the Na^+-K^+ dipole-dipole VDW constant. It is also clear why η is so sensitive to the variation from the "Mayer" to "iso-electronic" case for cation impurities: The VDW attraction between Br^- and Cl^- should be important in determining the displacement η, and it is this interaction which differs between these two cases.

(4) It is interesting to note that $|\delta|>|\eta|$ in the case of cation impurities but not for anion impurities. This indicates that the large anion A next to a cation impurity pushes out the C-type ions more than the B-type cations are pushed out by the impurity. The small cation next to the impurity plays no such role for the case of an anion impurity.

In concluding this discussion of the calculations of displacements and polarizations about these impurities, we may summarize roughly as follows: The displacements are affected strongly by the inclusion of polarizations on the ions and are sensitive to the assumed polarizabilities. To a somewhat lesser extent the displacements are affected by the inclusion of VDW interactions. The dipoles are relatively insensitive to VDW interactions, but are strongly affected by the assumed value for the polarizabilities.

II. HEATS OF FORMATION OF SOLID SOLUTION

As an application of the relaxation calculation, we consider first the problem of the heats of formation of solid solution for dilute substitutional solutions of the alkali halides.

By dilute solutions we mean solute concentrations less than about 1% in which the solute ions may be considered to be isolated. The definition of the heat of

TABLE II. van der Waals force constants.[a]

	λ_{dd} (10^{-60} erg cm^6)	λ_{dq} (10^{-76} erg cm^8)
Na-Cl	11.2	13.9
Na-Br	14.0	19
Na-Na	1.68	0.8
Cl-Cl	116	233
Br-Br	196	450
Cl-Br	160	360
	79	134

[a] Where two values appear, the upper one corresponds to the choice "M" and the lower to the choice "I".

TABLE III. Polarizabilities, in units 10^{-24} cm^3.

	Cl^-	Br^-	Na^+
TKS	2.97	4.17	0.41
Sternheimer	5.63	7.36[a]	0.145

[a] This value, not calculated by Sternheimer, is estimated roughly by using $(\alpha_{\text{Br}}/\alpha_{\text{Cl}})$ Pauling $\times$ (α_{Cl}) Sternheimer.

TABLE IV. Displacements and electronic dipoles.[a]

System	Case	ξ	η	δ	μ_A	μ_B	μ_C
NaCl–Br	1	0.027	0.0078	−0.00030	0.00008	−0.0046	0.0078
	2	0.027	0.0077	−0.0016	0.00012	−0.0049	0.0079
	3	0.030	0.012	−0.0032	0.00038	−0.0046	0.0090
	4	0.035	0.0094	−0.0016	0.00027	−0.011	0.020
	5	0.037	0.010	−0.0039	0.00032	−0.012	0.021
	6	0.040	0.014	−0.0052	0.00043	−0.011	0.024
NaBr–Cl	1	−0.029	−0.0078	−0.0078	−0.00011	0.0059	−0.010
	2	−0.031	−0.0088	0.00084	−0.00019	0.0061	−0.011
	3	−0.028	−0.0056	−0.00018	−0.000014	0.0061	−0.0092
	4	−0.046	−0.011	0.00050	−0.00032	0.016	−0.029
	5	−0.052	−0.015	0.0034	−0.00042	0.017	−0.033
	6	−0.047	−0.011	0.0023	−0.00033	0.017	−0.030
KBr–Na	1	−0.055	−0.0064	−0.017	−0.014	−0.0041	0.0041
	2	−0.052	−0.0085	−0.013	−0.012	−0.0037	0.0039
	3	−0.052	−0.0086	−0.013	−0.012	−0.0036	0.0039
	4	−0.063	−0.0024	−0.025	−0.029	−0.0057	0.0048
	5	−0.059	−0.0043	−0.020	−0.025	−0.0051	0.0045
	6	−0.059	−0.0044	−0.020	−0.025	−0.0051	0.0045
NaBr–K	1	0.050	0.0098	0.0097	0.011	0.0016	−0.0017
	2	0.050	0.011	0.0073	0.010	0.0015	−0.0017
	3	0.050	0.011	0.0075	0.010	0.0015	−0.0017
	4	0.051	0.0063	0.015	0.020	0.00071	−0.00065
	5	0.051	0.0076	0.013	0.018	0.00068	0.00065
	6	0.051	0.0073	0.013	0.019	0.00069	−0.00065

[a] The cases are designated as follows: 1—No (VDW), TKS; 2—$(\mathrm{VDW})^{\mathrm{M}}$, TKS; 3—$(\mathrm{VDW})^{\mathrm{I}}$, TKS; 4—No VDW, Sternheimer; 5—$(\mathrm{VDW})^{\mathrm{M}}$, Sternheimer; 6—$(\mathrm{VDW})^{\mathrm{I}}$, Sternheimer.

formation of solid solution ΔH_f is

$$\Delta H_f = U_{ss} - (N_1U_1^0 + N_2U_2^0), \tag{8}$$

where U_{ss}, U_2^0 are the lattice energies per mole of solid solution and the pure components 1 and 2, respectively. [This definition is the same as that used by Fumi and Tosi[8] and Fineman and Wallace.[9] It differs in sign from the definition by Durham and Hawkins.[10]] N_1 and N_2 are the mole fractions of components 1 and 2. Since the reference energy is that of a mixture of pure components, the ΔE which we have calculated is not the heat of formation of a solid solution per molecule of solute. For definiteness consider NaCl–Br: $\Delta E=$ (energy of Br^- at Cl^- site in NaCl) − (energy of Cl^- ion at Cl^- site in NaCl). To get the heat of formation we must add to this $\Delta E_0=$ (energy of Cl^- ion at Cl^- site in NaCl) − (energy of Br^- ion at Br^- site in NaBr). The energy of a Cl^- ion at a Cl^- site in NaCl is given by

$$-e^2(\alpha_M/a)+6A\exp(-a/\rho)-e'(A_6'/a^6)$$
$$-f(A_8'/a^8)-g(A_6''/a^6)-h(A_8''/a^8), \tag{9}$$

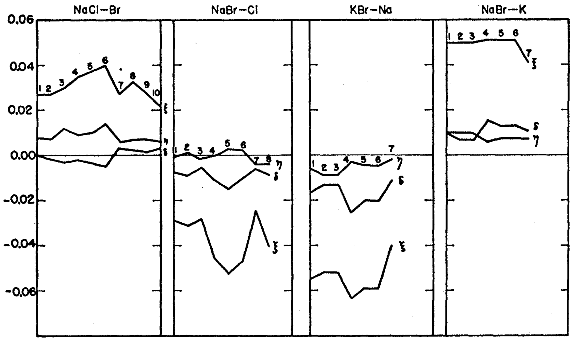

FIG. 2. Displacements ξ, η, and δ for the four systems studied. The approximations are designated by numbers as follows: 1—No VDW, TKS; 2—$(\mathrm{VDW})^{\mathrm{M}}$, TKS; 3—$(\mathrm{VDW})^{\mathrm{I}}$, TKS; 4—No VDW, Sternheimer; 5—$(\mathrm{VDW})^{\mathrm{M}}$, Sternheimer; 6—$(\mathrm{VDW})^{\mathrm{I}}$, Sternheimer; 7—BM, TKS; 8—BM, Sternheimer; 9—BM, TKS, next-nearest-neighbor repulsions included; 10—BM, no electronic dipoles.

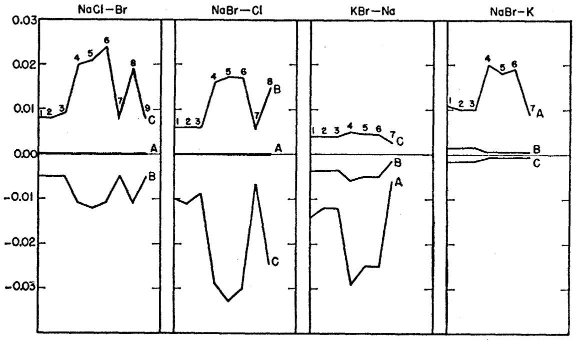

FIG. 3. Electronic dipoles μ_A, μ_B, and μ_C. The approximations are designated by numbers according to the same convention as that of Fig. 2.

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[8] F. G. Fumi and M. P. Tosi, Discussions Faraday Soc. 23, 92 (1957).

[9] M. Fineman and W. E. Wallace, J. Am. Chem. Soc. 70, 4165 (1948).

[10] G. S. Durham and J. A. Hawkins, J. Chem. Phys. 19, 149 (1951).

where a is the nearest-neighbor distance in NaCl; e', f, g, and h are the VDW constants defined in Sec. I for NaCl–Br; α_M is Madelung's constant for the NaCl structure and

$$A_s'=\sum_{l_1,l_2,l_3}{}' (l_1^2+l_2^2+l_3^2)^{-s/2}, \quad l_1+l_2+l_3 \text{ odd}$$

$$A_s''=\sum_{l_1,l_2,l_3}{}' (l_1^2+l_2^2+l_3^2)^{-s/2}, \quad l_1+l_2+l_3 \text{ even}$$

are sums defined and calculated by Jones and Ingham.[11] A and ρ are repulsive interaction constants for the anion-cation interaction of the host crystal NaCl. Similarly the energy of a Br^- ion at a Br^- site in NaBr is given by

$$-e^2(\alpha_M/b)+6B\exp(-b/\sigma)-i(A_6'/b^6) \\ -j(A_8'/b^8)-g^*(A_6''/b^6)-h^*(A_8''/b^8), \quad (10)$$

where b is the nearest-neighbor distance in NaBr; i and j are VDW constants defined above for the case NaCl–Br, and B and σ are NaBr repulsive constants. g^* and h^* are the dipole-dipole and quadrupole-dipole VDW constants for the Br^-–Br^- interaction. Thus, taking the difference of Eqs. (9) and (10),

$$\begin{aligned}\Delta E_0=&-e^2\alpha_M[(1/a)-(1/b)] \\ &+6[A\exp(-a/\rho)-B\exp(-b/\sigma)] \\ &-A_6'[(e'/a^6)-(i/b^6)]-A_8'[(f/a^8)-(j/b^8)] \\ &-A_6''[(g/a^6)-(g^*/b^6)] \\ &-A_8''[(h/a^8)-(h^*/b^8)]. \quad (11)\end{aligned}$$

To ΔE_0 must be added ΔE evaluated with those values of ξ, η, δ, μ_A, μ_B, μ_C, $(\equiv x_1,\cdots,x_6)$ which minimize it.

Since ΔE is of the form

$$\Delta E=A+\sum_{i=1}^{6} B_ix_i+\sum_{i,j=1}^{6} C_{ij}x_ix_j,$$

with $C_{ij}=C_{ji}$, it is easily shown that the minimum of ΔE is given by

$$\Delta E_{\min}=A+\tfrac{1}{2}\sum_{i=1}^{6} B_ix_i^0, \quad (12)$$

where

$$\partial\Delta E/\partial x_i^0=0, \quad i=1,\cdots,6.$$

The heat of formation of solid solution per molecule is then

$$\Delta H_f=\Delta E_0+\Delta E_{\min},$$

the coefficients and displacements for $\Delta E_{\min}$ being given in Sec. I and ΔE_0 being given by Eq. (11). This expression for ΔH_f does not include the contribution from the rest of the lattice beyond the A, B, and C ions, but this contribution will be shown to be small in Sec. III.

The calculated values of ΔH_f for assumed model constants and the inclusion or exclusion of VDW interactions are shown in Table V. Separate contributions to the total are listed there as well. The "Repulsive and Madelung" contribution lumps together the terms in $\Delta E_{\min}$ and ΔE_0 which contain Madelung's constant or the repulsive interaction parameters. The "VDW" contribution is a similar lumping of the terms of VDW origin. The "relaxation" terms are the terms linear in the displacements from $\Delta E_{\min}$ [Eq. (12)].

It is clear from Table V that all the contributions including the relaxation terms are important. It is also seen that the best agreement with experiment is obtained when Born-Mayer repulsive constants are used, the agreement being better for the TKS polarizabilities. It is gratifying that the heat of solution for NaCl–Br is calculated to be larger than for NaBr–Cl as found from experiment. The bad disagreement of the calculated heats of solution for the other approximations as compared with experiment is mostly due to the inaccuracies in the VDW constants. An examination of Table V seems to indicate that the VDW interactions contribute quite substantially to the calculated ΔH_f. The fact that the results obtained with Born-Mayer constants agree best with experiment suggests that the VDW contribution is really not important, but that its effect is grossly overestimated in the calculations using the Huggins-Mayer repulsive constants. The experimental values given are derived from the empirically fitted formula of Fineman and Wallace[9] in the limit of zero concentration. It should be remarked that the relaxation part of $\Delta E_{\min}$ is probably the most accurate part of ΔH_f since it is minimized. It is likely that the poorness of the calculated heats solution can be attributed to the other (constant) terms in ΔH_f. This would explain why it is that the field gradients and lattice constant changes calculated from the displacements of Sec. I do not show the great deviations from experiment that the calculated heats of solution do.

III. THE EFFECT OF THE REST OF THE LATTICE

In Sec. I only the A, B, and C ions have been allowed to polarize and move about the substitutional impurity. The displacements and polarizations extend, of course, throughout the crystal. In this section we shall show that the contribution of these additional deformations to the heat of solution is small and, further, that the displacement δ of the C ions is of the same order of magnitude as that calculated on the basis of an elastic continuum. The latter fact lends support to the validity of treating the rest of the lattice as an elastic and dielectric continuum. By the "rest of the lattice" we shall mean all of those ions beyond the impurity and its A, B, and C ions.

Treating the rest of the lattice as a dielectric continuum, let us first consider its polarization due to the displacement and polarization of the individual

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[11] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) **A107**, 636 (1925).

TABLE V. ΔH_f in calories per mole.

System	Case[a]	Repulsive plus Madelung	VDW	(Includes dipoles) Relaxation[b]	Calculated ΔH_f Total	ΔH_f Experiment[c]
NaCl–Br	No (VDW)	8.8	0	−10.8 −14.1	− 2.0 − 5.2	14.3
	(VDW)^M	8.8	−18.1	−10.1 −13.6	−19.4 −22.9	
	(VDW)^I	9.8	23.4	−11.8 −15.8	20.4 16.4	
	(BH)	26.4	0	−13.5 −16.5	12.9 9.8	
NaBr–Cl	No (VDW)	28.8	0	− 7.7 −12.0	21.2 16.8	12.5
	(VDW)^M	28.8	6.3	− 7.4 −12.4	27.8 22.8	
	(VDW)^I	28.8	− 5.9	− 6.4 −10.8	16.6 12.2	
	(BH)	19.5	0	− 7.5 −12.2	12.0 7.3	
KBr–Na	No (VDW)	65.7	0	−30.8 −34.9	34.9 30.8	
	(VDW)^M	65.7	4.6	−23.2 −26.1	47.1 44.2	
	(VDW)^I	65.7	5.4	−23.2 −26.2	47.9 45.0	
	(BH)	51.9	0	−18.4 ...	33.5 ...	
NaBr–K	No (VDW)	107.0	0	−63.2 −63.9	43.9 43.1	
	(VDW)^M	107.0	−37.0	−52.3 −52.7	17.7 17.3	
	(VDW)^I	107.0	−35.5	−52.1 −52.8	19.3 18.7	
	(BH)	92.0	0	−43.4 ...	48.7 ...	

[a] The first three cases for each system are based on Huggins-Mayer (reference 2) repulsive constants; the fourth case is based on Born-Huang repulsive constants (reference 4). In this latter case VDW interactions are not included.

[b] The top and bottom values are based on TKS (reference 6) and Sternheimer (reference 7) polarizabilities, respectively.

[c] See reference 9.

A, B, and C ions. These A, B, and C ions constitute a cubically symmetric charge distribution which we will treat as a set of electric multipoles. Although this charge distribution has a monopole moment, this monopole represents no alteration of the electrostatic configuration of the pure crystal and so may be neglected in considering the energy change associated with the introduction of an impurity. There are no nonzero odd multipole components. There are quadrupole components; however, a cubically symmetric charge distribution gives rise to zero external quadrupole field. The lowest order multipole of significance is a hexadecapole. The potential at an external point $\mathbf{r}$ with coordinates x_1, x_2, x_3 due to a hexadecapole arising from a charge distribution $\rho(\mathbf{r})$ is

$$\phi_0(\mathbf{r}) = (Q_{ijkl}/8r^9) \times (35x_ix_jx_kx_l - 30x_ix_j\delta_{kl}r^2 + 3\delta_{ij}\delta_{kl}r^4), \quad (13)$$

where

$$Q_{ijkl} = \int \rho(\mathbf{r}')x_i'x_j'x_k'x_l'd\tau', \quad (14)$$

and the summation convention has been used. For a cubically symmetric $\rho(\mathbf{r})$ there are only two different sets of nonzero hexadecapole components:

$$Q_{xxxx} = Q_{yyyy} = Q_{zzzz} \equiv Q_1,$$

$$Q_{xxyy} = Q_{xyxy} = Q_{yyzz} = \cdots \equiv Q_2,$$

so that for the cubic case

$$\phi_0(\mathbf{r}) = K[(x^4 + y^4 + z^4) - (3r^4/5)]/r^9, \quad (15)$$

where

$$K = (35/8)(Q_1 - 3Q_2). \quad (16)$$

This holds for a hexadecapole in free space. To calculate the energy associated with the polarization of the rest of the lattice due to this multipole, we must know the potentials inside and outside a spherical hole in a dielectric where this hole is centered on the hexadecapole. Evaluation of these potentials is a straightforward electrostatic boundary value problem and the results are

$$\phi_A = (K/r^5) \times [(1/420)P_4^4(\cos\theta)\cos 4\varphi + (2/5)P_4^0(\cos\theta)] + [K(1-\epsilon)r^4/(5\epsilon+4)R^9] \times [(1/84)P_4^4(\cos\theta)\cos 4\varphi + 2P_4^0(\cos\theta)], \quad (17)$$

$$\phi_B = [9K/(5\epsilon+4)R^5] \times [(1/420)P_4^4(\cos\theta)\cos 4\varphi + (2/5)P_4^0(\cos\theta)], \quad (18)$$

where ϕ_A is the potential inside the hole of radius R, and ϕ_B is that outside the hole and in the dielectric which has dielectric constant ϵ. The electrostatic energy in the rest of the lattice outside a radius R is that associated with the introduction of the dielectric and is given by

$$W_e=\frac{1}{8\pi}\int_0^R r^2dr\int d\Omega(\nabla\phi_A)^2+\frac{\epsilon}{8\pi}\int_R^\infty r^2dr\int d\Omega(\nabla\phi_B)^2 -\frac{1}{8\pi}\int_0^\infty r^2dr\int d\Omega(\nabla\phi_0)^2, \quad (19)$$

where ϕ_0 is the potential due to the hexadecapole in the absence of the dielectric given above. Performing the integrations, we find

$$W_e=[8(1-\epsilon)(10\epsilon^2-\epsilon+9)/21(5\epsilon+4)^2]K^2/R^9. \quad (20)$$

To compare W_e with H_f of Sec. II, it is necessary to estimate the values of Q_1 and Q_2. Since the electronic dipoles are small, they will be neglected in estimating the order of magnitude of Q_1 and Q_2. Knowledge of the displacements of the ions is not sufficient to find the fourth moments of the associated charge distribution; some charge distribution on the ion must be assumed. If the ions are assumed to be composed of a point core of charge $(Z_\pm\pm1)e$ and a uniformly charged shell of radius $r_\pm a$ and charge $Z_\pm e$, the hexadecapole components Q_1 and Q_2 may be evaluated to give (to first order in the displacements)

$$Q_1-3Q_2=4ea^4[(2-\tfrac{1}{3}Z_+r_+{}^2)\xi-(16+\tfrac{2}{3}Z_-r_-{}^2)\delta -(10(2^{\frac{1}{2}})+\tfrac{1}{3}8(2^{\frac{1}{2}})Z_-r_-{}^2)\eta], \quad (21)$$

where a is the nearest-neighbor distance in the host crystal. Suppose $r_+, r_-\sim1/2$; $Z_\pm\sim6$. It is then seen that the value of Q_1-3Q_2 is the same order of magnitude whether calculated for point-charge ions ($r_\pm=0$) or for core-shell ions. Therefore, we may use point-ion estimate with some confidence. Substituting Eq. (21) with $r_+=r_-=0$ into Eq. (20) and setting $R=2.5a$, which seems reasonable, we have

$$W_e=-\frac{e^2}{a}\frac{224}{3}(\tfrac{2}{5})^7\frac{(1-\epsilon)(10\epsilon^2-\epsilon+a)}{(5\epsilon+4)^2}(\xi-5(2^{\frac{1}{2}})\eta+8\delta)^2. \quad (22)$$

The energy calculated by this expression is in every case less than 10% of the calculated ΔH_f and in most cases is much less than this. Thus, it appears that the energy associated with the rest of the crystal is not great enough to alter significantly the calculated values of ΔH_f. A more consistent calculation of the displacement parameters ξ, η, and δ would result if W_e were added to ΔE of Sec. I before the minimization was carried out. This would not affect the values of ξ and η appreciably although it would alter δ somewhat. Most of the quantities which we have calculated from a knowledge of these displacements and the dipoles are very insensitive to δ, however, and so it was not considered important to carry out this modification.

Having discussed the electrical effects on the rest of the crystal, it remains to discuss those elastic displacements arising from the repulsive forces exerted by the impurity ion. The electrostatic energy just estimated and the elastic strain energy are added separately. This is permissible since piezoelectric effects are absent in the rest of the crystal, and electrostriction contributes terms to the energy of higher order than the second in the displacements. To estimate the elastic energy residing in the rest of the crystal, we treat it as an isotropic elastic continuum with forces applied outward from the impurity at the B and C ion positions. Thus, we consider a six-pronged set of forces $F_6(\pm1,0,0)$, $F_6(0,\pm1,0)$, and $F_6(-,0,\pm1)$ acting at positions $\mathrm{r}_0=2a(\pm1,0,0)$, $2a(0,\pm1,0)$, and $2a(0,0,\pm1)$, respectively, and a 12-pronged set $(F_{12}/\sqrt{2})(\pm1,\pm1,0)$, etc., at $\mathbf{r}_0=a(\pm1,\pm1,0)$, etc. F_6 arises because of the displacements δ and F_{12} from the displacements η. The displacement $\mathbf{U}$ at a point $\mathbf{r}$ in an isotropic elastic continuum due to a force $\mathbf{F}$ acting at a point $\mathbf{r}_0$ can be shown[12] to be

$$\mathbf{U}=(C_1\mathbf{r}/|\mathbf{r}-\mathbf{r}_0|)+C_2(\mathbf{r}-\mathbf{r}_0)\mathbf{F}\cdot(\mathbf{r}-\mathbf{r}_0)/|\mathbf{r}-\mathbf{r}_0|^3, \quad (23)$$

where

$$C_1=(C_{11}+C_{44})/8\pi C_{11}C_{44},\qquad C_2=(C_{11}-C_{44})/8\pi C_{11}C_{44}. \quad (24)$$

In assuming isotropy we have assumed $C_{11}-2C_{44}=C_{12}$, which is not true for the crystals under consideration, but the order of magnitude of the calculated strain energy should not be affected. Choosing the origin to be at the impurity ion, we expand the displacement $\mathbf{U}$ due to the sets of forces in powers of r_{0i}/r and find to first order

$$\mathbf{U}=(C_1/r^3)\textstyle\sum_i \mathbf{F}_i(\mathbf{r}_{0i}\cdot\mathbf{r}) +(C_2/r^3)\sum_i[3\mathbf{r}(\mathbf{F}_i\cdot\mathbf{r})(\mathbf{r}_{0i}\cdot\mathbf{r})r^{-2} -\mathbf{r}(\mathbf{F}_i\cdot\mathbf{r}_{0i})-\mathbf{r}_{0i}(\mathbf{F}_i\cdot\mathbf{r}), \quad (25)$$

where the sum over i is a sum over the members of the 6- and 12-prong sources. On carrying out the sums, it is found that

$$\mathbf{U}=K'\mathbf{r}/r^3, \quad (26)$$

where

$$K'=4(C_1-C_2)a(F_6+(2^{\frac{1}{2}})F_{12}) =(a/\pi C_{11})(F_6+(2)^{\frac{1}{2}}F_{12}). \quad (27)$$

Knowing $\mathbf{U}$, the strain components

$$e_{ij}=\left(\frac{\partial U_i}{\partial x_j}+\frac{\partial U_j}{\partial x_i}\right)(1-\tfrac{1}{2}\delta_{ij})$$

may be calculated and the strain energy density $dW/d\tau$

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[12] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, Inc., New York, 1944), 4th ed., p. 185, Eq. (12).

evaluated:

$$2(dW/d\tau)=C_{11}(e_{xx}+e_{yy}+e_{zz})^2+C_{44}(e_{yz}{}^2+e_{zx}{}^2+e_{xy}{}^2) -4C_{44}(e_{yy}e_{zz}+e_{zz}e_{xx}+e_{xx}e_{yy}), \quad (28)$$

$$dW/d\tau=6C_{44}K'^2/r^6.$$

Integrating this strain energy density over a region outside a sphere of radius R to infinity, we find the strain energy W_s to be

$$W_s=8\pi C_{44}K'^2/R^3, \quad (29)$$

where we shall choose $R\sim 3a$. It remains to calculate F_6 and F_{12}. The repulsive force which a displaced C ion exerts on its undisplaced nearest neighbor in the direction away from the impurity is

$$F_6=aA\exp(-a/\rho)\delta/\rho^2 \quad (30)$$

to first order in δ. Similarly,

$$F_{12}=aA\exp(-a/\rho)\eta/\rho^2, \quad (31)$$

so that

$$W_s=(8C_{44}a/27C_{11}{}^2\rho^4)A^2\exp(-2a/\rho)(\delta+(2^{\frac{1}{2}})\eta)^2. \quad (32)$$

When W_s is calculated, the contribution to ΔH_f is in all cases less than one percent of the calculated values shown in Table V. We may, therefore, neglect the contribution of W_s to an even better approximation than we neglected W_e. It is useful to compare the elastic displacement given by Eq. (26) at $r=2a$ with the value of δ calculated from the detailed considerations of Sec. I. The ratios $\delta a/U$ for this position are 1.6, 4.5, 2.2, 2.8 for the cases NaCl–Br, NaBr–Cl, KBr–Na, NaBr–K, respectively, (Born-Mayer constants, no VDW). Thus, the C-ion displacements calculated microscopically are somewhat in excess of the elastic continuum theory estimate. It is gratifying, though, that even without including W_e and W_s in the energy to be minimized, the δ's calculated are of the same order of magnitude as the elastic continuum estimate. This fact lends some confidence to the method of treating the rest of the crystal as an elastic and dielectric continuum.

IV. LATTICE CONSTANT CHANGES

The x-ray lattice constants of mixed crystals of the alkali halides are observed to be different from those

TABLE VI. Lattice constant changes.

System	Case[a]	Calculated[b] $\Delta a/f$	Vegard $n=1$	Preservation of atomic volume of $n=3$	Experiment[c]
NaCl–Br	No (VDW)	0.114 0.124	0.167	0.177	0.1776
	(VDW)$^{\mathrm{M}}$	0.099 0.109			
	(VDW)$^{\mathrm{I}}$	0.201 0.154			
	BH	0.127 0.136			
NaBr–Cl	No (VDW)	−0.130 −0.169	−0.167	−0.159	−0.146
	(VDW)$^{\mathrm{M}}$	−0.130 −0.200			
	(VDW)$^{\mathrm{I}}$	−0.091 −0.149			
	BH	−0.040 −0.170			
KBr–Na	No (VDW)	−0.229 −0.250	−0.312	−0.283	
	(VDW)$^{\mathrm{M}}$	−0.220 −0.229			
	(VDW)$^{\mathrm{I}}$	−0.221 −0.230			
	BH	−0.160 ...			
NaBr–K	No (VDW)	+0.264 0.268	0.312	0.346	
	(VDW)$^{\mathrm{M}}$	0.256 0.266			
	(VDW)$^{\mathrm{I}}$	0.259 0.266			
	BH	0.231 ...			

[a] See footnote a, Table V.
[b] Top and bottom values are based on TKS and Sternheimer polarizabilities, respectively.
[c] See reference 15.

of either of the constituents. Eshelby,[13] using isotropic elastic continuum theory, has shown that the change in volume associated with a mole fraction f of impurities is given by

$$\Delta V/V=4\pi\gamma K'f/a^3, \tag{33}$$

where

$$\gamma=3(1-\sigma)/(1+\sigma), \tag{34}$$

σ is Poisson's ratio, a^3 is the atomic volume, and K' is given by Eq. (27). What is measured is $\Delta a/f$, given by

$$\Delta a/f=a\Delta V/3fV. \tag{35}$$

We have calculated values of $\Delta a/f$ for the several cases considered for the displacements. These values are listed in Table VI. In the past there have been efforts to fit the observed lattice constant changes to a formula of the form:

$$a^n=a_1{}^n+(a_2{}^n-a_1{}^n)f. \tag{36}$$

Here a, a_1, and a_2 are the measured lattice constants of the mixed crystal and the two constituent crystals. The case $n=1$ is called Vegard's law. The case $n=3$ corresponds to the somewhat more plausible "preservation of atomic volumes."[14]

For very dilute solid solutions such as the ones we are considering, Eq. (36) takes the form

$$\Delta a/f=(a_2{}^n-a_1{}^n)/na_1{}^{n-1}. \tag{37}$$

For comparison with the $\Delta a/f$ calculated from Eqs. (33) to (35), Vegard's law ($n=1$) and $n=3$ cases have been calculated from Eq. (37). (See Table VI.) Nickels, Fineman, and Wallace[15] have measured $\Delta a/f$ for the NaCl–NaBr system. Their data indicate small positive deviations of $\Delta a/f$ from both the cases $n=1$ and $n=3$ and for both the NaCl–Br and the NaBr–Cl case. Our calculations are not conclusive on this point, including among the several cases both positive and negative deviations. It is worth noting that for both NaCl–Br and NaBr–Cl the (VDW)$^{\mathrm{I}}$-Sternheimer case calculated value comes nearest to experiment. As in the case of the heats of formation of solid solution, the VDW interactions and the polarizabilities strongly affect the calculation of $\Delta a/f$.

SUMMARY

The calculations of lattice deformations about monovalent substitutional impurities in alkali-halide crystals depend strongly on electronic polarization and van der Waals interactions. Uncertainties in the choices of polarizabilities can account for large variations in the calculated specific heats and somewhat smaller variations in the calculated lattice constant changes. Therefore, poor agreement with experiment is not necessarily an indication of the failure of the Born-Mayer model in these calculations. As will be seen in the following paper,[1] calculated field gradients are somewhat less sensitive to the permissible variation of parameters.

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[13] J. Eshelby, J. Appl. Phys. **25**, 255 (1954).

[14] A. Miller (to be published).

[15] J. E. Nickels, M. Fineman, and W. E. Wallace, J. Phys. Chem. **53**, 625 (1949).