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Experimental Difference between First and Zero Sound in KBr

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Long-wavelength acoustic phonons have been studied for each of the $[00\zeta]T$, $[00\zeta]L$, $[0\zeta\zeta]T_1$, and $[0\zeta\zeta]L$ branches in KBr at 95 and 463°K by means of inelastic neutron scattering. This study has shown that the elastic constants of KBr determined by inelastic neutron scattering (zero-sound regime) exhibit a different temperature dependence from those determined by ultrasonic techniques (first-sound regime). For example, the change in the zero-sound elastic constant for the $[0\zeta\zeta]T_1$ branch between 95 and 463°K is $(23\pm4)\%$, while the change in the first-sound elastic constant determined by Haussühl using ultrasonic techniques is $(35.1\pm1.2)\%$. Cowley's theory for first and zero sound shows reasonable agreement with experiment.

I. INTRODUCTION

In an anharmonic crystal, the mode of propagation of a phonon (or sound wave) depends on the relationship of its frequency ν to some typical inverse lifetime Γ of the phonons in the crystal.[1,2] If its frequency is sufficiently small ($\nu \ll \Gamma$), sufficient phonon-phonon collisions can occur during each period of the sound wave to alter the populations of the phonon states so as to set up local thermodynamic equilibrium. This "collision-dominated" mode of propagation is referred to as the hydrodynamic or first-sound regime. If, on the other hand, the frequency is sufficiently high ($\nu \gg \Gamma$), then sufficient collisions cannot occur during each period of the wave to significantly alter the populations of the phonon states, and the local temperature of the crystal is unaffected by the presence of the phonon. By analogy with the case of liquid He, this "collision-free" mode of propagation is referred to as the zero-sound regime.

As has recently been shown by Cowley,[2] anharmonic interactions influence the sound waves (or phonons) differently in the zero- and first-sound regimes so that the velocity of propagation should be different in the two regimes and should exhibit a different temperature dependence.

In the present study,[3] experimental evidence for the two modes of propagation in potassium bromide is obtained by showing that the temperature dependence of several high-frequency $[(0.3\text{–}1.6)\times10^{12}$ cps$]$ sound velocities, determined by means of inelastic neutron scattering, is different from the temperature dependence of the low-frequency ($\approx10^7$ cps) sound velocities determined by Haussühl[4] using ultrasonic techniques. Calculations carried out by Cowley and Cowley,[5] and earlier neutron-scattering measurements carried out by Woods *et al.*,[6] had shown that the inverse lifetimes of the phonons in KBr were $\lesssim 0.2\times10^{12}$ cps at 400°K except from some longitudinal optic (LO) modes. The phonons detected in the present study at temperatures $\leqslant 463$°K should therefore be propagating largely in the zero-sound regime, whereas the ultrasonic measurements[4] belong to the first-sound regime.

The neutron-scattering measurements and results are described in Sec. II. In Sec. III, these results are compared with those of ultrasonic measurements[4] and with the theory[2] for first and zero sound.

II. MEASUREMENTS AND RESULTS

The high-frequency elastic constants of potassium bromide have been studied by determining the frequencies of long-wavelength normal modes for the $[00\zeta]T$, $[00\zeta]L$, $[0\zeta\zeta]T_1$, and $[0\zeta\zeta]L$ branches of the dispersion relation. Measurements were carried out for reduced wave vectors $\zeta=0.1$, 0.15, 0.20, and 0.25 at 95 and 463°K. The main difficulty with the measurements was to avoid the systematic errors in frequency which occur because of the finite resolution of the instrument. Consequently, measurements were carried out at different temperatures so that the temperature dependence of the elastic constants could be determined. With this procedure, the systematic errors would be expected to largely cancel. That they did so was verified by measurements made with different experimental configurations.

The KBr specimen crystal was 2 in. in diam×2 in. long with a mosaic spread of about 0.2°. It was oriented with a [100] axis vertical. The measurements were carried out at constant **Q** using the new triple-axis crystal spectrometer at the C4 facility of the NRU reactor in Chalk River. (Methods of neutron spectroscopy have been described by Brockhouse.[7]) The monochromatic beam (frequency ν_0, wavelength λ_0) incident on the specimen is produced by Bragg scattering of neutrons from the reactor through a fixed angle

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[1] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960).

[2] R. A. Cowley, Proc. Phys. Soc. (London) **90**, 1127 (1967).

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[5] E. R. Cowley and R. A. Cowley, Proc. Roy. Soc. (London) **A287**, 259 (1965).

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

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

Table I. Temperature dependence of long-wavelength acoustic modes in KBr from measurements carried out with $\nu_0=4.374\times10^{12}$ cps, beam divergences $(d_1, d_2, d_3)=(0.41°, 0.41°, 1.03°)$ (see text), and mosaic spreads $M=0.25°$ and $A=0.33°$ for the monochromating and analyzing crystals, respectively.

Branch	ζ	Frequency (10^{12} cps) ν_L (95°K)	ν_H (463°K)	$\Delta\nu/\nu_L$ (%)	Average shift
$[0\zeta\zeta]T_1$	0.25	$1.33_5\pm0.01_5$	$1.19_5\pm0.02$	10.6 ± 1.8	11.5 ± 2.7
	0.20	$1.07\pm0.01_5$	0.95 ± 0.03	11.3 ± 3.1	
	0.15	0.80 ± 0.01	$0.70_5\pm0.02$	11.7 ± 2.7	
	0.10	$0.52_5\pm0.01_5$	0.46 ± 0.01	12.5 ± 3.1	
$[00\zeta]L$	0.25	$1.42_5\pm0.03$	1.28 ± 0.02	10.2 ± 2.4	9.8 ± 3.8
	0.20	1.14 ± 0.02	1.02 ± 0.02	10.5 ± 2.4	
	0.15	0.85 ± 0.02	$0.77_5\pm0.03$	8.8 ± 4.1	
	0.10	$0.56_5\pm0.02$	0.51 ± 0.03	9.8 ± 6.2	
$[0\zeta\zeta]L$	0.25	$1.62_5\pm0.02$	$1.52_5\pm0.02$	6.3 ± 1.7	6.8 ± 2.7
	0.20	1.32 ± 0.02	$1.22_5\pm0.02$	7.3 ± 2.1	
	0.15	0.99 ± 0.02	0.92 ± 0.02	7.2 ± 2.8	
	0.10	$0.64_5\pm0.02$	$0.60_5\pm0.02$	6.3 ± 4.2	
$[00\zeta]T$	0.25	0.52 ± 0.01	$0.50_5\pm0.01$	2.5 ± 2.7	2.6 ± 3.4
	0.20	$0.42_5\pm0.01$	$0.41_5\pm0.01$	1.7 ± 3.3	
	0.15	0.33 ± 0.01	0.32 ± 0.01	3.6 ± 4.2	

of about 54°. Several monochromating crystals are available so that various incident energies are readily obtained. The resolution of the instrument is determined mainly by three collimators with vertical blades of variable spacing which limit the horizontal divergences of the beam incident on the specimen, the beam scattered by the specimen, and the beam scattered by the analyzing crystal, to the angles d_1, d_2, and d_3, respectively.

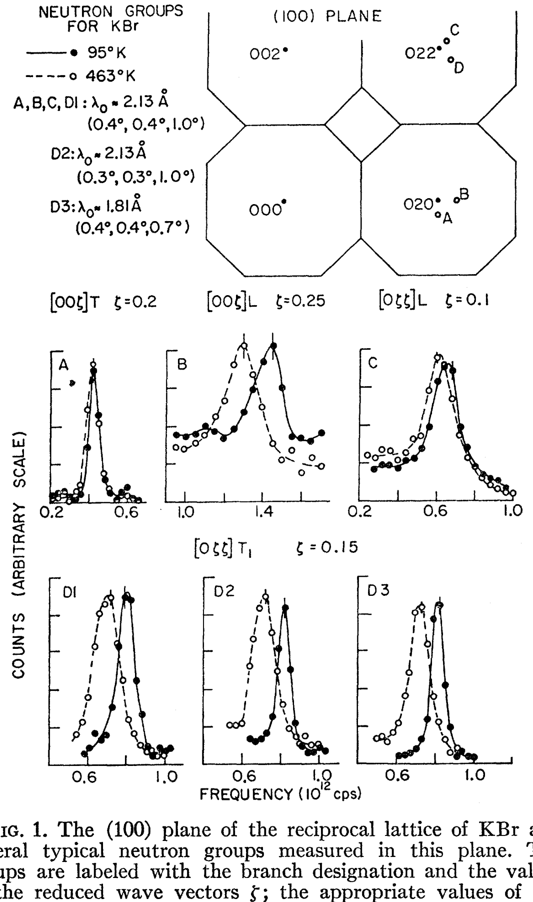

Fig. 1. The (100) plane of the reciprocal lattice of KBr and several typical neutron groups measured in this plane. The groups are labeled with the branch designation and the values of the reduced wave vectors ζ; the appropriate values of the incident neutron wavelength λ_0 and the beam divergences (see text) are also given.

Several typical pairs of neutron groups measured at 95 and 463°K are shown in Fig. 1 together with a section of the (100) plane of the reciprocal lattice of KBr which illustrates where the various groups were measured. Note that the groups labeled $D1$, $D2$, and $D3$ represent the same normal mode studied with three different resolutions as indicated on the diagram. The frequency shifts $\Delta=\nu_L-\nu_H$ between low (L) and high (H) temperatures for these three pairs of groups are in excellent agreement, being $0.09_5\pm0.02$, $0.10_5\pm0.02$, and $0.09_5\pm0.01_5$ (units of 10^{12} cps), respectively.

The results obtained for one particular experimental configuration are given in Table I. The relative frequency shifts $\Delta\nu/\nu_L$ are also given. The errors in ν_L and ν_H are estimated from the shapes and statistics of the neutron groups. There is no well defined procedure for making this assignment, but the errors were usually chosen to be about $\frac{1}{10}$ the full width at half-maximum. These errors are believed to be two standard deviations. The errors in the relative differences (column 5) are determined by the rms addition of the errors assigned to ν_L and ν_H and are therefore also two standard deviations.

In addition to random errors, systematic errors arise from the finite resolution of the apparatus but are expected to largely cancel in the relative frequency shifts. The magnitude of the systematic errors and their cancellation cannot be calculated reliably, but it is believed that for column 5, they do not exceed the random errors in magnitude but may possibly be of the same sign for each wave vector on one branch. Accordingly, we have quoted an error for the average shift (column 6) which is the average of the errors for each wave vector and is considered to be two standard deviations or greater. That this is so is borne out by the data (Table II) for different experimental configurations which will be discussed later, and by the recent investigation[8] of the significance of errors in neutron scattering.

To ensure that the results obtained were independent of the particular instrumental resolution employed, measurements were repeated at the same temperatures with two different incident neutron wavelengths [$\lambda_0 \approx 2.13$ Å from the (111) planes of an Al monochromator of mosaic spread 0.25°, and $\lambda_0 \approx 1.81$ Å from the (220) planes of a Ge monochromator of mosaic spread 0.33°] and with different values of the horizontal divergences (d_1, d_2, d_3). In all cases, it was found that the values for the relative frequency shifts with temperature agreed well within the estimated errors. Measurements carried out with the vertical divergences of the neutron beams incident on and scattered by the specimen both reduced to 1.4° from 2.4° and 4°, respectively, showed that the effect of the vertical divergence of the neutron beams was negligible.

The average shifts given in Table I for $\lambda_0 = 2.13$ Å and $(d_1,d_2,d_3) = (0.41°,0.41°,1.03°)$ are compared in Table II with the results for $\lambda_0 = 1.81$ Å and $(d_1,d_2,d_3) = (0.41°,0.41°,0.67°)$. It is seen that the two sets of results are in very good agreement. The $[0\zeta\zeta]T_1$ branch was also studied using other instrumental resolutions; in all cases, the results were in excellent agreement with those listed in Table II. We therefore believe that the relative frequency shifts obtained in the present study are independent of instrumental resolution.

TABLE II. Average frequency shifts for different experimental configurations.

Frequency ν_0 (10^{12} cps)	4.374	6.039
Collimation (d_1,d_2,d_3)	0.41°, 0.41°, 1.03°	0.41°, 0.41°, 0.67°
Mosaic spread: M, A	0.25°, 0.33°	0.33°, 0.25°
Branch	$\Delta\nu/\nu_L$ (%)	
$[0\zeta\zeta]T_1$	11.5±2.7	11.4±1.8
$[00\zeta]L$	9.8±3.8	8.1±3.1
$[0\zeta\zeta]L$	6.8±2.7	6.8±2.4

III. COMPARISON WITH ULTRASONIC RESULTS AND WITH THEORY

The averages for each branch of the relative frequency shifts obtained with the various experimental configurations are given in Table III (column 3) together with the number of individual values comprising the averages (column 2). For comparison with the results of ultrasonic measurements and with the theory, it is most convenient to convert these frequency shifts into relative changes in elastic constants. If C is the elastic constant for a particular branch, then the relative frequency shift (for a particular reduced wave vector ζ) between a high (H) and a low (L) temperature is given by

$$\frac{\Delta\nu}{\nu_L}\equiv\frac{\nu_L-\nu_H}{\nu_L}=\frac{(a_LC_L)^{1/2}-(a_HC_H)^{1/2}}{(a_LC_L)^{1/2}}, \tag{1}$$

where a is the lattice constant. It follows that

$$\Delta C/C_L \equiv (C_L-C_H)/C_L = 1-(a_L/a_H)(1-\Delta\nu/\nu_L)^2. \tag{2}$$

The values of $\Delta C/C_L$ obtained from the neutron results of column 3 using Eq. (2) are listed in column 4 of Table III.

The values of $\Delta C/C_L$ given by the ultrasonic measurements of Haussühl[4] at a frequency of 9×10^6 cps are listed in column 6 of Table III. Haussühl gives values for $C^{-1}\,dC/dT$ at $T=0$°C. In calculating the values of $\Delta C/C_L$ from these quantities, it has been assumed that dC/dT is constant for $T>95$°K which appears to be a good approximation.[4,9]

The results given in column 7 of Table III show that there is a significant difference between the temperature dependences of the elastic constants of KBr as determined by high-frequency (neutron scattering) and low-frequency (ultrasonic) techniques. The high-frequency elastic constants are seen to decrease more slowly with temperature than the low-frequency ones. The difference is not significant for the $[00\zeta]T$ and $[0\zeta\zeta]L$ branches, but it is outside the assigned error for the $[00\zeta]L$ branch, and for the $[0\zeta\zeta]T_1$ branch the discrepancy is three times the assigned error. (These

TABLE III. Temperature dependence of the high (10^{12} cps) Z and low (10^7 cps) F frequency elastic constants of KBr. The results shown are fractional shifts (in percent) between 95 and 463°K.

Branch	Number of individual values	$(\Delta\nu/\nu_L)_Z$	$(\Delta C/C_L)_Z$		$(\Delta C/C_L)_F$	$(\Delta C/C_L)_F-(\Delta C/C_L)_Z$	
		Expt.	Expt.	Theory[a]	Expt.[b]	Expt.	Theory[c]
$[0\zeta\zeta]T_1$	16	11.4±2.0	23±4	24	35.1±1.2	12±4	24
$[00\zeta]L$	8	9.0±3.4	18±7	19	27.2±0.5	9±7	21
$[0\zeta\zeta]L$	7	6.8±2.6	14±5	11	18.5±0.3	4±5	17
$[00\zeta]T$	3	2.6±3.4	6±7	1	8.3±0.4	2±7	3

[a] From the calculation of first-sound elastic constants (Ref. 5) and of the difference between the first- and zero-sound elastic constants (Ref. 2).
[b] Reference 4.
[c] Reference 2.

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[8] E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. **155**, 619 (1967).

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

errors are believed to be about two standard deviations as mentioned earlier.) It is concluded that a difference has been observed between the temperature dependence of the high- and low-frequency elastic constants.

These results provide evidence that phonons in KBr with frequencies of the order of 10^{12} cps in the temperature range of this experiment do not propagate as first sound. That they propagate essentially as zero sound is suggested by the lifetimes given in Sec. I.

Although the present study of zero-sound elastic constants by means of inelastic neutron scattering was designed specifically to determine their temperature dependence, it is worth noting that the absolute value obtained for C_{11} at 95°K is $(3.9\pm0.2)\times10^{11}$ dyn/cm^2, which agrees within experimental error with Galt's[9] ultrasonic value of 4.02×10^{11} dyn/cm^2. It is expected that the difference between the zero- and first-sound elastic constants (which is zero at 0°K) will still be very small at 95°K.

It is of interest to compare our results with current theories of zero sound. Cowley[2] has calculated the difference in the temperature dependence of the zero- and first-sound elastic constants of KBr. His differences may be combined with the temperature dependence of the first-sound elastic constants of KBr calculated by Cowley and Cowley[5] to yield the temperature dependence of the zero-sound elastic constants. The resulting values given in column 5 of Table III are seen to be in excellent agreement with the values determined from the neutron scattering measurements (column 4). However, this agreement is probably fortuitously good since the theory is not expected to be reliable to this accuracy.

A comparison of Cowley's[2] differences (column 8) with the differences between the neutron and ultrasonic results (column 7) shows that his predicted differences are in the correct relative order and of the correct sign. This indicates the essential correctness of the approach used by Cowley. However, the magnitude of the theoretical prediction is larger than experiment by about a factor of two. This may be because the measurements were not carried out at sufficiently low temperatures that the condition for zero-sound propagation $\nu\gg\Gamma$ held for all the modes; it is known that, for some longitudinal optic modes, it does not hold for the lowest frequencies determined in this experiment.[5] Also, the measurements were carried out at finite though small wave vector, whereas the theory applies to limitingly small wave vector. Furthermore, the accuracy of the theoretical predictions is limited by the approximations made in carrying out the calculations. For example, there is some evidence[5] that the same model for anharmonic effects in alkali halides overestimates the size of effects by 20–30%. Therefore, we believe that the agreement of theory with experiment is as good as can be expected, although a more refined calculation would be useful.

IV. CONCLUSIONS

Neutron inelastic scattering from potassium bromide has revealed that the temperature dependence of the elastic constants determined at frequencies of the order of 10^{12} cps is significantly different from that of the elastic constants obtained at frequencies of 10^7 cps by Haussühl[4] using an ultrasonic technique. Since the typical inverse lifetime of most of the modes in KBr at the temperature of the measurements is less than the probe frequency for the neutron measurements, this result has been interpreted as evidence that the modes studied in the present experiment propagated as zero sound, while those studied in the ultrasonic measurement propagated as first sound. Comparison with theoretical calculations for first sound[5] and for the difference between first and zero sound[2] gives agreement with experiment to within the expected accuracy.

The present experiment shows that care must be taken in comparing the prediction of harmonic models of lattice dynamics with experimental data obtained at high and low frequencies. In particular, force models determined from neutron scattering results should not be expected (or constrained) to reproduce the first-sound elastic constants.

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