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Brillouin Scattering and Elastic Constants of Potassium Bromide

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The Brillouin scattering of KBr crystals was measured by using a helium-neon laser and a pressure-scanned Fabry-Perot interferometer. The Brillouin shifts were measured for various crystal orientations with the scattering vector in the [110] plane. In addition to the strong Brillouin peaks due to the longitudinal acoustic mode, relatively weak Brillouin peaks due to the transverse mode with admixture of the longitudinal mode were clearly resolved for a certain range of crystal orientations. From these Brillouin shifts, the frequencies and velocities of thermally excited sound waves of the wavelength 286.9 nm were obtained, and the three independent elastic constants of the KBr crystal for sound waves of microwave frequencies 6—12 GHz were determined as $C_{11}=3.37\times10^{11}$, $C_{12}=0.61\times10^{11}$ and $C_{44}=0.51\times10^{11}$ dyn/cm^2. The elastic constants determined in the present study were close to the ultrasonic values, indicating little dispersion of the sound velocities for the regions between 10 MHz and 10 GHz.

Brillouin spectroscopy has become a valuable technique for studying thermal and transport properties of matter, with the introduction of lasers as intense monochromatic sources, combined with high-resolution interferometers. One of the important applications is the measurement of velocities of thermal sound-waves in crystals in the microwave region. The sound-wave velocity obtained from Brillouin scattering is used to determine the elastic constants, without any external acoustic excitation. The Brillouin scattering technique has been employed for determining the elastic constants of some alkali halide crystals. The elastic constants determined accurately for KCl, RbCl and KI crystals[1] agreed very well with the results of ultrasonic measurements, indicating that there was no dispersion of sound-wave velocities for the regions between 10 MHz and 10 GHz.

In the present study, the Brillouin scattering of KBr crystals was measured by using a helium-neon laser and a pressure-scanned Fabry-Perot interferometer. The elastic constants determined are compared with ultrasonic values and the sound velocity dispersion is discussed. The present results are also compared with previous results of a Brillouin scattering study on KBr.[2]

1) G. B. Benedek and K. Fritsch, *Phys. Rev.*, **149**, 647 (1966).

2) H. Kaplan, J. Shaham, and W. Low, *Phys. Lett.*, **31A**, 201 (1970).

TABLE 1. FREQUENCIES AND VELOCITIES OF SOUND WAVES OF 286.9 nm WAVELENGTH AS A FUNCTION OF PROPAGATION DIRECTION IN THE [110] PLANE IN KBr

Angle ϕ (deg)	Longitudinal mode (L)		Mixed mode (M)	
	Frequency[a] (GHz)	Velocity[a] (m/sec)	Frequency[a] (GHz)	Velocity[a] (m/sec)
24	11.52	3306		
25	11.44	3284		
26	11.39	3270		
29	11.18	3207		
30	11.08	3181	6.19	1776
31	11.00	3157	6.27	1800
34	10.79	3097	6.46	1855
36	10.68	3063	6.61	1896
39	10.46	3002	6.83	1960
40	10.39	2981	6.89	1976
41	10.36	2973	6.97	1999
44	10.16	2916	7.07	2030
46	10.08	2891		
49	9.97	2861		
51	9.93	2851		
55	9.91	2843		
60	9.99	2866		
65	10.12	2903		
70	10.24	2938		
75	10.38	2980		
80	10.44	2997		
85	10.53	3021		
90	10.54	3025		

a) Averaged experimental errors for the frequency and the velocity are ± 0.07 GHz and ± 20 m/sec, respectively.

Experimental

The experimental arrangement for the observation of Brillouin scattering spectra used in the present study is shown schematically in Fig. 1. The light source was a helium-neon gas laser (Nippon Electric Co., Model GLG 108), which was operated in the fundamental transverse mode at 632.8 nm with an output of about 50 mW. The laser beam passed through the sample which was rotated in such a way that any direction in a [110] plane could be set parallel to the scattering vector. The light scattered at 90° away from the direction of the incident beam was led to a pressure-scanned Fabry-Perot interferometer of Mizojiri Kogaku

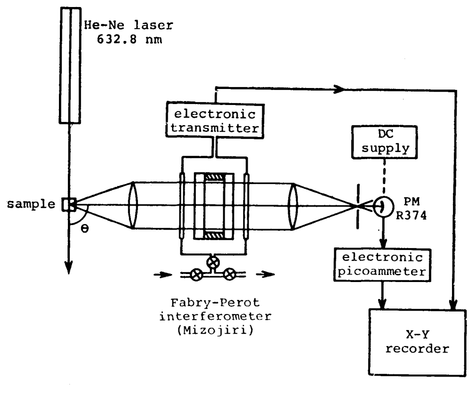

Fig. 1. Experimental arrangement for Brillouin scattering measurements.

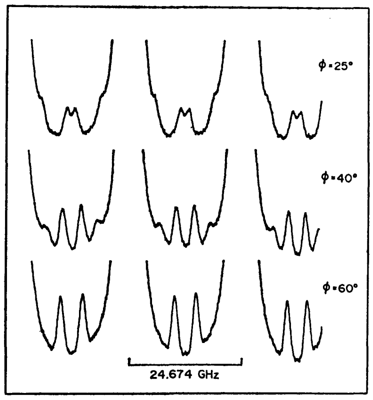

Fig. 2. Brillouin spectra of KBr for $\phi = 25°$, 40° and 60°.

Kogyo Co. The ring pattern was centered on an aperture of a 1 mm diameter and the intensity of the emerging light was detected by an S20 photomultiplier (Hamamatsu Corp., R374), whose output was measured by an electronic picoammeter and recorded on an X–Y recorder. The electric vector of the incident laser light was set perpendicular to the scattering plane. The spacer between the interferometer etalons had a thickness of 6 mm, giving a free spectral range of 25 GHz. The exact thickness was measured by a micrometer to within 4 μm. The interferometer was scanned by evacuating the optical chamber and then allowing air leakage slowly.

In the measurements of the Brillouin scattering, the crystal sample of KBr, a cube with 5 mm on an edge, was immersed in anethole ($CH_3CH{=}CHC_6H_4OCH_3$). This liquid had nearly the same index of refraction as KBr, and surface scattering from KBr crystal was largely eliminated. The sample was supported by a rotatable holder so that the scattering vector was kept in the [110] plane of the crystal. The Brillouin spectra were measured as a function of the angle ϕ (24°—90°) between the scattering vector and the [001] direction. For $\phi<25°$, the Stokes Brillouin line overlapped the anti-Stokes line (and *vice versa*) of the adjacent spectral order. The spectra were scanned as slowly as about ten minutes over one free spectral range of 25 GHz, so as to resolve relatively weak Brillouin lines due to the transverse mode with admixture of the longitudinal mode. The scattering measurements were made at 20±1 °C at least six times for each orientation of the crystal.

Typical examples of the observed spectra for $\phi=25°$, 40° and 60° are shown in Fig. 2, and the observed frequency shifts and sound velocities are listed in Table 1.

Brillouin Scattering and Elastic Constants

Brillouin scattering shifts are proportional to the velocity of thermally excited sound waves whose wavelengths are of the same order as the wavelength of light. The sound velocity, V, in the medium is related to the frequency shift, Ω, due to the Doppler effect on the light from reflection by the sound wave:[1,3]

$$\Omega/\omega=\pm 2(V/c)n\sin(\theta/2), \tag{1}$$

where ω is the frequency of the incident light wave, c is the velocity of light in vacuum, n is index of refraction of the medium and θ is the angle of scattering. The frequency shift, Ω, is equal to the frequency of the sound wave responsible for the light scattering.

In a crystal, there are in general three modes of elastic waves, one longitudinal and two transverse modes, propagating with different velocities. Thus, V in Eq. (1) can take three values and accordingly one should observe generally three pairs of Brillouin components with different frequency shifts in the scattering by any crystal.[4] Also, in the crystal, one may obtain from the Brillouin spectra the frequencies and velocities of sound waves as a function of crystal orientation. This observation can be made by bringing different crystal directions parallel to the scattering vector. For a cubic crystal, each of the three acoustic waves which propagate in the direction of principal symmetry, namely the [001], [111] or [110] direction, is a pure longitudinal or transverse wave, and the two transverse modes are degenerate for the [001] and [111] directions. In general for the cubic crystal, the sound waves which propagate in the [110] plane have the following polarizations; the first acoustic wave (T) is purely transverse for any crystal direction, the second wave (M) is largely transverse with admixture of the longitudinal mode, and the third wave (L) is almost entirely longitudinal.

The elastic constants are closely related to the sound velocities of the three waves in the acoustic branches. The sound velocities, V, are given as roots of the following equation[5]

$$\begin{vmatrix} \lambda_{11}-\rho V^2 & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \lambda_{22}-\rho V^2 & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \lambda_{33}-\rho V^2 \end{vmatrix}=0, \tag{2}$$

where ρ is the mass density, and λ_{ab} is given by

$$\lambda_{ab}=l^2C_{1a1b}+m^2C_{2a2b}+n^2C_{3a3b}+mn(C_{2a3b}+C_{3a2b}) + nl(C_{3a1b}+C_{1a3b})+lm(C_{1a2b}+C_{2a1b}), \tag{3}$$

where l, m and n are the direction cosines of the propagation direction of the sound wave and the suffixes to the elastic constants are written in full. However, the elastic constants C_{iajb} in Eq. (3) may be converted into C_{pq} in the more usual notation by changing the suffixes ia and jb to p and q, respectively, in manner that 11→1, 22→2, 33→3, 23→4, 31→5 and 12→6. The general expression in Eq. (2) is specialized for the case of a cubic crystal as a function of the propagation direction, ϕ, in the [110] plane, where ϕ is the angle between the [001] direction and the propagation direction of the sound wave,

$$\begin{vmatrix} \frac{1}{2}[(C_{44}+C_{11})+(C_{44}-C_{11})\cos^2\phi]-\rho V^2 & -\frac{1}{2}(C_{44}+C_{12})\sin^2\phi & -\frac{1}{\sqrt{2}}(C_{44}+C_{12})\sin\phi\cos\phi \\ -\frac{1}{2}(C_{44}+C_{12})\sin^2\phi & \frac{1}{2}[(C_{44}+C_{11})+(C_{44}-C_{11})\cos^2\phi]-\rho V^2 & \frac{1}{\sqrt{2}}(C_{44}+C_{12})\sin\phi\cos\phi \\ -\frac{1}{\sqrt{2}}(C_{44}+C_{12})\sin\phi\cos\phi & \frac{1}{\sqrt{2}}(C_{44}+C_{12})\sin\phi\cos\phi & C_{44}-(C_{44}-C_{11})\cos^2\phi-\rho V^2 \end{vmatrix}=0. \tag{4}$$

Equation (4) may be rewritten into a more convenient form by transforming the coordinates a, b and c into $(1/\sqrt{2})(a+b)$, $(1/\sqrt{2})(a-b)$ and c. Of these new coordinates, the first one is perpendicular to the [110] plane and corresponds to the pure transverse mode (T), and the hybridization of the second and third, both in the [110] plane, gives the longitudinal mode (L) and mixed mode (M). The transformed equation is given by

$$\begin{vmatrix} \frac{1}{2}[(C_{11}-C_{12})+(2C_{44}+C_{12}-C_{11})\cos^2\phi]-\rho V^2 & 0 & 0 \\ 0 & \frac{1}{2}[(2C_{44}+C_{11}+C_{12})-(C_{11}+C_{12})\cos^2\phi]-\rho V^2 & -(C_{44}+C_{12})\sin\phi\cos\phi \\ 0 & -(C_{44}+C_{12})\sin\phi\cos\phi & C_{44}-(C_{44}-C_{11})\cos^2\phi-\rho V^2 \end{vmatrix}=0. \tag{5}$$

3) R. S. Krishnan, "The Raman Effect," ed. by A. Anderson, Marcel Dekker, New York (1971), p. 343.

4) If the birefringence is taken into consideration, there should in general be twelve pairs of Brillouin components.[3]

5) M. J. P. Musgrave, *Proc. Roy. Soc. London*, **A226**, 339 (1954).

Accordingly, the velocities of the three sound waves, V_T, V_L and V_M, are obtained as

$$\rho[V_T(\phi)]^2 = \frac{1}{2}[(C_{11}-C_{12}) + (2C_{44}+C_{12}-C_{11})\cos^2\phi], \tag{6}$$

$$\rho[V_L(\phi)]^2 = \frac{1}{4}[(4C_{44}+C_{11}+C_{12}) - (2C_{44}+C_{12}-C_{11})\cos^2\phi + \{(C_{11}+C_{12})^2 + (2C_{44}+C_{12}-C_{11}) \times [(8C_{44}+14C_{12}+6C_{11})\cos^2\phi - (6C_{44}+15C_{12}+9C_{11})\cos^4\phi]\}^{1/2}], \tag{7}$$

and

$$\rho[V_M(\phi)]^2 = \frac{1}{4}[(4C_{44}+C_{11}+C_{12}) - (2C_{44}+C_{12}-C_{11})\cos^2\phi - \{(C_{11}+C_{12})^2 + (2C_{44}+C_{12}-C_{11}) \times [(8C_{44}+14C_{12}+6C_{11})\cos^2\phi - (6C_{44}+15C_{12}+9C_{11})\cos^4\phi]\}^{1/2}]. \tag{8}$$

For the directions of principal symmetry [001], [111] and [110], corresponding to $\phi=0°$, 54.7° and 90°, respectively, Eqs. (6), (7) and (8) are reduced to the following simplified forms; for the [001] direction, $\rho V_L^2=C_{11}$ and $\rho V_M^2=\rho V_T^2=C_{44}$; for the [111] direction, $\rho V_L^2=[2(2C_{44}+C_{12})+C_{11}]/3$ and $\rho V_M^2=\rho V_T^2=(C_{44}+C_{11}-C_{12})/3$; and for the [110] direction, $\rho V_L^2=(2C_{44}+C_{12}+C_{11})/2$, $\rho V_M^2=C_{44}$ and $\rho V_T^2=(C_{11}-C_{12})/2$.

The intensity of the Brillouin scattering in a crystal is determined by the polarization directions of the incident and scattered light waves and of the sound wave, the propagation direction of the sound wave, and the magnitude of the elasto-optical constants.[6] The formulas for the Brillouin intensity have been derived for a cubic crystal as a function of the angle ϕ.[1] The formulas indicate that the Brillouin intensity of the longitudinal mode (L) in the entire ϕ region and of the mixed mode (M) in a certain ϕ region is strong enough, but the intensity of the purely transverse mode (T) is much weaker than the former two modes. Therefore, the Brillouin component due to the transverse mode is not expected to be observable in the spectra.

Results

In the present study, the Brillouin scattering measurements were made for the scattering angle $\theta=90°$, and the wavelength of the scattering sound wave λ_s is given from Eq. (1) by

$$\lambda_s = \lambda_0/(\sqrt{2}n), \tag{9}$$

where λ_0 is the wavelength of the incident light in vacuum. By substituting $\lambda_0=632.8$ nm for a helium–neon laser and $n=1.5594$ for KBr,[7] $\lambda_s=286.9$ nm is obtained, which is common to all orientations of the crystal.

The observed spectra in Fig. 2 exhibit two kinds of Brillouin components, a stronger one with a larger frequency shift and a weaker one with a smaller frequency shift. The former is assigned to the longitudinal mode (L) and the latter to the mixed mode (M) (a largely transverse mode with admixture of the longitudinal mode), as suggested from the theoretical relative intensities. The Brillouin component due to the mixed mode was resolved clearly for $\phi=30°$—44°. The intensity of this mode was previously expected to be strong enough only for this ϕ region.[1,2] Also, if ϕ is smaller than 30°, the velocity of the mixed mode is so low that the mixed-mode peak apparently merges into the strong central peak. Variation of the relative intensity of the longitudinal mode with the angle ϕ is also noted in Fig. 2. The intensity increases progressively as ϕ is increased up to 60°, and reaches maximum and finally decreases slightly as ϕ is further increased to 90°. This pattern is in agreement with the intensity variation previously calculated for KBr by Kaplan *et al.*[2]

The sound velocities listed in Table 1 were obtained from the observed frequency shifts by Eq. (1). In Fig. 3, the observed sound velocities V_L and V_M for the longitudinal and mixed modes are plotted against the angle ϕ. From the observed sound velocities, the three independent elastic constants C_{11}, C_{12} and C_{44} were determined from Eqs. (7) and (8) by the method of least squares. The mass density[8] of $\rho=2.744$ g/cm³ was used for the calculation. The values of the elastic constants are listed in Table 2, and the sound velocities V_L, V_M and V_T calculated from these

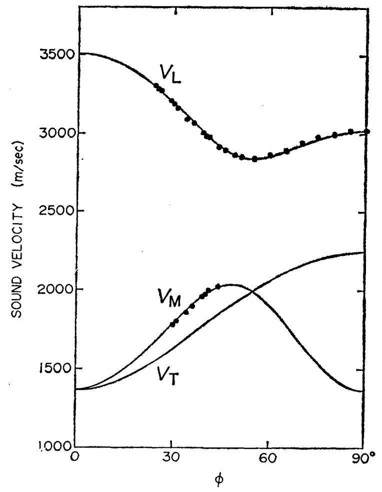

Fig. 3. Velocity of sound waves in KBr as a function of propagation direction in the [110] plane; ϕ is the angle between the propagation direction and the [001] axis. ●: observed value; ——: calculated value.

6) I. L. Fabelinskii, "Molecular Scattering of Light," Plenum Press, New York (1968), p. 139.

7) "Kagaku Benran," ed. by the Chemical Society of Japan, Maruzen, Tokyo (1966).

8) O. D. Slagle and H. A. McKinstry, *J. Appl. Phys.*, **38**, 437 (1967).

Table 2. Elastic constants of KBr at room temperature, in units of 10^{11} dyn/cm^2

	C_{11}	C_{12}	C_{44}
Brillouin scattering			
Present study (20 °C)	3.37±0.03	0.61±0.03	0.51±0.02
Kaplan *et al.*[a] (22.5 °C)	3.34±0.08	0.35±0.04	0.47±0.04
Ultrasonic technique			
Huntington[b]	3.45±0.07	0.54±0.03	0.508±0.005
Galt[c]	3.46	0.58	0.505
Merkulov[d]	3.50	0.62	0.506
Slagle and Mckinstry[e] (25 °C)	3.468	0.580	0.507
Thermal diffuse scattering of X-rays			
Ramachandran and Wooster[f]	3.8	0.60	0.64

a) Ref. 2. b) H. B. Huntington, *Phys. Rev.*, **72**, 321 (1947). c) J. K. Galt, *Phys. Rev.*, **73**, 1460 (1948). d) L. G. Merkulov, *Soviet Phys.-Acoustics*, **5**, 444 (1960). e) Ref. 8. f) Ref. 9.

elastic constants are shown in Fig. 3.

Discussion

In the present study, the elastic constants C_{11}, C_{12} and C_{44} of KBr were determined for sound waves of microwave frequencies 6—12 GHz by the Brillouin scattering technique. The elastic constants thus determined may be compared with the values for the ultrasonic region (10 MHz region) as measured by externally generated sound waves. In Table 2, previous results of ultrasonic measurements are also listed for comparison with the Brillouin results. Although there are some discrepancies among the ultrasonic results by different workers, the present hypersonic values by Brillouin scattering and the ultrasonic values are close to each other, indicating little dispersion of the sound-wave velocity for the regions between 10 MHz and 10 GHz corresponding to the frequency change of three orders of magnitude. Kaplan *et al.*[2] have also measured Brillouin scattering spectra of KBr and have obtained the elastic constants. However, their C_{12} value is appreciably smaller than ours (see Table 2). Comparison of Fig. 3 in this paper and Fig. 1b in Ref. 2 indicates that the sound velocity measured by Kaplan *et al.* is slightly smaller than the present result for the longitudinal mode but larger for the mixed mode; these differences make their C_{12} value smaller. The previous Brillouin study[1] on other alkali halides of KCl, RbCl and KI indicated the absence of dispersion of the sound-wave velocity for the hypersonic and ultrasonic regions. Accordingly, the little dispersion found for KBr in the present study seems to be reasonable.

The elastic constants of KBr have also been obtained by the technique of thermal diffuse scattering of X-rays,[9] in which measurements were made of the intensity of weak diffuse X-rays reflected from crystals. The elastic constants determined by this method are also listed in Table 2. However, the accuracy of this method is not high enough for discussing the dispersion of the sound velocity for the visible and X-ray regions.

In the present measurements of Brillouin scattering of KBr, the Brillouin component due to the mixed mode was observed for $\phi=25°$—$50°$, but the frequency-shift data for $\phi=30°$—$44°$ were used for the calculation of the elastic constants. The observation of the mixed mode is necessary for determining C_{12} and C_{44} separately; the velocity of the longitudinal mode depends largely on $(2C_{44}+C_{12})$ and C_{11}, as seen from Eq. (7), but the velocity of the mixed mode is sensitive to C_{44}. Our observation of the mixed mode for $\phi=30°$—$44°$ and the longitudinal mode for $\phi=24°$—$90°$ was good enough for the determination of the three elastic constants.

Numerical calculations in the present study were carried out with a NEAC 2200—700 computer at the Computer Center of Osaka University.

9) G. N. Ramachandran and W. A. Wooster, *Acta Crystallogr.*, **4**, 431 (1951).