

Observation of Low Energy Optical Phonon in the β -Phase of CuI

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Concerning high ionic conduction of superionic conductors(SICs), much attention has been focused on the role of phonon modes[1-4]. One of those is a low energy(LE-) mode which is observed in many SICs, and exhibits characteristic properties. Most popular LE-mode is the 17cm^{-1} mode in AgI. For its origin, several mechanism has been proposed[1]. Recently author assigns the LE-mode an optical phonon at the center of Brillouin zone by applying the idea of zone folding[1], and connects it the origin of high ionic conduction of SICs[4]. Therefore a LE-mode is much important for elucidating the mechanism of SICs. According the idea of the zone folding, a LE-mode must be observed in the β -phase of CuI because of its crystal structure having the same crystal symmetry with that of AgI. The γ - and β -phases of CuI take a zincblende and wurtzite structures below and above 368 K(=Tc), respectively. The LE-mode and phonon modes of CuI have been studied by neutron and Raman scattering spectra[5]. However a LE-mode has not been clearly observed yet, though a transverse acoustic(TA-) mode at the edge of Brillouin zone is observed near 40cm^{-1} , in addition to a large anharmonic optical mode.

In this report, we measure the reflectivity spectra in far-infrared region for a sintered CuI using a conventional equipment with the resolution of 1.0cm^{-1} and 0.5cm^{-1} in the temperature range from the γ - to β -phases through Tc. We observe a LE-mode which appears suddenly near and above Tc. This behavior is different from that of TA-mode, observed even at room temperature[5]. For the LE-mode, a sharp band is anticipated from the low energy of the mode, as observed. The spectra are analyzed using Kramers-Kronig relation, and the energy of the mode is assigned to 28cm^{-1} , that is lower than $30\text{-}40\text{cm}^{-1}$ of the TA-mode, observed in Raman and neutron scattering spectra[4-5].

From these behaviors, we assign this mode the E_2 -mode, characteristic in the crystal symmetry of the β -phase. The E_2 -mode is basically infrared inactive but it can be observed by infrared spectra under the appearance of many defects because of the destruction of the selection rule. Such defects near Tc can be suggested from the high ionic conductivity[6]. We indicate that this mode satisfies the properties of low energy optical phonon, originated from the TA-mode at the edge of Brillouin zone, and also the correlations with the squared root of atomic mass, ionic activation energy, and transition temperature[1,2,4].

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