Terahertz Spectra of GaSe: Fundamental and two-order phonon processes

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***Abstract*-Fundamental and high-order phonon-phonon interactions dominate the far infrared absorption and dispersion spectrum of most semiconductors and dielectrics. We present the detailed investigation of the temperature dependence of the dielectric function of the semiconductor GaSe in the frequency range below 4 THz, between 100 K and 310K, using terahertz time-domain spectroscopy (THz-TDS) technique. Combined with the Fourier translation infrared (FTIR) spectroscopy, the complete infrared absorption spectra, including both sum and difference two-phonon absorption, are obtained. From the dielectric function we determine the blue-shift of the fundamental phonon frequency E' at 0.59 THz with the decrease of the temperature. Furthermore, our experimental data enable assignment of the two-phonon terahertz absorption to difference combinations of fundamental phonon mode at critical points in the Brillouin zone center.**

I. INTRODUCTION

The resonance-like terahertz and far-infrared absorption in ion-bond crystals has been understood as a result of cation- and anion-sublattice vibration resonance driven by the light-wave electric field, which usually only involves phonons near the Brillouin-zone center. Apart from the transverse optical (TO) mode resonance, direct coupling of phonon oscillator pairs to light, which results from higher-order Born effective charges, occurs at sums and differences of phonon frequencies and in principle, involves phonon everywhere in the Brillouin zone. Despite the wealth of past studies, the light-lattice interaction is still far from maturity.

Our interest in two-phonon processes is motivated by the ultrafast response time of electro-optic crystals. The introduction of electro-optic materials for detection of subpicosecond electrical transients has kicked-off new research directions which complement techniques based on photoconductive materials for static spectroscopy in the far infrared. Recently developed terahertz time-domain spectroscopy (THz-TDS) with its high signal to noise ratio in the THz range facilitates the research of the frequency differences of fundamental phonon mode of crystals. And modern electronic structure calculation method has undergone sufficient recent improvements to warrant critical-point analysis of two phonon absorption spectra [1].

Gallium selenide (GaSe) is a promising semiconductor for THz generation and detection. Recently, GaSe was used in the generation of 0.18-5.27 THz tunable waves using a difference-frequency technique [2] and also used in phase-matched optical rectification with a Ti:sapphire laser from 0.4-41 THz [3]. GaSe is becoming a material of choice of for a THz emitter and sensor. In this paper, we present a measurement of the absorption and dispersion spectra of GaSe below 4 THz, in the temperature range between 100 K and 310 K, with an emphasis on the importance of interactions between THz photos and vibration modes of the crystal lattice in the interpretation of the spectra.

II. EXPERIMENTAL SETUP

We measure the absorption and refractive index spectra of GaSe with a conventional terahertz time domain spectrometer. Photoconductive dipole antennas, driven by 90 fs pulses from a mode-locked Ti:sapphire oscillator, are used to generate and detect the terahertz pulses, which consist of a single cycle of the electro-magnetic fields with 500 fs duration. The emitter and detector are fabricated on LT-grown GaAs and the active area is 5 μm wide. The terahertz system can provide a useful bandwidth from 0.3 to 3.5 THz. The first off-axis paraboliodal mirror is used to focus the beam of THz pulses at the intermediate focus inside a cryostat where the sample and an identical reference aperture are mounted. The second off-axis paraboliodal mirror imagines the focus onto the detector. The THz beam path is vacuumed to avoid absorption induced by rotational transitions in water molecules.

GaSe is a layered crystal in which each layer consists of four mono-atomic sheets in the order of Se-Ga-Ga-Se. Several polytypes have been reported, which differ in the stacking pattern sequence of the basic layer units. Bridgeman grown samples are commonly found to follow the ε stacking pattern and said to be optically uniaxial crystals. In our experiment, a 2.4-mm-thick z-cut GaSe wafer is inserted into the cryostat which can be cool down to 100 K.

The dielectric function of the sample may be represented by the intensity absorption coefficient and the refractive index, and is calculated at each frequency within the bandwidth of the pulses from the ratio of the Fourier transforms of the sample pulse and reference pulse. The material parameters are extracted following the method presented by Duvillaret [4] which included the phase shift associated with the transmission over the dielectric interfaces of the crystal.

III. RESULTS

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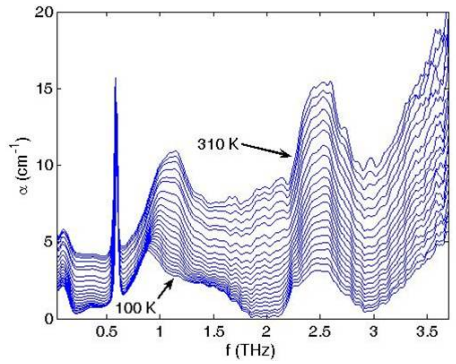

Figure 1. Absorption coefficient of GaSe crystal at temperatures between 100 K and 310 K with interval of 10 K.

In Fig. 1, the absorption coefficient of GaSe crystal between 100 K and 310 K is shown. At all temperatures, a slow increase of absorption coefficient towards high frequency is observed. This increase is caused by the TO phonon, which in GaSe is located at 6.33 THz. The sharp absorption peak at 0.59 THz is the resonance of phonon mode E', which is the rigid movement between the two different Se-Ga-Ga-Se layers. The absorption intensity of the single phonon mode is independence of temperature. The peak position is shifted slightly towards higher frequency when the crystal temperature is decreased. The same result obtained by temperature-dependent Raman scattering spectra of GaSe crystal [5].

Superposed on the low-frequency TO wing two features are visible in the absorption spectra. These broad absorption peaks are known to be the contributions of two-phonon difference mode, respectively. As the temperature of the crystal is lowed, the contribution from the two-phonon differences becomes less prominent in the absorption spectrum. Although transitions between the phonon branches can occur anywhere in the Brillouin zone, they are most likely to take place at critical points, where the density of state is highest. The corresponding two-phonon sums are observed in the FTIR spectrum. Combined with the thermally weighted two-phonon density of state contributing to the absorption spectrum, we assign the specific phonon pairs to the corresponding difference mode absorption. Fig. 2 shows the relative peak-absorption strength of phonon band at 83 cm^{-1} at different temperatures and the agreement with the population difference of two fundamental phonon modes $E^{'}(TO)$ and $A_1^{'}$. From the good agreement, we can identify unambiguously the broad absorption peak with difference phonon process which occurs in the center of Brillouin zone.

The interpretation of the different mode at about 40 cm^{-1} needs much more effort. Fig. 1 shows that the peak position is shifted to lower frequency when the temperature decreased. This indicates that the broad absorption peak may be the addition of two or more difference phonons. The assignment of these features call for the third-order density-functional perturbation calculation and critical-points analysis.

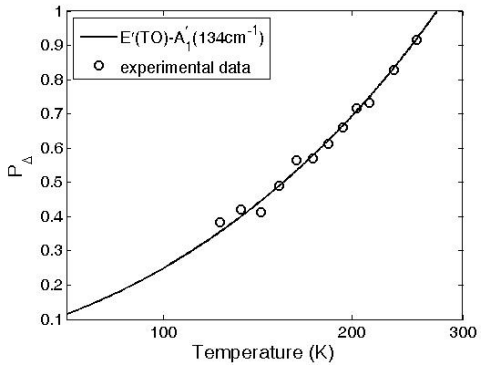

Figure 2. Temperature dependent of the peak absorption strength of phonon band at 83 cm^{-1} in GaSe together with theoretical curve.

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