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Comments and Addenda

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Alkali-Halide Mixed Crystals*

B. G. DICK AND KYLER F. NELSON†
University of Utah, Salt Lake City, Utah 84112

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In earlier work we have used a model for dilute mixed crystals in which the sole perturbing effect of a foreign ion is a change in the nearest-neighbor Born-Mayer repulsion parameters. A simple experimental criterion for the validity of this model is deduced and compared with experiment for the cases NaF-Li and NaF-K. For these cases, the validity criterion is violated; hence, the model is inadequate.

INTRODUCTION

THERE has been continuing experimental[1–10] and theoretical[11–17] interest in dilute alkali-halide solid solutions. This interest has been prompted by the supposition that a substitutional foreign halide or alkali ion in an alkali halide should be one of the gentlest and simplest point defects in these rather well-understood crystals. In particular, the absence of a net charge for such defects greatly simplifies efforts at theoretical analysis.

We have previously[11,12,15] used a simple model for the defect and lattice which we hoped would be adequate to account for measured nuclear quadrupole effects in dilute alkali-halide solid solutions. This model, which we will refer to as the DD model, supposes that the sole effect of the defect ion is a change in the Born-Mayer repulsion parameters between the substitutional defect and its nearest neighbors. The resulting relaxation of the lattice is then calculated treating the host-lattice ions as polarizable shell-model ions. This relaxation produces electric field gradients which interact with nuclear quadrupole moments. This interaction is the object of the experimental investigations. Recently, Ikenberry and Das[17] have pointed out that finite ion-size effects can lead to field gradient contributions comparable to those coming from the DD model.

It is the purpose of this paper to point out a simple prediction of the DD model and to provide new experimental data which are in violation of this prediction. The importance of this prediction is that it is independent of the particular parameters (polarizabilities, Born-Mayer parameters, lattice constants, dielectric constants, and elastic constants) which are used in the model. Our conclusion is that in at least one pair of cases, NaF-Li and NaF-K, the DD model cannot account for the experimental results for *any* choice of these parameters.

THEORY

We shall show that for a given host crystal the DD model predicts ion displacements, electronic dipoles, and field gradient components which are all proportional to a single quantity which can be taken, for instance, to

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† Present address: Xerox Research Laboratories, Rochester, N. Y.

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be the nearest-neighbor ion displacement. If the defect occupying the lattice site is changed, then, according to the DD model, all the calculated quantities just mentioned will change while their ratios will remain unaltered.

To see this, consider the equations which determine ion displacements and induced electronic dipoles in the DD model when five shells of neighbors are considered [see Ref. 15, Eq. (25)]. We write them in matrix form,

$$\begin{pmatrix} a_{11}a_{12} & \cdots a_{1,10} \\ \vdots & \\ a_{10,1}a_{10,2} & \cdots a_{10,10} \end{pmatrix} \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_5 \\ \mu_1 \\ \vdots \\ \mu_5 \end{pmatrix} = \begin{pmatrix} b_1 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix} . \tag{1}$$

Here the ξ_i are radial ion displacements (Fig. 1, Ref. 15) and the μ_i are radially directed electronic dipoles induced on the corresponding ions. As shown in Ref. 15, for the form of the model used there, only a_{11} and b_1 depend on the parameters of the Born-Mayer repulsion defect-nearest-neighbor interaction. All the other a_{ij}'s depend only on parameters of the host crystal. Thus a_{11} and b_1, along with the designation of whether the impurity is an anion or a cation, characterize the impurity in the model. This feature is a direct consequence of limiting the perturbation to that of a nearest-neighbor repulsion change in the DD model. This is not the case for that form of the DD model used in Ref. 11, where van der Waals interactions were included.

Now imagine that the last nine lines of Eqs. (1) are solved to give $\xi_2, \ldots, \xi_5, \mu_1, \ldots, \mu_5$ in terms of ξ_1. Because of the linearity of the equations, these nine quantities will all be proportional to ξ_1. Further, because only a_{11} and b_1 depend on anything but the host lattice, the constants of proportionality between $\xi_2, \ldots, \xi_5, \mu_1, \ldots, \mu_5$, and ξ_1 will be characteristic of the host lattice and the sign of the electric charge on the defect. ξ_1 can then be found by substituting our solutions for $\xi_2, \ldots, \xi_5$ and $\mu_1, \ldots, \mu_5$ into the first line of Eq. (1). Thus, we have all the ξ_i and μ_i proportional to ξ_1. If the defect species is changed without changing its sign, ξ_1 will change and all the other ξ_i and μ_i will change with it in proportion.

One alternative way to express this is to say that all the ξ_i and μ_i are proportional to the fractional volume change $\Delta V/V$ associated with the defect. This is the case if, as for the DD model, $\Delta V/V$ can be written as a linear combination of ξ_i and μ_i.[11]

Now we have shown[12] that, within the DD model, all field gradient tensor components arising at various lattice sites because of the relaxation of the lattice around the defect can be written as linear combinations of the ξ_i and μ_i. The field gradient components, thus, are proportional to ξ_1 or $\Delta V/V$, say, for a sequence of anion (or cation) impurities in a given host lattice. According to this, the quadrupole coupling constant measured, say, at the (0,0,1) site relative to the impurity in NaF-Li, NaF-K, NaF-Rb plotted against $\Delta V/V$ for these defects should lie on a straight line intersecting the origin if the DD model were valid. Without measuring $\Delta V/V$ there is another way of checking the DD model. Consider lattice sites such as (1,0,1), for example, where the asymmetry parameter

$$\eta = (|V_{y'y'}| - |V_{x'x'}|)/|V_{z'z'}|$$

is not zero by the symmetry of the site. Being the ratio of field gradient components, η should be independent of impurity in a sequence of dilute mixed crystals with a common host and common sign of impurity ions such as that mentioned above.

EXPERIMENT

To check this prediction of the DD model, quadrupole coupling constants were measured in NaF-Li and NaF-K mixed crystals.

The first-order quadrupole splittings of the Na^{23} nuclei located at (1,0,1)- and (0,0,2)-type sites [relative to the impurity anion at the (0,0,0) coordinate] were experimentally determined by a high-field nuclear magnetic double-resonance technique.[10] Both crystals were grown from the melt using ultrapure NaF.[18] An atomic absorption analysis showed that the NaF-LiF crystal contained a ratio of 0.25% Li^+ ions to NaF molecules and that the NaF-KF crystal contained 0.036% K^+ ions to NaF molecules.[19] Both crystals were oriented such that the magnetic field was contained in a (100) plane. A rotation pattern for each first-order Na^{23} quadrupole shift was then generated by rotating the crystal about a ⟨100⟩ direction. All experiments were done at 77°K and were performed with identical experimental parameters.[10]

The first-order quadrupole splittings of the Na^{23} nuclei at (1,0,1)-type sites were found to be $e^2qQ/h = \pm(544\pm10)$ kHz and $e^2qQ/h = \pm(832\pm10)$ kHz for the Li^+ and K^+ anion impurities, respectively. The corresponding asymmetry parameters were $\eta = 0.65 \pm 0.05$ and 0.45 ± 0.05. The experimental data do not allow the specific assignment of a plus or minus sign to the first-order splittings due to the symmetry of the $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ and the $\frac{3}{2} \leftrightarrow \frac{1}{2}$ transitions about the central $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions. For the same reason, a single assignment of principal axes cannot be made. The experimental results showed that, for both crystals, the principal x', y', and z' axes for the (1,0,1)-type Na^{23} sites were directed either along the crystalline ⟨010⟩, ⟨$\bar{1}$01⟩, and ⟨101⟩ directions, respectively, or along the crystalline ⟨010⟩, ⟨101⟩, and ⟨10$\bar{1}$⟩ directions, respectively, in agreement with assumed symmetry.

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[18] The crystals were grown by F. Rosenberger, Department of Physics, University of Utah.

[19] This analysis was done by D. Barber, Engineering Experiment Station, University of Utah.

TABLE I. Quadrupole coupling parameters, asymmetry parameters, and electric field gradients in NaF-Li and NaF-K.

	Electric quadrupole (1,0,1) (10^{13} esu)		η (1,0,1)		Electric quadrupole (0,0,2) (10^{13} esu)	
Impurity	Expt	Calc[a]	Expt	Calc[a]	Expt	Calc[a]
Li^+	$\pm(1.36\pm0.03)$	-2.137	0.65 ± 0.05	0.705	$\pm(2.14\pm0.03)$	$+2.378$
K^+	$\pm(2.07\pm0.03)$	$+1.419$	0.45 ± 0.05	0.705	$\pm(3.79\pm0.03)$	-1.580

(1,0,1) crystalline electric field gradients

	$V_{z'z'}=V_{x'x'}=-\frac{1}{2}V_{y'y'}$ (10^{13} esu)		$V_{x'z'}$ (10^{13} esu)	
	Expt	Calc[a]	Expt	Calc[a]
Li^+	±0.119	-0.158	±1.24	-1.98
K^+	±0.285	$+0.105$	±1.78	$+1.31$
Electric-field-gradient absolute change from Li^+ to K^+ (sign change included)	0.404	0.263	3.02	3.29

[a] Using the method of Ref. 15.

The first-order quadrupole splittings of those Na^{23} nuclei at (0,0,2)-type sites were found to be $e^2qQ/h=\pm(856\pm10)$ kHz and $e^2qQ/h=\pm(1520\pm10)$ kHz for the Li^+ and K^+ anion impurities, respectively. The principal axes and the crystalline axes are the same due to the symmetry of the (0,0,2)-type sites and, consequently, the asymmetry parameter η is zero.

The data shown in Table I were obtained by assuming $Q=0.1\times10^{-24}$ cm^2,[20] and an antishielding factor of $1-\gamma_\infty=5.53$.[21]

DISCUSSION

It is seen that the predictions of the DD model are in conflict with experiment for NaF-Li and NaF-K taken together.

From this we must conclude that the DD model as used in Ref. 15 is inadequate for calculating quadrupole coupling constants in dilute mixed crystals. This failure may indicate:

(1) The defect perturbs the crystal in a more extensive way than just altering the repulsion of the defect and its nearest neighbors.

(2) It may be inadequate to find the displacements and dipoles by keeping only linear terms in the derivatives of the energy which are set equal to zero. [Equation (1) was derived in this way.]

(3) The electric field gradients at the nuclei may not be linearly related to the ξ_i and μ_i. This is what happens when wave-function distortions other than those involved in electronic polarization come into play. Ikenberry and Das[17] have treated such distortions, but their treatment does not yet yield satisfactory agreement with experiment in the case of anion impurities.

Going to more neighbors in a DD model does not alter the model's prediction of constant η at sites where $\eta\neq0$ in a sequence of anion (or cation) impurities in a common host crystal. Thus, going to more neighbors cannot rescue a DD model.

Lithium has become an interesting impurity in alkali halides since, in KCl, it occupies an off-lattice-site position.[22] It is not known whether this happens in NaF. However, if Li^+ did occupy an off-center location in NaF such as to give an electric dipole moment of the order of that which it has in KCl, then there would be field gradients in the vicinity of the Li^+ approximately 4 orders of magnitude greater than those observed. Furthermore, evidence in KCl-Li indicates that at 77°K, thermal motion averages out the effects of the off-center dipole. We see no experimental evidence which would indicate Li^+ is off center in NaF.

Note added in proof. The validity criterion discussed in this paper has been pointed out previously by A. Hartland [Proc. Roy. Soc. (London) **A304**, 361 (1968)]. We are grateful to Dr. L. O. Andersson for drawing this fact to our attention.

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