Phonon density of states in γ-, β- and α-AgCuS

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(Received April 12, 2007.
In final form June 25, 2007)

This paper describes studies of ternary superionic conductor AgCuS by means of inelastic neutron scattering at temperatures from 150 to 398 K. Experimental time-of-flight spectra were recalculated into the generalized phonon density of states ($G(\varepsilon)$) in the frame of incoherent approximation. It is shown that $G(\varepsilon)$ of AgCuS has a nontrivial temperature dependence in the low-energy range. The relation between the temperature dependence of $G(\varepsilon)$ and existence of the *LE*-mode in AgCuS is discussed.

PACS: 63.20.-e, 66.10.Ed, 78.70.Nx

1. Introduction

The superionic conductors (SIC), or solid electrolytes, comprise the compounds whose crystal structure peculiarities provide high ion mobility in one of the sublattices. In the superionic phase these compounds are characterized by unusually high values of ionic conductivity for solid states ($\sigma \geq 0.01\,\Omega^{-1} \cdot \mathrm{cm}^{-1}$) and by low values of the activation energy ($E_a \approx 0.1\,\mathrm{eV}$) comparable with those of the melts [4]. The study of lattice dynamic properties in SIC gives a key to the understanding of „melting“ of the superionic crystal sublattice. The ions of the disordered sublattice, as well as the ions of the rigid sublattice, determine the crystal vibrational spectrum, and hence the changes of the phonon spectrum reflect the disordering processes in a superionic crystal. It is well known that the low-frequency region of the phonon density of states $G(\varepsilon)$ is sensitive to desorder. The low-energy (LE) mode in $G(\varepsilon)$ of superionic conductors also is the most intriguing peculiarity of lattice dynamics of this type compounds. It is suggested that the phenomenon of superionic conductivity in SIC is closely connected with *LE*-mode. In particular, it was assumed that diffusion in superionics can be considered as a process assisted with the low-energy optic vibration mode observed in the vibrational spectra of superionics [2]. The low-energy excitations have been observed by inelastic neutron scattering (INS) methods in the low-temperature phase of cation conducting superionics, and it was suggested that the *LE*-mode is connected with the localized vibration of the conducting type of ions [2,3]. Later on, Wakamura described the lattice dynamics in superionics by the example of a linear chain with two kinds of atoms [4]. He has shown that the high ionic conductivity originates from a double minimum potential originating from the third and forth order terms of thermal atomic displacements, wh ich are, in turn, closely related to the *LE*-optic-like (LEO) mode and „flat“ transverse acoustic (TA) modes with low dispersion and low energy. Wakamura has also shown that the energy of LEO- or TA-phonons is proportional to $1/\sqrt{m}$, where m is the atomic mass of the heavier sublattice, not necessarily the conducting one. Recently on the basis of INS results T. Sakuma confirmed that the values of the *LE*-excitation depend on the mass of the heaviest ion in the compound as $1/\sqrt{m}$ and does not depend on the mass of the conducting ions [5].

In spite of the great scientific interest in superionic conductors during the last several decades, the role of the *LE*-modes in the phenomenon of superionicity is not clear. One of the primary problems is deficiency in experimental data on lattice dynamics in superionic conductors. In particular, there is a lack of experimental data on changes in $G(\varepsilon)$ of superionic compounds in a wide temperature range of order–disorder phase transitions.

In the present work we report the results on inelastic neutron scattering studies of lattice dynamics in powder of α-, β- and γ-AgCuS superionic conductors in the temperature range from 150 up to 398 K. Ternary compound AgCuS exists in three polymorphic modifications: α-, β- and γ-phases [6–8]. The low-temperature γ-AgCuS and the room-temperature β-AgCuS exist in the temperature ranges $T < 250\,\mathrm{K}$ and $250 < T < 366\,\mathrm{K}$, respectively. At 366 K, AgCuS exhibits a phase transition of the first order into the superionic α-phase. The structure of γ- and β-AgCuS was thoroughly studied in [8]. It was established that the structure of β- and γ-phases are closely related: β- and γ-AgCuS have the same orthorhombic symmetry with space groups $Cmc2_1$ (No. 36) and $Pmc2_1$ (No. 26), respectively. The main difference between the γ- and β-structures is a disorder of Ag atoms in β-phase accompanied by considerable increase of the amplitude of thermal vibration of silver atoms [8]. It was supposed that in α-AgCuS both silver and copper sublattices are disordered [7].

The main aim of the present work is the investigation of the modifications of $G(\varepsilon)$ in the low-energy region

during $\gamma \to \beta \to \alpha$ phase transitions. To perform INS studies at low and elevated temperatures, up-scattering (neutron energy gain) and down-scattering (neutron energy loss) INS regimes have been employed. Measurements at 150 K and room temperature (RT) have been performed in down-scattering regime (KDSOG-M spectrometer) [9], measurements at elevated temperatures (RT, 348 and 398 K) — in up-scattering regime (DIN-2PI spectrometer) [9]. Multiphonon correction, which is important for the analysis of the $G(\varepsilon)$ temperature dependence in wide energy range, could be taken into account only for DIN-2PI measurements. For KDSOG-M measurements, implementation of multiphonon correction was not possible because of the low statistical precision for background measurements. Thus for comparability of the results we present the data of KDSOG-M and DIN-2PI measurements both without multiphonon correction. Note that multiphonon processes play important role only at high frequency part of $G(\varepsilon)$ and are expected to produce only minor effects on the shape of low-energy part of $G(\varepsilon)$. Results on the comprehensive studies of lattice dynamics at the $\beta \to \alpha$ phase transition (DIN-2PI measurements) with implementation of multiphonon correction are presented in [10].

2. Experiment

Inelastic neutron scattering experiments were performed with the time-of-flight (TOF) spectrometer of inverse geometry KDSOG-M and TOF spectrometer of direct geometry DIN-2PI, which both are enstalled at the IBR-2 pulsed high-flux reactor of the Joint Institute for Nuclear Research in Dubna. The sample was powder silver copper sulfide (AgCuS) with a weight of about 60 g, which was placed in the hollow cylinder made of thin aluminum foil. The sample thickness was 1.5 mm in DIN-2PI measurements and 7 mm in KDSOG-M measurements. Spectra were recorded at 150 K and at RT with the KDSOG spectrometer and at RT, 348 and 398 K with the DIN-2PI spectrometer.

In the case of KDSOG-M spectrometer, the INS spectra were recorded in the same fashion for eight scattering angles ranging from 30 to 140°. This allowed studies of the lattice dynamics of the samples at low temperatures. The neutron energy loss was measured by the analyzer consisting of a polycrystalline beryllium filter cooled down to liquid nitrogen temperature and single crystals of pyrolytic graphite. In the case of DIN-2PI spectrometer, the INS spectra were recorded for 12 scattering angles in the range from 28 to 134° in the neutron energy gain regime with an initial neutron energy of $E_0 = 11.8$ meV. The signal accumulation time varied from 12 to 36 h. The energy resolution was about 5–8% for energy transfers between 0 and 60 meV in both measurement modes. Momentum transfer region Q was from 1 up to 4 Å^{-1} for KDSOG-M measurements and from 1 up to 7 Å^{-1} for DIN-2PI spectrometer. In both cases wave-vector range of scattered neutron is much larger than the dimension of the first Brillouin zone of the reciprocal crystal lattice. Therefore $G(\varepsilon)$ was derived in the frame of incoherent one-phonon approximation [11], and coherence effects were taken into account by averaging over the range of neutron momentum transfers

$$G(\varepsilon) = \frac{\varepsilon}{n(\varepsilon)+1} e^{2W(Q)} \sqrt{\frac{E_0}{E_1}} \frac{1}{Q^2} \frac{d^2\sigma}{d\Omega dE_1}, \qquad (1)$$

where E_0 and E_1 are initial and final neutron energy, respectively, $\varepsilon = (E_0 - E_1)$ is the energy transfer, $n(\varepsilon)$ is the Bose–Einstein distribution function, $2W(Q)$ is the Debye–Waller exponent and $\frac{d^2\sigma}{d\Omega dE_1}$ is a double differential cross section for neutron scattering. The standard background corrections of the empty container (taking into account self-shielding), normalization and detector efficiency corrections were applied to the measured differential cross section data by the standard data reduction procedure. Multiple and multiphonon processes were ignored.

3. Results and discussion

The $G(\varepsilon)$ of AgCuS extracted from the INS data at 150, 298, 348 and 398 K is shown in Fig. 1. The spectra were normalized in such a way that the area under the curve is equal to 1. The $G(\varepsilon)$ of γ- and β-AgCuS at the lowest temperature can be decomposed into a low-energy part extending from 0 meV to about 25 meV and a high-energy part at 27–42 meV. The low-energy and high-energy parts are well separated by a gap. Due to the finite instrumental resolution and the presence of the large elastic peak, the lowest energy for which we can have confidence is about 1.8 meV. Unreliable region of $G(\varepsilon)$ is marked by hatching in Fig. 1.

The low-energy part of $G(\varepsilon)$ consists of a set of peaks at about 3, 6, 10, 16 and 18 meV, which are well-resolved at 150 K. No significant changes of the phonon frequencies, with the exception of the lowest-energy peak at ~ 3 meV, were found in γ- and β-AgCuS as temperature increases from 150 to 348 K. The phonon widths increase when temperature rises from 150 to 348 K, with further increase near the $\beta \to \alpha$ phase transition. Peaks in $G(\varepsilon)$ which are very well resolved at 150 K and still can be distinguished at 348 K degenerate into a broad and structureless intensity distribution at 398 K with low-energy maximum at about 10 meV and high-energy tail extending up to 45–50 meV. The lowest energy peak with a maximum at ~ 3 meV at 150 K is considerably softened when temperature increases from 150 to 298 K. At 298 K, the lowest energy peak can not be resolved in $G(\varepsilon)$ spectra, but its position could be determined at about 2.5 meV as a barely perceptible bending. It should be noted that $G(\varepsilon)$ at 150 K exhibits a quadratic, Debye-like dependence at the energy range $\varepsilon < 3$ meV, whereas at higher temperature $G(\varepsilon)$ demonstrates a linear dependence rather than quadratic. To determine parameters of the *LE*-peak more precisely, we fitted the low-energy part of $G(\varepsilon)$ by superposition of a Lorentzian function corresponding to the *LE*-peak and the Debye law corresponding to acoustic phonons (Fig. 2). Fitting has shown that the acoustic part of

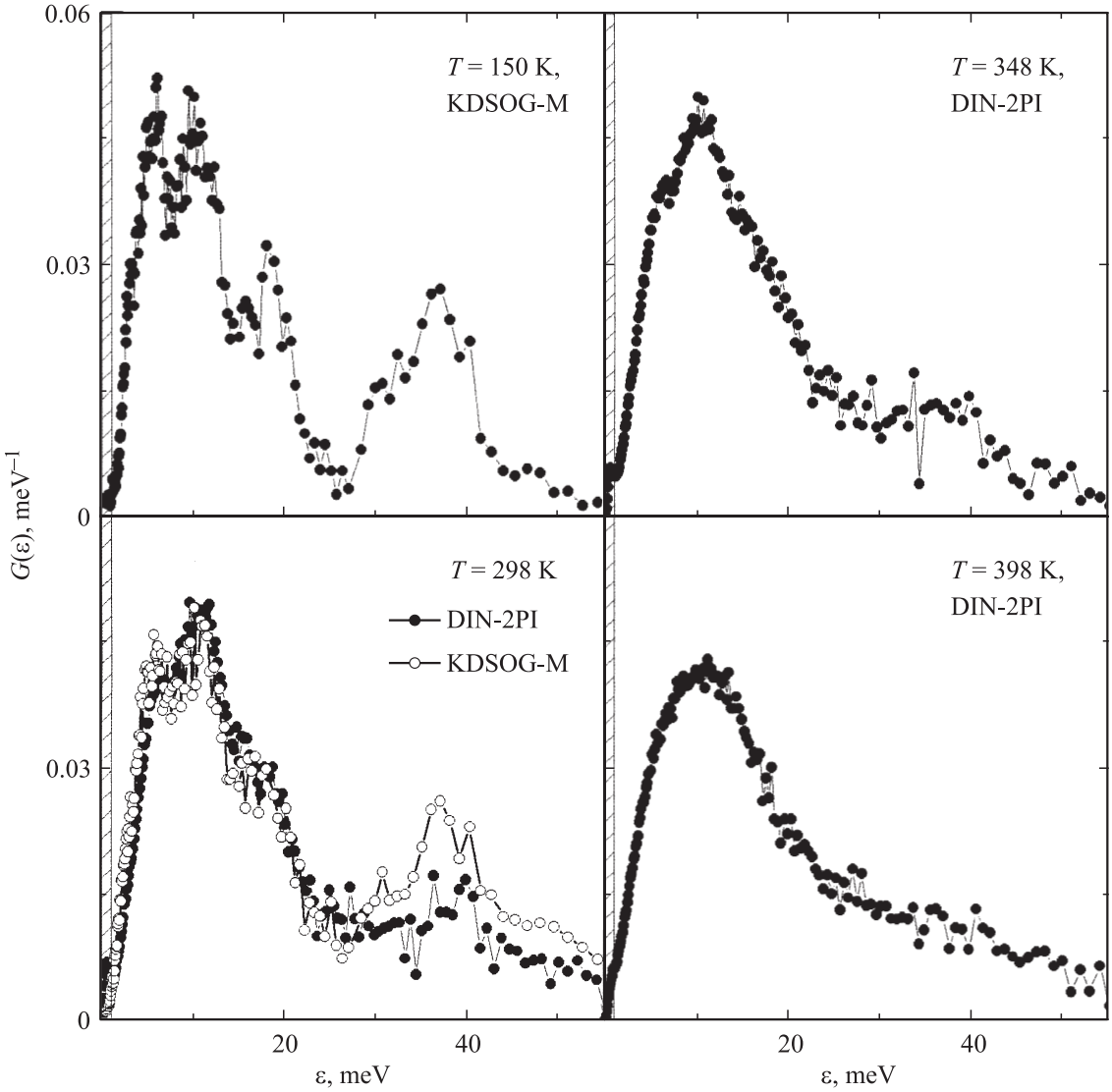

Figure 1. Spectra of $G(\varepsilon)$ at $T = 150$, 298, 348 and 398 K (KDSOG and DIN-2PI measurements).

$G(\varepsilon)$ ($G(\varepsilon) = Ax^2$) does not change when temperature increases from 150 to RT, characteristic Debye temperature calculated in the limit $\varepsilon \to 0$ is equal to 135 K for $T = 150$ and RT. Intensity of *LE*-mode also does not change with temperature, while width and position of the peak change substantially. Parameters of *LE*-peak are listed in the Table.

Analysis of the temperature dependence of $G(\varepsilon)$ suggests that the non-Debye-like behavior of $G(\varepsilon)$ at low energy in β and α phases originates from intense *LE*-mode. Namely, its considerable softening with the temperature increase results in a linear dependence of $G(\varepsilon)$ at $T \geq 298$ K. In α-AgCuS the *LE*-peak in $G(\varepsilon)$ is not detected, however the increasing of slope of the linear part of $G(\varepsilon)$ is an evidence of subsequent softening of *LE*-mode in α-AgCuS. Evidently, the width of the *LE*-peak in α-AgCuS is larger than the peak-position that corresponds to overdamped phonons.

Parameters of the *LE*-mode at low and room temperatures

Parameter	$T = 150$ K	RT
Intensity, a. u.	0.019 ± 0.003	0.019 ± 0.002
Width (FWHM), meV	1.1 ± 0.2	1.6 ± 0.2
Position (ε), meV	2.98 ± 0.05	2.52 ± 0.05

As AgCuS is a powder sample, and because the $G(\varepsilon)$ spectrum correspondes to an integration over the scattering angle, this peak is not a single mode but, instead, represents a band of modes. However, given the relative sharpness and strength of the peak at 150 K, it is reasonable to conclude that the band of modes giving rise to the peak form a relatively dispersionless branch over a large portion of the Brillouin zone. Such a description would closely fit the behavior of a low-energy optic mode. However, given that the peak is at such low energy, it is perhaps more likely that it is a transverse acoustic mode which has hybridized with a transverse optic mode. Such a speculation can only be verified by measurements on a single crystal specimen. It should be noted that INS

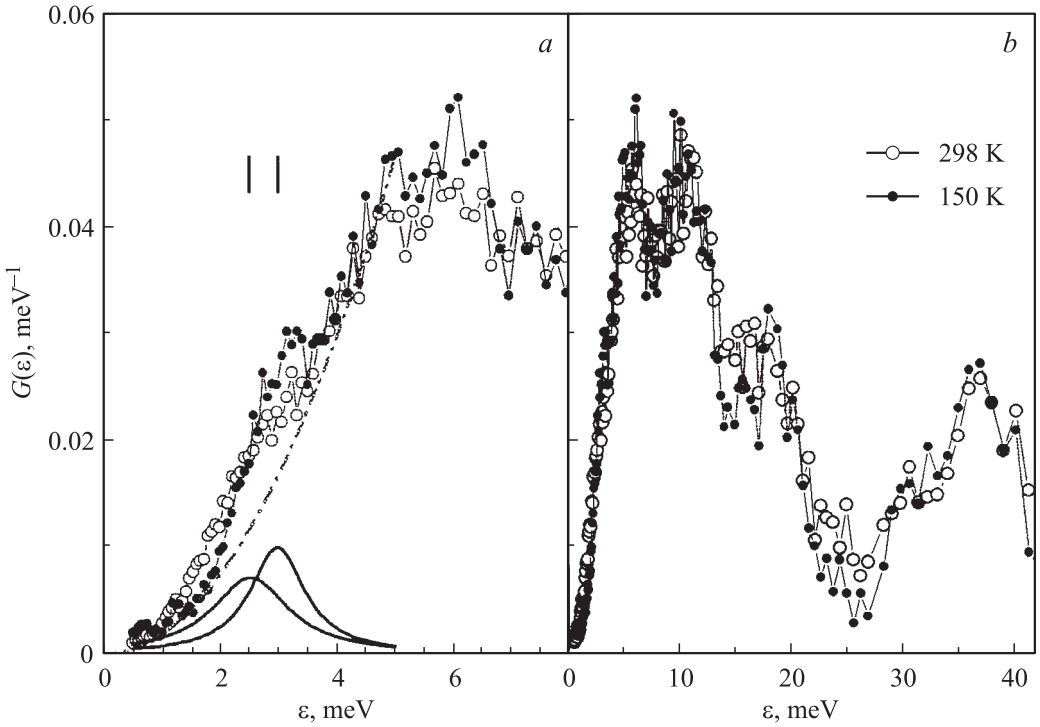

Figure 2. Low-energy part (a) and complete (b) $G(\varepsilon)$ in AgCuS at $T = 150$ and 298 K (KDSOG-M measurements). The low-energy part of the $G(\varepsilon)$ with fitting by a superposition of Debye law (dot dashed line) and Lorentzian function (solid line) are shown in part a. Vertical marks correspond to the center of Lorentzian function at $T = 150$ and 298 K.

experiments performed on $Cu_{2-\delta}Se$ single crystal have shown on LEO-modes in this superionic compound, though transverse acoustic modes in $Cu_{1.85}Se$ are unusually flat over the major part of the Brillouin zone [3]. In view of the fact that silver is the heaviest atom in AgCuS and taking into account the relation $E_{LE} \sim 1/\sqrt{m}$, most likely the lowest-energy peak corresponds to vibrations of silver atoms, while high-energy distribution could be attributed to vibrations of lightest sulfur atoms. This agrees with results of [8], which show that thermal motion of silver is greatly diminished in γ-AgCuS.

4. Conclusion

Inelastic neutron scattering measurements reported in this paper have shown the presence of the LE-mode in non-superionic γ- and β-AgCuS. The LE-mode exhibits considerable softening at $\gamma \to \beta$ phase transition. At the superionic $\beta \to \alpha$ phase transition, the LE-mode became overdamped. Presence of the LE-mode in AgCuS and its drastic softening at $\gamma \to \beta$ and $\beta \to \alpha$ phase transitions is a reason of non-Debye behavior of $G(\varepsilon)$ at the low energy in α- and β-AgCuS.

This work is supported by the Bundesministerium fuer Bildung und Forschung (German Federal Ministry of Education and Research). One of the authors (ANS) wishes to thank the Darmstadt University of Technology and Deutsche Forschungsgemeinschaft for hospitality and financial support during his visit to TU Darmstadt.

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