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Lattice Dynamics of Alkali Halide Crystals. III. Theoretical

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The "shell model" of an alkali halide is extended to take into account short-range forces between both first- and second-nearest neighbor atoms in the crystal, the polarizability of both ions, and the possibility that the ionic charge may be less than one electronic charge. The arbitrary parameters of the model have been obtained by means of a least-squares fit to the measured dispersion relations for the lattice vibrations, the dielectric constants, and the elastic constants. For NaI and KBr, models have been found which give excellent agreement both with these measurements and with measurements of the specific heat. This good agreement is, however, obtained only when the simple shell-model concept of the ions is to some extent abandoned. The reasons for this, and the connection with work of other authors, are discussed.

I. INTRODUCTION

IN earlier papers of this series, we described[1,2] experimental studies of the lattice vibrations in sodium iodide and in potassium bromide, carried out using the technique of neutron spectrometry. It was shown that the well-known rigid ion model,[3] originally due to Born, was inadequate to explain the experimental measurements. When, however, the polarizability of the negative ion was taken into account by using the "shell-model" formalism, greatly improved agreement with experiment was obtained though important discrepancies remained.

In this paper, we present computations based on more complicated shell models, which include the effects of (a) short-range interactions between second as well as first nearest neighbors, (b) arbitrary ionic charge, and (c) the polarizability of positive, as well as of negative, ions. With the more complicated models extremely good agreement was obtained with the neutron measurements, with the elastic and dielectric constants, and with the measured specific heat.

Although the shell-model formalism has been used throughout, the parameters obtained for the best models cannot be given a reasonable physical interpretation on this basis. We discuss later whether this may be an inadequacy of the dipolar approximation, to which the shell model is equivalent. Detailed comparisons are made with the methods of Tolpygo *et al.*[4] and of Hardy,[5] which also involve the dipolar approximation.

II. THEORY AND RESULTS

1. Basic Theory of the Models

The model, used in the preceding papers,[1,2] includes central short range forces between nearest neighbors, Coulomb forces between all the ions, and allows the negative ion to become polarized during the lattice vibrations. The three arbitrary parameters are then determined by the dielectric constants and one elastic constant. A brief discussion of the basic theory will be given before discussing the parameters required to specify more complicated models.

For crystals in which the energies of the electronic transitions are much larger than the energies of the lattice vibrations, as is the case for the alkali halides, the well known adiabatic, harmonic and electrostatic approximations to the equations of motion are adequate. When the ions are displaced, the forces between them are calculated from the change in the potential energy of the crystal. This change arises in part from the distortion of the electronic wave functions, the energy of which is calculated from the electric moments produced on the ions. The shell model is a first approximation, in which only the dipole moments are included, and these are placed at the centers of the ions. Six degrees of freedom, three from the displacement, and three from the dipole moment, are now associated with each ion in the crystal and, in general, there will be coupling between all of them. The forces are calculated by dividing the interactions into (a) long-range Coulomb forces between point dipoles; these are calculated using the dimensionless coefficients introduced by Kellermann,[6] and (b) short-range repulsive forces between neighboring ions. The equations of motion are then, in matrix notation,

$$\mathbf{m}\omega^2\mathbf{U}=(\mathbf{R}+\mathbf{ZCZ})\mathbf{U}+(\mathbf{T}+\mathbf{ZCY})\mathbf{W}, \tag{1}$$

$$0=(\mathbf{T}^T+\mathbf{YCZ})\mathbf{U}+(\mathbf{S}+\mathbf{YCY})\mathbf{W}. \tag{2}$$

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

[2] A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, preceding paper, Phys. Rev. **131**, 1025 (1963).

[3] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. II.

[4] V. S. Mashkevich and K. B. Tolpygo, Zh. Eksperim. i Teor. Fiz. **32**, 520 (1957) [translation: Soviet Phys.—JETP **5**, 435 (1957)]. Further references are given here.

[5] J. R. Hardy, Phil. Mag. 4, 1278 (1959); **6**, 27 (1961); **7**, 315 (1962); see also J. R. Hardy and A. M. Karo, *ibid.* **5**, 859 (1960).

[6] E. W. Kellermann, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

R, **T**, **S** are the matrices specifying the short-range interactions, while **C** is the matrix of Coulomb coefficients. ($\mathbf{T}^T$ is the transpose of **T**.) **m**, **Z**, and **Y** are diagonal matrices representing the mass, ionic charge, and the charge on the shells. **U** and **W** are vectors; **U** is the amplitude of the displacements of the ions, while **YW** is the electronic dipole moment on the ions.[7]

The number of independent parameters in the theory is most easily discussed by considering a wave propagating in a symmetry direction. The interaction matrices are then of dimension (2×2), and can be written[1] in the form

$$\begin{pmatrix} R_{11}+Z_1^2C_{11} & R_{12}+Z_1Z_2C_{12} \\ R_{21}+Z_1Z_2C_{21} & R_{22}+Z_2^2C_{22} \end{pmatrix}, \tag{3}$$

$$\begin{pmatrix} T_{11}+Z_1Y_1C_{11} & T_{12}+Z_1Y_2C_{12} \\ T_{21}+Z_2Y_1C_{21} & T_{22}+Z_2Y_2C_{22} \end{pmatrix}, \tag{4}$$

$$\begin{pmatrix} T_{11}+k_1+Y_1^2C_{11} & S_{12}+Y_1Y_2C_{12} \\ S_{21}+Y_1Y_2C_{21} & T_{22}+k_2+Y_2^2C_{22} \end{pmatrix}. \tag{5}$$

It is convenient to express the equations in terms of quantities which are more physically meaningful than the core-shell force constant k and shell charges Y. These quantities are the electrical polarizabilities of the ions,

$$\alpha_1=\frac{Y_1^2}{k_1+(T_{11})_0}, \quad \alpha_2=\frac{Y_2^2}{k_2+(T_{22})_0}, \tag{6}$$

and the short range or mechanical polarizabilities,

$$d_1=-\frac{(T_{11})_0Y_1}{k_1+(T_{11})_0}, \quad d_2=-\frac{(T_{22})_0Y_2}{k_2+(T_{22})_0}. \tag{7}$$

The expression $(T_{11})_0$ is the matrix element T_{11} when the wave vector, **q**, is zero. The invariance of the crystal under translations requires,

$$\begin{aligned} (R_{11})_0&=(R_{22})_0=-(R_{12})_0=-(R_{21})_0, \\ (T_{11})_0&=-(T_{21})_0, \\ (T_{22})_0&=-(T_{12})_0. \end{aligned} \tag{8}$$

Since both the charges, **Y**, on a shell and the displacements, **W**, have been introduced to specify one physical quantity per ion, viz., its electronic dipole moment, there are two parameters which are not independent. We have, therefore, chosen to set

$$(T_{11})_0=(T_{22})_0=(R_{11})_0. \tag{9}$$

Two parameters are needed to specify the nearest neighbor short-range forces and three for the second neighbor forces between the negative ions. In general, these parameters will be different for the different types of short-range interaction, **R**, **T**, and **S**, subject to the restrictions imposed by Eq. (9). Fifteen independent parameters are needed to specify these forces and so physically reasonable assumptions were sought which would reduce this number.

The **R** and **T** matrices were chosen to be identical at $\mathbf{q}=0$ [Eqs. (8) and (9)]. We now further assume that they are the same for all wave numbers. The **S** matrix is also assumed to be of the form $\mathbf{S}=\gamma_s\mathbf{R}$, where γ_s is a constant. Although there is no complete justification for the above assumptions, they appear plausible from the shell-model point of view. The polarizability arises from the relative motion of the outer electrons and in a shell model these motions are represented by the motion of the shells. The short-range interaction is expected to act mainly through these outer electrons, and the above approximation, together with the assumption that $\gamma_s=1$, are equivalent to assuming that all the short-range interaction acts through the shells. The validity of this approach will be further discussed in Sec. III 2.

The short-range interactions may now be calculated in terms of the derivatives introduced in the earlier paper.[1] Nearest neighbor forces are specified by

$$\left(\frac{\partial^2V_{12}}{\partial r^2}\right)_{\parallel}=\frac{e^2A}{2v}, \quad \left(\frac{\partial^2V_{12}}{\partial r^2}\right)_{\perp}=\frac{e^2(B+B'')}{2v}, \tag{10}$$

where B is defined by

$$\frac{1}{r}\left(\frac{\partial V}{\partial r}\right)_{\parallel}=\frac{e^2B}{2v},$$

and $B''=0$ if the forces are central forces. The second-nearest neighbor forces were assumed to be specified by two parameters. These were defined by

$$\left(\frac{\partial^2V_{22}}{\partial r^2}\right)_{\parallel}=\frac{e^2A'}{2v}, \quad \left(\frac{\partial^2V_{22}}{\partial r^2}\right)_{\perp}=\frac{e^2B'}{2v}. \tag{11}$$

B and B' were then related by the equilibrium condition

$$B+2B'=-\tfrac{2}{3}\alpha_MZ^2,$$

where α_M is the Madelung constant.

As simplified above, the model now has ten arbitrary parameters; five short-range force parameters, A, B'', $A'B'$, γ_s, two crystal polarizabilities α_1, α_2, two short range polarizabilities d_1, d_2, and the ionic charge, Z. In fact, we found that quite large changes in the parameter γ_s had little effect on the results, and we set $\gamma_s=1$ throughout the final iterations. The model then corresponds physically to polarizable atoms with a short-range interaction extending to second-nearest neighbors but involving only the outer electrons. Models which involve the various possible combinations of these parameters were fitted by a nonlinear least-squares analysis to the dispersion relations in symmetry directions,[2] and to the experimental measurements of the

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[7] W. Cochran, in *Advances in Physics,* edited by N. F. Mott (Taylor and Francis Ltd., London, 1961), Vol. 10, p. 401.

TABLE I. The parameters involved in each model. F represents a parameter which was allowed to vary during the least-squares fitting analysis.

Model	Short-range forces: Nearest neighbors A	Short-range forces: Nearest neighbors B''	Short-range forces: Second-nearest neighbor A'	Short-range forces: Second-nearest neighbor B'	Ionic charge Z	Electrical polarizability positive ion α_1	Electrical polarizability negative ion α_2	Short-range polarizability positive ion d_1	Short-range polarizability negative ion d_2
I	F	0	0	0	1	0	F	0	F
II	F	F	F	F	1	C^{a}	F	0	F
III	F	F	F	F	F	C^{a}	F	0	F
IV	F	F	F	F	F	F	F	$\alpha_1 d_2/\alpha_2$	F
V	F	F	F	F	F	C^{a}	F	F	F
VI	F	F	F	F	F	F	F	F	F

[a] C denotes the crystal polarizability, which was taken from a compilation by Born and Huang (see Ref. 10). (For KBr, $\alpha_1 = 1.13$; for NaI, $\alpha_1 = 0.28$.)

TABLE II. The results of the least-squares analysis for potassium bromide at 90°K.

Model	Short-range forces (units $e^2/2v$): Nearest neighbors A	Nearest neighbors B''	Second-nearest neighbors A'	Second-nearest neighbors B'	Ionic charge Units electronic charge Z	Electrical polarizability (10^{-24} cm^3) Positive α_1	Electrical polarizability Negative α_2	Short-range polarizability (electronic charge) Positive d_1	Short-range polarizability Negative d_2	Ratio of error of model to estimated experimental error
I	13.15 ± 0.36						5.21 ± 0.77		0.301 ± 0.093	55
II	13.61 ± 0.08	-0.064 ± 0.053	-0.496 ± 0.076	-0.079 ± 0.048			3.98 ± 0.17		0.244 ± 0.019	2.15
III	12.30 ± 0.17	-0.054 ± 0.031	-0.091 ± 0.067	-0.042 ± 0.031	0.896 ± 0.014		3.81 ± 0.11		0.187 ± 0.014	0.71
IV	11.74 ± 0.34	-0.055 ± 0.042	0.078 ± 0.117	-0.183 ± 0.075	0.832 ± 0.035	1.05 ± 0.35	3.70 ± 0.39		0.192 ± 0.023	1.22
V	13.21 ± 0.41	-0.011 ± 0.027	-0.411 ± 0.152	0.046 ± 0.029	0.969 ± 0.028		3.92 ± 0.09	-0.076 ± 0.027	0.186 ± 0.014	0.50
VI	13.15 ± 0.27	-0.034 ± 0.021	-0.399 ± 0.101	0.054 ± 0.027	0.965 ± 0.020	2.12 ± 0.21	3.05 ± 0.20	-0.101 ± 0.20	0.141 ± 0.014	0.28

TABLE III. The results of the least-squares analysis for sodium iodide at 100°K.

Models	Short-range forces (units $e^2/2v$): Nearest neighbors A	Nearest neighbors B''	Second-nearest neighbors A'	Second-nearest neighbors B'	Ionic charge (electronic charge) Z	Electrical polarizability (10^{-24} cm^3) Positive α_1	Electrical polarizability Negative α_2	Short-range polarizability (electronic charge) Positive d_1	Short-range polarizability Negative d_2	Ratio of error of model to estimated experimental error
I	11.43 ± 0.12						6.59 ± 0.39		0.322 ± 0.037	15.4
II	11.12 ± 0.18	-0.171 ± 0.213	0.440 ± 0.287	0.037 ± 0.150			6.30 ± 0.36		0.315 ± 0.033	11.0
III	8.93 ± 0.25	-0.102 ± 0.110	1.058 ± 0.157	-0.164 ± 0.077	0.806 ± 0.023		5.87 ± 0.20		0.201 ± 0.024	2.92
IV	7.77 ± 0.19	-0.051 ± 0.076	1.33 ± 0.112	-0.371 ± 0.061	0.662 ± 0.02	2.74 ± 0.33	3.30 ± 0.28		0.116 ± 0.027	1.40
VI	9.94 ± 1.03	-0.026 ± 0.068	0.618 ± 0.379	-0.041 ± 0.064	0.890 ± 0.077	1.98 ± 0.32	4.34 ± 0.14	-0.112 ± 0.076	0.136 ± 0.021	0.97

elastic[8,9] and dielectric constants[10] of sodium iodide and potassium bromide.

The numerical work was performed using the Edsac II computer at the Cambridge University Mathematical Laboratory.

2. The Results of the Fitting

The parameters of the models, which were obtained by the least-squares analysis described in the previous section, are summarized in Tables I, II, and III. Table I lists some of the models which were used, and specifies the parameters which were allowed to refine in each model. Tables II and III present the results of the computations for potassium bromide and sodium iodide, respectively. The error of a model is the weighted sum of squares of the deviations from the experimental measurements, and this is compared with the estimated experimental error. The more striking features of some of the models are described in this section.

a. Model I

Model I, the simplest, was used previously[1,2]; only the negative ion is polarizable, and only central nearest neighbor short-range forces are included. The iterations gave results very similar to those obtained when the three parameters were fitted to the dielectric and elastic constants, as described in the companion paper.[2] The error is 16 times the estimated experimental error for

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[8] R. N. Claytor and B. J. Marshall, Phys. Rev. **120**, 332 (1960).

[9] J. K. Galt, Phys. Rev. **73**, 1460 (1948).

[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Table 17, p. 85.

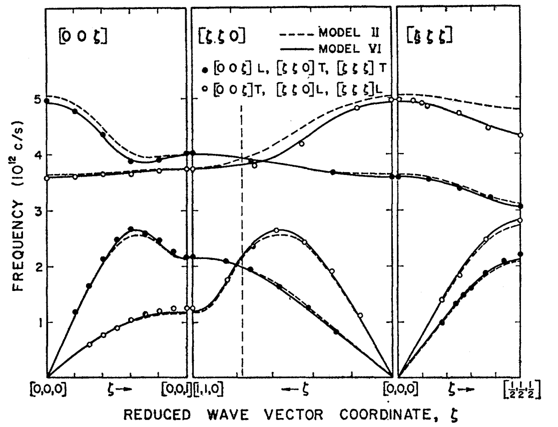

FIG. 1. The dispersion relations for potassium bromide in the $[00\zeta]$, $[\zeta\zeta 0]$, and $[\zeta\zeta\zeta]$ directions at 90°K. The dashed curves have been calculated using Model II and the solid curves using Model VI.

sodium iodide and 54 times for potassium bromide. The error for potassium bromide largely comes from a 25% error in the elastic constants c_{12} and c_{44}. The dispersion curves for these models are substantially similar to those shown in Figs. 1 and 2 of Ref. 2, and considerable discrepancies are observed, particularly for the longitudinal optic branches.

b. Model II

The inclusion of second neighbor forces, and noncentral first neighbor forces considerably improves the model; the error for potassium bromide is now reduced to only $2\frac{1}{2}$ times the estimated experimental error, though for sodium iodide, it is still 10 times the experimental error. Good agreement is obtained with the elastic constants, but the dispersion curves still show considerable discrepancies, Figs. 1 and 2.

c. Model III

The ionic charge was included as a variable parameter in this model and a considerable decrease in the error resulted; a factor of three decrease for potassium bromide and of four for sodium iodide. The elastic constants are in good agreement with experiment and the agreement with the dispersion curves is considerably improved. The parameters of the models have now changed considerably; the nearest neighbor forces are reduced by 10% for potassium bromide, and by 20% for sodium iodide, while the ionic charges are suspiciously low, 0.9 and 0.8 electronic charges, respectively.

d. Model IV

The polarizability of the positive ion was introduced in three different ways. Hanlon and Lawson[11] have suggested that the charge on a shell is the same for both atoms. In the present notation this leads to $\alpha_1/\alpha_2 = d_1/d_2$. The electrical polarizability of the positive ion, α_1, was treated as a parameter while d_1 was determined from the above relation. This resulted in the ionic charge being still further decreased, to 0.83 for potassium bromide and to 0.66 for sodium iodide. The electrical polarizability α_1 turned out to be almost exactly the crystal polarizability quoted by Born and Huang[9] for potassium bromide, but considerably larger than the value quoted for sodium iodide. The fitting error for sodium iodide was slightly lower than for Model III, but for potassium bromide, it was rather larger, even though Model III has one less arbitrary parameter.

e. Model V

An alternative way of introducing the positive ion polarizability is to fix the electrical polarizability of the positive ion to its quoted value,[10] and to allow the parameter d_1 to vary. This gives very good agreement with experiment; for potassium bromide the error turns out to be just half the experimental error. The ionic charge was 0.97 for potassium bromide, and the nearest neighbor forces increased correspondingly. The short-range polarizability of the positive ion was, surprisingly, negative. For sodium iodide the model was substantially the same as Model III.

f. Model VI

The best agreement with experiment was obtained when all the parameters were allowed to vary; the excellent agreement obtained with the experimental dispersion curves in symmetry directions is shown in Figs. 1 and 2 and the agreement with the experimental elastic and dielectric constants is shown in Table IV. The error is only one quarter of the estimated experimental error for potassium bromide and just equal to

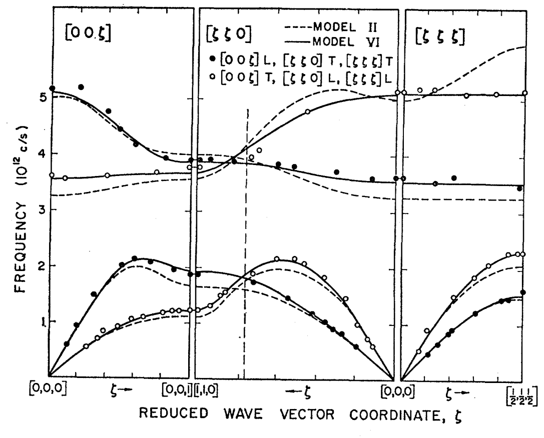

FIG. 2. The dispersion relations for sodium iodide in the $[00\zeta]$, $[\zeta\zeta 0]$, and $[\zeta\zeta\zeta]$ directions at 100°K. The dashed curves have been calculated using Model II and the solid curves using Model VI.

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[11] J. E. Hanlon and A. W. Lawson, Phys. Rev. **113**, 472 (1959).

TABLE IV. The dielectric and elastic constants, polarizability of the ions and volume of the unit cell for potassium bromide and sodium iodide. The experimental measurements are compared with those calculated using Model VI.

	Potassium bromide		Sodium iodide		
	Experimental	Model (VI)	Experimental	Model (VI)	Remarks
Elastic constants (10^{12} dyn/cm^2)					The elastic constants and high-frequency dielectric constant were used as experimental observations for the fitting and weighted by their estimated experimental errors. The experimental values were taken from Refs. 8–10.
C_{11}	0.398	0.398	0.353	0.353	
C_{12}	0.056	0.0552	0.0825	0.0797	
C_{44}	0.052	0.052	0.0767	0.0767	
High frequency dielectric constant					
ϵ	2.33	2.33	2.91	2.85	
Polarizability of the ions (10^{-24} cm^3)					These were parameters of the model and the experimental values were taken from Ref. 10.
α_1	1.13	2.12	0.28	1.98	
α_2	4.12	3.05	6.41	4.34	
Volume of unit cell (10^{-24} cm^3)					Refs. 10 and 14.
$v=2r_0^3$	70.4		66.0		

it for sodium iodide. However, the short-range polarizability of the positive ions turned out to be negative for both potassium bromide and sodium iodide, and the electrical polarizability of the same ions was larger than the crystal polarizability.[10]

The second neighbor short-range forces of potassium bromide are attractive. If we assume a potential of the form C/r^n, then C and n may be calculated from the second neighbor parameters A' and B'. Reasonable agreement is obtained with the expected size of Van der Waals forces. For sodium iodide the second neighbor forces are repulsive and about 7% of the nearest neighbor forces. The repulsion presumably arises from the overlap of the iodine ion wave functions; the ionic radii[10] suggest that this is likely.

The agreement with experiment is more satisfactory for potassium bromide than for sodium iodide. This is probably in part due to the greater difficulty in performing the experiments on sodium iodide, as described in the companion paper,[2] but it is also likely that the model is more satisfactory for those alkali halides for which the ions do not differ too greatly in size or polarizability.

Some of the models have been fitted to the potassium bromide measurements at 400°K, and the results are tabulated in Table V. The same general tendencies were present as at 90°K but the nearest neighbor forces were reduced by nearly 10%.

3. Calculations Using the Models

The models described above were fitted to give extremely good agreement with the experimental measurements of the dispersion curves of the normal modes in symmetry directions, of the elastic constants, and of the dielectric constants of potassium bromide and sodium iodide. A test of these models is whether they give as good agreement with independent experimental measurements of other quantities.

a. The Lattice Vibrations in Off-Symmetry Directions

Measurements of the frequencies of the normal modes in off-symmetry directions were described in the companion paper.[2] Figure 3 shows the excellent agreement with calculations of these frequencies from the models. The calculated frequencies appear to be even less sensitive to the details of the models than are the frequencies in the symmetry directions, and do not give good evidence in favor of any particular model.

TABLE V. The results of the least squares analysis for potassium bromide at 400°K.

	Short-range forces (units $e^2/2v$)				Ionic charge (electronic charge)	Electrical polarizability (10^{-24} cm^3)		Short-range polarizability (electronic charge)		Ratio of error of model to estimated experimental error
	Nearest neighbors		Second nearest neighbors			Positive	Negative	Positive	Negative	
Model	A	B''	A	B'	Z	α_1	α_2	d_1	d_2	
I	11.96±0.32						5.34±0.95		0.322±0.119	41.7
II	12.57±0.98	0.092±0.070	−0.653±0.099	−0.061±0.063					0.283±0.030	2.21
III	11.10±0.31	−0.086±0.053	−0.171±0.121	−0.173±0.052	0.888±0.025		4.05±0.19		0.225±0.027	1.27
IV	11.29±0.43	−0.088±0.062	−0.224±0.158	−0.140±0.093	0.905±0.040	0.07±0.43	5.06±0.53		0.265±0.035	1.65
V	11.88±0.11	−0.079±0.052	−0.433±0.40	−0.088±0.053	0.951±0.072		4.36±0.20	−0.058±0.072	0.236±0.037	1.12
VI	12.30±0.84	−0.069±0.048	−0.590±0.302	−0.065±0.057	0.979±0.058	2.21±0.50	3.25±0.49	−0.124±0.06	0.180±0.038	0.88

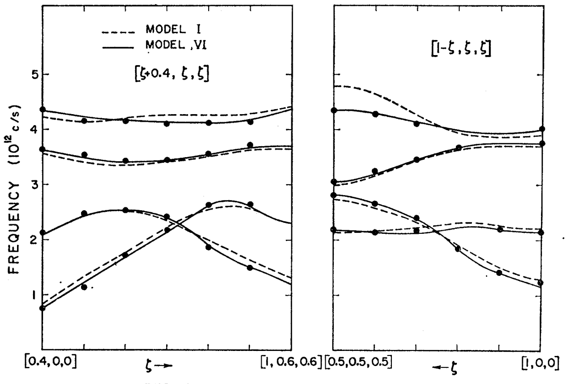


FIG. 3. The dispersion relations for two off-symmetry directions in potassium bromide at 90°K. The dashed curves have been calculated using Model I and the solid curves using Model VI.

b. The Specific Heat and the Frequency Distribution

Before the advent of inelastic neutron scattering techniques, nearly all detailed lattice dynamical calculations were directed towards calculating the specific heat of the crystal. The specific heat and frequency distributions of various models have been calculated using the Datatron computer at Chalk River. The frequencies of the normal modes were calculated at the 47 independent points in reciprocal space, for which Kellermann[6] has calculated the Coulomb coefficients. In the region near $\mathbf{q}=0$, the frequency distribution was calculated as a Debye function, so as to obtain the correct behavior of the specific heat at very low temperatures. The Debye temperature at 0°K, was then the Debye temperature of this small element, and was calculated from the model elastic constants using the method and table of de Launay.[12] The Debye function was taken from a table of Beattie.[13]

The specific heats of various models of potassium bromide and sodium iodide at 100°K are tabulated in Table VI together with the experimental measurements of Berg and Morrison.[14] The frequency distributions of the best models are shown in Fig. 4, and the temperature dependence of the Debye temperature in Fig. 5.

TABLE VI. The specific heat (cal/g atom) for several models of potassium bromide and sodium iodide at 100°K.

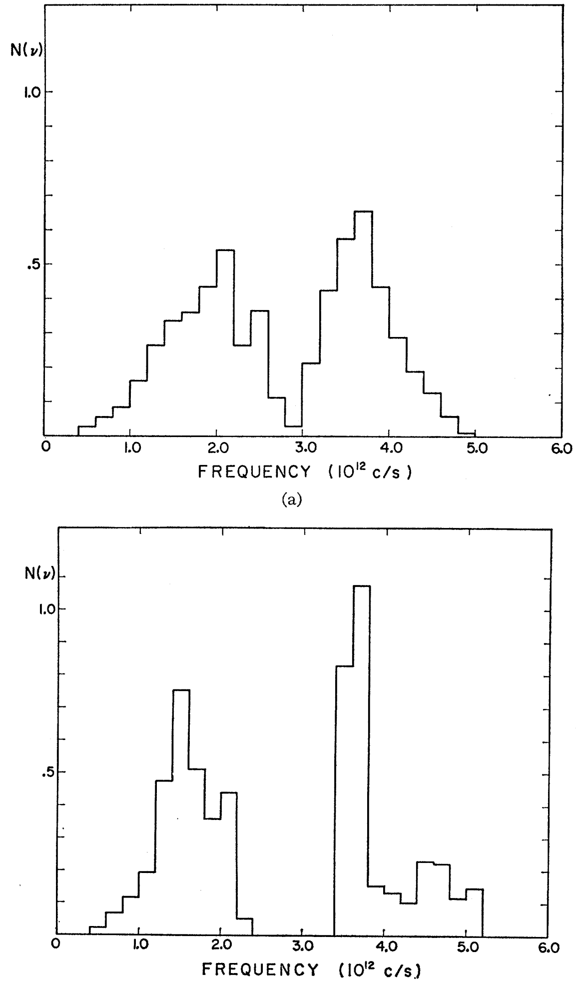
Model	KBr	NaI
I	5.0435	5.0474
II	5.0519	5.0867
III	5.0848	5.0773
VI	5.0811	5.0665
Experimental[a]	5.0755	5.0465

[a] See Ref. 14.

It is very difficult to estimate the error in calculating the frequency distributions and specific heats; the Debye temperature is probably accurate to 3°K, but the finer structure of the frequency distribution is probably not significant.

At temperatures other than 90°K for potassium bromide and other than 100°K for sodium iodide, a correction should be applied to the Debye temperatures for the change in frequency distribution with temperature. An estimate of this correction can be obtained from the temperature dependence of the elastic constants, and the correction increases the calculated Debye temperature by about 4°K at low temperatures. For potassium bromide the theoretical and experimental curves are then within 2.5°K of each other, which is well within the error of the calculations.

When this correction is applied, the curves for sodium iodide are also in good agreement above 4°K. Below 4°K the calculated Debye temperature is larger than



(a)

(b)

FIG. 4. The frequency distribution calculated using Model VI of (a) potassium bromide at 90°K, (b) sodium iodide at 100°K.

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[12] J. de Launay, J. Chem. Phys. **30**, 91 (1959).

[13] J. A. Beattie, J. Math. Phys. **6**, 1 (1926–7).

[14] W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **242**, 467 (1957).

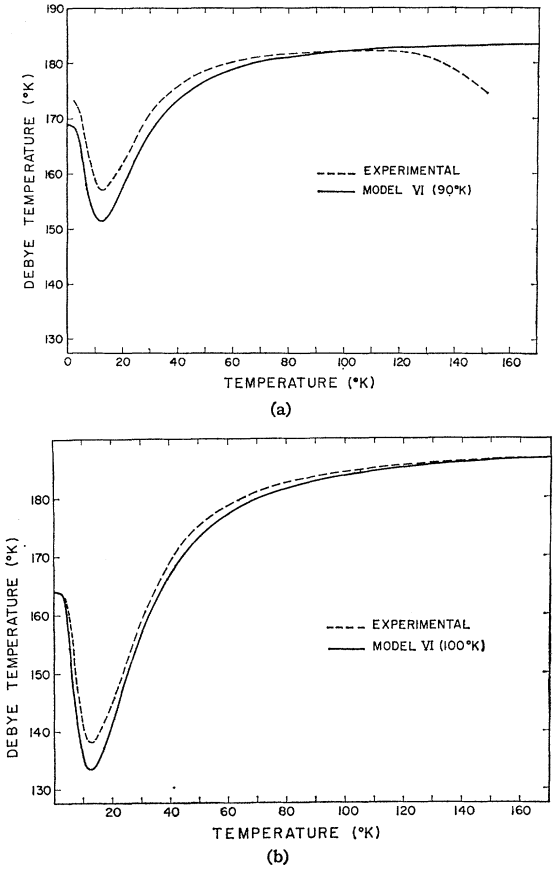

FIG. 5. (a) The specific heat of potassium bromide. The dashed line shows the Debye temperature determined experimentally by Berg and Morrison and the solid line calculations using Model VI. (b) The specific heat of sodium iodide. The dashed line shows the Debye temperature determined experimentally by Berg and Morrison and the solid line calculations using Model VI.

the experimental; this arises because the low temperature specific heat and elastic constants give different[8] Debye temperatures at 0°K, by 4.4±2°K. Ludwig and Leibfried[15] have shown that anharmonic effects may possibly explain this.

c. Cohesive Energy

Very good agreement with the experimental cohesive energies of alkali halides has been obtained by using a rigid ion model of the crystal.[3] By far the largest contribution is the Madelung electrostatic energy, which is proportional to the square of the ionic charge. However, this good agreement does not prove conclusively that the ions are fully charged. For example, when the theory is applied to Wurtzite and similar crystals whose ionic charges are almost certainly much less than two, the value used in the calculations, quite good agreement with experiment is also obtained.

Quantum-mechanical calculations[16,17] of the cohesive energy give the electrostatic energy as the sum of three terms: the Madelung energy, a term from the repulsion of the electrons, and a term from the attraction of the electrons and the nuclei. Although the last two terms are quite large, they are of opposite sign and hardly contribute to the cohesive energy, but it is by no means obvious that these two terms will cancel when the forces in the crystal are calculated.

The cohesive energy of the models has been calculated by representing the nearest-neighbor short-range forces by a potential C/r^n, where C and n have been calculated from the parameters A and B. Table VII shows the experimental and theoretical cohesive energies for a number of models. Good agreement is obtained for the models whose ionic charge is one or nearly one, but for the other models the results are significantly lower than the experimental measurements. (The change in cohesive energy between 0°K and the model temperatures and the neglect of the zero point energy are small compared with the errors of the calculations.)

TABLE VII. The cohesive energy (kcal/g mole) for several models of potassium bromide and sodium iodide.

Model	KBr	NaI
Experimental[a]	156.2	166.4
I	165.5±5	167.5±5
II	171.2±5	165.3±5
III	137.2±10	122.5±10
VI	154.5±10	136.5±10

[a] Reference 14.

III. DISCUSSION

1. Models Used by Other Authors

In the previous papers,[1,2] a rigid ion model was shown to be inadequate to describe the lattice dynamics of sodium iodide and potassium bromide. The electrical polarizability of the ions was included by Lyddane and Herzfeld[18] and Lundquist *et al.*,[19] and the importance of including the interaction between the polarizability and the short range forces was emphasized by Szigeti.[20]

Detailed calculations based on models which include both electrical and short range polarizability have been made by Hardy.[5] The equations of motion which he uses are the same as Eqs. (1) and (2) apart from the neglect of a term $\mathbf{T}\mathbf{S}^{-1}\mathbf{T}^T$ (see Appendix). This term

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takes account of the short range interaction on an ion by the neighboring dipoles and the present authors can see no justification for neglecting it. The short-range forces specifying the **S** matrix are also simplified and in our notation the matrix reduces in symmetry directions to

$$\mathbf{S}=\begin{pmatrix} k_1 & 0 \\ 0 & k_2 \end{pmatrix}. \tag{12}$$

Detailed calculations have been made for sodium and potassium chlorides using a model which is equivalent to our model I, except that in our notation the **R** and **T** matrices were not assumed to be identical for all wave vectors, although they are at $\mathbf{q}=0$ [Eqs. (8) and (9)].

Detailed calculations on sodium iodide and potassium bromide have been made by Tolpygo and coworkers.[22,23] Their theory is identical with ours, apart from the neglect of short range dipole-dipole forces; i.e., the **S** matrix is written as in Eq. (12). In the detailed applications the **R** matrix was not assumed to be identical with the **T** matrix, and the models include the effects of first and second-neighbor short-range forces, the electrical polarizability of both ions and the short-range polarizability of the negative ion. The results they obtain are similar to these given by our models II and III. The theories and notations used by these authors are further compared with ours in the Appendix.

2. The Approximation $\mathbf{R}=\mathbf{T}$

The parameters which we used to describe the models allow us to choose $\mathbf{R}=\mathbf{T}$ at $\mathbf{q}=0$. We have then made the further assumption that $\mathbf{R}=\mathbf{T}$ for all wave vectors. This assumption has not been made in the detailed calculations of Hardy *et al.*,[5] or of Tolpygo *et al.*,[4] and its only justification lies in the simple description of the ions by the shell model as outlined above. The surprising polarizability parameters of the best models suggest that a simple shell-model description is unrealistic and so the validity of the approximation must be further discussed.

The short-range force constants between the ions depend on the overlap of the ground state wave functions of the ions, while the forces between the dipoles and the ions represented by the **T** matrix, depend on the overlap of the ground-state wave functions of one ion with the excited states of the other. Tolpygo *et al.*[23] suggest that if we introduce short-range force constants A_{I}, A_{II}, B_{I}, B_{II}, specifying the **T** matrix, analogously to those introduced in Sec. II.1 and as detailed in the Appendix, then we expect

$$\left|\frac{A_{\mathrm{I}}}{B_{\mathrm{I}}}\right|<\left|\frac{A}{B}\right|,\quad \left|\frac{A_{\mathrm{II}}}{B_{\mathrm{II}}}\right|<\left|\frac{A}{B}\right|.$$

A more quantitative estimate is given by an argument originally due to Dick and Overhauser.[24] The parameters A_{I}, A_{II}, B_{I}, B_{II} can be used to describe the dipole moment associated with a short-range force in the crystal. It is suggested that this dipole moment is proportional to the square of the overlap integral S and further that $S^2 \propto rV(r)$, where r is the distance between the ions and $V(r)$ the short-range potential. If $V(r)=C/r^n$, then $|A_{\mathrm{I}}/B_{\mathrm{I}}|=|A_{\mathrm{II}}/B_{\mathrm{II}}|=n-1$, while $|A/B|=n+1$. The difference between the parameters of the **T** matrix obtained from these relations, and the assumptions which we made is quite small, and the changes in the frequencies of the lattice vibrations are correspondingly very small.

3. The Failure of the Simple Shell Model

The best agreement with experiment is given by models which give surprising polarizabilities to the ions: The short-range polarizability of the positive ions, d_1, is negative, and the electrical polarizability is shared between the two ions more than expected. Equations (7), (8), and (9) show that the negative short-range polarizability implies a positively charged shell and this is clearly unrealistic. However, it should be emphasized that particular charges on the shells are simply a mathematical consequence of the method used to eliminate the two arbitrary parameters in the equations of motion, in this case by using Eq. (9). If we rewrite this equation $(T_{11})_0=-(T_{22})_0=-(R_{11})_0$, then the charges on the shells are negative, but the short-range forces cannot be readily understood in terms of a shell model. These unexpected results occur only in models which give a good fit to the $[\zeta\zeta\zeta]$ zone-boundary frequencies, while keeping the ionic charge reasonably large.

Figure 6 pictures a two-dimensional analog of the motion of the ions in the zone boundary mode for which $\mathbf{q}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})(2\pi/a)$. In the longitudinal optic mode, with this wave vector, planes of positive ions move while the planes of negative ions remain fixed. Figure 6 shows a possible arrangement of dipoles produced on the negative ions, B, by the motion of the rigid positive ions, A. The frequency of this mode of vibration will clearly depend on these dipoles, but in the shell model or dipole approximation, no distortion of the negative ions occurs in this mode of vibration.

The distortions are not neglected, if instead of summing the dipoles over the negative ions, we sum them over the positive ions. In the shell-model formalism, this is achieved by associating a considerable part of the polarizability with the positive ion. The arrows, showing the direction of motion of the electrons in Fig. 6, indicate that the motions of the electrons under short-range forces are opposite to the expected motion of a shell on the positive ion. The short-range polarizability is, therefore, negative while the electrical polarizability

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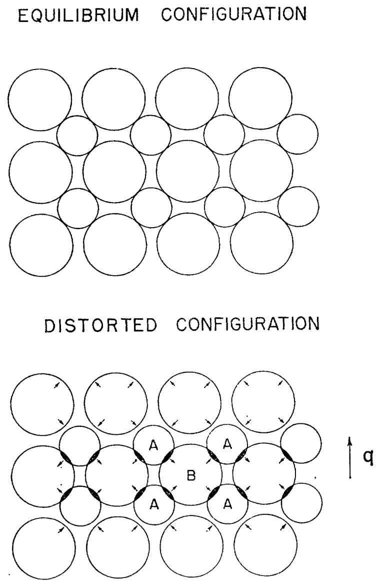

FIG. 6. A two-dimensional analog of the motion of the atoms in the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ longitudinal optic mode of vibration, in which alternate planes of positive ions move in opposite directions. The negative ions are labeled B and the positive ions A, while the arrows show the direction of motion of the electrons of the negative ions.

is fairly equally shared between the ions. These unexpected parameters are, therefore, required to describe adequately this mode.

The model could possibly be improved so as to describe the above phenomenon more realistically. The multiple dipoles on ions B, Fig. 6, are equivalent to quadrupole moments on the negative ions. The equations of motion of the model can be easily extended to include quadrupole moments produced both by short range forces and electrostatic forces. However, it is necessary to introduce a large number of additional parameters to specify all the forces, and we are not confident that it would be possible to demonstrate conclusively that quadrupole interaction is important.

An alternative approach, which is not unconnected, would be to use a model in which dipoles are placed on the bond between the two ions. The magnitude of these dipoles then depends on the short-range forces and electrostatic fields at the dipoles. The advantage of this procedure over the quadrupole model is that the number of arbitrary parameters, which are needed to specify the forces, is considerably less.

IV. CONCLUSIONS

In this paper, we have obtained models of the lattice dynamics of sodium iodide and potassium bromide which give good agreement with experimental measurements. The equations of motion of these models are derived from an expansion of the potential energy of the crystal which includes terms from the displacements of the ions and from the dipole moments producible on the ions during the vibrations. The models have been fitted to some of the experimental measurements and give good agreement both with these measurements, and also with other measurements to which they were not fitted. The models, therefore, probably give a very accurate description of the harmonic properties of these two alkali halides, at the temperature of the experimental measurements.

The good agreement is obtained however, only when some of the parameters have rather unrealistic values and the models cannot be readily interpreted in terms of shells of electrons. These artificial parameters are a direct result of a deficiency in the model, and more complicated models which include the effects of quadrupole moments have been suggested to overcome this deficiency. However, we have already obtained agreement which is well within the experimental errors of the measurements, and the more complicated models have even more arbitrary parameters.

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APPENDIX

In this Appendix the notation and theories of other authors, Hardy *et al.*[5] and Tolpygo *et al.*,[4,22,23] are compared with those presented in this paper. The approximation $\mathbf{R}=\mathbf{T}$ for all wave vectors is not made by the other authors, therefore, our notation must be extended to include the extra parameters which are required to specify the more general short-range interactions. These interactions for the $\mathbf{T}$ matrix are more complicated than for the $\mathbf{R}$ matrix. They correspond to two types of interaction: (a) The negative ion interaction with the electronic dipole moment on the positive ion is labeled I, (b) The positive ion interaction with the electronic dipole moment on the negative ion is labeled II. These two interactions will not necessarily be identical. In analogy with the parameters for the short-range interaction specifying the $\mathbf{R}$ matrix, for nearest neighbors two parameters are defined for each of the two types of interaction:

(a) Interaction I

$$\left(\frac{\partial^2 V_{\mathrm{I}}}{\partial r^2}\right)_{\parallel}=\frac{e^2 A_{\mathrm{I}}}{2v}, \quad \left(\frac{\partial^2 V}{\partial r^2}\right)_{\perp}=\frac{e^2 B_{\mathrm{I}}}{2v}$$

(b) Interaction II

$$\left(\frac{\partial^2 V_{\mathrm{II}}}{\partial r^2}\right)_{\parallel}=\frac{e^2 A_{\mathrm{II}}}{2v}, \quad \left(\frac{\partial^2 V}{\partial r^2}\right)_{\perp}=\frac{e^2 B_{\mathrm{II}}}{2v}.$$

These parameters are not independent, however, and Eq. (9) now reduces to

$$A_{\mathrm{I}}+2B_{\mathrm{I}}=A_{\mathrm{II}}+2B_{\mathrm{II}}=A+2(B+B'').$$

In general, similar parameters should be introduced both for the $\mathbf{S}$ matrix, and for second neighbor interactions in the $\mathbf{T}$ and $\mathbf{S}$ matrices. These additional parameters will not, however, be introduced here as the other authors have not included them.

(1) The Model of Hardy *et al.*

The equations of motion used by Hardy seem at first sight to be considerably different from Eqs. (1) and (2), which were used in this work. These equations may, however, be written in a similar form to those of Hardy if the effective electric field $\mathbf{E}$ is introduced. The equations of motion (1) and (2) then become

$$m\omega^2\mathbf{U}=\mathbf{RU}+\mathbf{TW}-\mathbf{ZE}, \tag{A1}$$

where

$$0=\mathbf{T}^T\mathbf{U}+\mathbf{SW}-\mathbf{YE}, \tag{A2}$$

$$\mathbf{E}=-\mathbf{C}(\mathbf{ZU}+\mathbf{YW}). \tag{A3}$$

When $\mathbf{W}$ is eliminated from Eqs. (A1) and (A3) and then $\mathbf{E}$ is eliminated, a single equation of motion remains;

$$\begin{aligned}m\omega^2\mathbf{U}=[&\mathbf{R}-\mathbf{TS}^{-1}\mathbf{T}^T+(\mathbf{Z}-\mathbf{TS}^{-1}\mathbf{Y})\mathbf{C}(\mathbf{Z}-\mathbf{YS}^{-1}\mathbf{T}^T)\\&-(\mathbf{Z}-\mathbf{TS}^{-1}\mathbf{Y})\mathbf{CYS}^{-1}\mathbf{Y}(\mathbf{I}+\mathbf{CYS}^{-1}\mathbf{Y})^{-1}\mathbf{C}(\mathbf{Z}-\mathbf{YS}^{-1}\mathbf{T}^T]\mathbf{U},\end{aligned}$$

where $\mathbf{I}$ is the unit matrix. The equation is now of the same form as Eq. (15) of Hardy (1962),[5] apart from Hardy's neglect of the term $\mathbf{TS}^{-1}\mathbf{T}^T$, which was mentioned in Sec. III.1.

(2) The Model of Toypygo *et al.*

When Eqs. (1) and (2) are compared with Eqs. (1) of Ref. 23, the equations of motion used by Tolpygo *et al.* are easily seen to be similar to those used in this paper. The only difference between the theories is the neglect of short-range dipole-dipole interactions in the $\mathbf{S}$ matrix, as described above (Sec. III.1).

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Observation of a Possible Large Crystalline Stark Splitting in Metallic Ce:LaAl$_2$†

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The susceptibility of polycrystalline Ce$_x$La$_{1-x}$Al$_2$ with several different concentrations of cerium has been found to decrease to about one fourth the value for free-Ce$_x^{3+}$ ions between room temperature and 4.2°K. The observed behavior is consistent with a cubic-crystal field splitting in the $J=\frac{5}{2}$ ground term of Ce^{3+} of 200°K. The observed splitting is close to that predicted on a point-charge ionic model ignoring shielding by conduction electrons if the rare-earth ions are assumed to be tripositive and the aluminums negative, and if the $4f$ electron of Ce^{3+} is represented by a Hartree-Fock function. It is about one third as large as might have been expected on the basis of experience with cubic nonconductors had the Ce:LaAl$_2$ been a nonconductor with this distribution of charges rather than a conductor.

INTRODUCTION

Although a considerable body of knowledge has accumulated on the crystalline Stark splittings of energy levels of rare-earth ions in nonconducting, ionic crystals, relatively little is known about the splittings in metallic environments. A broad anomaly in the specific heat of praseodymium metal centered about 50°K provided possibly the first clear evidence that Stark splittings might be appreciable in the rare-earth metals.[1] The anomaly could be fitted by assuming that it arises from a cubic Stark splitting of 80°K between a singlet and a triplet in the ground term of Pr^{3+} ions.[1,2] More detailed calculations based on the actual symmetry of this metal, which is hexagonal rather than cubic, are in progress,[3] and will hopefully also explain the susceptibility,[4] which in simplest approximation requires a considerably smaller Stark splitting.[2]

A maximum in the specific heat of metallic cerium at 100°K has been attributed by Murao and Matsubara[5] to a cubic Stark splitting in the ground term of Ce^{3+} of 200–250°K. A splitting of this size is also compatible with the susceptibility of the metal, which, especially on first cooling and warming shows departures from

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