

Lattice Dynamics and Specific-Heat Data for Rocksalt-Structure Alkali Halides

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Vibrational distribution functions are derived for a number of rocksalt-structure alkali halides using a more refined treatment of the interionic forces than that provided by regarding them as rigid point charges. The dipole moment at any given ion site is calculated taking into account the contribution from the deformation of the electron distribution resulting from both polarization and overlap repulsion between nearest neighbors. In this way the dipole-dipole part of the Coulomb interaction is treated self-consistently.

Both room temperature and 0°K input parameters are used, and the derived specific-heat data are compared with experimental results. The over-all agreement with experiment is significantly better than that obtained by treating the ions as rigid point charges.

Sets of phonon dispersion curves are also given. For NaI they are in much better agreement with those determined experimentally by inelastic neutron scattering than are the rigid ion curves. There appears to be close agreement with the results of the "shell-model" calculations.

I. INTRODUCTION

IN two classic papers on the lattice dynamics of NaCl, Kellermann¹ made the first serious attempt to apply the formal Born-von Kármán² theory to a real crystal and, in particular, to the evaluation of the specific heat³ as a function of temperature. This work was stimulated by a series of papers due to Blackman.⁴ These treated certain theoretical models exactly and demonstrated very clearly that, in these cases at least, the earlier simplified theory of Debye,⁵ which treated a crystal as an elastic continuum with a finite number of degrees of freedom, was inadequate. Blackman found that this failure can best be demonstrated, in any given case, by fitting a Debye function to the calculated specific heat at a sequence of temperatures T using the Debye characteristic temperature $\Theta_D(T)$ as a disposable parameter. One thus derives $\Theta_D(T)$ as a function of T , and any nonconstancy indicates a failure of the Debye theory.

The $\Theta_D(T)$ functions he obtained in this way for various three-dimensional models showed distinct minima in all cases. These occurred at temperatures low enough for the Debye specific heat to follow its limiting T^3 law. Consequently, the true specific heat

also displayed this behavior in the region of the minimum. This strongly suggested that a similar effect was responsible for the apparent close agreement between the Debye theory and the then-available specific-heat measurements for real crystals. Furthermore, the forms of the minima in Blackman's results were strongly influenced by the details of his models.

It was thus evident that more exact experimental work, particularly in the region of 0°K, was very necessary and that such work could well provide a detailed test of theoretical work on a real crystal using a specific force-constant model. Since the theory could only be tried in this way, there being no prospect of using specific-heat data to determine the interatomic forces directly (a statement that is still valid at present), NaCl was an obvious choice as a test case.

For this crystal, and indeed for all the alkali halides, Born⁶ had evolved a very simple model which reproduced the observed cohesive energy extremely well. He found that each of these crystals could be regarded as an array of alternating point charges held apart by short-range repulsions acting only between nearest-neighbor ions. A later refinement of this work by Born and Goeppert-Mayer⁷ which included non-Coulomb interactions between more-distant neighbors seemed least necessary for NaCl. It was, thus, the simplest crystal to treat theoretically.

Kellermann's results¹ confirmed the existence of a minimum in $\Theta_D(T)$ and agreed reasonably well with experimental data, although direct comparison should strictly only be made when theory and experiment both refer to fixed volume at 0°K.

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¹ E. W. Kellermann, *Phil. Trans. Roy. Soc. London* **238**, 513 (1940); *Proc. Roy. Soc. (London)* **A178**, 17 (1941).

² M. Born and T. von Kármán, *Physik. Z.* **13**, 297 (1912); **14**, 15 (1913).

³ Here, and elsewhere, this quantity is defined as the specific heat at any temperature derived assuming the volume of the crystal to remain fixed at the value appropriate to some given temperature. This is usually chosen to be 0°K, but for Kellermann's results, room temperature.

⁴ M. Blackman, *Z. Physik* **86**, 421 (1933); *Proc. Roy. Soc. (London)* **A138**, 384 (1935); **A159**, 416 (1937). See also *Reports on Progress in Physics* (The Physical Society London, 1941, Vol. 8, p. 11); *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1.

⁵ P. Debye, *Ann. Physik* **39**, 789 (1912).

⁶ M. Born, *Atomtheorie des Festen Zustandes* (J. B. Teubner, Berlin, 1923).

⁷ M. Born and M. Goeppert-Mayer, in *Handbuch der Physik*, edited by S. Flügge (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2.

Subsequently, Iona⁸ published a rather less detailed treatment of KCl, but it was not until recently that any further incentive to undertake calculations as detailed as Kellermann's was provided by experimental work. In 1957 Barron, Berg, and Morrison⁹ published an analysis of new specific-heat measurements on several alkali halides, made by Morrison and co-workers,¹⁰ (*cf.* earlier work by Clusius, Goldman, and Perlick¹¹), which extracted far more information than could have been derived from earlier data and offered a much more rigorous test of theoretical work. Subsequently, one of us (A.M.K.) published a systematic application of Kellermann's analysis, first to the Li and Na halides¹² and then to those K, Rb, and Cs halides¹³ which have the rocksalt structure. This work differed from Kellermann's in the use of the more recent crystal data published in Born and Huang,¹⁴ and results were derived for both room temperature (RT) and 0°K data. The second set were then directly comparable with the results of Barron, Berg, and Morrison.⁹ Agreement between theory and experiment was satisfactory for the K halides, but certain significant discrepancies were present in the cases of NaCl and NaI. The most likely origin of these was the oversimplified manner in which the Coulomb interactions were treated in the Born-Kellermann model. This view was confirmed when the second author (J.R.H.) derived a frequency spectrum for the NaCl crystal¹⁵ based on a self-consistent analysis of the dipole-dipole interactions in a perturbed lattice. This spectrum had a very different shape from that resulting from the Kellermann theory. In a joint paper¹⁶ it was shown that the use of the new theory led to results in closer accord with experiment. This theory has also been applied to KCl¹⁷ (we shall refer to this paper as I hereafter), and here too the results are, on balance, in better agreement with the empirical data.

The object of the present paper is to report the results of a systematic application of the new theory to all the more important rocksalt-structure alkali halides. These results provide us with a considerably more extensive test of the theory since we have included all the crystals investigated by Barron, Berg, and Morrison.⁹ Our data also indicate other salts for which

differences from the results of the Kellermann theory are large and for which further experimental work would seem to be most fruitful.

An important and independent stimulus to this type of theoretical work is provided by inelastic neutron scattering measurements. Recent work by Woods, Cochran, and Brockhouse¹⁸ on NaI resulted in the direct determination of frequency versus wave vector dispersion curves for plane-wave normal modes propagating along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions in this crystal. The measured curves are very different from those derived using the Born-Kellermann model. Consequently, these authors have given a theoretical analysis in the same paper based on the "shell model," originally developed by Dick and Overhauser¹⁹ to explain dielectric properties, which leads to dispersion curves much closer to those they measured.

It is evident that when empirical dispersion curves are known in this way they provide a quite independent test of a given theoretical model. Thus, in the case of NaI, if our model yields both dispersion curves and specific-heat data in agreement with experiment, it seems likely that it also provides a good description of the interionic forces. Conversely, should there be discrepancies for NaI or any other salt, one may hope by combining both sets of data to deduce what modifications of the model are necessary to remove them.

It is particularly important to apply the present theory to NaI since our approach differs from that of the shell model and is free from the more artificial assumptions of the latter. It was possible that we would not have produced as good an agreement between theory and experiment as that found by Woods, Cochran, and Brockhouse.¹⁸ However, this appeared unlikely as our earlier results¹⁶ for NaCl are virtually identical with those published previously by Cochran.²⁰ In addition, it does seem quite likely that our theory can provide a clearer insight into the meaning of any residual discrepancies. At all events it is highly desirable to have more experimental dispersion curves, particularly for salts for which detailed specific-heat measurements are available.

II. THEORY

This has been given in detail in I, and we shall merely outline the basic ideas and quote those results relevant to the present work.

For any molecular system one can write a Hamiltonian function governing the nuclear motion which involves only the coordinates \mathbf{X}_K and momenta \mathbf{P}_K of the nuclei (where K specifies a particular nucleus),

⁸ M. Iona, Jr., *Phys. Rev.* **60**, 822 (1941).

⁹ T. H. K. Barron, W. T. Berg, and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 478 (1957).

¹⁰ W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 467 (1957). See also J. A. Morrison, D. Patterson, and J. S. Dugdale, *Can. J. Chem.* **33**, 375 (1955); J. A. Morrison and D. Patterson, *Trans. Faraday Soc.* **52**, 764 (1956).

¹¹ K. Clusius, J. Goldmann, and A. Perlick, *Z. Naturforsch.* **4a**, 424 (1949).

¹² A. M. Karo, *J. Chem. Phys.* **31**, 1489 (1959).

¹³ A. M. Karo, *J. Chem. Phys.* **33**, 7 (1960).

¹⁴ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), pp. 26 and 54. See also R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. 1, Table III.

¹⁵ J. R. Hardy, *Phil. Mag.* **4**, 1278 (1959).

¹⁶ J. R. Hardy and A. M. Karo, *Phil. Mag.* **5**, 859 (1960).

¹⁷ J. R. Hardy, *Phil. Mag.* **7**, 315 (1962).

¹⁸ A. D. B. Woods, W. Cochran, and B. N. Brockhouse, *Phys. Rev.* **119**, 980 (1960). See also *Bull. Am. Phys. Soc.* **5**, 462 (1960), Sec. 48.

¹⁹ B. G. Dick, Jr., and A. W. Overhauser, *Phys. Rev.* **112**, 90 (1958).

²⁰ W. Cochran, *Phil. Mag.* **4**, 1082 (1959).

provided the electrons follow the nuclear motion adiabatically. For alkali-halide crystals this approximation is certainly valid, since their large band gaps ensure that electronic excitations have frequencies several orders of magnitude greater than the vibrating nuclei. Therefore, the nuclei behave as a closed system having an effective potential function $\Phi(\mathbf{X}_K)$.

To the lowest order, assuming one measures \mathbf{X}_K from the equilibrium configuration where $\partial\Phi(\mathbf{X}_K)/\partial\mathbf{X}_K=0$,

$$\Phi(\mathbf{X}_K) = \Phi_2 = \frac{1}{2} \sum_{KK'} \mathbf{X}_K \left(\frac{\partial^2 \Phi}{\partial \mathbf{X}_K \partial \mathbf{X}_{K'}} \right) \mathbf{X}_{K'}. \quad (1)$$

Thus, the Hamiltonian H is given by

$$H = H_2 = \frac{1}{2} \left[\sum_K \frac{\mathbf{P}_K^2}{m_K} + \sum_{KK'} \mathbf{X}_K (\Phi(KK')) \mathbf{X}_{K'} \right], \quad (2)$$

where m_K is the mass of the nucleus K and the second term is simply an abbreviated form of Φ_2 , $\Phi(KK')$ being a 3 by 3 matrix.

Our concern is with a large perfect rocksalt structure. We shall restrict the ensuing discussion to this system, which we shall treat assuming H_2 to provide an adequate Hamiltonian function. This approximation leads to harmonic nuclear vibrations. For alkali halides the theoretically derived specific heats are directly comparable with the corrected experimental data.⁹ The latter are appropriate to an "effective" harmonic lattice at 0°K as a consequence of the high cohesive energies of these crystals which ensures that anharmonic effects are small at low temperatures.

Theoretically, one considers a crystal containing L ion pairs, where L is Avogadro's number; the resultant specific heats are thus appropriate to one mole. To ensure full periodicity we assume that the crystal has the same shape as the basic face-centered monatomic primitive cell, each of which contains one ion pair, and impose the Born-von Kármán² boundary condition which constrains corresponding points on opposite faces to have the same displacements.²¹ It is then possible to reduce Eq. (2) by a Fourier decomposition of the displacements $\mathbf{X}_K \equiv \mathbf{X}(k^l)$, where l is the cell index and k is 1 or 2 according to whether K refers to a positive or a negative ion. Thus,

$$\mathbf{X}(k^l) = \frac{1}{L^{1/2}} \sum_{\mathbf{q}} \frac{\mathbf{Q}(\mathbf{k})}{(m_k)^{1/2}} e^{i\mathbf{q} \cdot \mathbf{r}(k^l)},$$

where the wave vectors \mathbf{q} satisfy the periodic boundary conditions, and $\mathbf{r}(k^l)$ is the position vector of the ion (k^l) in the undistorted lattice. Moreover, the lattice periodicity is such that there are exactly L physically distinct \mathbf{q} vectors evenly distributed over the first Brillouin zone.

²¹ See reference 17, Appendix (b) for a discussion and justification of the Born-von Kármán periodic boundary condition.

Equation (2) now reduces to

$$H_2 = \frac{1}{2} \left[\sum_{\mathbf{q}k} \dot{\mathbf{Q}}^*(k) \dot{\mathbf{Q}}(k) + \sum_{\mathbf{q}kk'} \mathbf{Q}^*(k) \mathbf{M}(k^{\mathbf{q}k'}) \mathbf{Q}(k') \right], \quad (3)$$

where

$$\mathbf{M}(k^{\mathbf{q}k'}) = \sum_l \Phi(k^l k'^0) \frac{e^{-i\mathbf{q} \cdot [\mathbf{r}(k^l) - \mathbf{r}(k'^0)]}}{(m_k m_{k'})^{1/2}},$$

and where we have used the fact that $\Phi(k^l k'^l)$ depends only on the relative cell index $l-l'$.

For a general value of \mathbf{q} no further reduction by symmetry is possible. However, Eq. (3) can be transformed to a sum of $6L$ harmonic oscillator Hamiltonians, one set of 6 for each \mathbf{q} value, whose frequencies are the positive roots of the eigenvalues of the 6 by 6 matrix $\mathbf{M} \equiv \mathbf{M}(k^{\mathbf{q}k'})$. These oscillations are the $6L$ independent normal modes for one mole of crystal, within the harmonic approximation.

Because the frequencies $\omega(j^{\mathbf{q}})$ ($j=1, \dots, 6$) are densely distributed over a range $0 \leq \omega(j^{\mathbf{q}}) \leq \omega_m$, a convenient and physically meaningful quantity is the distribution function $N(\omega)$, where $N(\omega)d\omega$ is the number of allowed frequencies between ω and $\omega+d\omega$. Any sum over normal modes can then be represented by an integral over this frequency distribution.

The form of \mathbf{M} , and thus of $N(\omega)$, depends strongly on the model one uses. The derivation of \mathbf{M} for our present model has been given in I. Here we shall only summarize the basic assumptions and the manner in which the various parameters are fixed from the appropriate input data.

The short-range contribution to \mathbf{M} is evaluated by Kellermann's method^{1,17} from the observed compressibility β and the equilibrium nearest-neighbor distance r_0 . We have not attempted to include short-range interactions between other than nearest-neighbor ions.

The Coulomb part of \mathbf{M} is derived by calculating the dipole-dipole interaction and neglecting higher order multipole effects which we believe to be much less important [see I, Appendix (a)]. Moreover, the dipole moment on a given ion is calculated in a way which allows not only for its displacement as a point charge, but also for the distortion induced in the electronic charge distribution. This is regarded as consisting of two parts:

(a) A component $\mathbf{u}_1(k^l) = \alpha_k E_{\text{eff}}$, where α_k is the appropriate crystal polarizability and is taken from the results of Tessman, Kahn, and Shockley (T.K.S.),²² using the values extrapolated to zero frequency.

(b) A component $\mathbf{u}_2(k^l)$ which depends on the relative positions of the given ion and its nearest neighbors, and which we refer to as the deformation dipole (D.D.) moment, associated with the ionic overlap responsible for the nearest-neighbor repulsion.

²² J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

This second concept was first introduced by Szigeti²³ to account for the discrepancies between the observed static dielectric constants ϵ_0 and those calculated assuming the ions to displace as point charges of magnitude $\mp e$, where $e = |\text{electronic charge}|$, and to acquire electronic dipole moments of the form $\mathbf{u}_1(k^j)$. In this way he found that it was perfectly consistent to regard the ions as carrying an "effective charge" $\mp e^*$, where $e^*/e \approx 0.7$ in most cases, when calculating ϵ_0 , while using the full value of e when calculating the Madelung contribution to the cohesive energy.

The reason for this is that electrons tend to be displaced from the regions of maximum overlap between nearest neighbors. Therefore, any given ion acquires a multipole moment which depends only on the relative configuration with respect to itself and its nearest neighbors. We are concerned with the resultant dipole moment, and this can be derived by regarding the charge distribution on a particular ion as equivalent to a monopole of $\mp e$, at the nucleus, together with six similarly situated dipoles each of the form $m_i^k(|\mathbf{r}_i|)(\mathbf{r}_i/|\mathbf{r}_i|)$. Here, i ($=1, \dots, 6$) denotes a particular nearest neighbor and \mathbf{r}_i is the position vector of this ion with respect to the central nucleus of type k .

In the undistorted lattice the resultant dipole moment is zero, but in the uniformly polarized crystal this is no longer true. A dipole moment, linear in the relative displacement of the two sublattices, is present and is a function of both $m^k(r_0)$ and $[dm^k(r)/dr]_{r_0}$. If one assumes that $m^2(r)$ is proportional to $e^{-r/\rho}$, where ρ is the screening radius in the repulsive potential, and that $m^1(r) \equiv 0$, then one may determine $m^2(r)$ and its derivative from the observed value of e^*/e for any given crystal. This implies that the positive ions ($k=1$) do not deform to any marked extent. This assumption seems reasonable for salts where $\alpha_1 \ll \alpha_2$ (e.g., for the Li and Na Halides), but it appears to hold even when this is not the case. In I it is shown that, for KCl, the assumption that $m^1(r)/m^2(r) \approx \alpha_1/\alpha_2$ produces results in very much worse agreement with experiment than those derived assuming $m^1(r) = 0$. Moreover, it was found that *any* departure from the latter restriction worsens the agreement.

Therefore, throughout the present analysis we have set $m^1(r) = 0$. Since this assumption is valid for KCl, it should also hold for all the salts considered in this paper, with the possible exception of KF for which $\alpha_1 > \alpha_2$.

Yamashita and Kurosawa²⁴ in their treatment of the dielectric constants of ionic crystals and Tolpygo *et al.*²⁵ in their work on the normal modes of alkali halides have similarly considered the polarization of the ions arising from the electric field due to the displacements

²³ B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950); see also reference 14 (Born and Huang), p. 111 for further discussion.

²⁴ J. Yamashita and T. Kurosawa, J. Phys. Soc. Japan **9**, 944 (1954); **10**, 610 (1955).

²⁵ Z. A. Demidenko and K. B. Tolpygo, Soviet Phys.—Solid State **3**, 2493 (1962). References are given to earlier papers.

of the ions. They have also taken into account deformation of the charge distribution resulting from overlap interaction. The results of the latter workers, although considerably less extensive than those reported here, are in essential agreement with both the shell model¹⁸ and the present work.

III. CALCULATION

Obviously one cannot derive the eigenvalues of \mathbf{M} for all the allowed \mathbf{q} vectors. We use the sample of 1000, evenly spaced throughout the first Brillouin zone, selected by Kellermann together with the zone corners which he also included although they are not true members of the sample.²⁶

Our results are thus directly comparable with those obtained for rigid ions (A.M.K.).^{12,13} (in the earlier paper¹⁶ the corners were excluded, but the derived quantities are unaffected within the limits of significance of the calculation.) From the eigenfrequencies for this sample of points it is then possible to derive any function ϕ of the form

$$\phi = \sum_{\mathbf{q}j} f[\omega_j(\mathbf{q})] = \int_0^{\omega_m} f(\omega) N(\omega) d\omega$$

by summing $f(\omega)$ over the sample of \mathbf{q} vectors, each appropriately weighted. One obtains the specific heat $C_V(T)$ by substituting for f the Einstein specific-heat function. From $C_V(T)$ the effective Debye temperature $\Theta_D(T)$ can be derived using Blackman's method⁴ described in the introduction.

Similarly, the n th moment of the frequency distribution function,

$$\mu_n = \int_0^{\omega_m} \omega^n N(\omega) d\omega / \int_0^{\omega_m} N(\omega) d\omega,$$

is given by summing appropriately weighted values of $(\omega_j)^n$ over the sample of \mathbf{q} vectors and dividing by the sum of the weighting factors.

From the resultant values of μ_n one can evaluate the moment function $\omega_D(n) = [\frac{1}{3}(n+3)\mu_n]^{1/n}$, used by Barron, Berg, and Morrison⁹ as a means of correlating values of μ_n derived from experimental data.

This function, which should be constant for a true Debye spectrum, provides a particularly useful means of comparing theory and experiment, since it contains most of the information which can reliably be derived from the sample of points we have employed. The curves of $\Theta_D(T)$ vs T contain a little more but are unreliable in the regions close to 0°K.

The eigenvalues and their associated eigenvectors, which also have been determined in each case for all the chosen \mathbf{q} vectors, are too numerous to tabulate in this paper. However, they are available from one of us (A.M.K.) upon request.

²⁶ The sample point omitted by Kellermann (references 1, 12) $\mathbf{q} = \pi/r_0(0.7, 0.7, 0.1)$, and those derived from it by symmetry have been included.

IV. RESULTS

A. Initial Calculations

We have treated all of the Na and K halides together with LiF and LiCl. Results for each crystal have been obtained for both room temperature (RT) and 0°K input data.²⁷ For the 0°K calculations we have assumed that e^*/e , α_1 , and α_2 are unchanged between RT and 0°K, except for KCl for which a slightly modified value of the effective charge has been used. Because e^*/e is unknown for all the lithium halides except LiF, the value used for LiCl is only a rough estimate. Compressibilities and lattice constants, which constitute the remainder of the input data, are the same as those used in the rigid-ion calculations.^{12,13}

Thus, most of the input data have been taken from Born and Huang²⁸ and T.K.S.²² and are displayed in detail as Table I.

At present any comparison of our results and those of the rigid ion (RI) calculations is best made between those derived from RT input data. Although the ionic polarizabilities probably change little between RT and 0°K, e^*/e may well vary significantly in many cases. This point will be considered in more detail in a later section. It is sufficient for our present purposes to remark that our results are very sensitive to e^*/e , which in turn depends on ϵ_0 which is only known to within a few percent even at room temperature.²⁹ In addition, to obtain e^*/e one also requires ω_0 , the reststrahlen frequency, which is also unknown at 0°K,

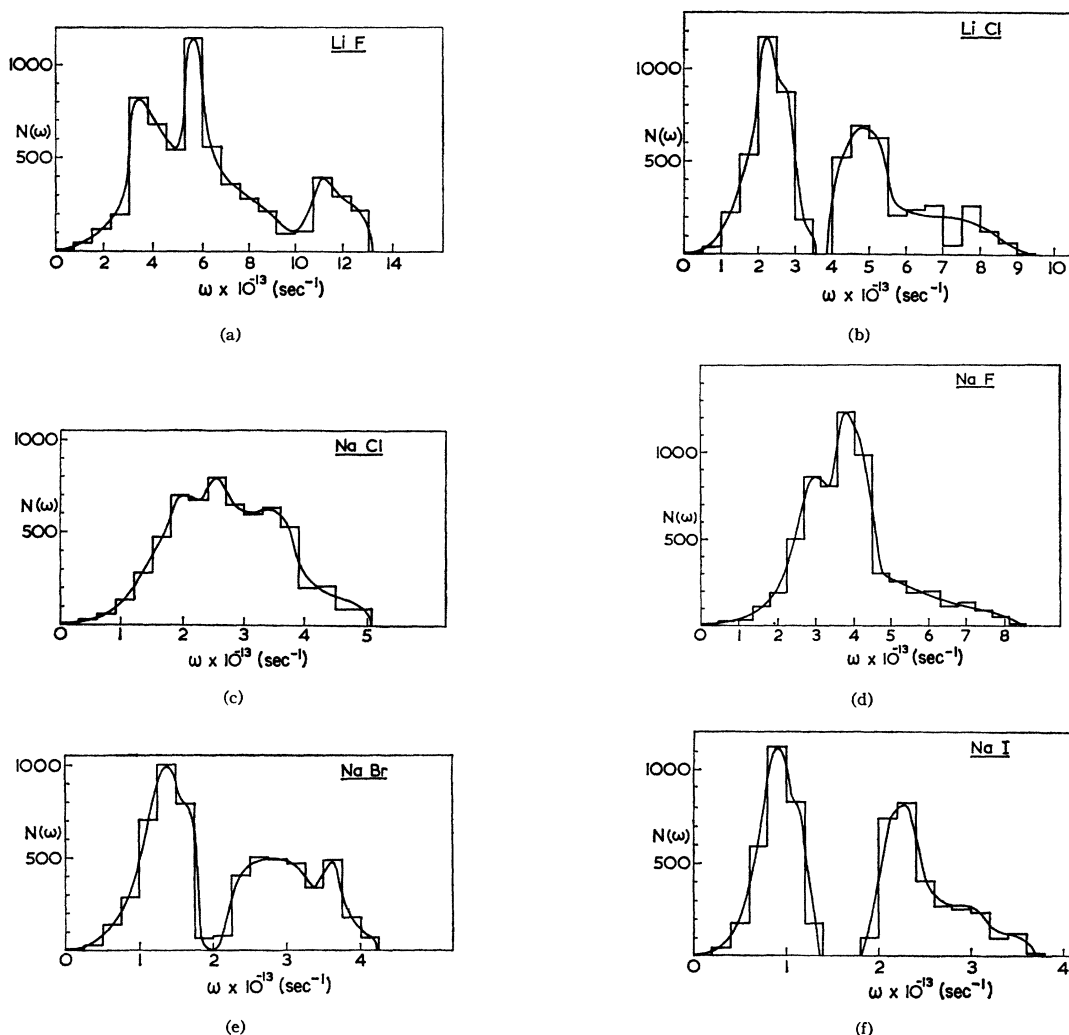


FIG. 1. Vibrational frequency distributions for the Li and Na halides (RT data).

²⁷ It is not practical to present here a complete set of results for each of the alkali halides we have studied. The reader is referred to the University of California Lawrence Radiation Laboratory Report UCRL-6893, (1962, unpublished) by the authors for a full presentation of the calculated data.

²⁸ Reference 14 (Born and Huang), pp. 85 and 112.

²⁹ The values given in Born and Huang, p. 85, and used by us disagree with the more recent data of S. Haussühl [Z. Naturforsch. 12a, 445 (1957)] by amounts of this order.

TABLE I. Input data for initial D. D. (deformation dipole) calculations.

Salt	Compressibility β (10^{-12} /barye)		"Effective charge" e^*/e		Lattice constant r_0 (10^{-8} cm)		Screening radius ρ (10^{-8} cm)		Ionic polarizabilities (RT & 0°K)	
	RT	0°K	RT	0°K	RT	0°K	RT	0°K	α_+ ($\equiv \alpha_1$)	α_- ($\equiv \alpha_2$)
LiF	1.54	1.43	0.80	0.80	2.0087	2.0004	0.2989	0.2858	0.029	0.759
LiCl	3.41	3.20	0.75	0.75 ^a	2.5648	2.5538	0.3346	0.3218	0.029	2.974
NaF	2.11	1.99	0.93	0.93	2.3100	2.2967	0.2878	0.2786	0.255	0.759
NaCl	4.26	3.98	0.74	0.74	2.8138	2.7935	0.3283	0.3163	0.255	2.974
NaBr	5.03	4.70	0.69	0.69	2.9805	2.9560	0.3335	0.3194	0.255	4.130
NaI	7.07	6.45	0.71	0.71	3.231	3.1975	0.3637	0.3462	0.255	6.199
KF	3.30	3.10	1.00	1.00	2.6650	2.6476	0.3020	0.2917	1.201	0.759
KCl	5.63	5.26	0.80	0.795 ^b	3.1390	3.1167	0.3236	0.3114	1.201	2.974
KBr	6.70	6.17	0.76	0.76	3.2930	3.2658	0.3348	0.3192	1.201	4.130
KI	8.54	7.75	0.69	0.69	3.5260	3.4918	0.3497	0.3305	1.201	6.199

^a Estimated from ionic radii.

^b Derived from 80°K data.

although the RT values measured by different workers are reasonably self-consistent.³⁰

We have first used our data to construct frequency distribution functions $N(\omega)$ for all the salts. This was done in each case by dividing the frequency range into about twenty equal intervals, $\Delta\omega$, and counting the properly weighted number of frequencies in each. This allows one to plot a histogram of the distribution function $N(\omega)$ against ω . In most cases it is then possible to fit a smooth curve to the histogram, which is a

reasonable approximation to the true distribution function. Frequency distributions for both 0°K and RT initial sets of parameters (Table I) were constructed, but except for the K halides the former are not displayed here. For 0°K parameters the structure of the curves in general is unchanged with only small shifts of the peaks to higher frequencies.

In Figs. 1 and 2 the resulting RT $N(\omega)$ vs ω curves are shown, together with the backing histograms. These curves have been checked, and in one or two

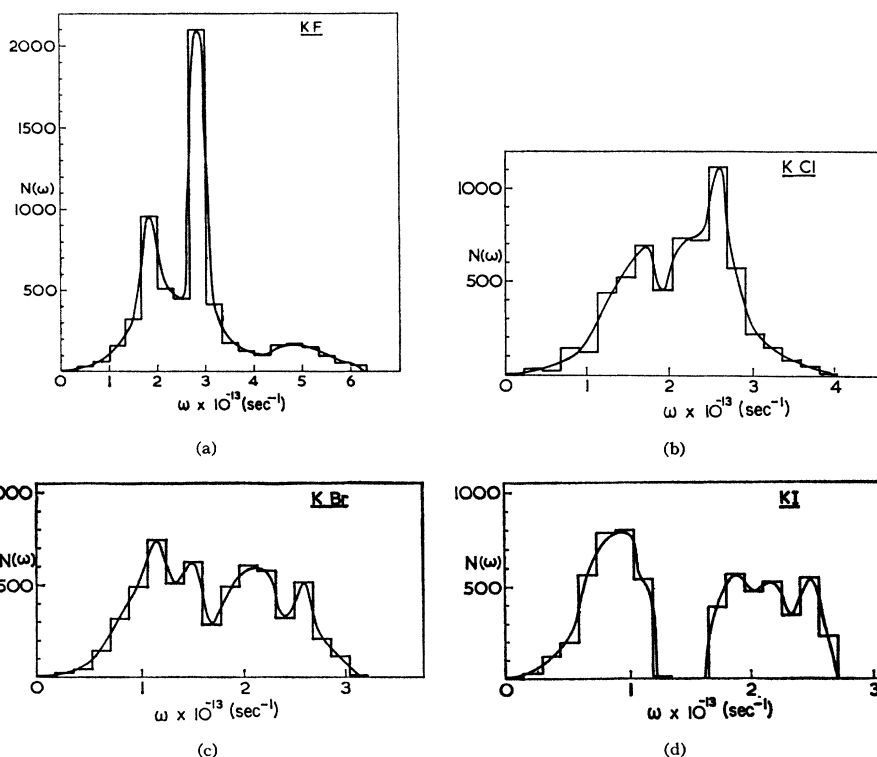


FIG. 2. Vibrational frequency distributions for the K halides (RT data).

³⁰ R. B. Barnes, Z. Physik **75**, 723 (1932); G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **A261**, 10 (1961); and M. Hass, Phys. Rev. **119**, 633 (1960).

dubious cases modified, by displacing the origin of $\Delta\omega$ by first $\Delta\omega/3$ and then $2\Delta\omega/3$ and recounting. As a result of this check one can say that all the features displayed by the smoothed curves are genuine, but that their relative strengths are somewhat uncertain. This is particularly true of the weaker features. The

curves for NaCl and KCl are slightly modified versions of earlier results^{16,17} and are given here for completeness. The use of a smaller $\Delta\omega$ for KCl has also revealed additional structure on the low-frequency side of the strongest peak.

In Figs. 3, 4, and 5 the associated sets of ω vs q

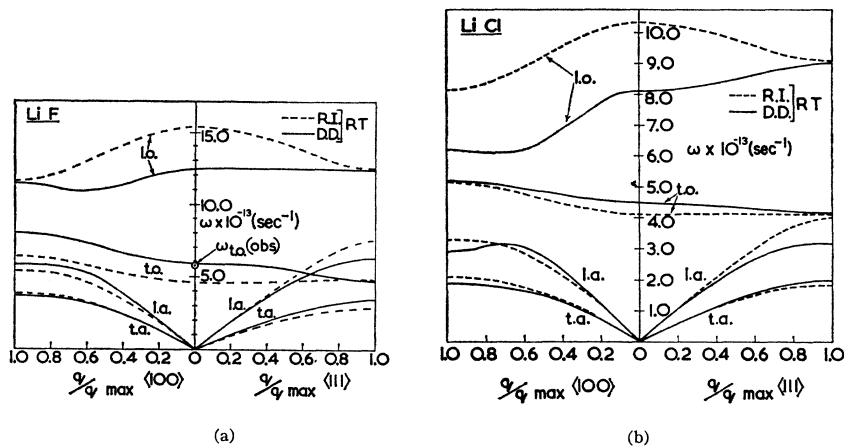


FIG. 3. Phonon-dispersion curves for LiF and LiCl (RT data).

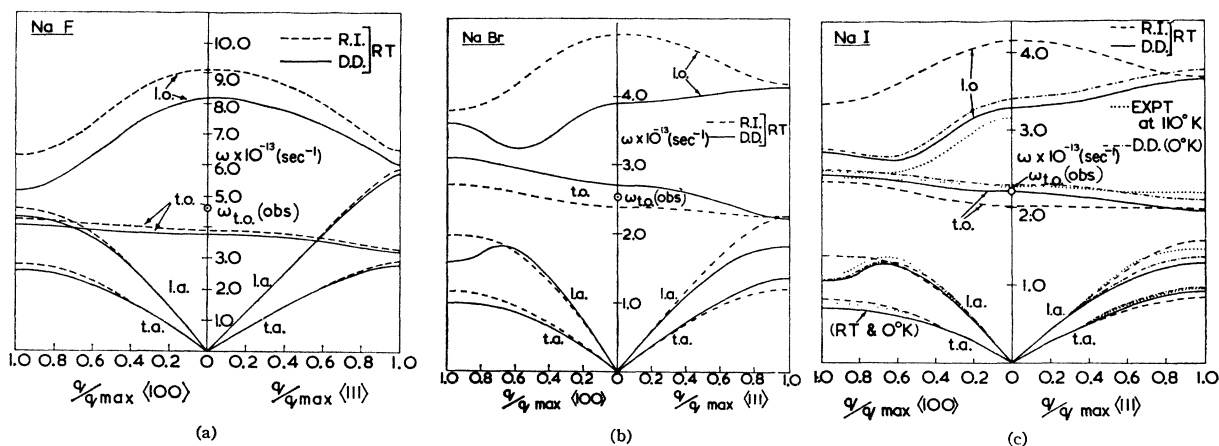


FIG. 4. Phonon-dispersion curves for the Na halides (RT data). For NaCl see reference 16.

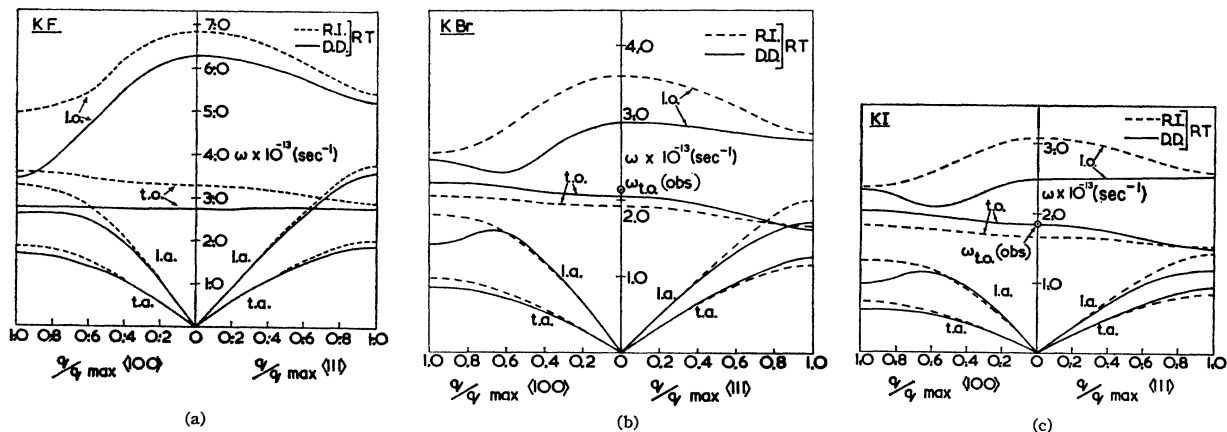


FIG. 5. Phonon-dispersion curves for the K halides (RT data). For KCl see reference 17.

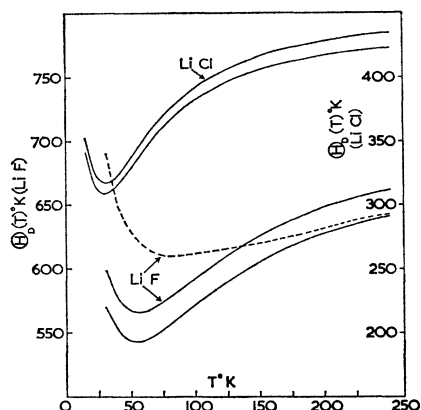


FIG. 6. Debye characteristic temperatures as functions of temperature for the Li halides. Upper and lower curves are for 0°K and RT parameters, respectively. Experimental values are indicated by the dashed curve.

dispersion curves, marked D.D., are shown for lattice waves propagating along $\langle 111 \rangle$ and $\langle 100 \rangle$ directions in these crystals. For comparison the appropriate rigid-ion (RI) curves^{12,13} are also shown together with the measured RT reststrahlen frequency³⁰ which provides a direct measure of the transverse optical (t.o.) frequency at $\mathbf{q}=0$. Once again all the results are derived from RT data. The transverse branches (t.a. and t.o.) are doubly degenerate for these directions, hence there are only four distinct ω 's for a given \mathbf{q} vector. The curves which one obtains from 0°K data differ very little in over-all shape from those given here. To illustrate the general trend we have shown both sets of curves for NaI together with the results derived by inelastic neutron scattering at 110°K.¹⁸ By comparing our results with those of Woods, Cochran, and Brockhouse it can be seen that the D.D. (0°K) curves fit the experimental results as well as do those of the "shell" model used by these authors.

In Figs. 6, 7, and 8 are plotted the $\Theta_D(T)$ curves which we obtain from the theoretical specific heats. Also shown are the experimental curves derived from values of $C_V(T)$ for those salts for which data are available.^{10,11} Each curve is terminated near 0°K when it ceases to be reliable. Tables of the calculated and experimental heat capacities which correspond to these

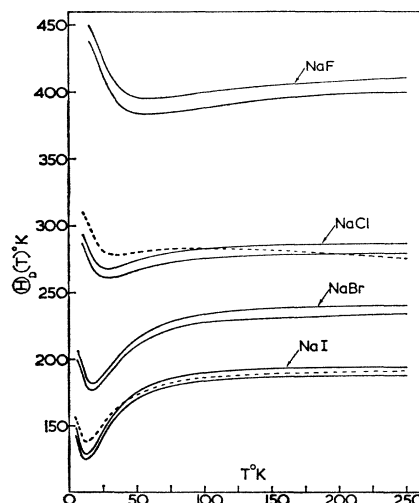


FIG. 7. Debye characteristic temperatures as functions of temperature for the Na halides. Upper and lower curves are for 0°K and RT parameters, respectively. Experimental values are indicated by the dashed curves.

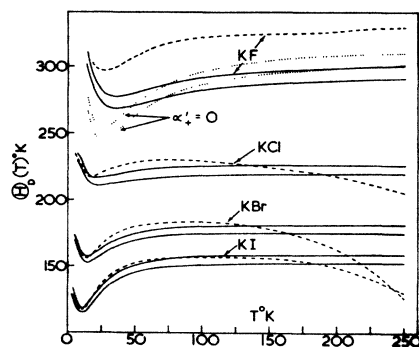
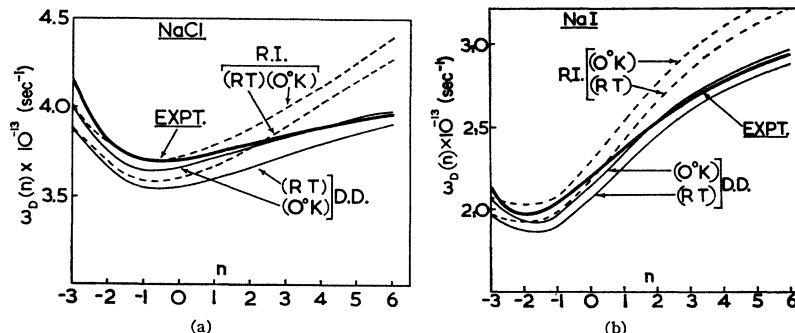


FIG. 8. Debye characteristic temperatures as functions of temperature for the K halides. Upper and lower curves are for 0°K and RT parameters, respectively. Experimental values are indicated by the dashed curves.

Debye characteristic temperatures are collected in reference 27.

In Figs. 9 and 10 we show in more detail the derived moment functions, $\omega_D(n)$, denoted by D.D. Also plotted are the curves obtained from the rigid-ion (RI) model^{12,13} and from the available experimental

FIG. 9. The moment function $\omega_D(n) = [\frac{1}{3}(n+3)\mu_n]^{1/n}$ vs n for NaCl and NaI. The experimental curve for NaI has been modified and is appropriate to $\Theta_\infty = 193^\circ\text{K}$ rather than 195°K (reference 9).



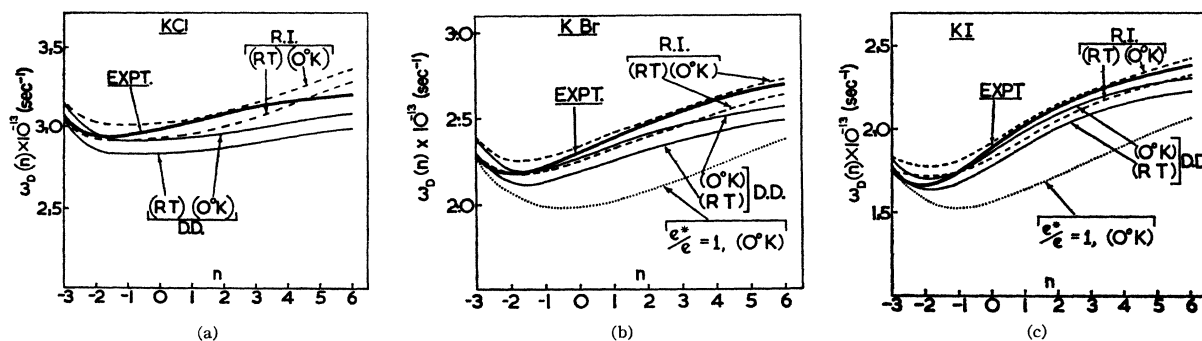


FIG. 10. The moment function $\omega_D(n) = [\frac{1}{3}(n+3)\mu_n]^{1/n}$ vs n for KCl, KBr, and KI.

data.⁹ The RT results for NaCl and KCl have appeared previously¹⁶ (see also I). In the present paper, the curves have been extrapolated to the true limiting value of $k_B\theta_0/\hbar$ as $n \rightarrow -3$; where k_B is Boltzmann's constant and θ_0 is the limiting value of $\theta_D(T)$ at 0°K evaluated from the *theoretical* elastic constants.⁹ For our model these limiting values are the same as those derived previously for rigid ions.^{12,13}

In Fig. 10 we have also shown for KBr and KI the $\omega_D(n)$ curves obtained by neglecting the deformation polarization, which is equivalent to setting $e^*/e=1$. (A similar curve is drawn in Fig. 13 for the KCl calculation described in the next section.) We note that deformation polarization in KF has also been neglected because of our initial choice of the parameter e^*/e (see Table I). It is evident that this neglect introduces a discrepancy between theory and experiment at least as marked as that found in the case of NaCl¹⁶ and completely destroys the accord between the RI results and experiment.

B. Variations of Parameters

We see that the results in any one case are sensitive to the input values of e^*/e , the compressibility β , and the lattice parameter r_0 . Changes in the first affect the shape of the resultant $\omega_D(n)$ curve very markedly; while variations in β and r_0 , which are partially compen-

sating, produce an almost uniform change in the absolute level of this function.

It might also be expected that our results are sensitive to the ionic polarizabilities α_k . To check this we have calculated frequency distributions for all the alkali halides considered with $\alpha_1' = \alpha_1 = 0$ and $\alpha_2' = \alpha_1 + \alpha_2$, the sum of the T.K.S.²² polarizabilities. The resulting distribution curves are shown in reference 27. Except in the case of KF (cf. Fig. 16), which we shall consider in more detail later, the distributions are not greatly affected. The derived $\theta_D(T)$ and $\omega_D(n)$ curves are so little different from those in Figs. 6 through 10 that, apart from the $\theta_D(T)$ curve for KF, we have not displayed them. In every case, KF excluded, the results are in slightly *worse* agreement with experiment indicating that one should retain the T.K.S. α 's during subsequent work.

We decided to take as our test cases the three salts KCl, NaCl, and KF, and we shall discuss each separately.

1. KCl

For this crystal we have used a revised value of β in the 0°K calculation, since more recent results³¹ indicate that the value given in Table I is an underestimate. Revised input data for KCl and for the other two salts are listed in Table II.

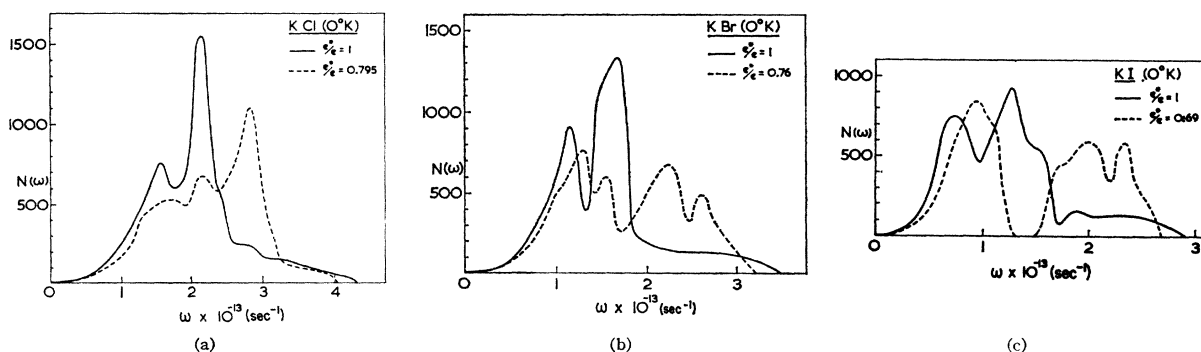


FIG. 11. Superimposed vibrational frequency distributions for the K halides (0°K data) corresponding to including or neglecting deformation polarization.

³¹ M. H. Norwood and C. V. Briscoe, Phys. Rev. **112**, 45 (1958).

TABLE II. Variations of 0°K input data. (Parameters not shown explicitly are the same as those appropriate to 0°K in Table I.)

Salt	Compressibility β (10^{-12} /barye)	"Effective charge" e^*/e	Screening radius (used to derive D. D. moment) ρ (10^{-8} cm)
KCl	5.08	...	0.3028
NaCl a	...	0.756	...
b (original run)
c	3.89	...	0.3107
d	3.89	0.756	0.3107
e	3.89	0.756	0.3729 [=1.2(0.3107)]
KF a	...	0.95	...
b	...	1.05	...
c	...	0.85	...

It can be seen that we have used the same value of $(e^*/e)_{0^\circ\text{K}}$ as that given in Table I and that it is virtually the same as the RT value. The low-temperature value is obtained from recent measurements by Hass^{30,32} on the reststrahlen frequencies of NaCl and KCl at 82°K which provide a much improved estimate of $(e^*/e)_{0^\circ\text{K}}$.

In Fig. 11 we show the resultant distribution function for these input data together with the distribution function derived with $e^*/e=1$. For comparative purposes we also show those functions obtained for KBr and KI, superimposing the distributions corresponding to either including or neglecting deformation polarization. Similar curves for KF are given in Fig. 16. Comparing Fig. 2 (RT distributions) with Figs. 11 and 16 (0°K distributions) clearly shows the relatively small changes in shape which in general occur between room temperature and 0°K. On the other hand, the complete change in character of the distribution function when deformation polarization is neglected is quite apparent. We may also note that the effect appears to be enhanced for the larger, more deformable ions.

Thus, in general, the drastic changes in shape which can occur are due mainly to setting e^*/e equal to unity

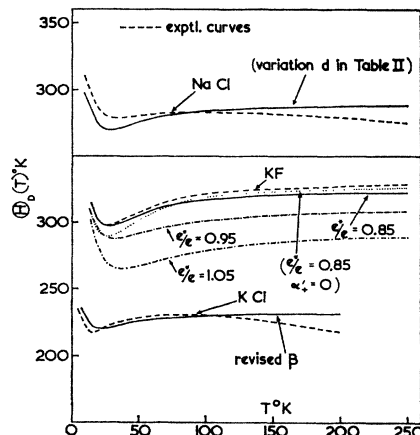


FIG. 12. Revised Debye characteristic temperatures as functions of temperature (0°K data). For NaCl only the best fit (variation *d*) is shown. Curves for the other variations are shown in Fig. 13.

and not to the changes in β and r_0 between RT and 0°K.³³

In Figs. 12 and 13 the derived functions $\Theta_D(T)$ and $\omega_D(n)$ are shown. Most of the discrepancy between theory and experiment, present in Figs. 8 and 10, has been removed, the agreement being at least as good as that for KBr and KI.

2. NaCl

For this salt the data of Hass³⁰ indicate an appreciable change in $(e^*/e)_{0^\circ\text{K}}$. We have tried a number of variations of the input parameters, all of which are listed in Table II. The resulting Debye temperatures and moment functions are shown in Figs. 12 and 13. In Fig. 14 we show the distribution function which combines the most reliable input data and leads to the best fit of the specific-heat data.

Thus, from Fig. 13 we see that the use of the improved value of e^*/e worsens the agreement with experiment,

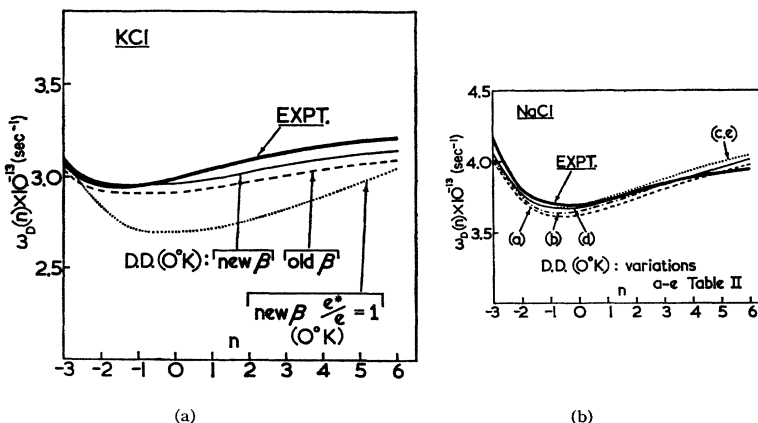


FIG. 13. The moment function $\omega_D(n) = [\frac{1}{3}(n+3)\mu_n]^{1/n}$ vs n for various 0°K input data.

³² We should like to express our thanks to Dr. Hass for access to unpublished data on these salts.

³³ The relative effect is significantly larger for the D.D. results than for the R. I. curves although small in absolute terms.

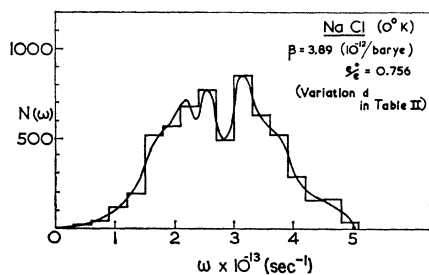


FIG. 14. Revised vibrational frequency distribution for NaCl resulting from the most reliable set of input data.

but that the use in addition of a more recent value³⁴ of β removes this discrepancy and leads to better over-all agreement than any other set of parameters.

It is particularly interesting to notice that the use of a different value of ρ , the screening radius, when deriving $m^2(r)$ worsens the agreement between theory and experiment. This indirectly supports the assumption that deformation due to overlap occurs only on the negative ion. If the displaced charge came from both types of ion, its "center of gravity" would probably move, relative to the nucleus of the negative ion, in a uniformly polarized crystal (as predicted by the "shell model"¹⁹), and this would effectively increase ρ . Such an effect need not occur if only one type of ion deforms.

3. KF

As mentioned earlier this salt is unique among those considered here in that the positive ion has the larger polarizability. This suggests that, if deformation polarization occurs, it may also take place on the positive ion. In the initial calculation we set $e^*/e=1$ and thus neglected any deformation polarization. The resulting poor agreement between the theoretical and experimental³⁵ $\Theta_D(T)$ curves indicates that this assumption is invalid. Also, as we noted in Sec. IV B, it is disturbing to observe the relatively large improvement in this agreement brought about by assuming all the polarization dipole to lie at the center of the negative ion.

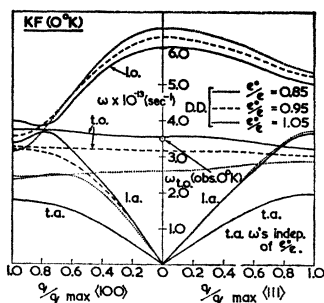


FIG. 15 Phonon-dispersion curves for KF for various 0°K input data.

³⁴ W. C. Overton and R. T. Swim, Phys. Rev. **84**, 758 (1951)

³⁵ E. F. Westrum and K. S. Pitzer, J. Am. Chem. Soc. **71**, 1940 (1949). $\Theta_D(T)$ is derived from $C_V(T)$ estimated as described in reference 13, footnote 13.

We have therefore repeated the calculations for $e^*/e=0.85, 0.95,$ and 1.05 (see Table II). The last value is used in a calculation in which only the positive ion is allowed to deform.

The Debye characteristic temperature is shown in Fig. 12 and the associated sets of dispersion curves and frequency distributions in Figs. 15 and 16. In every case we have confined our attention to the results derived from 0°K input data. It is evident from Fig. 12 that assuming $e^*/e=0.85$ gives a theoretical $\Theta_D(T)$ curve in excellent agreement with the experimental curve. The slight discrepancy above 150°K may well represent a systematic error in the derivation of $\Theta_D(T)$ from the *measured* specific heat at constant pressure.³⁵ While subsequent measurements may indicate some slight revision of e^*/e to be required, it is almost certain that the value of 0.85 is not greatly in error.

Thus, we may say conclusively that the deformation occurs essentially on the *negative* ion in this as in the other salts. Moreover, for $e^*/e=0.85$ the results obtained assuming that only the negative ion polarizes are now in significantly worse agreement with experiment. Perhaps the most striking confirmation of the revised value of e^*/e for KF comes from the observed reststrahlen frequency at 80°K for this salt.³⁶ This is shown on the dispersion curves in Fig. 15 (assuming the value unchanged at 0°K). It is seen that this point lies on the calculated transverse optical (t.o.) branch at $q=0$. Such good agreement does not follow implicitly from that found between the theoretical and experimental specific-heat data. It may be taken, therefore, as an independent piece of evidence in support of our final model for which the frequency distribution is shown in Fig. 16. In Fig. 16 a comparison is given of this distribution and those corresponding to neglecting deformation polarization or placing all ionic polarization on the negative ion.

Finally we note that it would be particularly interesting to determine experimentally the value of $\omega_m=\omega_{1,0}(q=0)$ (the highest frequency) for this salt to provide a further test of this model.

V. DISCUSSION

It is evident that our theory leads to results which are in general in reasonable agreement with the experimental data that exist. It should be emphasized that the input values of β and e^*/e are subject to experimental revision. Any discrepancies with respect to present results of the theory revealed by subsequent experimental work could well be reduced by improved values of these parameters (*cf* the revisions for KCl

³⁶ Molecular and Solid State Spectroscopy Report 1959-1960, Physics Department, King's College, London, U. S. Army Contract DA-91-591-EUC-1308 OI-4201-60 (unpublished). We are particularly indebted to Dr. G. R. Wilkinson and C. Smart for access to their data in this report which also confirms results reported in reference 30.

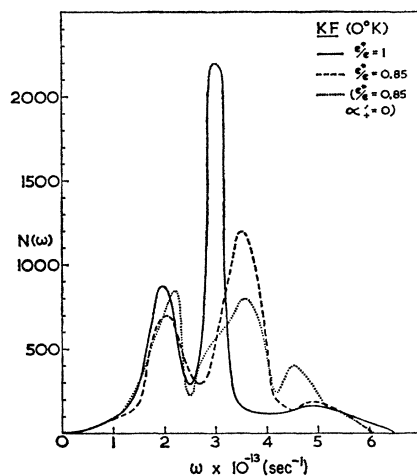


FIG. 16. Superimposed vibrational frequency distributions for KF for various 0°K input data.

and NaCl). This possibility applies to some extent to the significantly worse agreement between the present D.D. $\omega_D(n)$ curves and the experimental curves, as compared with the RI results for KBr and KI.

However, at least for KBr other reasons for the present discrepancy exist. This is apparent in Fig. 5 where one can see that $\omega_{t.o.}(q=0)$ disagrees with the measured RT value. It is probable that a similar discrepancy exists at 0°K. Since the calculated reststrahlen value is too low, one also expects the calculated values of $\omega_D(n)$ to lie below the experimental results. This is seen to be the case.

It also seems likely that a similar, but smaller, discrepancy is present in the 0°K results for KI,³¹ and in the revised 0°K data for KCl. For the latter salt this could explain much of the residual disagreement between the theory and experiment.

The probable origin of these discrepancies was first described by Szigeti.³⁷ Prior to introducing the "deformation dipole" concept to explain the observed values of e^*/e , he considered the effect of short-range interactions between second-neighbor ions. When these are present one must calculate both nearest and next nearest neighbor force constants separately. While both influence β , $\omega_{t.o.}(q=0)$ depends only on the former. We hope shortly to present the results of more refined calculations designed to include both types of interaction.

With this reservation, it is evident that the D.D. model reproduces the frequency spectra and the derived quantities determined experimentally from specific heat data rather better (particularly for NaCl and NaI) than the RI theory. This improvement is particularly satisfying when one recalls how sensitive the results are to the manner in which the dipole induced on a given ion is calculated.

It thus seems that future experimental work designed

³⁷ B. Szigeti, *Trans. Faraday Soc. (London)* **45**, 155 (1949).

to test the D.D. model would be very profitable. This is particularly true of neutron scattering measurements to determine dispersion curves, but also applies to experimental determinations of β and e^*/e to establish accurately the values that one should use as input data. It perhaps should be emphasized here that our model does not contain any adjustable parameters: The results of the calculations are uniquely defined with respect to the input parameters, which in turn can eventually be precisely determined by experiment.

The only safe comparisons would appear to be those made between our theoretical results and the corresponding experimental data for an "effective" harmonic spectrum at 0°K.⁹ Provided that anharmonic effects are small in this temperature region, as is generally the case, it seems to us reasonable to assume that by using the *observed* values of e^*/e and β at 0°K we obtain results which are appropriate to this spectrum. That is, the most important anharmonic effects are probably implicitly included by using these input data.³⁸

It seems likely that the use of more precisely determined experimental parameters and the introduction of next-nearest-neighbor interactions between ions will remove most discrepancies except those in the $\omega_D(n)$ curves for some salts (e.g., NaCl) as $n \rightarrow -3$. These differences reflect disagreements between theoretical and ultrasonically determined elastic constants,^{12,13,31,34} and, in particular, the failure of the latter to satisfy the Cauchy relation $C_{12}=C_{14}$. Alternative measurements of C_{12} seem desirable in order to confirm and determine the exact extent of this violation, since C_{12} determined ultrasonically is somewhat unreliable. Such an alternative method is provided by direct measurements of β , which one requires in any case to establish the input data reliably. (The "improved" values of β for KCl and NaCl were determined from the experimental values of C_{11} and C_{12} ,^{31,34} and are thus still to be considered somewhat unreliable.)

However, for LiF³⁹ the failure of the Cauchy relation is undoubtedly real and is reflected in the specific-heat data below 100°K. To properly interpret this discrepancy a more refined theory along the lines developed by Löwdin⁴⁰ and his school is probably necessary.

These workers have made detailed quantum-mechanical calculations of the charge distributions in several alkali halides using free-ion functions. The derived potential function for the nuclear motion involves terms which depend simultaneously on the coordinates of three or more ions. These terms can lead to violations of the Cauchy relation. However, in I

³⁸ B. Szigeti, *Proc. Roy. Soc. (London)* **A252**, 217 (1959); **A258**, 337 (1960).

³⁹ C. V. Briscoe and D. F. Squire, *Phys. Rev.* **106**, 1175 (1957).

⁴⁰ P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1956), Vol. 5. See also S. O. Lundqvist, *Arkiv Fysik* **9**, 435 (1955); **12**, 263 (1957).

[Appendix (a)] it has been demonstrated that these terms are essentially equivalent to the inclusion of higher order multipole interactions, and that it is plausible to infer that their influence is most marked for the long-wavelength acoustic modes, whose frequencies depend only on the elastic constants. It follows that both frequency distributions and dispersion curves should be almost unaffected, except in the low-frequency regions, and it would be interesting to test these assertions experimentally.

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Interaction of Ultrasonic Waves with Electron Spins

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We discuss the interaction between paramagnetic atoms and elastic waves at microwave frequencies by means of a total Hamiltonian comprising sound field, interaction, and spins. From this Hamiltonian and the Heisenberg commutation rules we obtain a set of coupled equations of motion. The condition of compatibility leads in the usual way to a secular determinant, the solution of which is a dispersion relation exhibiting the familiar anomalous change in velocity and absorption of waves near resonance.

I. INTRODUCTION

WITH the advent of methods for generating and detecting ultrasonic waves at microwave frequencies, it has become possible to study the interaction between lattice vibrations and electron spin systems directly. Such studies have been carried out by observing the effects of ultrasonic waves on paramagnetic resonance^{1,2} and, conversely, by noting the effects of paramagnetic ions on the propagation of ultrasonic waves.³⁻⁶ It is the purpose of this paper to discuss the latter phenomenon, and, in particular, to develop a theory of elastic wave propagation in a solid containing resonant spins.

II. DISPERSION OF SOUND BY RESONANT SPIN SYSTEMS

The experimentally observed change in the velocity of sound propagation⁶ when the ultrasonic frequency

approaches the resonant frequency of allowed spin transitions closely parallels the behavior of electromagnetic waves propagating in a medium containing resonant atoms. The latter phenomenon of electromagnetic dispersion is well known and easily described by Maxwell's equations for the electromagnetic field and the dynamical equations for the atomic system. When the atomic system is represented by a harmonic oscillator, the problem is particularly simple and readily formulated in terms of Maxwell's equations and Newton's equations of motion for the oscillator, these same ideas being extendable to purely quantum-mechanical systems by means of time-dependent perturbation theory. To treat the dispersion of sound, we employ a model analogous to that of the harmonic oscillator used in elementary treatments of electromagnetic dispersion and derive a set of equations of motion for the composite sound field and spin system, a simultaneous solution of which yields a dispersion relation. We expect the scheme to be extendable to spin systems obeying purely quantum laws of motion by the use of quantum theory. As we shall see, such a program can be carried out subject to the assumption that the spins are uniformly distributed and that there are many spins per sonic wavelength. The system of spin $S=1/2$ is the counterpart of the harmonic oscillator in the optical case.

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¹ E. H. Jacobsen, N. S. Shiren, and E. B. Tucker, *Phys. Rev. Letters* **3**, 81 (1959).

² N. S. Shiren and E. B. Tucker, *Phys. Rev. Letters* **6**, 105 (1961).

³ E. B. Tucker, *Phys. Rev. Letters* **6**, 183 (1961).

⁴ N. S. Shiren, *Phys. Rev. Letters* **6**, 168 (1961).

⁵ E. B. Tucker, *Phys. Rev. Letters* **6**, 547 (1961).

⁶ N. S. Shiren, *Phys. Rev.* **128**, 2103 (1962).