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1989 J. Phys.: Condens. Matter 1 2279

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LETTER TO THE EDITOR

Low-temperature elastic anomalies in lithium tetraborate

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Received 19 December 1988

Abstract. Anomalies in the elastic stiffness C_{33}^D have been observed at 75, 125, 215 K in tetragonal lithium tetraborate. Corresponding peaks in the attenuation of ultrasound have been observed. Changes in the inter-layer force constants are briefly considered.

The crystal structure of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) has been determined and refined by Krogh-Moe (1962, 1968). More accurate bond lengths and angles have been calculated by Natarajan *et al* (1979). The structure at room temperature is tetragonal, with space group IH_1cd (C_{4v}^{12}), and point group 4mm, with the polar axis along the crystallographic c axis. All the elastic stiffness, piezoelectric, and relative dielectric constants have been determined by Shorrocks *et al* (1981) at room temperature. From ultrasonic data and the density ($\rho = 2451 \text{ kg m}^{-3}$), Shorrocks *et al* (1981) also examined the longitudinal elastic stiffness C_{33}^D corresponding to the [001] direction between 253 and 353 K.

In the Letter we report on ultrasonic studies of tetragonal $\text{Li}_2\text{B}_4\text{O}_7$ at lower temperatures. Crystals of $\text{Li}_2\text{B}_4\text{O}_7$ grown by the Czochralski method were obtained from Barr and Stroud Ltd. They were supplied roughly polished and oriented in the form of 0.5 cm cubes. After the crystals had been finely polished, sound velocity and attenuation measurements were made using the ultrasonic pulse–echo overlap technique.

The velocity and attenuation changes in longitudinal sound waves propagated along the [001] direction over the temperature range 30–373 K are shown in figure 1. Anomalies in the temperature variation of the sound velocity and attenuation were found at 318, 215, 125 and near 75 K. There was a measurable anomalous change in the sound velocity of about 0.3% near 215 K.

The two-way transit times of short 30 MHz pulses propagated along the c axis were determined and combined with the appropriate values of length and density to give C_{33}^D as a function of temperature as shown in figure 2. Values of the lattice constants given by Natarajan *et al* (1979) were used to calculate the room-temperature density (2430 kg m^{-3}). The elastic constant C_{33}^D decreases markedly as the temperature is lowered reaching a minimum at approximately 75 K. Below this temperature the elastic constant starts to increase with decreasing temperature. The data in figure 2 show that whilst there is a slight softening of C_{33}^D near 215 and 125 K, there is a significant softening near 75 K. It was not possible to complete the attenuation curve at 75 K because of the very large attenuation encountered.

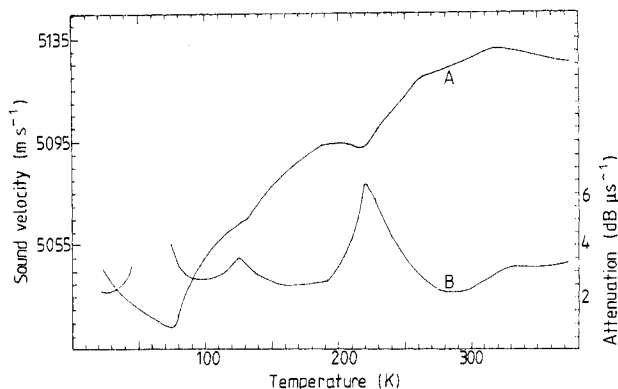


Figure 1. The temperature dependence of the longitudinal sound velocity (A) and attenuation (B) along [001] in $\text{Li}_2\text{B}_4\text{O}_7$.

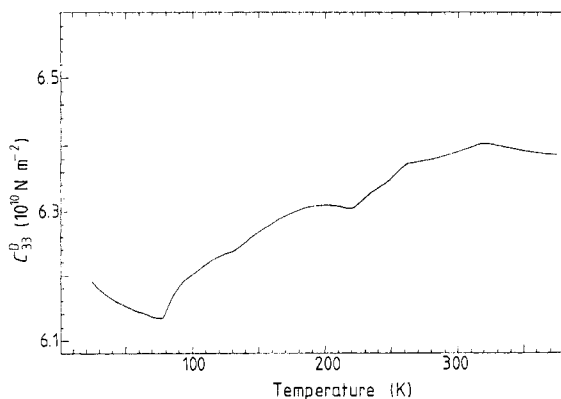


Figure 2. Temperature dependence of the elastic stiffness constant C_{33}^D in $\text{Li}_2\text{B}_4\text{O}_7$.

Experimental data on sound velocities have also been obtained in other crystallographic directions down to a temperature of 100 K. Anomalies at 125 and 215 K have again been seen, but they are significantly smaller than those shown in figure 1.

It is significant that the sound velocity along the c axis is very much lower than velocities measured in either the a or b direction. This points to a difference between the bond strengths in these two directions, and Shiosaki *et al* (1985) have suggested that $\text{Li}_2\text{B}_4\text{O}_7$ is indeed a layer crystal. Hence we would expect to see larger changes taking place along the c axis.

A single-crystal sample of $\text{Li}_2\text{B}_4\text{O}_7$ has also been examined, in these laboratories, using Raman spectroscopy by Sehery (1988). In this work the intensity, half-width and shift of the Raman modes have been found. At room temperature strong peaks at 152, 175, 204 and 218 cm^{-1} were observed. The Raman data indicate decreases in intensity for the lattice modes near 125 and 75 K. The linewidth data give an anomaly at 215 K and the possibility of one near 125 K. The Raman shift variation again indicates 215 and 125 K as temperatures at which anomalies occur. For example, the single 175 cm^{-1} mode at 130 K splits into two at 165 and 171 cm^{-1} near 125 K. Below this temperature the 171 cm^{-1} mode grows in intensity as the temperature is lowered to 10 K. It is suggested

that any explanation must involve a change in force constants within the crystal which may be attributable to a phase transition involving displacement or motion of layers or molecular groups within each layer. The absence of additional Raman splittings suggests that there are no structural changes within the molecular groups.

In conclusion, we note that the C_{33}^D elastic stiffness data show anomalies at 215, 125 and 75 K. These anomalies coincide with changes taking place in a direction normal to the planes, where changes in the weaker van der Waals' forces are likely to be greater than corresponding changes in the covalent bonding within the layers. Work now in progress aimed at deriving a complete set of elastic constants, together with a calculation of inter- and intra-layer forces, should further clarify the nature of these anomalies.

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