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Lattice Dynamics of NaCl, KCl, RbCl, and RbF

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In a series of earlier papers, experimental results on phonon dispersion relations at 80 °K in NaCl, KCl, RbCl, and RbF have been reported. We now present calculations on these halides using the extended-shell-model approach with both ions polarizable and including next-nearest-neighbor interactions. The parameters obtained in a least-squares fit to the experimental points in the symmetry directions have been used to calculate the phonon frequencies in 512 000 equally spaced points in an octant of the Brillouin zone, whereby, after sorting these into intervals of width $\Delta\omega = 2\times 10^{11}$ rad sec^{-1}, the frequency spectrum was obtained. From these spectra the variation of the Debye temperature with temperature was also calculated. The agreement with results from specific-heat measurements for NaCl and KCl is quite satisfactory at low temperatures.

I. INTRODUCTION

The lattice dynamics of alkali halides has been described in terms of gradually more complicated models developed since about 1940. The original rigid-ion approach of Kellermann[1] has been the foundation of the development of these models of the ionic interactions in the alkali halides. Among such models are the simple-shell model (SM) first used in lattice dynamics by Cochran,[2] and the generalized-shell model of Woods *et al.*,[3] which is an extended version of the SM. A minor modification of this model has been made by Schröder[4] in the so-called "breathing" shell model (BSM). Slightly different approaches have been made in a series of papers by Karo and Hardy[5] using various versions of their deformed-dipole model (DD). Dick and Overhauser[6] proposed the exchange-charge model (ECM) which is closely related to the SM. These models all take into account the polarizability of the ions in the lattice, though in somewhat different manners. So far the extended-shell model seems to be the most successful and widely used of these models and we have used it for calculations of dispersion curves, frequency spectra, and Debye temperatures for the four halides we have studied.[7-9]

Sections II to IV present the results of these calculations.

II. MODEL AND A CALCULATION OF DISPERSION CURVES

A considerable number of papers describing the model are now available[10] and we will not go into any great detail here. A short account of the basic assumptions of the model is, however, appropriate. Basically one has to take into account the short-range "overlap" repulsion between the ions, the Coulomb forces, and also forces between the ion cores and the outer electrons arising because of the distortion of the configuration of these outer electrons, the "shell." The Coulomb forces may be described in terms of an electric multipole expansion on the ion sites. If higher-order terms than dipole are neglected, this leads to the shell model. The general form of this model contains a large number of adjustable parameters, and simplifying assumptions must be made to reduce this number. Assuming the overlap forces to be axially symmetric and to extend no further than second-nearest neighbors, and making the approximation that short-range forces act exclusively through the outer electron shell one ends up with 11 adjustable parameters. This is the procedure introduced by Cowley *et al.*[11] The model also includes the harmonic and adiabatic assumptions. The 11 parameters are A_{12}, B, A_{11}, B_{11}, A_{22}, B_{22} [i.e., the radial and tangential force constants between the (1)-(2), (1)-(1), and (2)-(2) near-neighbor ions, (1) and (2) designating the positive and negative ions, respectively], the ionic charge Ze, and the electrical and mechanical polarizabilities α_1, α_2, d_1, and d_2. The parameter B is related to B_{11}, B_{22}, and Z by a stability condition for the lattice and may be replaced by $B+B''$ in the equations of motion, B'' taking into account noncentral forces between nearest neighbors. Cochran showed that the equations of motion may be written

$$\underline{m}\omega^2\underline{U} = (\underline{R} + \underline{Z}\underline{C}\underline{Z})\underline{U} + (\underline{T} + \underline{Z}\underline{C}\underline{Y})\underline{W} \;,$$
$$0 = (\underline{\tilde{T}} + \underline{Y}\underline{C}\underline{Z})\underline{U} + (\underline{S} + \underline{Y}\underline{C}\underline{Y})\underline{W},$$

where $\underline{R}$, $\underline{T}$, and $\underline{S}$ are matrices describing the short-range interactions and $\underline{C}$ is a matrix of Coulomb coefficients, while $\underline{m}$, $\underline{Z}$, and $\underline{Y}$ are diagonal matrices designating the ion masses, the ion charges, and the shell charges, $\underline{U}$ is the displacement vector of the ions, and $\underline{YW}$ is the electronic dipole moment of the ions.

We have solved these equations using a varying number of adjustable parameters, including the rigid-ion case where polarization is not taken into account. A good fit to the experimental points was obtained for two models with nine parameters and for an 11-parameter model. The latter gave a slightly better fit than the other two but the improvement was not very significant. The numerical results for these models are presented in Tables I and II. Model 1 includes second-neighbor interactions between positive ions only, while model 3 includes these interactions between negative ions only. Model 2 is the 11-parameter model taking all second neighbors into account. The calculated dispersion curves for model 2 are compared to the experiments in Figs. 1(a)–1(d). The fitting to the experimental points in the symmetry directions was performed using a nonlinear least-squares procedure. Also included in the tables are the standard errors and the quantity χ^2 calculated from

$$\mathrm{SE}=\left(\sum_{i=1}^{N}[\omega_i(\mathrm{expt})-\omega_i(\mathrm{model})]^2(N-K)^{-1}\right)^{1/2}$$

and

$$\chi^2=\sum_{i=1}^{N}\left(\frac{\omega_i(\mathrm{expt})-\omega_i(\mathrm{model})}{\sigma_i}\right)^2(N-K)^{-1},$$

where N is the number of observations, K is the number of adjustable parameters, ω_i is the phonon frequencies (in units of 10^{13} rad sec^{-1}), and σ_i is the estimated experimental error for the ith phonon. In Fig. 1, one finds the agreement between model and experiment to be quite satisfactory. More than two-thirds of the experimental frequencies differ from the model values by less than 1% and less than one-tenth of all experimental points differ by more than 2%.

A look at the Tables I and II reveals that the estimated uncertainties in the parameters are often rather large. This makes it difficult to draw any conclusions as to any significant variation of a specific parameter from one halide to another. A

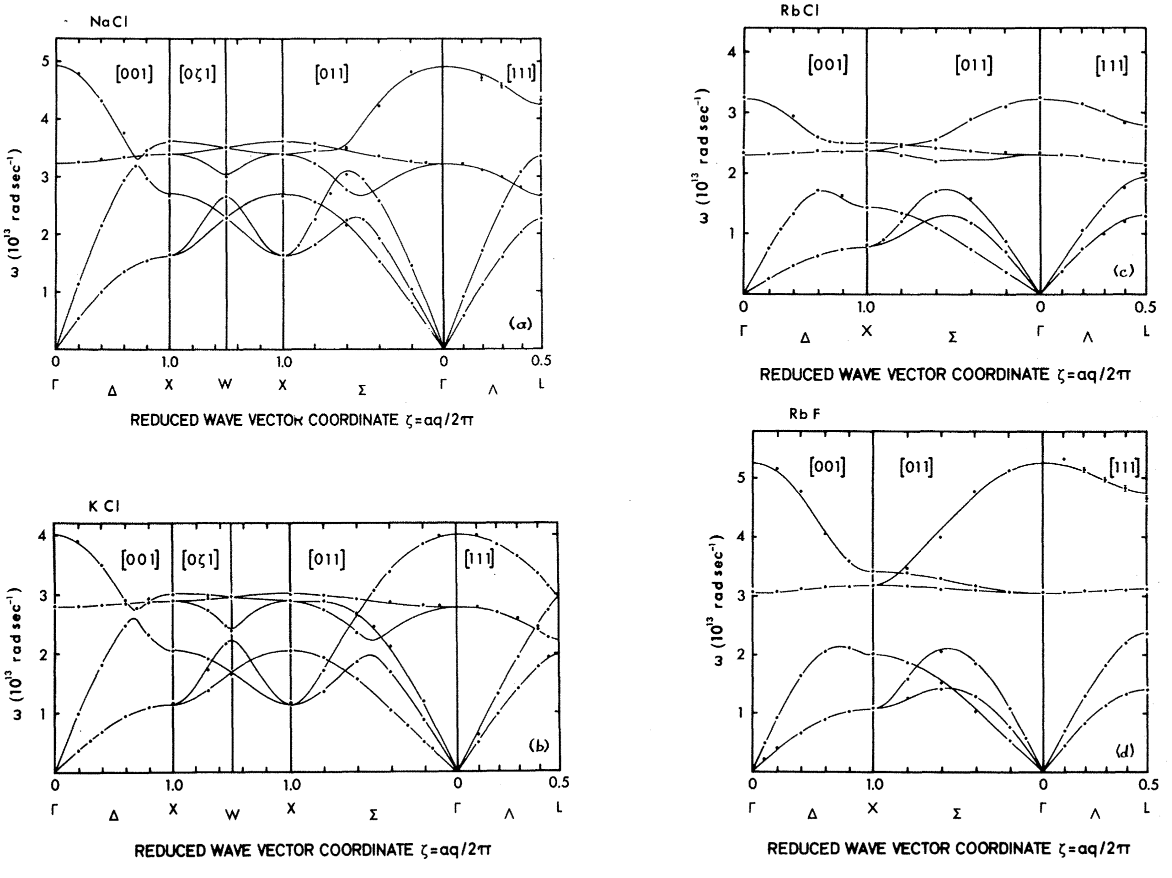

FIG. 1. Dispersion curves at 80 °K for (a) NaCl, (b) KCl, (c) RbCl, and (d) RbF obtained from the parameters of model 2. The dots are the experimental values from Refs. 7–9.

TABLE I. Shell-model parameters for three different calculations of NaCl and KCl. r_0 is the nearest-neighbor separation. The parameters of model 2 have been used in the calculations discussed in the paper. The relatively large values of χ^2 occur because of the method of analysis using the computer program described in Ref. 12 giving smaller errors than the visual inspection method.

Model parameters	Units[a]	NaCl model 1	NaCl model 2	NaCl model 3	KCl model 1	KCl model 2	KCl model 3
A_{12}	$e^2/2v$	9.75 ±0.47	9.77 ±0.49	11.86 ±0.49	11.47 ±0.36	11.17 ±0.58	10.88 ±0.58
A_{11}	$e^2/2v$	0.56 ±0.15	0.56 ±0.17	...	0.29 ±0.14	0.15 ±0.17	...
B_{11}	$e^2/2v$	0.012 ±0.024	−0.006 ±0.04	...	0.02 ±0.04	0.08 ±0.06	...
A_{22}	$e^2/2v$	...	−0.006 ±0.15	− 0.058 ±0.18	...	0.27 ±0.22	0.54 ±0.23
B_{22}	$e^2/2v$	...	0.004 ±0.04	0.009 ±0.033	...	− 0.074 ±0.059	− 0.017 ±0.046
B''	$e^2/2v$	0.066 ±0.028	0.055 ±0.032	0.029 ±0.034	0.032 ±0.045	0.011 ±0.045	− 0.028 ±0.050
Z	e	0.89 ±0.03	0.89 ±0.03	1.03 ±0.03	0.84 ±0.03	0.82 ±0.05	0.80 ±0.05
α_1	10^{-24} cm^3	0.29 ±0.34	0.18 ±0.32	0.83 ±0.13	1.67 ±0.31	1.61 ±0.31	1.30 ±0.50
α_2	10^{-24} cm^3	2.33 ±0.13	2.35 ±0.13	2.81 ±0.13	0.93 ±0.62	0.99 ±0.62	1.18 ±0.93
d_1	e	−0.030 ±0.032	−0.031 ±0.035	− 0.015 ±0.016	0.012 ±0.018	0.019 ±0.016	− 0.005 ±0.039
d_2	e	0.124 ±0.014	0.131 ±0.029	0.192 ±0.035	0.080 ±0.029	0.064 ±0.042	0.025 ±0.078
r_0	Å	2.80	...	...	3.14	...	...
SE	10^{13} rad sec^{-1}	0.035	0.034	0.039	0.023	0.021	0.023
χ^2		3.00	2.69	5.20	2.67	2.38	2.63

[a] Here $v = 2r_0^3$ is the volume of the trigonal unit cell.

TABLE II. Shell-model parameters for three different calculations on RbCl and RbF. r_0 is the nearest-neighbor separation. The parameters of model 2 have been used in the calculations discussed in the paper.

Model parameters	Units[a]	RbCl model 1	RbCl model 2	RbCl model 3	RbF model 1	RbF model 2	RbF model 3
A_{12}	$e^2/2v$	12.73 ±0.24	12.01 ±0.78	11.94 ±0.87	12.32 ±0.31	12.31 ±0.57	11.16 ±0.59
A_{11}	$e^2/2v$	0.38 ±0.13	0.31 ±0.13	...	− 0.17 ±0.13	− 0.17 ±0.15	...
B_{11}	$e^2/2v$	− 0.22 ±0.50	− 0.01 ±0.6[illegible]	...	0.050 ±0.036	0.050 ±0.040	...
A_{22}	$e^2/2v$	...	0.36 ±0.35	0.69 ±0.39	...	0.02 ±0.12	0.32 ±0.22
B_{22}	$e^2/2v$	...	− 0.04 ±0.07	− 0.10 ±0.10	...	0.0003 ±0050	− 0.052 ±0.052
B''	$e^2/2v$	− 0.16 ±0.06	− 0.20 ±0.08	− 0.22 ±0.09	− 0.15 ±0.05	− 0.15 ±0.05	− 0.24 ±0.05
Z	e	0.85 ±0.02	0.79 ±0.06	0.77 ±0.08	1.01 ±0.02	1.00 ±0.04	0.92 ±0.04
α_1	10^{-24} cm^3	0.77 ±0.28	0.66 ±0.26	0.13 ±0.09	1.54 ±0.18	1.54 ±0.18	1.46 ±0.18
α_2	10^{-24} cm^3	2.59 ±0.21	2.31 ±0.42	2.45 ±0.49	1.15 ±0.18	1.15 ±0.27	0.75 ±0.27
d_1	e	0.070 ±0.008	0.066 ±0.008	0.038 ±0.009	− 0.007 ±0.018	− 0.008 ±0.022	0.009 ±0.012
d_2	e	0.164 ±0.015	0.103 ±0.065	0.061 ±0.079	0.100 ±0.013	0.099 ±0.029	0.040 ±0.042
r_0	Å	3.27	...	...	2.805	...	...
SE	10^{13} rad sec^{-1}	0.026	0.026	0.029	0.041	0.042	0.043
χ^2		2.95	2.41	3.17	5.36	5.45	5.20

[a] Here $v = 2r_0^3$ is the volume of the trigonal unit cell.

common quality, however, is that no parameters have physically unrealistic values. The negative values of d_1 that occur in some cases are smaller than the errors and of no significance. It is, of course, important to realize that the shell model is somewhat intuitive and that its parameters have not been deduced from basic theory. Nevertheless, they seem to give a useful description of the interionic forces. An indication of this is the good agreement between model and experiment obtained in the $[1\xi 0]$ direction in NaCl and KCl [Figs. 1(a) and 1(b)], where no fitting to the experimental points was performed. Also a calculation of the Szigeti effective charge using $e^* = Z(1 + d_1 - d_2)$ gives reasonable agreement for models 1 and 2 with values obtained in Ref. 9, whereas model 3 is somewhat less satisfactory in this case. From a study of Tables I and II one may draw the general conclusion that a satisfactory fit to the experimental points may be obtained for a rather large range of values for some of the parameters.

III. FREQUENCY SPECTRUM

Using the parameters from model 2 we have calculated the frequencies in 512 000 equally spaced points in an octant of the Brillouin zone giving a

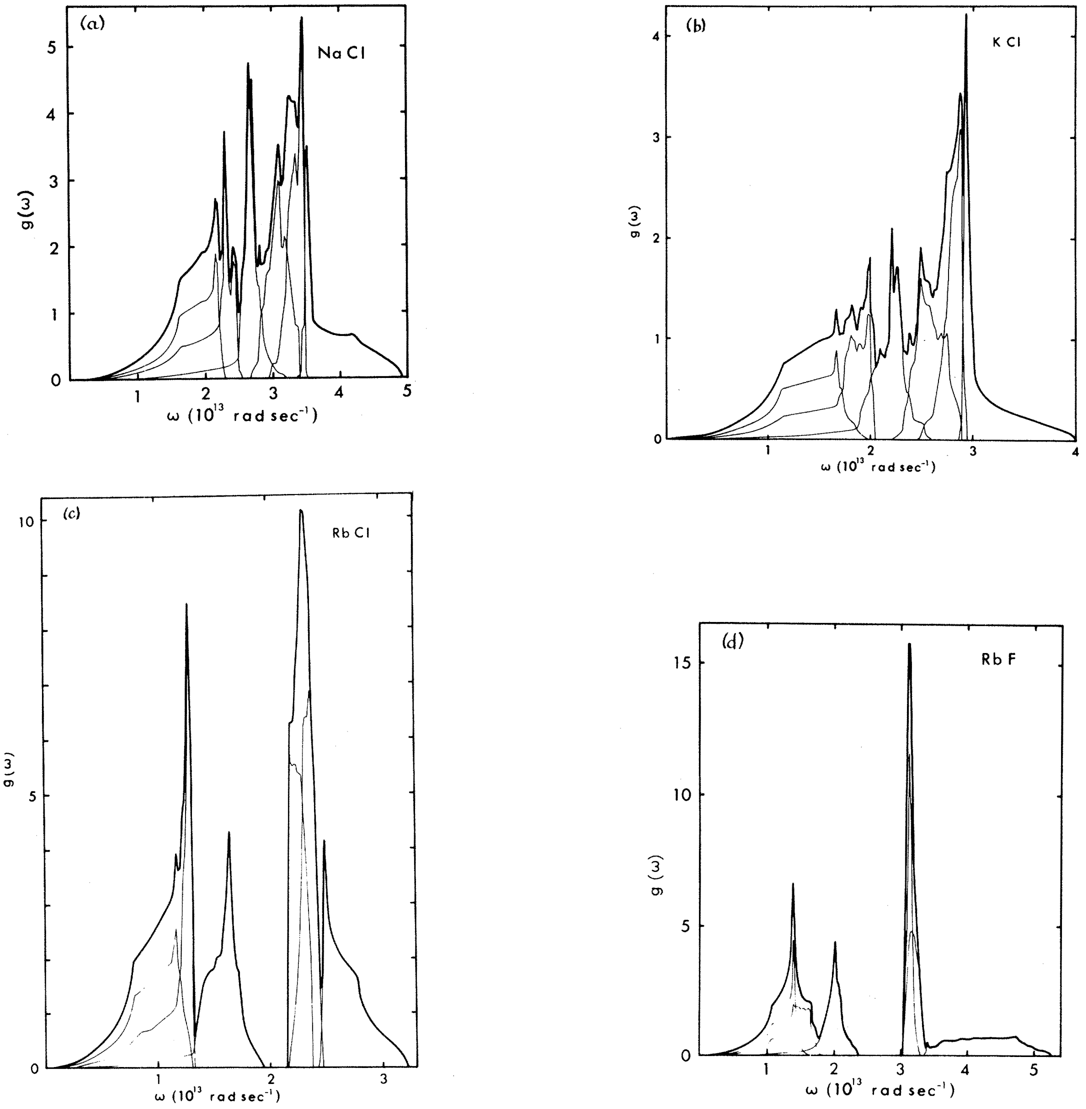

FIG. 2. Frequency spectra of (a) NaCl, (b) KCl, (c) RbCl, and (d) RbF. Also shown are the individual spectra of each branch, which may easily be identified by a comparison with Fig. 1. The unit on the vertical axis is 10^4 when totally 3 072 000 frequencies have been sorted into intervals of width 0.02×10^{13} rad sec^{-1}.

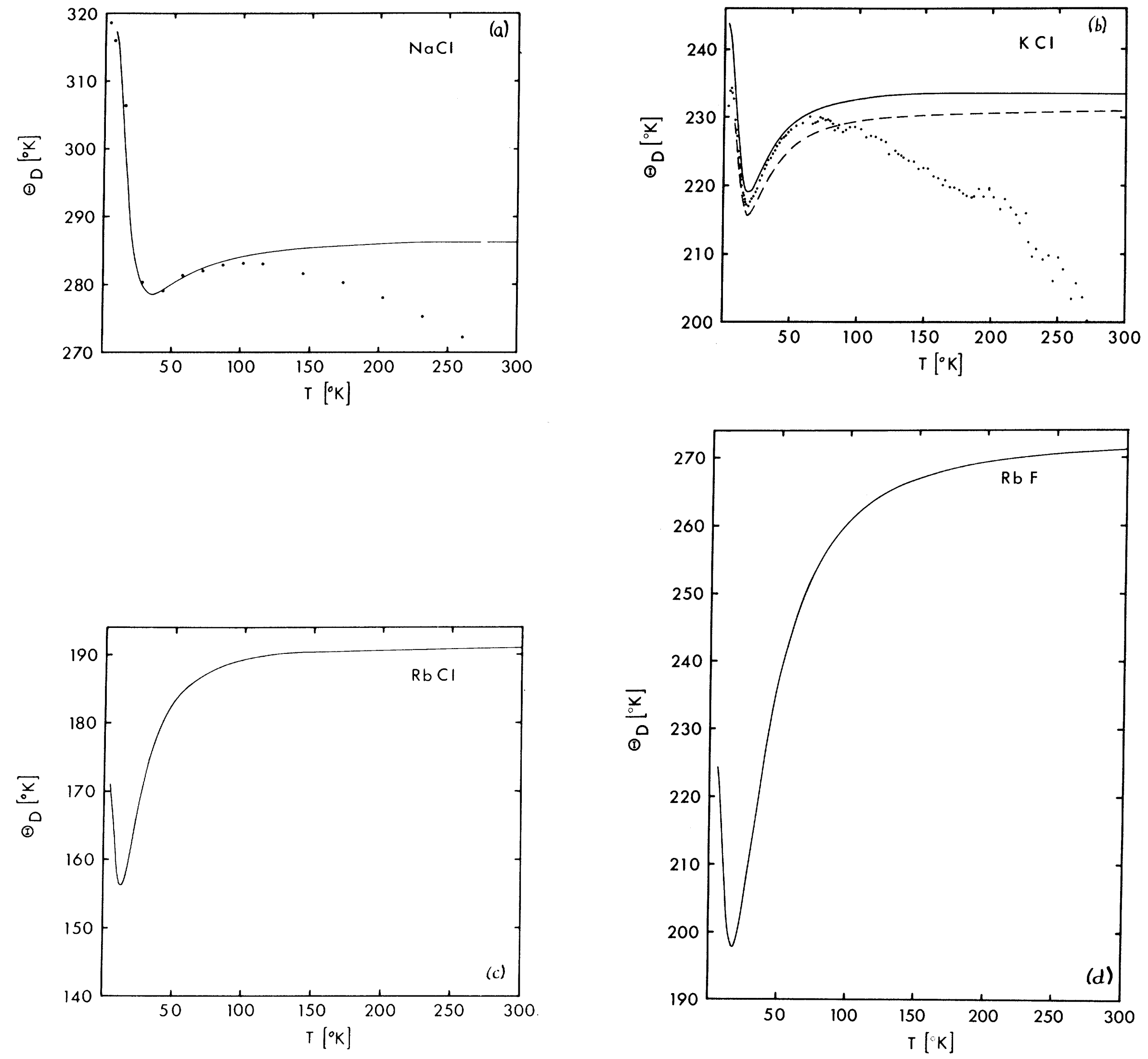

FIG. 3. Temperature variation of the Debye temperature of (a) NaCl, (b) KCl, (c) RbCl, and (d) RbF (full lines), calculated from the spectra in Fig. 2. For NaCl and KCl the results are compared to specific-heat measurements by Barron *et al.* (Ref. 15) and by Berg and Morrison (Ref. 16). The deviations at higher temperatures are ascribed to anharmonic effects. The dashed curve in (b) shows the results obtained for a shell model by Copley *et al.* (Ref. 17). Their model is equivalent to our model 3. The difference between the two sets of Debye temperatures is less than 1% at all temperatures. Also the over-all agreement between the experimental frequencies in Refs. 17 and 18 is quite satisfactory.

total number of 3072000 phonon frequencies. These were sorted into frequency intervals of width 0.02×10^{13} rad sec^{-1}, giving the frequency spectra presented in Figs. 2(a) – 2(d). Briefly, the procedure was the following: An octant of the Brillouin zone was divided into 1000 small cubes and the dynamical matrix solved for the q vectors corresponding to the center of each such cube. The following interpolation procedure was then applied. The frequencies in a network of $8\times8\times8$ equidistant points inside each cube were obtained from a second-degree Taylor expansion of the frequency in the cube, and the constants of this Taylor series were derived from the calculated frequencies in the centers of the adjacent cubes. This method is rather similar to the one by Gilat and Raubenheimer[13] and is expected to give about the same accuracy.

Comparing the frequency spectra with the corresponding dispersion curves, one finds that most of the more salient features of the spectra may be readily interpreted in terms of maxima, minima,

TABLE III. Debye temperatures at 0 °K calculated from three sets of elastic constants using the formulas given by de Launay (Ref. 19).

Halide	Θ_0 model 2 this work (°K)	Θ_0 neutron data Ref. 9 (°K)	Θ_0 ultra-sonic data Ref. 9 (°K)
NaCl	324	325	322
KCl	240	238	234
RbCl	171	177	168
RbF	242	222	222

or accidental degeneracies of the dispersion curves We have not made any written assignments in the figures since this could lead to confusion. Such assignments can easily be made from the figures by anyone interested in the details of the spectra.

IV. DEBYE TEMPERATURE

It was shown by Blackman[14] that the simple theory of Debye leading to the so-called Debye frequency spectrum was inadequate. The failure of the Debye theory may be best demonstrated by fitting a Debye spectrum to the specific heat at a series of temperatures using the Debye characteristic temperature $\Theta_D(T)$ as a parameter. One tnus obtains $\Theta_D(T)$ as a function of T, and any variation of $\Theta_D(T)$ indicates a failure of the Debye theory. Using the relations given by Blackman, we have calculated $\Theta_D(T)$ from the frequency distributions in Fig. 2. The results are presented in Figs. 3(a)–3(d). For NaCl and KCl, where experimental results on the specific heats are available, a comparison is also made between those results and ours. The agreement is good at lower temperatures and we have no reason to suspect the results for RbCl and RbF to be much less reliable. The deviations at above about 100 °K are caused by anharmonic effects. In this temperature range one should take into account the temperature dependence of the frequency spectrum. This requires, however, a knowledge of the phonon frequencies at more than one temperature. Only in the case of KCl[8] have we to some extent studied these temperature shifts, and the results of calculations on these effects will be published elsewhere.[18] At very low temperatures ($\lesssim 5$ °K) the statistical uncertainties in the frequency spectra are too large to allow any reliable calculations of $\Theta_D(T)$ and this range has been omitted in the figures. Using the formulas given by de Launay[19] and the elastic constants calculated from the parameters of model 2, we have calculated $\Theta_D(0)$. These values are listed in Table III together with the values obtained when the elastic constants are estimated from the slopes of the dispersion curves for small wave vectors and with results from ultrasonic measurements. The errors in these data are relatively large but we believe the neutron results from Ref. 9 to be about as accurate as the model results.

Although the specific heat of a solid is comparatively insensitive to details of the frequency spectrum, the good agreement we have obtained is an indication of the validity of our data.

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