Observation of anomalously increasing phonon damping constant in the β phase of the fast-ionic conductor Ag$_3$SI

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The correlation of phonon frequency ω_j and phonon damping γ_j to the ionic conductivity σ has been observed from the temperature dependence of infrared-reflectivity spectra of a Ag$_3$SI single crystal. Two reststrahlen bands and a rapid increase of reflectivity in low-frequency region were observed above T_c (≈ 157 K), the β-γ phase transition temperature, and described by the dispersion relation due to the phonons and the diffusing ions. The γ_j exhibits the drastic change at T_c and has an anomalously large magnitude above T_c. The shifts of γ_j and ω_j also showed appreciable changes at about 250 K. Furthermore, the ω_j of the low-frequency mode in the β phase increases with increasing temperature. We can qualitatively interpret these results from the disorder arrangement of the Ag ion above T_c and the coupling of mobile ions above 250 K with phonons near the Brillouin-zone boundary.

I. INTRODUCTION

Fast-ionic conductors are characterized by a high density of mobile ions and also by the intense anharmonic crystal potential. We are interested in the effect of such an anharmonic potential on a phonon mode since the coupling between the phonons and the mobile ions would be dominantly related to the mechanism of ionic motion. The large anharmonic potential, however, makes it difficult to observe a clear reststrahlen band and, therefore, detailed information for the phonons in the fast-ionic state has not been reported to date.

For the investigation of phonon parameters, Ag$_3$SI is an appropriate compound since a clear phonon structure is observed on the infrared spectra in the β phase of the fast-ionic state.[1,2] The phonon parameters, therefore, can be determined with a considerable degree of accuracy. The infrared-reflectivity spectra at room temperature or at several low temperatures were reported by Gras and Funke[1] and by Brüesch et al.[2] The former gives two bands[1] and the latter gives three main bands.[2] The difference between the spectra may depend on the quality of the crystal used for the measurements.

Furthermore, both reports remark little on the values characterizing the phonon modes. Recently, Wakamura and Hirokawa found a clear correlation for the temperature dependences of the phonon frequency ω_j and the phonon damping constant γ_j to that of ionic conductivity σ in the isomorphous compound Ag$_3$SBr.[3] They considered the origin due to the coupling of mobile ions to the phonons at the boundary of the Brillouin zone (hereafter abbreviated ZB phonons), but could not account for its microscopic mechanism. To ascertain the correlation reported, similar behavior must be present in other fast-ionic conductors.

In this paper we report the temperature dependence of infrared-reflectivity spectra for single-crystalline Ag$_3$SI in the β and γ phases. A microscopic mechanism for the temperature dependence of ω_j and γ_j is proposed by considering the coupling of the ZB phonons to the mobile ions. The mechanism explains some characteristic correlations among ω_j, γ_j, and σ.

II. EXPERIMENTS

A large single crystal was grown from the equimolar mixture of AgI and Ag$_2$S powders with a modified vertical Bridgman method. Details of the method were mentioned elsewhere.[4] The crystal obtained was heated once above the α-β phase-transition temperature (246 °C), and was annealed approximately at 230 °C for a few hours to obtain the stable β phase, which was ascertained by the x-ray-diffraction method.

An x-ray-diffraction pattern for the surface of a sample showed only a sharp peak characterizing a single crystal. After the optical polishing of a fresh sample, we measured the infrared-reflectivity spectra with a Fourier-transform spectrometer (FTS-20E, Digilab, Inc.) for the entrance angle of 14° in the energy range 15–500 cm^{-1}. The reflectivity at each temperature was obtained by averaging the data measured with 8- and 25-μm beam

splitters with a resolution of 1.0 cm^{-1}. For the reflectivity measurements with decreasing temperature, details of the method were described elsewhere.[5]

III. RESULTS AND ANALYSES

Ag$_3$SI exhibits three crystallographic structures, that is, the α ($T > 513$ K), the β ($513 > T > 157$ K), and the γ (157 K $< T$) phases.[6-9] The α phase has the antiperovskite-type structure (O_h^5) with the mobile Ag ion distributed statistically on 12(d) sites. The S or I ions distribute randomly at the corner or the body-centered sites of a cube. In the β phase, the structure undergoes a slight deformation and takes a simple-cubic structure (O_h^1) in which anions I and S locate in a CsCl-type array and also the mobile Ag ions distribute statistically on 12(h) sites. The α and β phases exhibit the fast-ionic conduction. In the γ phase the crystal assumes a rhombohedral structure (C_3^4) in which the rhombohedral angle is almost 90°.[7] The Ag ions are orderly and fixed near one of 12(h) sites in the β phase and make many domains, having 16 domain orientations.

Some of observed reflectivity spectra in the β and γ phases are shown in Fig. 1. The features of the spectra are different from the previous results[1,2] in several ways. The spectra at 302 K are similar to the results reported by Gras and Funke,[1] except for their low reflectivity. The low reflectivity perhaps arises due to the polycrystalline pressed pellet. On the other hand, the complex structure of the spectra was observed by Brüesch et al.[2] with a polycrystal containing many single domains. Such domains may give a larger number of structures in the spectra than the present data.

Only two bands, a and b, were observed at the β and γ

phases above 100 K. The b band was assigned by Brüesch et al.[2] to a resonance band due to the local motion of silver ions, which is called an attempt mode. However, we assign both bands to the broadened reststrahlen bands since the bands in the γ phase show a feature characteristic of the reststrahlen band. This assignment will be supported by the reasonable magnitude of the Szigeti effective charge e_s^*, which is calculated from the frequencies of both bands and also exhibits a reasonable relation to the optical dielectric constant ϵ_∞ as will be mentioned later.

We observed three or four bands below 90 K and, in addition, the other weak structures at 18 K. These may originate from the multidomain structure having different electric dipole moments. We also observed an appreciable increase of reflectivity R below 30 cm^{-1} above T_c and a small increase even below T_c, which had been already observed and considered to be a precursor effect of the phase transformation by Brüesch et al.[2]

We determined the magnitudes of the phonon parameter by the fitting of R with the factorized form of the dielectric function $\epsilon(\omega)$. We employ a procedure that applies to a cubic crystal since the influence of small-crystal anisotropy in the γ phase will reflect little on the macroscopic dielectric parameters found in ZnO and chalcopyrite compounds.[10]

The R at normal incidence is related to the real and imaginary parts of the refractive index, n and k, and also those of the dielectric functions ϵ_1 ($= n^2 - k^2$) and ϵ_2 ($= 2nk$), as

$$R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2] . \tag{1}$$

The $\epsilon(\omega)$ above T_c is given by the phonon term ϵ_{ph} (Ref. 11) and also the diffusive-ion term ϵ_d,[12]

$$\epsilon(\omega) = \epsilon_{\mathrm{ph}} + \epsilon_d = \epsilon_\infty \prod_j (\omega_{Lj}^2 - \omega^2 - i\gamma_{Lj}\omega)/(\omega_{Tj}^2 - \omega^2 - i\gamma_{Tj}\omega) + S/(\bar{\omega}^2 - \omega^2 - i\omega\Gamma) , \tag{2}$$

Here, ω_{Tj}, ω_{Lj}, γ_{Lj}, and γ_{Tj} indicate the frequencies of the jth transverse-optical (TO) and longitudinal-optical LO modes, and the damping constants of the jth LO and TO modes, respectively. The suffix j takes two infrared-active modes above 110 K, and three or four modes below 90 K. Γ represents the frequency-dependent damping, $\bar{\omega}$ the resonance frequency averaged by diffusive ions, and S its oscillator strength. The former two values are the functions of both the frequency ω_0 and damping γ_0 of diffusive ions.[12] The contribution of the second term on the phonon having the lowest energy is not small. The fit with Eqs. (1) and (2) is shown by the dashed line in Fig. 1. Excellent agreement was obtained over the measured temperature range and it indicates the reliability of the determined phonon parameters. The determined value of ω_{TO} for the b band is slightly larger than the resonance frequency assigned by Brüesch et al.[2] The determined values of γ_j and ω_j are shown as a function of temperature by the squares in Figs. 2 and 3, respectively.

The abrupt change of γ_j is found at T_c and the appre-

ciable increase is also found approximately above 250 K. To depict these anomalies, we first analyze the γ_j below T_c by employing the cubic and quartic phonon-decay processes.[13] Under the assumption that each decayed phonon has the same frequency, the phonon-damping constant γ_j is

$$\gamma_j = a_j[N(\hbar\omega_{aj}) + 0.5] + b_j\{[N(\hbar\omega_{bj}) + 0.5]^2 + \tfrac{1}{12}\} , \tag{3}$$

where ω_{aj} ($= \omega_j/2$) and ω_{bj} ($= \omega_j/3$) mean the frequencies of decayed phonons. For those phonons, the ZB phonon is important because of its high density of states. The phonon population number $N(\hbar\omega_{aj})$ is given by $N(\hbar\omega_a) = 1/[\exp(\hbar\omega_a/kT) - 1]$. The coefficients a_j and b_j are the cubic and quartic derivatives of the crystal potential U with respect to the phonon displacements, respectively. We take the constant values for the a_j and b_j as employed in several ionic crystals.[14,15] The results are shown by the solid line in Fig. 2. The agreements with the observed values below 150 K are fairly good. The
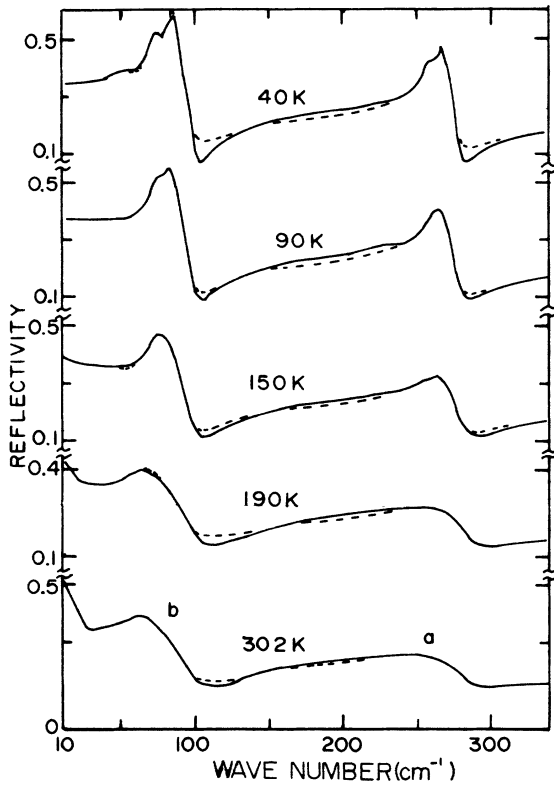
FIG. 1. Temperature dependence of reflectivity spectra. Solid line shows the observed spectrum, the dashed line the value fitted with Eqs. (1) and (2).
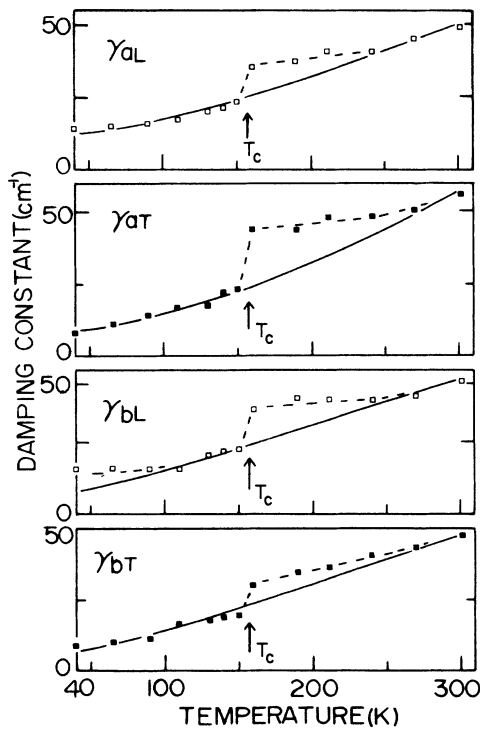

FIG. 2. Temperature dependences of γ_{LO} and γ_{TO}. Solid and dashed lines represent the results fitted with Eq. (3) and the smooth curve through the observed points, respectively.
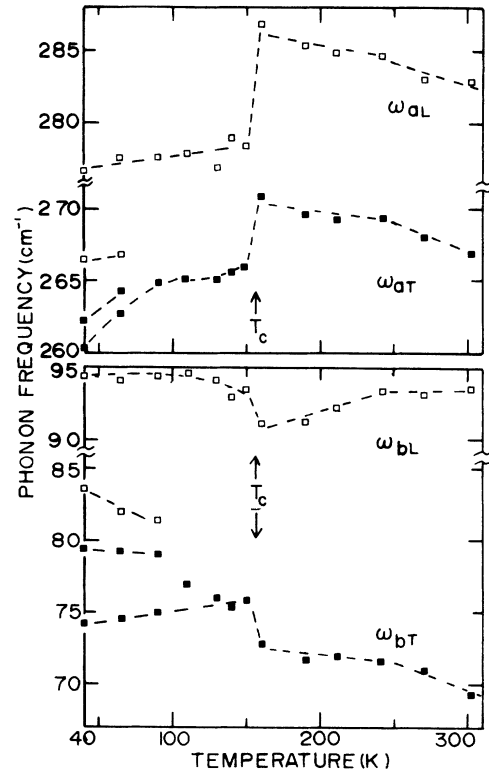

FIG. 3. Temperature dependences of ω_{LO} and ω_{TO}. The open and solid squares indicate the observed values for LO and TO phonons, respectively. Below 90 K, the LO and TO modes for a split band are represented by the same symbol. The dashed lines were drawn through the observed points.

agreement is also good over the temperature range 250–300 K, and the calculated line is likely to agree with the measured values above 300 K, if measured. The values a_j and b_j are 22 and 3 for the LO mode of the a band, 14 and 6 for the TO mode of the a band, 10 and 0.1 for the LO mode of the b band, and 7 and 0.1 for the TO mode of the b band, respectively. These values are 2 or 3 times larger in comparison with those of normal ionic crystals.[13,14] This result indicates that the large anharmonic crystal potential is realized even below T_c.

Concerning the shifts of ω_{TO} and ω_{LO} in Fig. 3, we can find the drastic variation at T_c and the small temperature dependence between T_c and 250 K. The a band shows small variation and the ω_{LO} for the b band shows an increase with temperature.

Furthermore, the splitting of the reststrahlen band has been observed below 90 K. The energy of the split band shifts appreciably with decreasing temperature. This result suggests that the continuous variation of electric dipole moments arises even in fairly low temperature below T_c, and may relate to the large anharmonicity below T_c.

IV. DISCUSSION

The corresponding variation of γ_j and ω_j to the ionic conductivity σ is obvious by comparing those with the σ observed by Chiodelli et al.[16] and Kojima et al.[17] Chiodelli et al. observed the drastic change of σ at T_c

and the additional increase of σ above 250 K in addition to the linear relation between T_c and 250 K.[16] They analyzed this increase with another exponential term arising from an additive element such as the order-disorder transition of Ag ions. On the other hand, the drastic change of γ_j or ω_j takes place at T_c and the appreciable increase of γ_j and decrease of ω_j were observed above 250 K, as seen in Figs. 2 and 3.

With these correspondences in mind, three characteristic features of γ_{TO} and γ_{LO}—that is, the drastic variation at T_c, the constant value between T_c and 250 K, and the appreciable increase above 250 K—are understood by considering the coupling of phonons with the mobile ions, in addition to the effect of a disordered arrangement of Ag ions.

Near T_c, the effect of a disordered arrangement of Ag ions may have a large contribution to the magnitude of γ_j because the ordered Ag ions below T_c begin to move in a disordered manner at T_c. Contrary to the γ_j value, the shift of ω_j above T_c is small. This result may also suggest the effect of a disordered arrangement of Ag ions since the large value of γ_j due to the strong anharmonic phonon-phonon interactions does not induce such small frequency shifts.

With respect to the further increase of γ_j above 250 K, we can consider an additional term arising from the coupling of ZB phonons to the mobile ions. For the coupling, we propose a microscopic mechanism. If a phonon couples to the mobile ions, the coupling takes place dominantly on phonons of short wavelength, since the ionic motion arises within the local sites at low temperature in the superionic state. The energy of ZB phonons at each local site in a crystal would, then, be shifted depending on the strength of the coupling. The energy levels may overlap with each other and the bands can be formed. Such bands induce a greater number of phonon-decay processes since the satisfied conditions for the phonon decay, i.e., the energy and momentum conservation, are realized more easily by the band. The decay time decreases and γ_j increases. The brief schema for the decay process are shown in Fig. 4. The dashed lines indicate the energy levels below T_c and the hatched parts indicate the bands above T_c. The decay channels below and above T_c are shown by the dashed and solid arrows, respectively.

Since the ZB phonon contributes dominantly to the decay process of optical phonons because of its high density, the effect of coupling increases the magnitude of γ_j and must appear on both a and b bands in spite of the large frequency difference. This prediction also explains the further decrease of frequency for the a and b bands above 250 K because the large anharmonicity arises from the coupling.

For the LO mode of the b band in the β phase, the frequency increases monotonically with temperature. This behavior also supports the large anharmonic crystal po-
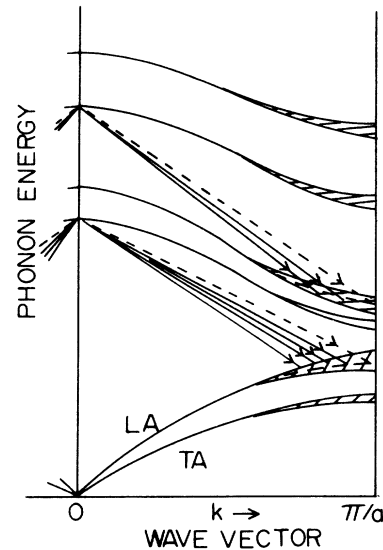

FIG. 4. Brief energy schema for the phonon dispersion. The hatched area indicates the broadened energy level. The dashed and solid arrows indicate the decay processes below and above T_c, respectively.

tential since similar behavior observed in Ta halides is explained by the large quadratic phonon-phonon–interaction process.[18]

The influence of increasing σ was also observed in the appreciable increase of R below 30 cm^{-1}, which appeared above about 200–250 K and corresponds to the temperature change taking place upon the decrease of activation energy.[17]

The assignment of the a and b bands to the reststrahlen band will be justified owing to the reasonable magnitude of the Szigetti effective charge e_s^* of a Ag ion. It is calculated with the procedure proposed by Wakamura and Arai,[10] in which the charge of an I ion reduced by the chemical valency Z_0 was assumed to be larger than that of a S ion. The calculated value of e_s^* for a Ag ion takes the value 0.30–0.43. It is considerably smaller in comparison with that of AgI ($e_s^* \approx 0.6$), as expected from the difference in electronegativity between I and S ions. The value is, however, reliable since e_s^* is plotted reasonably in the empirical interrelationship $\epsilon_\infty - 1 = 2/(X + X^2)$ ($X = e_s^*/Z_0 e$) for $Z_0 = 1.5$. The value of 1.5 for z_0 is a common number for the Ag halides.[10]

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