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Lattice Dynamics of Sodium Halides

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A modified shell model developed earlier by the authors which included the effect of three-body forces has been used to study the lattice dynamics of sodium halides. The model has been ascribed a fundamental basis by pointing out that amongst the current phenomenological models, this one makes the nearest approach to the shell model recently derived by Sinha on rigorous quantum-mechanical considerations. Excellent agreement has been obtained with experimental data on phonon dispersion relations, specific heats at constant volume, and the infrared absorption and Raman scattering spectra of the solids.

I. INTRODUCTION

The shell model of ionic crystals proposed by Dick and Overhauser[1] presents a simple description of the electronic polarization in these solids. The basic ideas of this model were developed by Woods *et al.*[2] into a theory of lattice dynamics which, with its various modifications,[3-5] has since proved to be the most successful among the current theories. Woods *et al.* (see also Cochran[6] and Cowley[7]) further observed a certain degree of similarity between the mathematical description of their theory and that formulated by Tolpygo[8] and Tolpygo and Mashkevich[9] on quantum-mechanical considerations. This fact provides a fundamental basis to the apparently phenomenological model, so that it can be accepted as a convenient representation of a relatively exact theory of lattice dynamics.

The shell model begins by assuming that every ion is divided into a rigid spherical shell of a portion of the electron cloud and a rigid spherical core of the nucleus and the rest of the electron cloud. The two are coupled together by an isotropic spring and have a common center in the equilibrium configuration. This departure from the rigid-ion picture produces a different response to the long-wave optical (electromagnetic) waves, but does not make any impression on the long-wave acoustical (mechanical) vibrations, with the result that while the model permits a better description of the dielectric polarization in ionic crystals, it does not go beyond the rigid-ion model with respect to the elastic behavior of these solids. In particular, the shell models employing only central interactions lead to the Cauchy relation $c_{12} = c_{44}$. However, the low-temperature measurements of elastic constants, now available for a large number of ionic solids, do not support this result.

Phenomenologically, the Cauchy discrepancy can be accounted for by including various kinds of noncentral interactions amongst the ion pairs. In fact, some of the later modifications of the shell model include noncentral short-range interactions and give a better description of the vibrational properties of the solids under consideration. However, in general, these modifications are not based on the existing knowledge about the nature of the interaction responsible for the Cauchy discrepancies in ionic solids. Thus these modified models effectively replace a part of the operative forces by others of an entirely different nature. This replacement of one force by another could modify the parameters of the rest of the interactions also, particularly when the model is constrained to give agreement with experiments. This is exactly the observation of Cowley *et al.*[10] and Dolling *et al.*,[11] who find that some of the parameters of their best models attain unrealistic values when they are made to give an almost exact agreement with the experimental dispersion curves.

The theoretical investigations into the basic cause for the Cauchy discrepancy in ionic solids have been made along two different lines. One of these is due to Herpin,[12] who begins by deriving the Coulomb interaction between electronic clouds of polarizable particles in the adiabatic approximation. He used the quantum-mechanical perturbation theory and obtained the forces in the form of a series in powers of the distance between ion pairs. The successive terms in this series can be identified as dipole, quadrupole, etc., coupling between ions. In solids, with every ion situated at a center of inversion symmetry, the dipole coupling does not contribute to the Cauchy discrepancy, while the quadrupole term does. Herpin suggested that the entire Cauchy discrepancy in ionic solids is due to this quadrupole coupling between polarizable ions and found a fair amount of agreement in some cases. But, in general, the theory does not give a satisfactory explanation of the Cauchy discrepancy in the class of compounds under consideration and has even the wrong sign for many solids.

The second approach is that due to Löwdin[13] and his school and is based on a quantum-mechanical calculation of the cohesive energy of ionic crystals in the Heitler-London approximation. The calculation leads to a many-body potential apart from the central two-body terms. This many-body interaction owes its origin to the nonorthogonality of the free-ion one-electron wave functions and accounts for a Cauchy discrepancy which is of the right sign, although it is somewhat larger in magnitude. It is possible that the observed discrepancy is the resultant of both the effects mentioned above, but it could also well be that the large value of the discrepancy obtained by Löwdin is due to the fact that his calculations refer to a static lattice and in this respect are only approximate. Accepting the latter point of view, we may ignore the quadrupole terms of the polarizability forces and modify the magnitude of the many-body energy term so as to give the correct value of the Cauchy discrepancy without affecting the functional dependence of this energy on the nuclear coordinates.

The many-body energy term can be expressed as a series of terms of successively decreasing order of magnitude and the first important member of this series is a three-body potential of the central type. Lundqvist[14] gave a simple expression for this three-body potential, which in the harmonic approximation gives three distinct contributions. One of these contributions adds to the Coulomb interaction and the second goes with the nearest-neighbor overlap potential. The third term has been put in the form of a slowly convergent series and represents a purely three-body interaction, long-range in nature. Since the nearest-neighbor overlap potential is always taken as an undetermined function whose parameters are to be evaluated by letting the theory give correct values of certain experimentally measured quantities, the modification of this term by the three-body potential contribution is trivial. Verma and Singh[15] (hereafter referred to as I) studied the exact nature of the purely three-body potential term of Lundqvist and evaluated the contribution of this potential to the dynamical matrix of alkali halides. These authors then injected these elements into the shell model and thus developed a new modified shell model[16] (hereafter referred to as II), which has given excellent results with many alkali halides.[16,17]

The model described in II differs from the shell model of Woods *et al.* only in as much as the Coulomb interaction matrix is modified to the form $\underline{C}' = \underline{C}\chi^2 + \underline{V}$, where χ is a function depending on the overlap integrals of the Heitler-London wave functions and $\underline{V}$ is the purely three-body interaction matrix. This matrix enters the shell-model equations in the form $\underline{Z}\underline{C}'\underline{Z} = \underline{Z}\chi\underline{C}\chi\underline{Z} + \underline{Z}\underline{V}\underline{Z} = \underline{\bar{Z}}\underline{C}\underline{\bar{Z}} + \underline{V}'$, say. Recently Sinha[18] gave a quantum-mechanical derivation of the shell model based on a systematic self-consistent Born-Oppenheimer perturbation expansion. He showed that the equations of the shell model could be obtained rigorously, with minor modifications in the meanings of the different terms. The equation of motion of the shells in this scheme appears as a self-consistency condition. The ionic charge $\underline{Z}$ is modified to the value less than 1, and additional terms appear with the short-range interaction matrices $\underline{R}$, $\underline{T}$, and $\underline{S}$, so that they cease to be equal. However, a matrix $\underline{X}$, which represents the bonding coefficients between ions due to the short-range exchange and correlation corrections to the bare interaction between the valence charge distributions, can be considered together with the Coulomb interaction matrix modifying it to the form $(\underline{Z}\underline{C}\underline{Z} + \underline{X})$. Apparently $\underline{X}$ replaces the three-body interaction matrix $\underline{V}'$ of the Heitler-London scheme, which itself represents the interaction between charge deformations produced at the ion sites and other ions in the lattice regarded as point charges. Apart from the matrix $\underline{X}$, the differences in the three short-range matrices $\underline{R}$, $\underline{T}$, and $\underline{S}$ are due to terms which are quite small. These terms involve certain overlap integrals and a possible dependence of the polarizability tensor on the wave vector $\vec{q}$. For well-localized wave functions the overlap integrals vanish; further, if we ignore the $\vec{q}$ dependence of the polarizability tensor, the short-range matrices assume the same forms as used in the conventional shell model. In the case of alkali halide crystals these assumptions can be regarded as approximately true, so that the assumption $\underline{R} = \underline{T} = \underline{S}$ should be a good approximation. We have retained this assumption in our model also because otherwise the number of parameters of the theory would increase without possibly giving any significant improvement. It is clear that among the current phenomenological models the modified shell model described in II is the nearest approach to the model derived by Sinha. We give a brief description of the model in Sec. II and the results obtained by applying this model to the four sodium halides in Sec. III. In these calculations we have ignored the effect of anharmonicity, including that due to the zero-point vibrations of the lattice. A look at the work of Plendl[19] shows that the anharmonic effects in sodium halides should be rather weak except possibly in the case of NaF. We have compared our results with those of Melvin *et al.*,[20] obtained on the basis of a radially deformable shell model; we observe that our model gives better agreement with experimental phonon-dispersion curves. Section IV of this paper consists of a discussion of these results and the conclusions.

II. BRIEF DESCRIPTION OF METHOD

Lundqvist's expression for the potential energy per unit cell reads as

$$\phi(r) = e^2\left(\frac{\epsilon\alpha_M}{r}\{1 + 12f(r)\} + 12V(r)\right), \tag{1}$$

TABLE I. Input data for calculation of model parameters. Elastic constants are in units of 10^{11} dyn/cm^2, polarizabilities of ions in 10^{-24} cm^3, long-wave optical vibration frequencies in 10^{12} sec^{-1}, and interionic distance in 10^{-8} cm; calculated values refer to least-squares-fit values of the model parameters.

Property	NaF			NaCl			NaBr			NaI		
	Obs	Ref.	Calc	Obs	Ref.	Calc	Obs	Ref.	Calc	Obs	Ref.	Calc
c_{11}	11.039	23	11.040	5.838	27	5.807	4.010	29	3.855	3.530	32	3.445
c_{12}	2.242	23	2.243	1.194	27	1.306	1.090	29	0.873	0.852	32	0.761
c_{44}	2.947	23	2.946	1.327	27	1.351	0.990	29	0.970	0.767	32	0.774
α_1	0.255	24	0.355	0.255	24	0.255	0.255	24	0.155	0.255	24	0.155
α_2	0.908	24	0.808	3.008	24	0.038	4.133	24	4.233	6.009	24	6.109
ν_L	12.650	25	12.708	7.830	28	7.805	6.345	30	6.416	5.170	10	5.104
ν_T	7.510	25	7.405	5.173	28	5.160	4.051	30	3.952	3.600	10	3.650
a	2.3025	26	2.3025	2.7935	23	2.7935	2.9870	31	2.9870	3.2875	2	3.2075

where $e = |\text{electronic charge}|$, $\epsilon = |\epsilon_{(\kappa)}|\,(\epsilon_{(\kappa)} = \pm 1$ denotes the sign of the charge on the κth ion in any cell), $\alpha_M (= -1.7476)$ is the Madelung constant, $V(r)$ represents the non-Coulomb interaction potential, which is supposed to be significant between the nearest neighbors only, and r is the interionic distance.

For the equilibrium of the lattice we must have

$$\left(\frac{d\phi}{dr}\right)_0 = B - \tfrac{2}{3}\alpha_M\{1 + 12f(r)\}_0 = 0$$

which gives

$$B = 8a^2\left[\left(\frac{dV}{dr}\right) + \frac{\epsilon\alpha_M}{r}\left(\frac{df}{dr}\right)\right]_0 = -1.165\{1 + 12f(a)\}$$
$$= -1.165\,\chi^2 \qquad (2)$$

where we have put $\{1 + 12f(a)\} = \chi^2$. The suffix 0 has been used to indicate the equilibrium values and a is the equilibrium lattice constant.

The elements of the dynamical matrix can be conveniently expressed as a sum of three components:

$$D_{\alpha\beta}(\kappa\kappa') = C_{\alpha\beta}(\kappa\kappa') + R_{\alpha\beta}(\kappa\kappa') + V_{\alpha\beta}(\kappa\kappa'),$$

where $C_{\alpha\beta}(\kappa\kappa')$ represents the Coulomb interaction matrix $\underline{C}$ as defined by Kellermann[21] multiplied by the factor χ^2, $R_{\alpha\beta}(\kappa\kappa')$ is the nearest-neighbor overlap repulsion matrix $\underline{R}$ and can be expressed in terms of the usual parameters B and A related to the first and second space derivatives of the short-range potential $[V(r) + (\epsilon\alpha_M/r)f(r)]$, and $V_{\alpha\beta}(\kappa\kappa')$ is the long-range three-body interaction matrix $\underline{V}$ which can be computed by evaluating the sums involved by a method due to Born and Bradburn.[22] Expressing the long-range interaction matrix then as $\underline{C}' = \underline{C}\chi^2 + \underline{V}$, the shell-model equations of motion take the form

$$4\pi^2\nu^2\underline{m}\,\underline{U} = (\underline{R} + \underline{Z}\,\underline{C}'\underline{Z})\underline{U} + (\underline{T} + \underline{Z}\,\underline{C}'\underline{Y})\underline{W}, \qquad (3)$$

$$0 = (\underline{T}^T + \underline{Y}\,\underline{C}'\underline{Z})\underline{U} + (\underline{\mathcal{S}} + \underline{Y}\,\underline{C}'\underline{Y})\underline{W}, \qquad (4)$$

where $\underline{U}$ and $\underline{W}$ are the column matrices specifying the displacements of the (two) cores and the (two) shells, respectively; $\underline{m}$, $\underline{Z}$, and $\underline{Y}$ are diagonal matrices representing the mass, ionic charge, and the charge on the shells. $\underline{\mathcal{S}} = \underline{S} + e^2\underline{Y}^2\alpha^{-1}$; $\underline{T}^T$ is the transpose of $\underline{T}$.

Solving these equations for long waves, we obtain the following expressions for the elastic constants and the long-wave optical vibration frequencies:

$$c_{11} = \frac{e^2}{4a^4}\left[-5.112\,\chi^2 + A + 9.3204\left(a\frac{df}{da}\right)\right],$$
$$c_{12} = \frac{e^2}{4a^4}\left[0.226\,\chi^2 + B + 9.3204\left(a\frac{df}{da}\right)\right], \qquad (5)$$

TABLE II. Values of parameters obtained before and after the least-square fit (LSF).

Parameters	NaF		NaCl		NaBr		NaI	
	Initial	LSF	Initial	LSF	Initial	LSF	Initial	LSF
A	11.0019	11.0020	11.4548	11.4550	10.4193	10.4190	11.5459	11.5450
B	−1.2029	−1.2029	−1.1736	−1.1736	−1.1445	−1.1445	−1.1790	−1.1793
χ^2	1.0325	1.0320	1.0074	1.0174	0.9812	0.9712	1.0120	1.0170
$[a(df/da)]$	−0.0369	−0.0368	−0.0151	−0.0051	0.0148	−0.0143	0.0114	−0.0026
d_1	0.0054	0.0074	0.0124	0.0237	0.0050	0.0075	0.0050	0.0150
d_2	0.1440	0.1459	0.2748	0.2648	0.2342	0.2344	0.4084	0.3664
Y_1	−1.7957	−1.6892	−4.3073	−1.983	−0.7784	−0.4723	−0.6698	−1.4385
Y_2	−2.2564	−2.1913	−2.2866	−0.7359	−2.3260	−2.7512	−2.0826	−2.2830

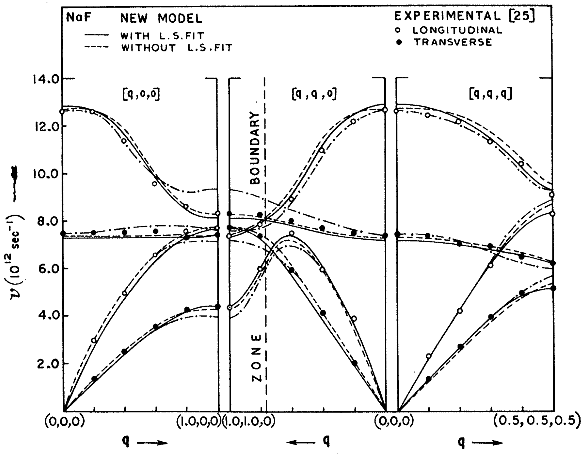

FIG. 1. Dispersion curves for NaF. Dot-dashed curves from Melvin *et al.* (Ref. 20).

$$c_{44}=\frac{e^2}{4a^4}\,(2.556\chi^2+B);$$

$$4\pi^2\mu(\nu_L^2)_{q=0}=R_0-e^2\left(\frac{d_1^2}{\alpha_1}+\frac{d_2^2}{\alpha_2}\right)+\frac{8\pi}{3}\,\frac{(eZ')^2}{vf_L}\left\{\chi^2+6\left(a\,\frac{df}{da}\right)\right\}, \tag{6}$$

$$4\pi^2\mu(\nu_T^2)_{q=0}=R_0-e^2\left(\frac{d_1^2}{\alpha_1}+\frac{d_2^2}{\alpha_2}\right)-\frac{4\pi}{3}\,\frac{(eZ')^2}{vf_T}\,\{\chi^2\},$$

where μ is the reduced mass of the two ions in the unit cell, v is the volume of the unit cell, and

$$f_L=1+\frac{(\alpha_1+\alpha_2)}{v}\,\frac{8\pi}{3}\left\{\chi^2+6\left(a\frac{df}{da}\right)\right\},\quad R_0=\frac{e^2}{v}\,(A+2B), \tag{7}$$

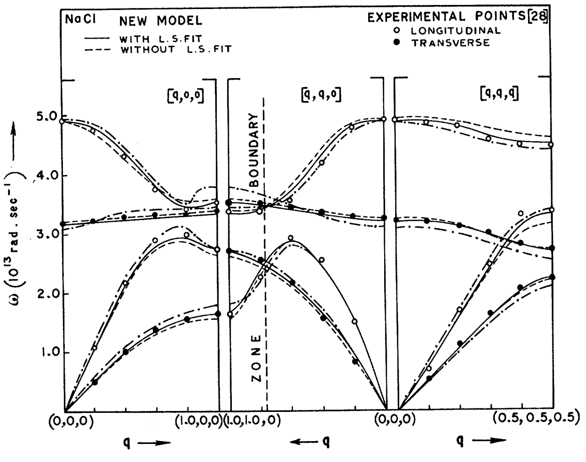

FIG. 2. Dispersion curves for NaCl. Dot-dashed curves from Melvin *et al.* (Ref. 20).

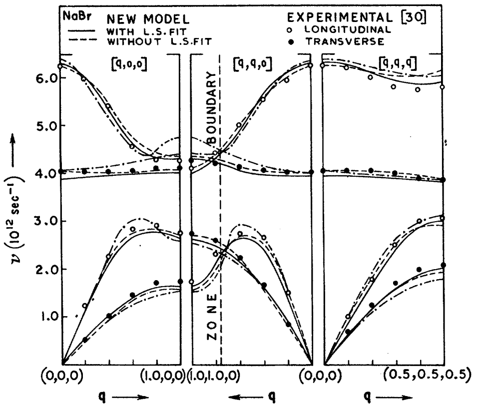

FIG. 3. Dispersion curves for NaBr. Dot-dashed curves from Melvin *et al.* (Ref. 20).

$$f_T=1-\frac{(\alpha_1+\alpha_2)}{v}\,\frac{4\pi}{3}\{\chi^2\},\qquad Z'=Z+d_1-d_2, \tag{8}$$

$$\alpha_1=\frac{y_1^2e^2}{k_1+R_0},\qquad d_1=-\frac{y_1R_0}{k_1+R_0},$$
$$\alpha_2=\frac{y_2^2e^2}{k_2+R_0},\qquad d_2=-\frac{y_2R_0}{k_2+R_0}. \tag{9}$$

α_1 and α_2 are the electronic polarizabilities of the positive and negative ions, respectively. k_1 is the core-shell force constant and y_1 the shell charge of positive ions, while k_2 and y_2 similarly refer to negative ions.

As discussed in the Introduction, we take the function $\{1+12f(a)\}$ and the derivative $[a(df/da)]$ as parameters of the theory. The other parameters are A and B, belonging to the short-range repulsion; d_1 and d_2, the distortion polarizabilities of the positive and negative ions, respectively; and y_1 and y_2 (or k_1 and k_2). A knowledge of the lattice constant, the elastic constants, the optical vibration frequencies, and the electronic polarizabilities enables us to determine these parameters through the relations expressed in (5)–(9). Once the parameters are determined, all the matrices of Eqs. (3) and (4) can be evaluated and the equations solved for any desired wave vector. In those cases in which the experimental dispersion curves are available, through neutron spectroscopic experiments, a method of least-square fit can be used for further refinement of the parameters, and final solutions can be obtained using these values.

III. APPLICATION TO SODIUM HALIDES

In Table I are given the input data for the four sodium halides with relevant references, while the values of the parameters $Z(=1)$, A, B, χ^2, $[a(df/da)]$, d_1, d_2, y_1, and y_2 are given in Table II obtained before and after the least-square fit.

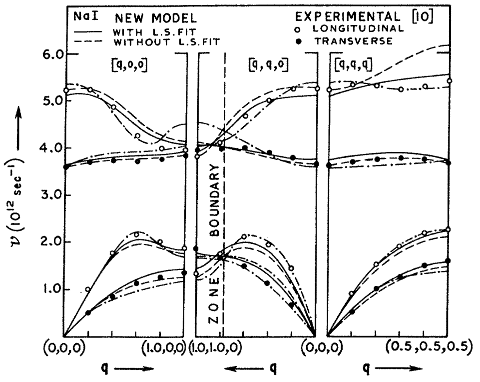

FIG. 4. Dispersion curves for NaI. Dot-dashed curves from Melvin *et al.* (Ref. 20).

We have solved the equations of motion for the 48 irreducible wave vectors of the first Brillouin zone corresponding to a division in $10\times10\times10$ equal parts. The dispersion curves obtained with and without least-square fit (LSF) in the symmetry directions are shown in Figs. 1–4.

The complete spectra have been used to compute the specific heats in the usual way, and $\Theta_D - T$ curves so obtained are shown in Fig. 5. The two-phonon combined density of states (CDS) curves, shown in Figs. 6–9, have also been worked out following the method of Smart *et al.*,[33] and the maxima have been compared with the positions of infrared (ir) absorption maxima[33] and Raman scattering shifts.[34,35]

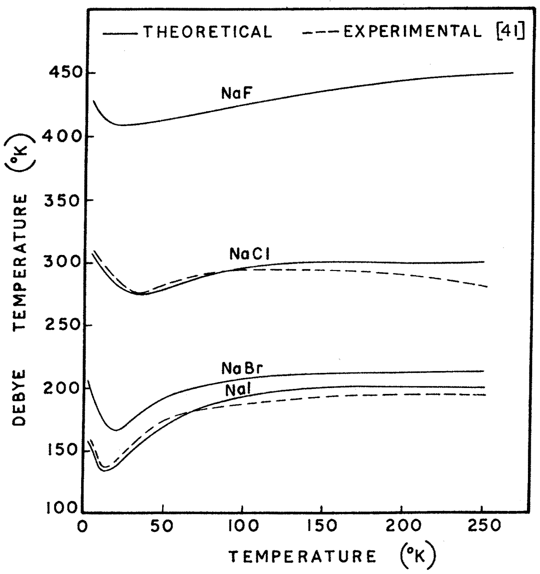

FIG. 5. Debye characteristic temperatures as functions of temperature for sodium halides.

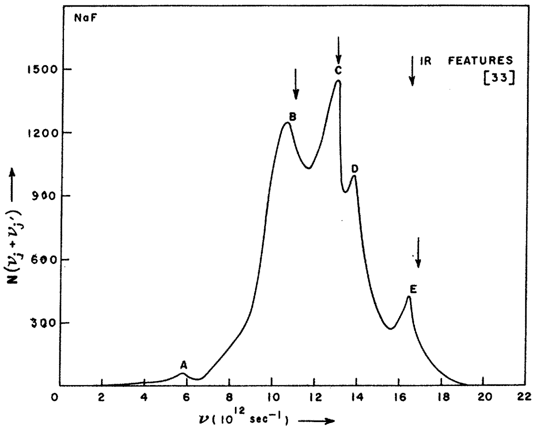

FIG. 6. Combined density-of-states curve for NaF.

IV. DISCUSSION

Lattice dynamics of sodium halides has been studied by various workers (NaF,[25,36] NaCl,[28,37–39] NaBr,[20] and NaI [3,5,10,40]). Recently Melvin *et al.*[20] investigated the ionic form-factor changes in NaCl using a radially deformable shell model which goes by the name of the breathing shell model. They, however, used the model to compute the vibration spectra of the four sodium halides. The dispersion curves obtained by these authors have also been shown along with the curves obtained by us and the experimental ones in Figs. 1–4. These figures show that the over-all agreement between theory

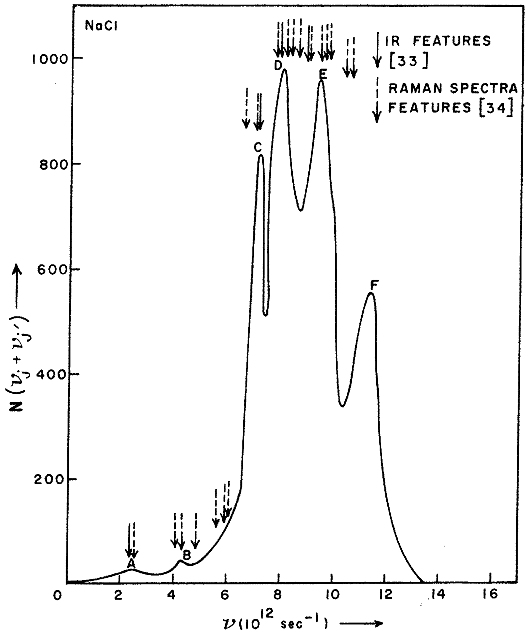

FIG. 7. Combined density-of-states curve for NaCl.

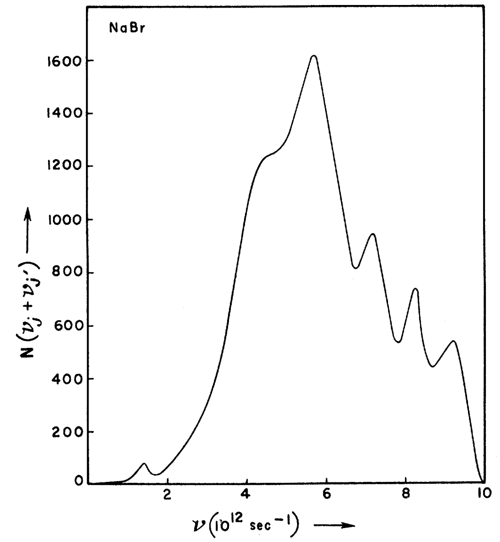

FIG. 8. Combined density-of-states curve for NaBr.

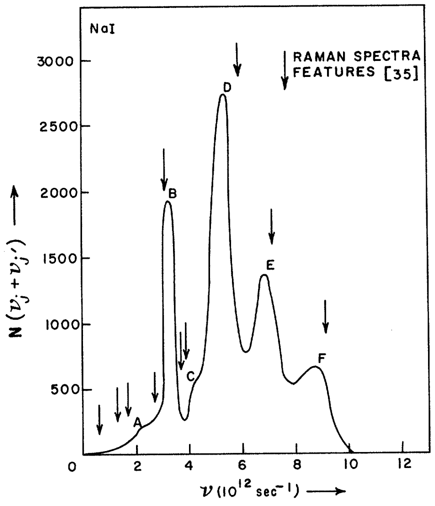

FIG. 9. Combined density-of-states curve for NaI.

and experiment is much better in our case. The small differences observed at places, however, show that the model deserves to be refined further. A possible direction of improvement is perhaps the consideration of anharmonic effects.

A look at the LSF parameters given in Table II shows that these parameters do not change in a systematic way as we go from NaF to NaI. Most of the values which do not fit in the sequences correspond to NaCl. This is, however, not quite unexpected because our model is strongly based on the Cauchy discrepancy which does not form a systematic sequence for the four halides under study and has the maximum value for NaCl.

The breathing shell model, which is supposed to be the best amongst the deformable shell models, is obtained by introducing a radial expansion rate of the shells as an additional parameter. However, the basis for the introduction of this additional degree of freedom is not clearly understood. In contrast to this, our model is based on taking a more realistic account of the long-range interactions by including the contribution of the three-body forces, whose existence in ionic crystals is well founded. This contribution has been computed exactly and satisfies the symmetry requirements in reciprocal space. The injection of these forces into the shell model is somewhat intuitive but is strongly supported by the quantum-mechanical derivation of the shell model by Sinha. There is, however, an important difference between our model and that of Sinha: While the charge parameter $|Z|$ in Sinha's model is necessarily less than 1 ($|Z|<1$), the parameter $|\chi|$ in our scheme is generally greater than 1 ($|\chi|>1$). This parameter is fixed by the equilibrium condition and the shear constant c_{44} and is not expected to undergo the desired change (from $|\chi|>1$ to $|\chi|<1$) unless the interaction potential is extended by including an additional term contributing significantly to c_{44}. Such an interaction is the second-neighbor overlap repulsion which is capable of producing the desired effect. Another point that warrants the necessity of including the second-neighbor repulsion is the fact that the largest deviation from the experimental curves is observed for the longitudinal optical branch in the $[q,q,q]$ direction in the case of NaI, which has the largest ratio between the radii of the negative and positive ions amongst the four alkali halides under study.

In general, however, our model gives good agreement with the dispersion curves, the specific-heat data,[41] and the infrared absorption and Raman scattering spectra, and has a smaller number of parameters than those used in similar models giving no better results. These agreements between theory and experiment also prove the validity of our contention that the equality of the short-range force matrices $\underline{R}$, $\underline{T}$, and $\underline{S}$ is a sufficiently good approximation. The results obtained in this study and those of similar studies with other alkali halides[16,17] show that our model presents a good description of this class of solids, and can perhaps be developed into an excellent model by introducing the effects of anharmonicity of vibrations and by including second-neighbor overlap repulsion.

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Ionic Raman Effect. I. Scattering by Localized Vibration Modes

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A theory is presented of the Raman scattering of infrared light by the modulation of the ionic contribution to the polarizability of a crystal by the displacements of the atoms from their equilibrium positions. It is applied to the calculation of the scattering efficiency for the scattering of light by the localized vibration modes due to H^- U centers in CaF_2. The results of these calculations indicate that such scattering should be readily observable when a CO or He-Ne laser is used as the source of incident light.

It is convenient to regard the Raman scattering of light by the elementary excitations of a crystal as the scattering of light by the inhomogeneities in the refractive index, or the polarizability, of the crystal caused by the elementary excitations being probed. In the case of the inelastic scattering of