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Picosecond Ultrasound for Studying Anomalous Temperature Dependence of Elastic Constants of the Negative-Thermal-Expansion Zirconium Tungstate

ピコ秒超音波による負の熱膨張を示す ZrW_2O_8 の弾性定数の異常温度依存性の研究

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1. Introduction

Zirconium tungstate (ZrW_2O_8: ZWO) shows negative thermal expansion (NTE) over a wide range of temperature (0-1050 K).[1] It has been expected to develop composites, showing no thermal expansion, which will improve precision devices' performance. Because of its unusual cubic structure, ZWO exhibits characteristic low-frequency phonon modes called 'rigid unit modes' (RUMs), which are considered to be responsible for the negative thermal expansion.[2] These mode have low energies ranging from 3 to 10 meV, corresponding to low frequencies from 700 GHz to 2.4 THz.[3]

Migliori *et al.* measured ZWO's elastic constants by resonant-ultrasound spectroscopy (RUS) and showed that its bulk modulus increases by 40% from room temperatue to 0 K despite increasing volume.[4] Considering that the bulk-modulus increments of tungsten and zirconium are 1.0% and 2.6% at the same temperature range, respectively[5], the relationship between the thermal expansion and the bulk modulus of ZWO is remarkable.

Ogi *et al.* established the elastic-costant measurement with Brilluin oscillations excited by picosecond ultrasounds[6] and extended this method at cryogenic temperatures.[7,8] In this method, we exicite ultrahigh-frequency coherent phonons in crystals by a ultrafast light pulse and observe propagation of a specific phonon mode whose frequency satisfies Bragg's condition with the probe light pulse. The strain pulse induced in the crystal includes a broad frequency band and should stimulate the RUMs directly. (No study has succeded in excting RUMs directly.) We thus expect to observe the elastic constants of ZWO different from the previous study and get infromation about relationship between temperature dependence of elastic constants of ZWO and RUMs.

While RUS can determine all elastic constants from a single specimen, we can measure only one elastic-constant component, the longitudinal-wave stiffness along the normal direction to the surface. Then, we prepare several small specimens whose orientation are known previously and measure their sound velocity by the Brillouin-oscillation method to determine the three cubic elastic constants of ZWO between 9 and 300 K. The results showed different tempearature dependence of the elastic constants from the previous work as expected, indicating significant contribution of stimulated RUMs.

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2. Experiments

We use an ultrafast light pulse to excite the strain pulse, which propagates in the specimen. A delayed probe light pulse is applied, which is diffracted in the specimen by the strain pulse exited by the pump light pulse. The diffracted light pulse causes interference with the surface reflected probe light. Brillouin oscillation is a phenomenon that intensity of interference light oscillates in a definite period. Its frequency f_{BO} is approximated by Bragg's condition[6]:

$$f_{BO} = \frac{2nv}{\lambda_{Pr}} \tag{1}$$

where n, v, and λ_{Pr} are the refractive index of the specimen, longitudinal sound-wave velocity, and the wavelength of the probe light, respectively.

Fig. 1 shows a schematic illustration of the experiment setup for low-temperature picosecond ultrasound spectroscopy developed in this study. We use a titanium-sapphire pulse laser with 140 fs duration and 80 MHz repetition rate. An output light pulse is separated into a probe light pulse and a pump light pulse by a polarizing beam splitter (PBS). Their power ratio is adjusted by a $\lambda/2$ plate. The probe light's frequency is doubled by a second harmonic generator (SHG) crystal, so the wavelength of the pump light and that of the probe light are 800 and 400 nm, respectively. The pump light is modulated at 100 kHz by an acousto-optical (AO) crystal. We move two corner-cube reflectors

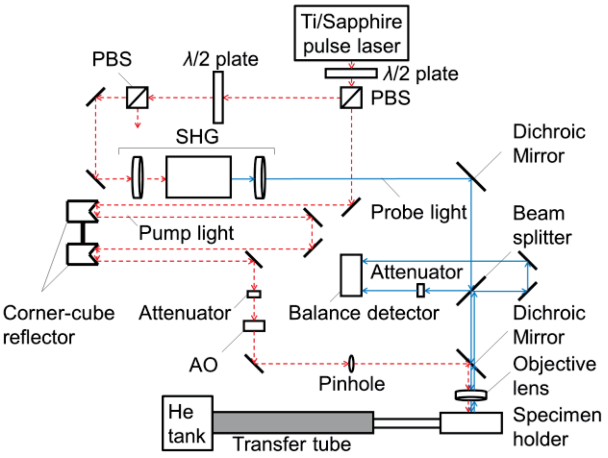

Fig. 1. Schematic of the experimental setup for low-temperature picosecond ultrasound spectroscopy. Solid and dashed lines represent 400-nm and 800-nm wavelength lights, respectively.

for the delay line, The specimen is fixed in the cryostat with a glass window and cooled by liquid helium through a copper heat exchanger. A RhFe resistance thermometer is set on the heat exchanger, which adjusts the specimen temperature. We deposit a 10-nm Al thin film on specimens as a sound generator.

3. Results and Discussions

Fig. 2(a) shows examples of Brillouin oscillation waveforms at 295 K and 10 K, whose backgrounds are subtracted. We can observe Brillouin oscillations even below 10 K. **Fig. 2(b)** shows their FFT spectra, clearly showing that the frequency is increased by cooling the specimen. We need to know the temperature dependence of the refractive index for precise elastic-constant determination, but such a frequency increase should be caused by the elastic-constant increase. From the measurements of eight specimens with different crystallographic orientations, we inversely determined the three independent elastic constants of ZWO. They behave quite differently at low temperatures compared with the previous low-frequency (~ 1MHz) study.[4] The bulk-modulus increase, for example, is less than half that reported. We attributed this to be the stimulated RUMs, which remained the apparent crystal temperature higher.

4. Conclusion

We succeeded in observing Brillouin oscillations in ZWO between room temperature and cryogenic temperatures by picosecond ultrasound spectroscopy. The Brillouin oscillation frequency increases at low temperatures, but the elastic constants behave differently from the previous

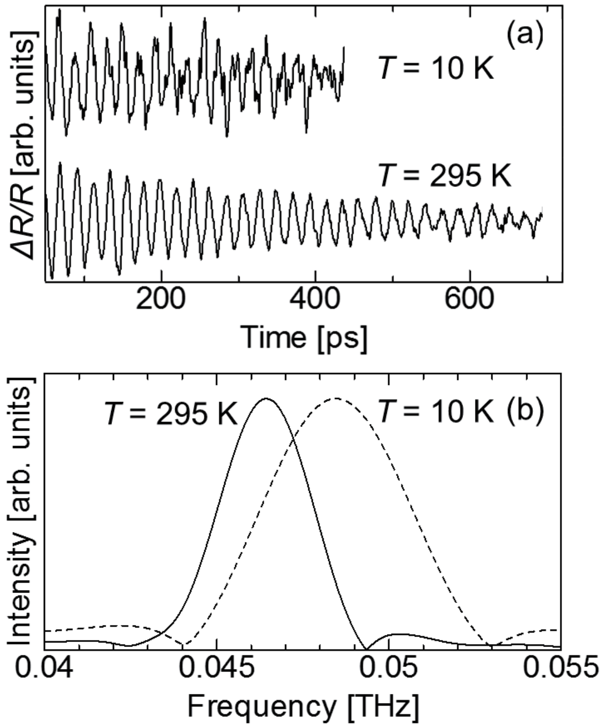

Fig. 2. Examples of (a) Brillouin oscillation wave forms and (b) their Fourier spectra.

study. This observation indicates the successful direct excitation of RUMs.

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