Brillouin scattering on rubidium iodide under high pressure

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Brillouin scattering measurements were made on single crystals of rubidium iodide (RbI) in the ⟨100⟩ and ⟨110⟩ directions at high pressures up to 4 kbar. RbI shows a pressure-induced first-order phase transition from the NaCl ($B1$) to CsCl ($B2$) structure at about 3.5 kbar. The elastic constants C_{11} and C_{44} determined from the Brillouin shifts (at frequencies at about 10^{10} Hz) show a linear pressure dependence in agreement with ultrasonic measurements (at sound frequencies at about 10^6 Hz). No significant deviations from the linear pressure dependence were found in the vicinity of the pressure-induced phase transition. The results from the present Brillouin measurements, probing the long-wavelength limit of the phonon dispersion of the transverse-acoustic (TA) ⟨110⟩ branches, contrast with earlier neutron scattering data, which exhibit small anomalies in frequency and intensity in the pressure dependence of the TA ⟨100⟩ and ⟨110⟩ phonons with small values of the reduced wave vector ($q < 0.5$) at the onset of the phase transition.

I. INTRODUCTION

The propagation of sound waves in RbI has attracted considerable interest in the past years. Experimental and theoretical investigations were focused on two properties of the RbI system, i.e., the anharmonicity of thermal vibrations[1–4] and the martensitic phase transition from the NaCl to the CsCl structure occurring above 3.5 kbar.[5–7] Anharmonicity leads to different values for the adiabatic elastic constants depending on whether they were observed by ultrasonic methods or obtained from the phonon dispersion curves measured by neutron scattering techniques.[8,9] In qualitative accordance with theory the elastic constants derived from phonon measurements are higher by 10% than those obtained by ultrasonic methods.

Recently the softening of the low-lying transverse-acoustic phonon branches of RbI was investigated under pressures up to 4 kbar by neutron scattering with special attention to the martensitic NaCl-CsCl phase transition above 3.5 kbar.[5,6] Within the pressure region where small nuclei of the CsCl phase were already present small anomalies were observed in the phonon frequencies for some long-wavelength transverse-acoustic phonons in the ⟨002⟩ direction. In addition, the NaCl-CsCl transformation was found to occur stepwise via an intermediate defect structure, probably consisting of stacking faults on close-packed {002} NaCl planes.

The present Brillouin scattering measurements were undertaken to probe the pretransitional phenomena in RbI occurring in the long-wavelength limit for transverse elastic waves propagating along the ⟨100⟩ and ⟨110⟩ directions in the vicinity of the martensitic shear transformation. The measurements were done up to 4 kbar, where the transition is entirely completed. Furthermore, Brillouin scattering probes the phonons at 10^9 Hz between the zero- and first-sound regime and gives additional information on the elastic constants at these intermediate frequencies.

II. EXPERIMENTAL

The Brillouin scattering apparatus consisted of a five-pass electronically stabilized Fabry-Perot interferometer (Burleigh Das-1) and a single-mode argon-ion laser (Lexel model No. 95) of about 250 mW operating at 514.5 nm. The interferometer had a mean effective finesse of about 30 obtained with dielectric-coated 85%-reflecting mirrors. Different free spectral ranges (FSR's) of 10.04, 11.97, 12.96, and 34.21 GHz were used to optimize the position of the Brillouin peaks of interest in the experimental spectra to avoid the parasitic scattered light which is often more intense than the Brillouin peaks. A Peltier-cooled photomultiplier (ITT FW 130) with a dark count rate of about three counts per second was used as a light detector. The photon pulses were stored in a multichannel analyzer for data analysis and plotting.

The RbI single crystals were grown by Dr. Karl Korth, Monokristalle-Kristalloptik. The crystals were oriented parallel to the {100} planes by x-ray diffraction and cubes were cut from these with an edge length of approximately 4 mm. The cube with the {100} surfaces was placed inside a high-pressure cell[10] provided with three optical windows. Plexol was used as the pressure-transmitting medium. The high-pressure system consisted of a straight hand pump for pressures up to 1000 bars. For higher pressures a second hand pump connected to an intensifier was used and this enabled us to reach 4000 bars. Pressure was measured with an error of ± 10 bars. The temperature of the sample was 295 K within ± 0.2 K.

Right-angle and backscattering geometries were used for measuring the three elastic constants in the NaCl phase. For both geometries the laser beam and the scattered light were perpendicular to a {100} surface of the RbI cube. Therefore for 90° scattering the phonon wave vector was parallel to a ⟨110⟩ direction and parallel to the ⟨100⟩ direction for backscattering.

The elastic constants C_{11} and C_{44} were obtained from the fitted spectra of the longitudinal (sound velocity V_l) and the transverse (sound velocity V_t) acoustic phonons (ρ is the density):

$$C_{11}=\rho V_l^2(\mathbf{q}\|\langle 100\rangle)\ ,$$

$$C_{44}=\rho V_t^2(\mathbf{q}\|\langle 110\rangle)\ .$$

The pressure dependence of the density was taken from Ref. 11.

For the evaluation of the sound velocity from the Brillouin shifts a knowledge of the density-dependent index of refraction n of RbI is required. However, only a single data point[12] for RbI could be found in the literature. Therefore, the density dependence of n was calculated using the Lorentz-Lorenz equation, taking into account the correction for the density-dependent molar polarizability[13,14] by a phenomenological strain-polarizability constant Λ which is 0.43 for RbI. This value was calculated from Ref. 12 and is in rough agreement with values for KBr and KI, calculated from Ref. 15. As a reference value at 295 K, at 5145 Å, and at atmospheric pressure $n=1.6597$ (Ref. 16) was taken.

We have assumed that n varies linearly with density in RbI in the vicinity of the phase transition in analogy with the case of β-PbF_2 (Ref. 14) where n has been measured as a function of pressure.

III. RESULTS

The pressure dependence of the elastic constants C_{11} and C_{44} of RbI obtained by Brillouin scattering is shown in Figs. 1 and 2 together with ultrasonic and neutron scattering data. In Fig. 1, the C_{44} values obtained from the present Brillouin scattering measurements and the ultrasonic data behave similarly except that the latter show a somewhat steeper decrease for the ⟨100⟩ shear waves than that observed by neutron scattering techniques at considerably higher q values. In contrast to the neutron data the present Brillouin data for C_{44}, corresponding to $q\times 10^{-3}$ phonons, give only a rather poor indication of a deviation from linearity up to 4 kbar.

In Fig. 1, just above 3 kbar the measured values deviate from the straight line obtained from the ultrasonic results. These deviations are at the limit of statistical significance but are however reminiscent of the stronger deviations in the THz region observed for small-q phonons by neutron scattering techniques. The C_{11} data obtained in backward scattering geometry are shown in Fig. 2 along with neutron data.

In the present experiment the phase transition was en-

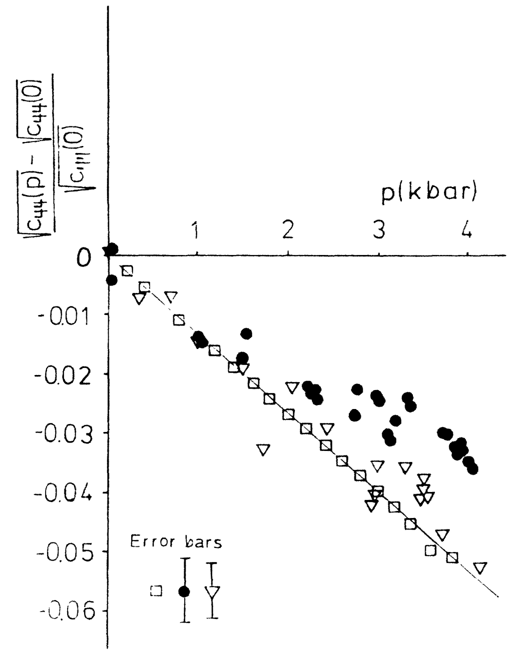

FIG. 1. Relative pressure dependence of the square root of the C_{44} elastic constant in RbI determined by Brillouin scattering (inverted open triangles) and by ultrasonic methods (open squares). The straight line is a linear least-squares fit to the ultrasonic data points. The filled circles indicate neutron scattering results deduced from the pressure dependence of transverse acoustic TA⟨002⟩ phonons at longer wavelengths ($q=0.3$).

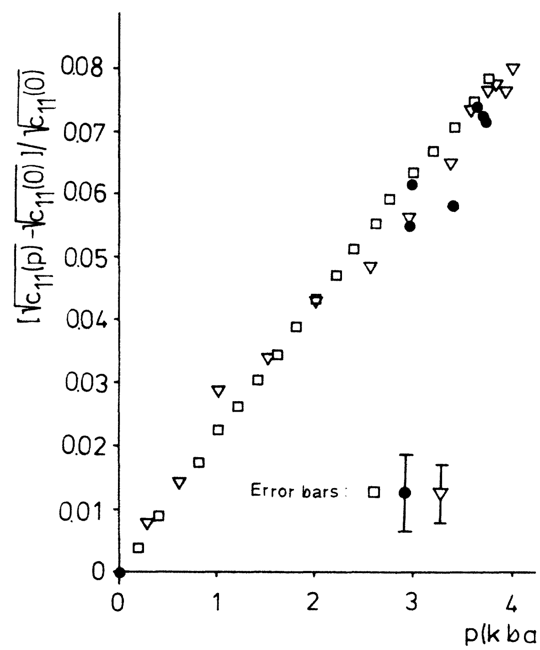

FIG. 2. Relative pressure dependence of the square root of the C_{11} elastic constant determined by ultrasonic (□) and Brillouin scattering (▽) techniques. The filled circles denote neutron scattering results obtained from the longitudinal acoustic LA⟨100⟩ phonon branch.

countered at 4 kbar where opalescent scattering of the entire sample is observed and the phonon peaks disappeared simultaneously. After reduction of the pressure the longitudinal Brillouin peaks reappeared at 2.55 kbar at the same frequency as observed in the upward run shown in Fig. 2. The Brillouin peaks regained about 90% of their original intensity, indicating the presence of a shape memory effect.

IV. DISCUSSION

The elastic constants of RbI at atmospheric pressure were measured by means of ultrasonic techniques by Haussuehl,[17] Bolef and Menes,[18] Reinitz,[19] and Lewis, Lehoczky, and Briscoe.[20] The pressure dependence of C_{44} was first measured by Daniels and Smith.[21] In subsequent studies, the pressure dependence of all three elastic constants of RbI was measured by Barsch and Chang,[22] Fontanella and Schuele,[23] Ghafelehbashi, Dandekar, and Ruoff[11] and Chang and Barsch[24] using ultrasonic techniques.

The adiabatic elastic constants c_{ij} of RbI at atmospheric pressure determined in this experiment in the GHz region are shown in Table I and are compared with previously published data.

The present results show that both C_{11} and C_{44} remain unchanged if we proceed from the MHz to the GHz region. In contrast to this, neutron scattering, which probes the THz frequency region, yields a value for C_{11} that is about 10% higher, whereas C_{44} as measured by neutron scattering is nearly equal to the ultrasonic and Brillouin values within the experimental error of the neutron measurements.

The data qualitatively confirm calculations of Loidl and co-workers[1,2] for the frequency dependence of the elastic constants in the transition region between the first- and zero-sound regime and indicate that in RbI the transition to the zero-sound regime occurs at frequencies somewhat higher than the Brillouin frequency of 18 GHz, corresponding to C_{11} (see Fig. 3).

Furthermore, the experiment also yields the pressure dependence of the elastic constants in the GHz region which is found to be similar to that obtained by ultrasonic measurements.

The experiment does not give a very significant indication of a deviation from linearity within the experimental error in the vicinity of the transition, compared to neutron scattering results for long-wavelength transverse acoustic phonons in the ⟨100⟩ direction (Fig. 1). In the neutron investigations the pretransitional phenomena, i.e., the small anomalies for small q transverse phonons in the ⟨100⟩ direction and the appearence of nuclei in the CsCl phase occurred well below 4 kbar, whereas the present Brillouin scattering results give no clear evidence of pretransitional phenomena in the macroscopic elastic behavior up to 4 kbar where the transition takes place.

Therefore, the deviations from linearity of the pressure dependence of transverse acoustic phonons in the ⟨100⟩ direction may be restricted to finite wavelengths and are not reflected in the macroscopic constants. It should be concluded that the anomalies in the phonon frequency behavior for the TA⟨002⟩ branch observed for q values near 0.2 are due to a resonancelike interaction with the microscopic intermediate defect structure appearing before the overall transition.

TABLE I. Elastic constants of RbI at 295 K and atmospheric pressure. The units are 10^{10} dyn/cm^2.

Experimental method	C_{11}	C_{44}	C_{12}	Refs.
Ultrasonic	25.83 ± 0.05	2.78 ± 0.005	3.7 ± 0.07	17
Ultrasonic	25.6	2.87	3.1	18
Ultrasonic	25.40 ± 0.05	2.76 ± 0.003	4.07 ± 0.02	19
Ultrasonic	25.63 ± 0.13	2.78 ± 0.01	3.4 ± 0.1	20
Ultrasonic	25.68 ± 0.05	2.78 ± 0.01	3.8 ± 0.02	11
Ultrasonic	25.66 ± 0.1	2.79 ± 0.003	3.77 ± 0.006	24
Brillouin	25.55 ± 0.25	2.76 ± 0.05	3.45 ± 0.3	This work
Neutron Scattering	28.15 ± 0.5	2.85 ± 0.1	3.7 ± 0.5	1,2

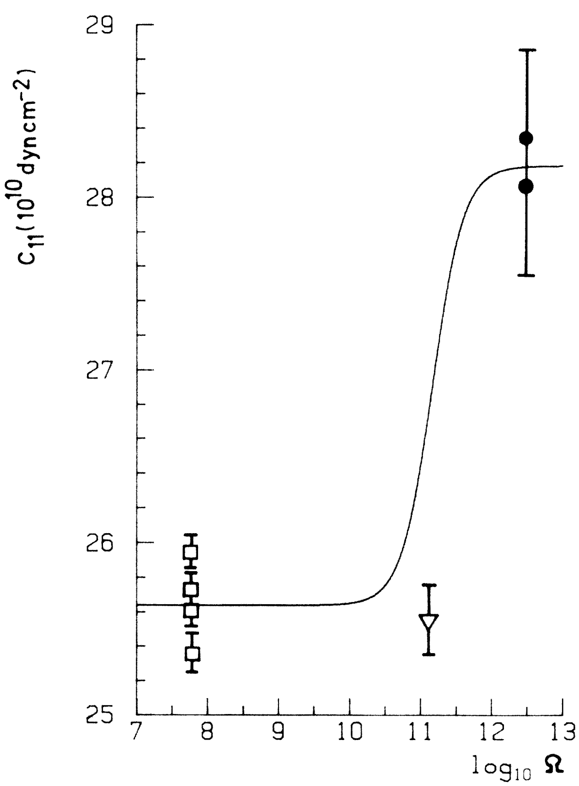

FIG. 3. The C_{11} elastic constant determined by ultrasonic (□), hypersonic (▽), and neutron (●) techniques. The value of C_{11} obtained in the present experiment was determined at sound angular frequencies $\Omega = 2\pi\ 18.10^9\ s^{-1}$ and is in agreement with ultrasonic data. The solid line shows the theoretical curve from Ref. 1. The transition between first and zero sound should therefore occur in RbI at frequencies between 10^{11} and 10^{12}. There is no quantitative agreement between the Brillouin value and that calculated by theory which could be interpreted with a slightly smaller mean lifetime of the phonons according to Ref. 1.

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