

Lattice Dynamics of Alkali Halide Crystals. II. Experimental Studies of KBr and NaI

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Dispersion curves for the lattice vibrations propagating in the $[00\xi]$, $[\xi\xi0]$, and $[\xi\xi\xi]$ directions in NaI at 100°K and in KBr at 90°K have been measured using neutron spectrometry, and the results compared with calculations based on a simple shell model. Both substances obey the Lyddane-Sachs-Teller relation. In addition, some measurements were made on KBr at 400°K; most frequencies showed a decrease of a few percent. At this temperature, the acoustical modes show no significant energy broadening, the transverse optical modes show slight broadening, and the longitudinal optical modes show very considerable broadening. The anomalous broadening of the LO modes is not yet understood and requires further study. It appears to be specimen-dependent as well as temperature-dependent.

I. INTRODUCTION

IN an earlier paper¹ we presented measurements of the lattice vibrations propagating in the symmetry directions $[00\xi]$, $[\xi\xi0]$, and $[\xi\xi\xi]$ of sodium iodide, made using neutron inelastic scattering. The measurements were compared with calculations based on a simple model for ionic crystals, the "shell model," which takes account of the fact that the ions in crystals can be polarized during lattice vibrations. In this paper we present additional measurements² on sodium iodide and extensive new measurements on potassium bromide. In a companion paper³ we compare these measurements with calculations based on more complicated versions of the shell model.

In the earlier study¹ the dispersion relation between the frequencies (ν) and wave vectors (\mathbf{q}) of the lattice waves propagating in the symmetry directions of NaI was well determined except for the longitudinal optical (LO) branch. For this branch, it was observed that the neutron groups became broad for $q \rightarrow 0$ ($q = 2\pi/\lambda$). Further experimental work was difficult at that time for two reasons. Firstly, the large incoherent cross section of sodium (about 50% of the total scattering cross section) gave rise to a neutron group with an energy change corresponding to the average frequency of the almost flat transverse optical (TO) branch. This peak was a nuisance, as it was necessary to subtract it quantitatively from the measured distributions in order

to observe the coherent contribution of the optic modes. The ratio of the intensities of the peaks produced by incoherent and coherent scattering is a factor of ten more favorable for potassium bromide than for sodium iodide. It was, therefore, decided to continue the studies of the alkali halides using potassium bromide. Secondly, in the methods of obtaining energy distributions of inelastically scattered neutrons employed in the earlier experiments¹ it was necessary to cover a rather considerable range of reciprocal space. It was impossible to tell how much error this introduced into the experiment because the details of the dispersion relations, in the off-symmetry directions particularly, were unknown. This difficulty was eliminated when the spectrometer was so controlled that, in any one measurement, the momentum transferred from the neutron to the crystal ($\hbar\mathbf{Q}$) remained constant and at a desired value, i.e., that measurements were made at a predetermined point in reciprocal space. This new procedure⁴ greatly facilitated the observations, especially of the optical modes.

The measurements on sodium iodide and potassium bromide presented in this paper were undertaken to clear up the difficulties encountered in the earlier experiments on sodium iodide, and to provide a larger body of experimental data for the testing of crystal models. Experiments were carried out as follows:

- (1) The frequencies of the LO branches in the symmetry directions of NaI at about 100°K were determined.
- (2) The complete dispersion relations for lattice vibrations in the symmetry directions of potassium bromide at 90°K were determined. Some measurements in off-symmetry directions were also made.

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

² Preliminary reports were given by A. D. B. Woods, B. N. Brockhouse, W. Cochran, M. Sakamoto, and R. N. Sinclair, *Bull. Am. Phys. Soc.* **5**, 462 (1960); and by R. A. Cowley, A. D. B. Woods, B. N. Brockhouse, and W. Cochran, *ibid.* **7**, 237 (1962).

³ R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, following paper, *Phys. Rev.* **131**, 1030 (1963).

⁴ B. N. Brockhouse, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 113.

- (3) The frequencies of lattice vibrations in two symmetry directions of KBr at 400°K were determined, and some observations of phonon lifetimes were made.
- (4) The longitudinal optical mode for $q \rightarrow 0$ was extensively studied in both KBr and NaI. The Lyddane-Sachs-Teller relation⁵ between the longitudinal and transverse optical frequencies

$$\left(\frac{\nu_{LO}}{\nu_{TO}} \right)_{q=0} = \left(\frac{\epsilon_0}{\epsilon_\infty} \right)^{1/2}, \quad (1)$$

(ϵ_0 and ϵ_∞ being the low- and high-frequency dielectric constants) was observed to be satisfied for both materials. Anomalous temperature broadening seemed to occur for this mode, however, and two different specimens of NaI gave quite different results.

The measured dispersion curves are compared with calculations based on the rigid ion model⁶ and on the simple shell model,¹ in which the negative ion alone is polarizable.

II. THE EXPERIMENTS

Measurements were carried out using two different single crystals of sodium iodide and a crystal of potassium bromide. All were obtained from the Harshaw Chemical Company. One of the sodium iodide specimens (A) was that described in Ref. 1 and had a mosaic spread about $1\frac{1}{4}$ deg. The other sodium iodide crystal (B), obtained more recently, had a 2.5-cm square face parallel to its $(1\bar{1}0)$ plane and was about 6.2 cm long. Its mosaic spread was not accurately determined but was certainly less than 0.3 deg and was estimated to be ~ 0.1 deg. The potassium bromide crystal had faces (3.2-cm square) parallel to its $(1\bar{1}0)$ plane and was 6.2 cm long. The mosaic spread of the $\{222\}$ planes of this crystal, as measured against a $\{220\}$ plane of a silicon crystal, was 0.05 ± 0.01 deg. The specimens were mounted in a metal cryostat and cooled from above for temperatures below room temperature. For temperatures above room temperature, the specimens were mounted in the same vacuum chamber but were heated from below. Measurements were made at 8, 90, 210, and 400°K with the $(1\bar{1}0)$ plane of each crystal horizontal.

In the experiment, the neutrons interact with the crystal in such a way as to create or annihilate a single phonon. The scattering, which results in well defined neutron groups, is governed by the conservation equations

$$\mathbf{Q} \equiv \mathbf{k}_0 - \mathbf{k}' = 2\pi\boldsymbol{\tau} - \mathbf{q},$$

and

$$E_0 - E' = \pm h\nu. \quad (2)$$

In these equations \mathbf{k}_0 and \mathbf{k}' are the wave vectors

⁵ R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).

⁶ E. W. Kellermann, Phil. Trans. Roy. Soc. (London) **238**, 513 (1940).

of the incoming and outgoing neutrons, respectively, $\boldsymbol{\tau} = a^{-1}(h, k, l)$ is a reciprocal lattice vector, \mathbf{q} is the phonon wave vector ($|\mathbf{q}| = 2\pi/\lambda$), E_0 and E' are the incoming and outgoing neutron energies, and ν is the phonon frequency. The expression for the intensities of the one phonon neutron groups has been discussed previously.¹

All of the experiments were carried out using the triple axis crystal spectrometer at the Chalk River NRU reactor. The spectrometer was so controlled that energy distributions were obtained at any desired and predetermined position in reciprocal space.⁴ This was accomplished by changing the angle of scattering and the crystal orientation simultaneously with the incident energy in such a manner that, for each point in the energy distribution, the vector \mathbf{Q} terminated at the same point in reciprocal space.

III. RESULTS

1. The Dispersion Curves of Sodium Iodide at 100°K

A new attempt was made to measure the frequencies of the LO modes in the specimen (A) used previously¹ but employing the crystal spectrometer in its constant- \mathbf{Q} mode of operation.⁴ However, as will be elaborated on in a later section, the measurements for the LO modes were still unsatisfactory. Specimen B was then used in the same way and gave satisfactory results. The frequencies of the LO branches for the symmetry directions were completely determined at a temperature of about 100°K. In addition, several frequencies in the acoustical branches were remeasured, without significant changes being observed from the earlier¹ results. The complete

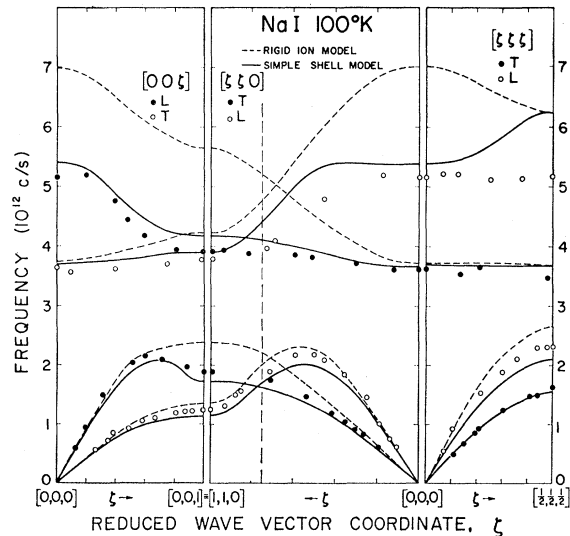


FIG. 1. The dispersion curves for the lattice vibrations of sodium iodide measured at temperatures within 10° of 100°K. The measurements are compared with calculations based on the rigid ion and simple shell models. The broken vertical line indicates the $[110]$ zone boundary.

dispersion curves for sodium iodide at temperatures within 10° of 100°K are shown in Fig. 1 and the frequencies of some specific modes are tabulated in Table I.

TABLE I. Frequencies of some selected modes in NaI at 100°K (from smoothed curves).

Mode	Frequency (10^{12} cps)
(0, 0, 0)TO	$3.6_0 \pm 0.1$
(0, 0, 0)LO	$5.1_7 \pm 0.1$
(0, 0, 1)TA	1.24 ± 0.03
(0, 0, 1)LA	1.87 ± 0.04
(0, 0, 1)TO	$3.8_0 \pm 0.1$
(0, 0, 1)LO	$3.9_1 \pm 0.1$
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ TA	1.58 ± 0.05
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ LA	2.31 ± 0.05
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ TO	$3.5_0 \pm 0.1$
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ LO	$5.1_7 \pm 0.1$

Figure 1 also shows calculated dispersion curves for the rigid ion and the simple shell models.¹ The parameters in these models were obtained from the measured elastic and dielectric constants. No fitting to the neutron results was involved. The agreement with the shell model is much better than with the rigid ion model, especially for the LO modes, but considerable discrepancies remain. More complicated models are discussed in the accompanying paper.

The results show unmistakably that the Lyddane-Sachs-Teller⁵ relation holds for sodium iodide within the experimental accuracy. It was shown previously to hold for potassium bromide,² and more recently also for calcium fluoride.⁷ A comparison of the measured frequencies and dielectric constants is made in Table II.

TABLE II. Comparison of frequencies of optical modes at $q=0$ and dielectric constants, demonstrating the Lyddane, Sachs, and Teller relation (Eq. 1).

	NaI	KBr
ν_{LO}	$5.1_7 \pm 0.1$	5.00 ± 0.05
ν_{TO}	$3.6_0 \pm 0.1$	3.60 ± 0.03
$(\nu_{\text{LO}}/\nu_{\text{TO}})_{q=0}$	1.44 ± 0.05	1.39 ± 0.02
ϵ_0^a	6.16 ± 0.2	4.46 ± 0.15
ϵ_∞^b	2.94 ± 0.03	2.36 ± 0.03
$(\epsilon_0/\epsilon_\infty)^{1/2}$	1.45 ± 0.03	1.38 ± 0.03

^a Estimated from Table XVII, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954) and from S. Roberts, *Phys. Rev.* **76**, 1215 (1949).

^b Estimated from Table XVII, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954) and from change in unit cell dimensions with temperature.

2. Dispersion Curves for KBr at 90°K

The complete dispersion curves for the $[00\xi]$, $[\xi\xi 0]$, and $[\xi\xi\xi]$ symmetry directions, as seen in a $(1\bar{1}0)$ plane, have been measured for potassium bromide at 90°K and are shown in Fig. 2 and Table III. The results once again are compared with calculations based on a rigid ion model and on a simple shell model, with parameters obtained from the high- and low-frequency

⁷ D. Cribier, B. Farnoux, and B. Jacrot, *Phys. Letters* **1**, 187 (1962).

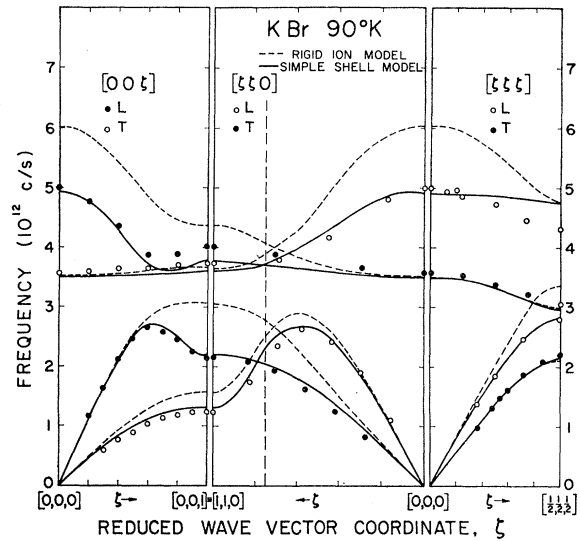


FIG. 2. The dispersion curves for the lattice vibrations of potassium bromide measured at 90°K , compared with calculated curves based on the rigid ion and simple shell models.

dielectric constants and the elastic constant c_{11} . As with sodium iodide, the shell model gives a much better fit to the experimental results than does the rigid ion model, but again it fails to fit the LO mode for which $q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})2\pi/a$. The Lyddane, Sachs, and Teller relation is verified to within the experimental accuracy (see Fig. 3 and Table II). The apparently large discrepancies

TABLE III. Phonon frequencies (units 10^{12} cps) in KBr at 90°K . Points marked with asterisk are included on more than one branch.

$\xi = aq/2\pi$	ν	$\sqrt{2}\xi = aq/2\pi$	ν	$\sqrt{3}\xi = aq/2\pi$	ν
[00\xi]LA	0.2 1.19±0.05 0.3 1.64±0.04 0.4 2.12±0.04 0.5 2.48±0.05 0.6 2.68±0.07 0.7 2.58±0.05 0.8 2.47±0.04 0.9 2.27±0.04 1.0* 2.15±0.03	[ξξ0]LA	0.23 1.13±0.04 0.43 1.93±0.05 0.63 2.42±0.06 0.83 2.63±0.06 0.99 2.36±0.05 1.19 1.75±0.04 1.41* 1.25±0.02	[ξξξ]LA	0.31 1.40±0.03 0.43 1.84±0.03 0.52 2.16±0.04 0.62 2.48±0.05 0.78 2.78±0.04 0.87 2.82±0.04
[00\xi]TA	0.3 0.61±0.03 0.4 0.77±0.02 0.5 0.90±0.03 0.6 1.04±0.02 0.7 1.15±0.02 0.8 1.21±0.02 0.9 1.26±0.02 1.0* 1.25±0.02	[ξξ0]TA	0.4 0.82±0.04 0.6 1.26±0.05 0.8 1.64±0.06 1.0 1.95±0.06 1.2 2.09±0.05 1.41* 2.15±0.03	[ξξξ]TA	0.31 0.98±0.04 0.38 1.29±0.04 0.42 1.33±0.04 0.47 1.48±0.03 0.52 1.60±0.04 0.62 1.82±0.04 0.74 2.09±0.04 0.87 2.20±0.03
[00\xi]LO	0.0* 5.00±0.05 0.2 4.77±0.1 0.4 4.37±0.1 0.6 3.80±0.08 0.8 3.80±0.06 1.0* 4.02±0.07	[ξξ0]LO	0.0* 5.00±0.05 0.04 5.01±0.1 0.24 4.80±0.1 0.64 4.16±0.2 0.97 3.80±0.05 1.41* 3.72±0.04	[ξξξ]LO	0.0* 5.00±0.05 0.10 4.93±0.08 0.17 4.89±0.05 0.21 4.85±0.06 0.43 4.71±0.08 0.64 4.46±0.06 0.87 4.34±0.05
[00\xi]TO	0.0* 3.60±0.03 0.2 3.59±0.05 0.4 3.66±0.07 0.6 3.66±0.06 0.8 3.71±0.05 1.0* 3.72±0.04	[ξξ0]TO	0.0* 3.60±0.03 0.41 3.67±0.05 1.00 3.86±0.05 1.41* 4.02±0.07	[ξξξ]TO	0.0* 3.60±0.03 0.22 3.55±0.05 0.43 3.40±0.04 0.65 3.23±0.07 0.87 3.06±0.05

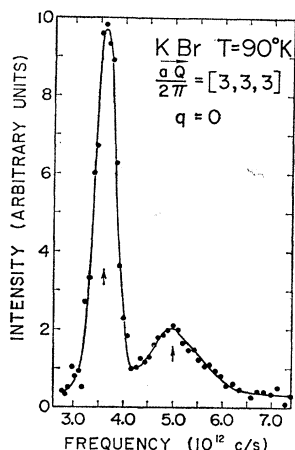


FIG. 3. Energy distribution of scattered neutrons from KBr at 90°K for $q=0$. Arrows indicate positions of TO and LO modes.

in the relative intensities of the LO and TO modes at $q=0$ may be explained in terms of the vertical divergence of the crystal spectrometer.⁸

In addition to the measurements in symmetry directions, the frequencies of some modes in non-symmetry directions were determined at 90°K. The modes were chosen to lie on two lines in the $(1\bar{1}0)$ plane of the reciprocal lattice well removed from the symmetry directions already studied. The frequencies are compared with the predictions of the shell model.³ The experimental results are given in Table IV.

TABLE IV. Frequencies (units 10^{12} cps) of some nonsymmetric modes in KBr at 90°K.

ξ	ν_1	ν_2	ν_3	ν_4
	[$\xi, \xi, 1-\xi$]			
0.1	1.41 ± 0.04	2.20 ± 0.04
0.2	1.85 ± 0.07	...	3.68 ± 0.07	...
0.3	2.22 ± 0.04	2.42 ± 0.03	3.47 ± 0.05	4.09 ± 0.08
0.4	2.14 ± 0.06	2.64 ± 0.04	3.26 ± 0.06	4.28 ± 0.08
	[$\xi, \xi, \xi+0.4$]			
0.1	1.14 ± 0.03	2.48 ± 0.04	3.55 ± 0.05	4.14 ± 0.1
0.2	1.70 ± 0.05	2.52 ± 0.07	3.43 ± 0.06	4.16 ± 0.08
0.3	2.22 ± 0.04	2.42 ± 0.03	3.47 ± 0.05	4.09 ± 0.08
0.4	1.86 ± 0.06	2.64 ± 0.04	3.57 ± 0.05	4.16 ± 0.08
0.5	1.49 ± 0.06	2.64 ± 0.04	3.73 ± 0.07	4.14 ± 0.06

3. Dispersion Curves for KBr at 400°K

Less extensive measurements of the dispersion curves of KBr were made at 400°K in the $[00\xi]$ and $[\xi\xi\xi]$ directions. These results are shown in Fig. 4. The dashed lines represent the curves measured at 90°K and are shown for comparison. The TO modes show an almost constant decrease in frequency of about 8% between 90 and 400°K. The average decrease in frequency of the LO modes is about 4%. The initial slopes of the acoustical branches are consistent with the velocities

⁸ B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).

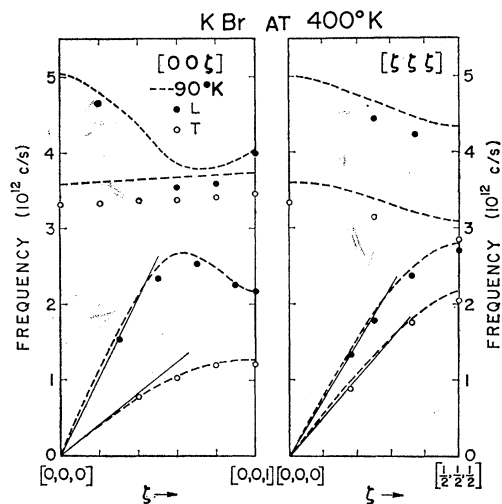


FIG. 4. The dispersion curves for the $[00\xi]$ and $[\xi\xi\xi]$ directions of potassium bromide at 400°K compared with measurements at 90°K (dashed lines). The straight lines through the origin have the slopes of the appropriate velocities of sound.

of sound calculated from extrapolated values of the elastic constants.⁹

4. Energy Widths and the Lifetimes of Phonons

The frequencies of the acoustical branches were quite straightforward to measure and showed no anomalous behavior. Measurements were made at 90 and 400°K in KBr in an effort to observe changes in widths. The distributions for the LA mode at the zone boundary $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are shown in Fig. 5 for these two temperatures; no change in width is apparent. The measured distributions for the other acoustical modes gave similar results.

The neutron groups corresponding to TO modes at 400°K show only a very slight broadening. Some results are shown in Fig. 5. At 400°K, the width of the mode for which $q \rightarrow 0$ is a few percent of its frequency, in rough agreement with that estimated from infrared measurements^{10,11} on KBr and other alkali halides.

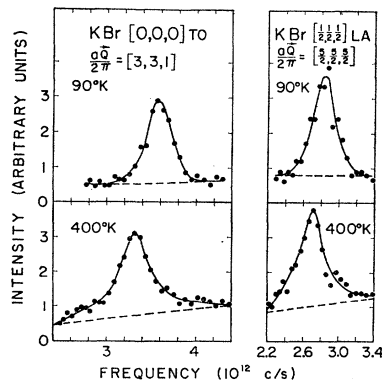


FIG. 5. Neutron energy distributions for scattering from LA and TO modes of KBr at 90 and 400°K. The dashed lines have been drawn to make the intensities consistent with the one-phonon intensity formula.

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

¹⁰ G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **A261**, 10 (1961).

¹¹ M. Hass, Phys. Rev. **117**, 1497 (1960).

5. The Longitudinal Optical Modes

The anomalous behavior of the longitudinal optical modes discussed earlier¹ has been studied further, but the experimental facts are still somewhat uncertain and the theoretical interpretation more so. The improved techniques now available allow the LO modes to be measured to a precision comparable with that for other branches, and there is little doubt about the frequencies (Figs. 1 and 2, Tables I and III). However, the neutron groups for LO modes show anomalous energy broadening; the widths are apparently structure sensitive as shown by the different results from two specimens, and increase more rapidly with temperature than do the widths for other modes.

Figure 6 shows neutron energy distributions for two specimens of sodium iodide at the same position in reciprocal space, $\mathbf{Q} = (2\pi/a)(2.63, 2.63, 2.63)$, at which position the longitudinal optical mode propagating in a $[\xi\xi\xi]$ direction (of the zone) with a reduced wave number $|\mathbf{q}| = 0.64(2\pi/a)$ should be visible. The pattern for specimen A shows a group on the high frequency side of the incoherent peak from the TO modes. This group varied little in both frequency and intensity over a considerable region of reciprocal space. Specimen B shows a group which has the expected behavior for the LO mode. As mentioned earlier specimen A had a comparatively large mosaic spread ($\sim 1\frac{1}{4}$ deg). An attempted chemical analysis of A was partially frustrated by the fact that the thin soldered copper case protecting the crystal developed a leak, and the surface of the crystal became heavily contaminated with water, and with copper, tin, and lead. However, the spectrographic analysis showed no important impurities other than these in the surface layers, and no important impurities (larger than 20 ppm) at all in the interior of the crystal.

For specimen B, normal neutron groups were obtained and these yielded the frequencies given in Fig. 1 and Table I.

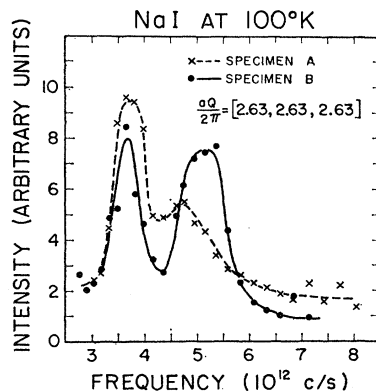


FIG. 6. Neutron energy distributions, corresponding to $(0.37, 0.37, 0.37)$ LO, scattered from two different specimens of NaI at 100°K .

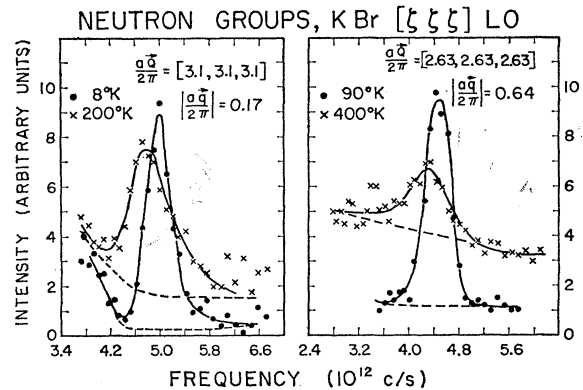


FIG. 7. Neutron energy distributions from KBr corresponding to the mode $(0.1, 0.1, 0.1)$ LO at 8 and 200°K and $(0.37, 0.37, 0.37)$ LO at 90 and 400°K . The dashed lines under the peaks make the relative intensities conform with the one-phonon intensity formula.

Figure 7 shows energy distributions for a potassium bromide crystal at two temperatures at each of two different positions in reciprocal space. At these positions LO modes propagating in the $[\xi\xi\xi]$ directions of the reduced zones should be visible, the two phonons having reduced wave numbers $a|\mathbf{q}|/2\pi$ of (a) 0.17 and (b) 0.64.

The width of the groups increases markedly with temperature. The widths are greater at the smaller wave number, and this has been borne out to some extent by other experiments. The LO group in Fig. 3 at $q=0$ is considerably broader than expected, though we are not completely certain that this is not due to geometric effects.

The energy broadening shown by the experiments at these comparatively low temperatures (the melting point of KBr is about 1003°K) is much larger than the broadening found to exist in certain other materials studied, or for other modes of KBr. The LO mode must, therefore, be especially sensitive to interaction with other modes (and also with some type of impurity or defect). This may come about because the LO mode has associated with it a much larger electric field than do other modes in ionic crystals, or than do the modes in other types of crystals.

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