An Investigation of the Structural Dynamics in the Fast Ionic Conductor $Cu_{2-\delta}Se$ using Neutron Scattering

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A neutron scattering study with energy analysis was performed on polycrystalline $Cu_{2-\delta}Se$ samples. Experiments show that the diffuse scattering in the super-ionic α-$Cu_{2-\delta}Se$ phase is mainly inelastic and most probably comes from correlated thermal displacements of the ions.

1. Introduction

The compound $Cu_{2-\delta}Se$ ($0 \leq \delta \leq 0.25$) is a mixed ionic-electronic conductor. For stoichiometric Cu_2Se the phase transition temperature to the super-ionic α - phase is 414K, but transition temperature depends on the composition and decreases with increasing values for δ. At room temperature the super-ionic α-phase exists over the composition range from $\delta = 0.15$ to 0.25 [1].

The structure of the α-phase is reported as cubic with Se atoms in fcc positions and Cu ions randomly distributed over interstitial sites [2]. The low-temperature β-$Cu_{2-\delta}Se$ phase is a triclinic fluorite-based superstructure with vacant Cu sites forming a $\sqrt{3} \times \sqrt{3}$ network in the [111] plane [3]. The vacant Cu layers stack at every fourth metal layer along the [111] axis.

Characteristic of super-ionic conductors is the presence of strong diffuse scattering. The copper selenide is no exception showing diffuse scattering features in neutron diffraction patterns of polycrystalline and single crystal samples [4, 5]. Diffuse scattering originates from static disorder and/or correlated dynamic displacement. In a conventional diffraction experiment the diffuse background contains both these components. In order to separate static and dynamical contributions in Cu_2Se Sakuma *et al.* [4] used a triple-axis spectrometer in $\Delta E \approx 0$ mode with the analyser crystal adjusted to reflect elastically scattered neutrons from the sample. The contribution of inelastic scattering processes was then estimated from the data measured with the analyser crystal and without it, in conventional double-crystal mode. The experiment showed that the inelastic component in the diffuse background was small, probably because of an insufficient energy resolution of the spectrometer [4].

In order to clarify the role of static disorder versus low-energy phonons in the diffuse scattering we performed energy resolved neutron scattering measurements at higher resolution. The paper presents the results of these neutron diffraction measurements taken in $\Delta E \approx 0$ mode together with conventional diffraction data from the super-ionic α - phase ($Cu_{1.98}Se$ at 435K and $Cu_{1.75}Se$ at 300K) and the ordered β - $Cu_{1.98}Se$ at 300K.

2. Sample preparation

The samples were prepared by solid-state reaction of high purity Cu and Se powders in evacuated ($p < 10^{-5}$ mbar) sealed quartz ampoules. The mixed components were heated up to 720K for about 100 hours with subsequent annealing for 48 hours at 420-520K. After slow cooling to room temperature the product was ground and then homogenised under vacuum for 100 hours at 670 K.

Neutron diffraction patterns of the samples were measured with the E1 triple-axis spectrometer (HMI, Berlin) using a PG monochromator and analyser at a wavelength of

2.355 Å [6]. The collimation of the spectrometer was 40′-40′-40′-80′ with a resolution at the elastic line of $\Delta E \approx 0.7$ meV. The cylindrical samples of $Cu_{1.75}Se$ and $Cu_{1.98}Se$, with masses of 4.8 and 8.5 g respectively, were measured in a standard cryofurnace at room and elevated temperatures.

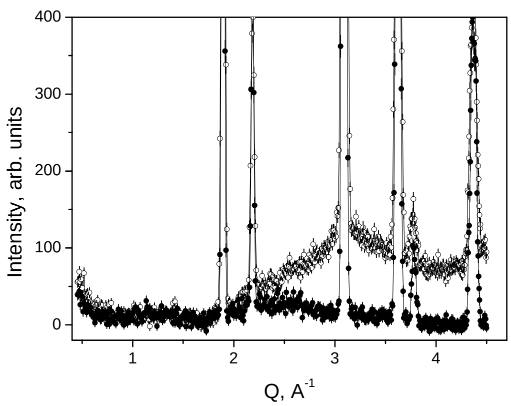

Fig. 1. Diffraction pattern of $Cu_{1.75}Se$ in the α - phase at 300K.

○ – double–axis scan, ● – triple–axis ($\Delta E \approx 0$) scan.

Figures 1 and 2 show diffraction patterns of the $Cu_{1.75}Se$ and $Cu_{1.98}Se$. The data were taken with and without the analyser crystal in otherwise identical experimental conditions. After subtraction of the flat background, the spectra of $Cu_{1.98}Se$ and $Cu_{1.75}Se$ were normalised to the sample mass and counts of the incident neutron beam monitor. Spectra measured with and without the analyser crystal, were normalised to the area intensity of Bragg reflections.

3. Results and Discussion

In α - $Cu_{1.75}Se$ the diffraction peaks correspond to an fcc structure (Fig. 1) with the lattice parameter ***a*** = 5.75 Å in agreement with data of Tonejc [7]. The diffraction pattern of α - $Cu_{1.98}Se$ at 435K also corresponds to the cubic phase, although the intensities of the (200) and (222) reflections ($Q \approx 2.2$ and 3.8 $Å^{-1}$ respectively) are lower. In addition to the peaks from the fcc structure, α - $Cu_{1.98}Se$ at 435K also has two small additional maxima at $Q \approx 2.6$ and 4.2 $Å^{-1}$ which are probably related to ordering of the Cu atoms even at temperature slightly above the reported phase transition. Note that our diffraction experiments with a single crystal of $Cu_{1.85}Se$ performed at ambient temperature - thus according to literature [1, 2] in "disordered" α - phase, in fact show the presence of superstructure reflections at the ***G*** ± 1/2 <111> and ***G*** ± 1/3 <220> positions of reciprocal space [5].

Along with these Bragg peaks, the diffraction pattern of the α - phase taken in the conventional two-axis geometry has a broad maximum related to diffuse scattering centred at $Q \approx 3$ $Å^{-1}$, close to the (220) Bragg reflection (Fig. 1 and 2(a)). The observed diffuse peak resembles the spectrum of α - Cu_2Se at 470 K measured in two-axis geometry in paper [4]. Contrary to earlier findings [4], our measurements show a strong suppression of this diffuse component in the spectrum measured with the analyser crystal. On the other hand, the diffraction pattern of the non super-ionic β - phase (Fig. 2b) shows only minor differences between spectra measured with and without the analyser crystal (Fig. 2b). This clearly indicates a strong contribution to the diffuse scattering in the super-ionic phase from inelastic scattering.

As mentioned above, in experiment [4] the spectrum taken in $\Delta E \approx 0$ mode was very similar to the diffraction pattern measured by the conventional double - axis technique in the region of the first diffuse maxima at $Q \approx 3$ $Å^{-1}$. This can occur if the contribution from the low-energy phonons and the quasielastic scattering are not filtered off by analyser crystal due to the limited energy resolution of the spectrometer. Such phonons with energies about 2 - 4 meV were observed in the phonon frequency distribution of $Cu_{2-\delta}Se$ compounds and in phonon dispersion curves. The density of states of low- energy phonons is relatively high because the dispersion curves change slope at wavevectors of q>0.2-0.4 and acoustic branches become nearly flat having an energy of about 4 meV [8].

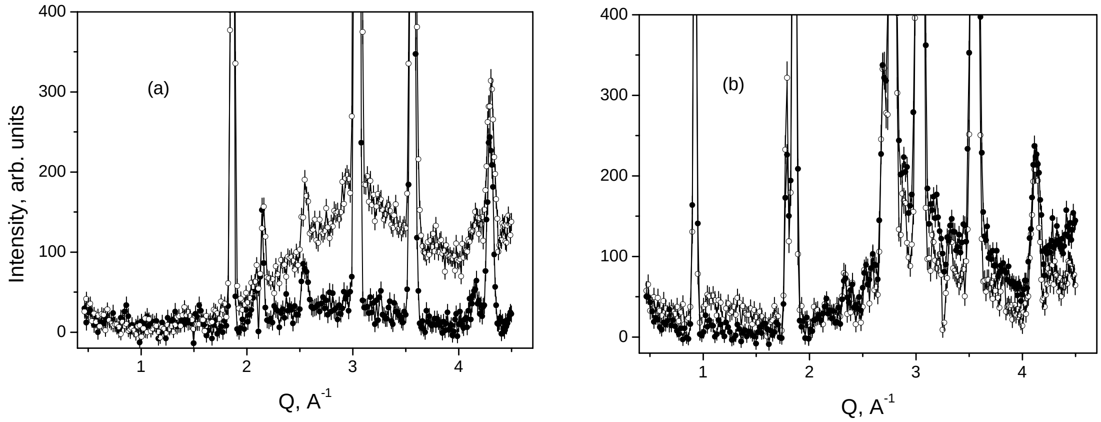

Fig. 2. Diffraction patterns of $Cu_{1.98}Se$ in the α - phase at 435K (a) and the β - phase at 300K (b).

○ – double–axis scan, ● – triple–axis ($\Delta E \approx 0$) scan.

The high spectral density of low-energy phonons, they can play a role in the transport of Cu ions. A calculation of diffuse scattering performed in paper [4] shows strong correlations between the thermal displacement of Se and Cu atoms at short distances. Such correlations are probably responsible for the strong dampening of acoustic phonons observed in α - $Cu_{1.85}Se$ at $q/q_m \geq 0.4$ [8] and indicate a coupling of low-energy phonon modes with displacement of mobile ions.

Acknowledgments

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References

[1] N.H. Abrikosov, V.F. Bankina, M.A. Korzhuev, G.K. Demski and O.A. Teplov, *Sov. Phys. - Solid State* **25,** 1678 (1983).
[2] M. Oliveria, R.K. McMullan and B.J. Wuensch, *Solid State Ionics*, **28-30,** 1332 (1988).
[3] S. Kashida and J. Akai, *J. Phys. C.: Solid State Physics* **21,** 5329 (1988).
[4] T. Sakuma, T. Aoyama, H. Takahashi, Y. Shimoto and Y. Morii, *Physica B* **213-214,** 399 (1995).
[5] S. Danilkin, Phase transformations in $Cu_{2-\delta}Se$, BeNSC (Experimental Reports 2001, HMI Berlin), p 96.
[6] Neutron-Scattering Instrumentation at the Research Reactor BER II Berlin Neutron Scattering Center (BENSC, March 2001), p 6.
[7] A. Tonejc, *J. Mater. Sci*. **15,** 3090 (1980).
[8] S.A. Danilkin, A.N. Skomorokhov, A. Hoser, H. Fuess, V. Rajevac and N.N. Bickulova, *J. Alloys and Compounds* **361,** 57 (2003).