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Isomorphous phase transition of 1,2,4,5-tetrabromobenzene jumping crystals studied by Brillouin light scattering

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ABSTRACT

The isomorphous phase transition of 1,2,4,5-tetrabromobenzene (TBB) jumping crystals was studied by Brillouin light scattering. The temperature dependence of the sound velocity and the corresponding elastic constants of three acoustic modes propagating along the [110] direction were measured as a function of temperature covering the β–γ phase transition temperature for the first time. All three elastic constants showed discontinuities at the jumping transition temperature with a large thermal hysteresis. While the longitudinal and one of the two transverse acoustic modes did not exhibit any appreciable changes in both the β and the γ phase, the lowest transverse acoustic mode showed substantial softening on approaching the jumping transition from both phases. This clearly showed that the jumping transition of this molecular crystal is driven by the elastic instability and that large intermolecular anharmonic interaction is associated with the molecular motions in the (110) plane.

1. Introduction

Recently, the thermosalient effect, also called the "jumping crystal" effect (or "hopping effect"), has attracted attention because of the interesting physics related to this phenomenon and possible applications [1]. Jumping crystals usually exhibit mechanical movements during the phase transition, the heights of which are in some cases several centimeters [2]. The jumping transition may be induced either by temperature variation or by ultraviolet irradiation [3]. One of the potential applications of the thermosalient effect may be efficient actuators based on the thermal–mechanical energy conversion process. Jumping crystals show large discontinuities in their lattice parameters and cell volumes at the phase transition temperature. It may induce substantial deterioration of the crystal quality during the mechanical movements, which makes it difficult to investigate the microscopic mechanism that drives the jumping phase transition.

1,2,4,5-Tetrabromobenzene (abbreviated as TBB) is one of the well-known jumping crystals. TBB is found in two polymorphic forms. The β phase is stable at room temperature, and the high-temperature phase is γ phase [4,5]. Fig. 1 shows the phase sequence of TBB as a function of temperature and thermal history. The jumping transition is usually observed at approximately 43–47 °C (T_c^+) upon heating. The thermal hysteresis amounts to approximately 10 °C, indicating the strong first-order nature of the phase transition. As in the case of many other organic jumping crystals, there is no change in the space group when TBB undergoes the β–γ phase transition. Both phases are monoclinic with the same space group $P2_1/a$–C_{2h}^5, exhibiting a primitive cell that includes two molecules located at the center of inversion [4,5]. Various experimental methods have been applied to TBB to get more insights into the nature of the jumping transition [6–11].

Elastic properties are one of the fundamental information necessary for getting more insights into the phase transition, because the elastic constants are determined by the intermolecular forces and lattice anharmonicity. Elastic properties are usually investigated by ultrasonic pulse-echo method [12], resonant ultrasonic spectroscopy (RUS) [13], impulsive stimulated thermal scattering (ISTS) [14] or Brillouin light scattering [15]. Detailed Brillouin scattering investigation was carried out on TBB single crystals by Dye and Eckhard at room temperature [8]. The 13 independent elastic constants, sound velocity diagrams and anharmonicity diagrams were suggested. According to this study, the longitudinal acoustic (LA) mode behaviors were dominated by the usual lattice anharmonicity, but some transverse acoustic (TA) velocities exhibited substantial changes along certain directions [8]. In particular, they reported that the TA mode velocity exhibited a very low value along the direction at approximately 45° off-axis in the *ab* plane [8]. This clearly suggests large anharmonicity associated with some TA modes and their possible role in the

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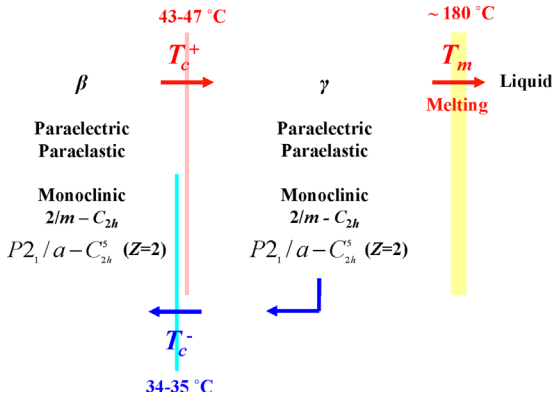

Fig. 1. (Color online) The schematic phase sequence of TBB as a function of temperature and thermal history.

jumping transition. However, they failed to observe the temperature dependence of the acoustic modes over the whole temperature range. The phonon velocities did not exhibit any shift as a function of temperature close to the phase transition point in the β phase. This is the motivation of the present study. We carefully investigated the acoustic properties of the TBB single crystals in a certain temperature range covering both the β and γ phases. Significant softening of the TA mode propagating along the [110] direction was revealed for the first time.

2. Experimental

TBB crystals were grown by slow evaporation after recrystallization of the commercially available compound from hot toluene. They are colorless and brittle. The crystal morphology is nearly the same to the previous reports, exhibiting needle-shaped morphology with predominant (110) surfaces (See Fig. 2 in Ref. [7]).

The Brillouin spectrum was measured by using a conventional tandem six-pass Fabry–Perot interferometer (TFP-1, JRS Co.). A compact cryostat cell (THMS600, Linkam) was put on a microscope (BX41, Olympus) for carrying out backscattering experiment. A solid state laser (Excelsior 532–300, SpectraPhysics) at a wavelength of 532 nm was used as an excitation source. Two few different free spectral ranges (FSRs), 30 and 15 GHz, were used to cover both high and low frequency ranges. In particular, the FSR of 15 GHz had to be used to measure the lowest transverse acoustic (TA) mode, which exhibited a substantial softening on approaching the phase transition temperature. The details of the Brillouin spectrometer can be found elsewhere [16,17].

Since the dominant surfaces are (110), the laser beam was incident on this surface, indicating that the phonon wavevector is along the [110] direction. The polarization direction of the incident laser beam on the (110) plane was rotated to check the birefringence effect and the Brillouin spectrum was measured. As suggested from previous study (See Figs. 2 and 3 in Ref. [7]), the principal directions were inclined by 15° with respect to the *c* axis. In other directions, all the Brillouin doublets were split into two due to the birefringence effect when the polarization direction was arbitrarily set with respect to the principal directions, making the spectrum much more complex.

In the first run, we did not align the polarization direction to any crystallographic axes and measured the Brillouin spectrum from room temperature up to T_c^+ located between 43.5 and 44 °C. After the jumping transition occurred, the crystal was broken into smaller parts and the crystallographic axes of these samples became random in the temperature cell. We selected one large sample and continued the experiment with the birefringence

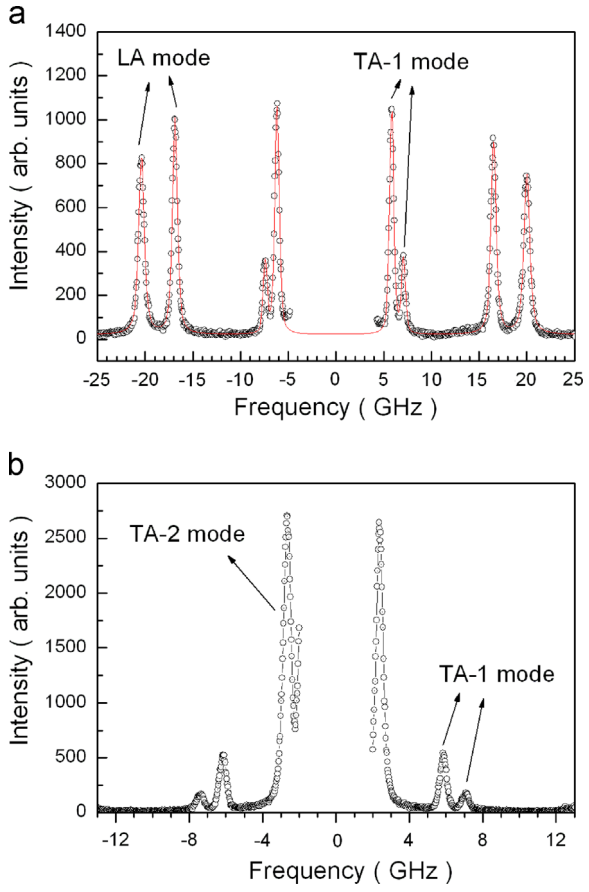

Fig. 2. (Color online) The Brillouin spectrum of TBB measured at room temperature in (a) a wide and (b) narrow frequency range. The red solid curve in (a) is the best-fit result.

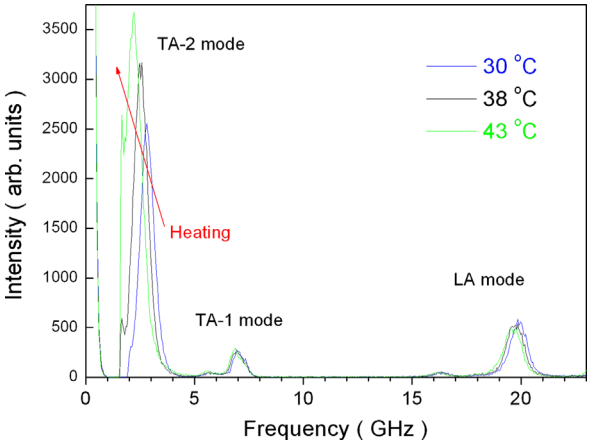

Fig. 3. (Color online) Brillouin spectra of TBB at three temperatures measured upon heating.

effect being present in the spectrum. After the measurement of the Brillouin spectrum at 50 °C, the crystal was cooled while recording the Brillouin spectrum. This sample underwent the jumping effect at around 35 °C (T_c^-), below which the sample was broken again and it was not possible to continue the experiment. In the second run, the polarization direction of the laser beam was aligned along the principal direction, by which the number of the Brillouin doublet became three. The TBB crystal underwent the jumping transition at approximately 43.7 °C (T_c^+),