NEUTRON SCATTERING TECHNIQUES FOR SOLID STATE IONICS

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ABSTRACT

Neutron scattering methods are very informative for the investigations of microscopic properties of solid state ionic and often provide information which can not be obtained by other diffraction techniques. This paper starts with a brief overview of the neutron scattering formalism including Bragg diffraction, diffuse scattering, quasi-elastic and inelastic scattering. The application of neutron scattering methods is demonstrated by the example of Cu$_{2.5}$Se compound. Copper selenide is a mixed ionic-electronic conductor and received attention from the technological and physical points of view in particular due to a high ionic conductivity. Because of the relatively simple crystal structure it is also a good model system for investigation of correlation between ionic transport, short-range order and lattice dynamics. Examples include the refinement of the average crystal structure; analysis of diffuse scattering and short order correlations; quasi-elastic neutron scattering study of self-diffusion and investigation of phonon softening in superionic conductor using inelastic neutron scattering.

Keywords: cationic conductors, crystal structures, diffusion, phonons, fluorites, Cu-conductors

INTRODUCTION

Properties of neutron like mass, the zero net charge and magnetic moment make it an ideal probe for the investigations of structure and dynamics of condensed matter. As with X-rays, thermal neutrons have wavelength comparable with lattice parameter of solids and therefore are widely used in the investigations of crystal and magnetic structures. One advantage of neutron diffraction is that the scattering length does not show systematic dependence on the atomic number. This is useful in studies of alloys consisting of atoms with similar weight. Another advantage of thermal neutrons is that neutrons coming from reactor have energies in the range of 1 – 100 meV appropriate for studying of dynamical phenomena in solids and liquids. The typical examples of applications of neutron scattering are studies of location and dynamics of light atoms in the crystal lattice; investigations of crystal and magnetic structures; energy dispersive studies of diffusion; spin and lattice dynamics.

The scheme of the scattering experiment in real and reciprocal space is shown in Figure 1. In the experiment the intensity distribution of scattered neutrons is measured as function of the scattering vector $Q$ and energy transfer. Neutron intensity is proportional to differential cross sections defined as the following ratio [1, 2]:
\[
\frac{d^2\sigma}{d\Omega dE} = \frac{\text{current of scattered neutrons into } (\Omega, d\Omega) \text{ and } (E, dE)}{\text{current of incident neutrons}} \\
= \frac{k_f}{k_i} b^2 S(\vec{Q}, \omega) 
\]

(1)

where \(S(\vec{Q}, \omega)\) is the scattering function (dynamic structure factor), \(N\) denotes the number of atoms in the sample and \(b\) is the scattering length.

\[ \text{Figure 1: Scattering geometry: Incident beam from the source defined by wavevector } k_i \text{ and corresponding energy } E_i \text{ scatters by a sample into a detector with solid angle } d\Omega. \text{ Scattering angle between incident and scattered beams is } 2\Theta. \text{ Wavevector and energy after scattering are } k_f \text{ and } E_f. \]

In general form the dynamic structure factor is expressed as the space and time Fourier transform of pair correlation function \(G(r, t)\):

\[
S(\vec{Q}, \omega) = \frac{1}{2\pi i} \iiint G(\vec{r}, t)e^{-i(\vec{Q}\cdot\vec{r} - \omega t)} d\vec{r} dt 
\]

(2)

Function \(G(r, t)\) is the probability of finding an atom at position \(r\) at time \(t\), if another atom was at \(r=0\) at time \(t=0\). It relates to correlated motions of atoms and defines the elastic and inelastic coherent scattering processes like phonon coherent scattering and Bragg diffraction [1, 2]:

\[
\left\{ \frac{d^2\sigma}{d\Omega dE} \right\}_{\text{coh}} = N \frac{k_f}{k_i} b_{\text{coh}}^2 S(\vec{Q}, \omega) 
\]

(3)

The self-correlation function \(G_s(r, t)\) is the probability of finding an atom at position \(r\) at time \(t\), if it was at \(r=0\) at time \(t=0\). This function related to motions of individual atoms and represents the incoherent scattering processes such as phonon incoherent scattering and quasi-elastic scattering [1, 2]:

\[
\left\{ \frac{d^2\sigma}{d\Omega dE} \right\}_{\text{inc}} = N \frac{k_f}{k_i} b_{\text{inc}}^2 S_s(\vec{Q}, \omega) 
\]

(4)
A more detailed introduction to neutron scattering can be found in the books [1-4].

**ELASTIC & QUASI-ELASTIC SCATTERING**

1. **Bragg Diffraction. Crystal structure.**

In case of elastic scattering \((k_i = k_f)\) the cross section for coherent scattering \((3)\) defines the Bragg scattering \([1, 2]\):

\[
\frac{d\sigma}{d\Omega}^{coh} = \sum_{i,j} e^{-i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)} e^{-2W} \Rightarrow \sum_{hkl} \delta(\vec{Q} - \vec{G}_{hkl}) |F_{hkl}(\vec{G})|^2
\]

where \(\vec{G}_{hkl}\) is reciprocal lattice vector and \(F_{hkl}\) is the unit cell structure factor.

![Diagram](image)

**Figure 2:** The Ewald construction for single crystal. A sphere has radius \(k_i\); diffraction peaks are observed when vector \(\vec{Q}\) coincides with reciprocal vector \(\vec{G}_{hkl}\). In case of polycrystalline sample the scattered wavevectors lie on the cone shown by dashed line.

The scattering diagram (Ewald construction) of Bragg scattering is shown in Figure 2. It can be seen from Figure 2 that Bragg reflection takes place when \(\vec{Q} = \vec{G}_{hkl} = 2k_i \sin\Theta_s\). This is a Bragg equation, which also can be written as \(\lambda = 2d_{hkl} \sin\Theta_s\), where \(\lambda\) is wavelength and \(d_{hkl}\) is planar spacing (\(d\)-spacing).

In diffraction experiment the intensity of scattered neutrons is proportional to the square of the structure factor (Eq. 5), which contains the complete information on the distribution of the atoms in the unit cell. The information on the crystal system and the basis vectors of the unit cell may be directly deduced from the diffraction pattern. In case of powder diffraction the Rietveld refinement is a standard method of data analysis and structure determination [5]. During Rietveld refinement the intensity at each point in the diffraction pattern is calculated using the expression:

\[
I_{c,i} = I_{b,i} + \sum_k P_{ik} I_{B,k}
\]

where \(I_{c,i}\) is calculated intensity at point \(i\) in the diffraction pattern; \(I_{b,i}\) is background intensity; \(P_{ik}\) is value of normalized peak profile function at point \(i\) for reflection \(k\); \(I_{B,k}\) is Bragg intensity of reflection \(k\). The principle of the Rietveld Method is to minimize the difference between a calculated profile and the observed data.
2. Average Structure of Superionic Compounds

The analysis of neutron powder diffraction data is demonstrated by the example of superionic \( \text{Cu}_{2-\delta}\text{Se} \) compound. For stoichiometric \( \text{Cu}_2\text{Se} \) the phase transition temperature to the cubic superionic \( \alpha \)-phase is 414K, but the transition temperature depends on the composition and decreases with increasing \( \delta \). Over the concentration range of \( \delta = 0.15 \) to 0.25 the superionic \( \alpha \)-phase \( \text{Cu}_{2-\delta}\text{Se} \) exists at room temperature [6]. Ionic conductivity of \( \alpha - \text{Cu}_2\text{Se} \) is about 2 S/cm at 600 K and decreases gradually with deviation from stoichiometry, vanishing at the boundary of the homogeneity region at \( \delta \approx 0.25 \) [7, 8].

The structure of \( \alpha \)-phase is of antifluorite with Se atoms in face-centred cubic positions and Cu atoms distributed over the large number of interstitial sites, many of which are vacant. The high temperature \( \alpha \)-phase is considered to have randomly distributed Cu ions over interstitial sites; however, information about the fractions of Cu in different interstitial positions is controversial. In the low-temperature \( \beta \)-\( \text{Cu}_{2-\delta}\text{Se} \) the Cu cations form an ordered structure in large distorted antifluorite-type unit cell [9, 10].

Neutron powder diffraction data of \( \text{Cu}_{2-\delta}\text{Se} \) compounds were measured with the Echidna high-resolution diffractometer at ANSTO using wavelength \( \lambda = 1.300 \text{ Å} \) [11]. The data were collected for the powder samples loaded in cylindrical vanadium containers in a standard cryofurnace. The diffraction patterns were corrected for the scattering from an empty sample container collected in the same conditions. Typical diffraction pattern from \( \text{Cu}_{1.98}\text{Se} \) in superionic \( \alpha \)-phase at 430K is shown in Figure 3.

![Figure 3: Least-squares refinement of the diffraction data from \( \text{Cu}_{1.98}\text{Se} \) at 430K. The crosses are experimental points; full line is the profile calculated using structural model; lower curve shows the difference between measured and calculated and the tick marks correspond to the calculated positions of the Bragg peaks.](image)

The distribution of Cu atoms over crystallographic positions in \( \alpha - \text{Cu}_{2-\delta}\text{Se} \) compounds has been analysed by Rietveld method using the GSAS software [5]. Different split-site models of the average structure were tested assuming the overall \( Fm\bar{3}m \) symmetry. During analysis, the total content of Cu atoms was fixed to the nominal composition. We found that the model with occupation of both \( 8c \) and \( 32f \) (\( x = 0.33 - 0.39 \)) sites gives better agreement
with experiment compared to the model with only 8c site occupied (Figure 4, Table 1) [12]. Our results are in general agreement with previous X-rays studies [13]. We did not find statistically significant improvement of refinement quality when allowing Cu atoms occupy the 4b position. This is in contradiction with the results of Yamamoto and Kashida obtained using X-ray single crystal diffraction and the maximum entropy method [14]. They found that the Cu ions have a noticeable population of the octahedral 4b positions in addition to 8c at elevated temperature in the $\alpha$-phase. This discrepancy demonstrates the difficulty in standard analysis of crystallographic data from disordered systems due to high correlation between parameters, in particular in separation of the positional disorder and vibrational displacements.

Table 1: The Cu atom distribution over crystallographic sites in $\alpha$-Cu$_{2+\delta}$Se compounds at 430K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$n_{\text{Cu}(8c)}$</th>
<th>$n_{\text{Cu}(32f)}$</th>
<th>$x$</th>
<th>$a$, Å</th>
<th>$R_p/\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{1.75}$Se</td>
<td>0.77(1)</td>
<td>0.028(2)</td>
<td>0.387(3)</td>
<td>5.7677(5)</td>
<td>4.4/1.3</td>
</tr>
<tr>
<td>Cu$_{1.85}$Se</td>
<td>0.73(2)</td>
<td>0.048(6)</td>
<td>0.332(3)</td>
<td>5.7988(6)</td>
<td>5.0/1.2</td>
</tr>
<tr>
<td>Cu$_{1.98}$Se</td>
<td>0.71(2)</td>
<td>0.069(6)</td>
<td>0.337(2)</td>
<td>5.849(1)</td>
<td>3.5/2.7</td>
</tr>
</tbody>
</table>

3. Diffuse Scattering

The key to the structural model for superionic conductors are positions and fractions of mobile atoms in different interstitial sites. Because the mobile atoms are delocalised the standard analysis of the average structure suffers from strong correlations between parameters, particularly the positional parameters and vibrational/thermal displacements. At the same time disorder gives rise to broad diffuse maxima observed in neutron diffraction patterns of polycrystalline and single crystal samples of superionic conductors. In diffraction pattern the diffuse scattering presents as the broad oscillating features, such as the peaks at $Q \sim 3$, 5.5 and 8 Å$^{-1}$ in Cu$_{1.98}$Se (Figures 3 and 5).
In general, the diffuse component arises from the different types of disorder in the crystal lattice such as lattice vibrations, stacking faults, substitutional or orientational disorder. The analysis of diffuse component provides information about the local structure, short-range correlations, which is often lost in the average structure.

The cross section of diffuse scattering can be written in terms of deviation of the structure factor from the mean value [10]:

$$\frac{d\sigma_{\text{diffuse}}}{d\Omega} \propto \sum_{i,j} e^{-i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \left\langle \Delta F_i \Delta F_j^* \right\rangle$$

where structure factor is defined as sum of mean structure factor and deviation from the mean value due to the disorder: $F_i = <F> + \Delta F_i$.

The diffuse background generally contains both elastic and inelastic scattering components which originate from the static disorder and dynamic correlations. According to [10, 16] the diffuse intensity including the term related to thermal displacements of atoms is expressed as follows:

$$I_D = N_0 \sum_i b_i b_i^* (1 - p_i \exp(-2M_i))$$

$$+ N_0 \sum_{i,j} b_i b_j \left\{ \alpha_{r_{(i)(j)}} \left[ \exp\left(-\left(M_i + M_j\right)(1 - \lambda_{r_{(i)(j)}})\right) - \exp\left(-\left(M_i + M_j\right)\right) \right] \right\}$$

$$+ (1 - p_i) (\alpha_{r_{(i)(j)}} - \beta_{r_{(i)(j)}}) \exp\left(-\left(M_i + M_j\right)\right) Z_{r_{(i)(j)}} S_{r_{(i)(j)}}$$

where $N_0$ is the number of unit cells per unit volume; $b_i$ is the neutron scattering length; $p_i$ is the probability of finding an atom $i$ in any site $s$; $M_i$ is the Debye-Waller factor of an atom $i$; $Z_{r_{(i)(j)}}$ is the number of sites at a distance $r$ around an atom $i$ occupied by an atom $j$; and $S_r =$
\[ \sin(Qr)/Qr \] is the distance between sites \( s(i) \) and \( s(j) \). The parameters \( \alpha \) and \( \beta \) relate to static correlations: \( \alpha_r \) gives the probability of finding an atom at distance \( r \) from the occupied site and \( \beta_r \) is the probability of finding an atom at a distance \( r \) from a vacant site. Correlation parameters between thermal displacements \( \lambda_r \) are given by:

\[
\lambda_{\tau(i)\tau(j)} = \frac{2\langle \Delta s_{\tau(i)} \Delta s_{\tau(j)} \rangle}{\langle \Delta s_{\tau(i)}^2 \rangle + \langle \Delta s_{\tau(j)}^2 \rangle}
\]

where \( \Delta s \) is the displacement caused by thermal vibrations.

In order to distinguish contributions from static and thermal distortions/correlations the experiment should be performed in the energy dispersive mode. This can be done with triple-axis spectrometer using the “elastic window” method. Contrary to a conventional diffraction experiment, in this setup the neutrons scattered by a sample are filtered by an analyser crystal before reaching the detector. The analyser crystal reflects only (within the instrument resolution) the scattering processes with zero energy transfer, which correspond to elastic scattering. As a result the thermal/inelastic contributions to the scattering intensity are filtered out.

Figure 5 shows diffraction patterns of \( \alpha\)-Cu\(_{1.98}\)Se at 430K measured with Echidna diffractometer and triple-axis spectrometer E1 [15]. It can be seen that spectra from E1 taken in conventional 2-axis mode match well with diffraction pattern from Echidna. In contrast, data taken in an energy-dispersive “elastic window” mode show strong suppression of diffuse intensity. This indicates that the predominant contribution to the diffuse scattering comes from inelastic scattering and related to dynamic correlations of thermal/vibrational displacements in the superionic phase.

**Figure 6.** Contributions to diffuse scattering in Cu\(_{1.75}\)Se at T = 430K
(a) Experiment (Echidna); (b) Calculated diffuse scattering (total + incoherent); Contributions: (c) Thermal diffuse; uncorrelated; (d) Thermal diffuse; Se\(\leftrightarrow\)Cu(8c, 32f) correlations; (e) Thermal diffuse; Cu(8c)\(\leftrightarrow\)Cu(8c) correlations; (f) Thermal diffuse; Cu(8c)\(\leftrightarrow\)Cu(32f) correlations

In order to get more information about the dynamic correlations the calculations of diffuse scattering have been performed. The model used in calculations takes into account both static and dynamic correlations (Eq. 8) [10, 16]. The occupation both 8c and 32f sites by
Cu was assumed using parameters from the structural refinement (Table 1). The static correlations between Cu atoms were taken into account at distances \( r \leq 3.0 \) Å. The correlations between thermal vibrations of Se-Cu and Cu-Cu atoms were considered at distances \( 2.3 < r \leq 4.0 \) Å and were described by 2 parameters depending on distance between atoms. Correlations between Se atoms were not included due to the larger interatomic distance. The oscillating contribution shown in Figure 6 originates from Se-Cu and Cu-Cu thermal correlations. The major contributions are from Se\( \leftrightarrow \)Cu(8c, 32f) and Cu(8c)\( \leftrightarrow \)Cu(8c) correlations. The diffuse scattering arising from Cu(8c)\( \leftrightarrow \)Cu(32f) correlations is also rather strong and comparable with contribution from Se\( \leftrightarrow \)Cu(32f). This is consistent with simultaneous occupation of 8c and 32f sites in the average structure and essential for the overall agreement of the calculations with experimentally observed diffuse scattering. Calculations show an increase in diffuse intensity both with temperature and increasing Cu content caused mainly by the contribution from Se-Cu and Cu-Cu thermal correlations.

4. Quasi-elastic scattering.

The incoherent differential cross section (Eq. 4) relates to motions of individual atoms and defines processes such as quasi-elastic scattering arising from the diffusive (non-periodic) motions of atoms. Diffusive processes manifest themselves as a broadening of elastic line, measured in the energy dispersive mode. In case of translational jump diffusion in the lattice the incoherent structure factor in Eq. 3 is represented by a Lorentzian function [4]:

\[
S_{\text{inc}}(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma^2(Q) + (h\omega)^2}
\]

(10),

where \( \Gamma(Q) \) is the half width of Lorentzian at half maximum and \( D_s \) is the coefficient of self-diffusion.

In the analysis of quasi-elastic broadening the isotropic Chudley-Elliott model is widely used as a first approach [4, 17] to gain some insight into the mechanism of diffusion. In this model the mobile atom remains in the crystal site for the time \( \tau \) (residence time) taking part in atomic vibrations. After this time the mobile atom moves to another site in the lattice. It is suggested that the sites are equivalent; jumps have a single length and jump direction is random.

In the Chudley-Elliott model the \( Q \)-dependence of \( \Gamma(Q) \) is given by following equation [17]:

\[
\Gamma(Q) = \frac{h}{\tau} \left( 1 - \frac{\sin(Ql)}{Ql} \right)
\]

(11),

where \( l \) is the average jump length and \( \tau \) is the residence time.

Important are the limiting cases of small and large \( Q \). At small \( Q \), in continuous (macroscopic) regime of diffusion, the linewidth is proportional to \( Q^2 \) and the coefficient of self-diffusion: \( \Gamma(Q) = h \cdot D_s \cdot Q^2 \). At large \( Q \) the linewidth comes out to the reciprocal residence time: \( \Gamma(Q) = h/\tau \).

The quasi-elastic neutron scattering (QENS) study of diffusion in Cu\(_{1.75}\)Se, Cu\(_{1.90}\)Se and Cu\(_{1.98}\)Se compounds were performed with NEAT time-of-flight spectrometer at Helmholtz - Zentrum Berlin [18]. The neutron scattering spectra were collected at incident wavelength of 6.5 Å from the powder samples. The data were corrected for background,
Neutron Scattering Techniques For Solid State Ionics

detector efficiency, transmission, self-attenuation and converted to constant $Q$ and linear energy scale spectra with FITMO2 software [19]. The quasi-elastic peaks were analysed in a model with one Lorentzian component plus elastic peak using LAMP QENS_FIT software [20].

The typical quasi-elastic data are shown in Figure 7 for detectors centred at scattering angle $2\Theta = 100.4^\circ$ ($Q = 1.49 \text{ Å}^{-1}$). In the non-superionic $\beta$-Cu$_{1.98}$Se compound at $T = 313K$ only elastic component is observed with the peak shape defined by the resolution function (Figure 7(a)). However the broad quasi-elastic component is clearly seen after transition to the superionic $\alpha$-phase at $T=430K$. By contrast, the Cu$_{1.75}$Se compound which is superionic at both temperatures, but with much lower conductivity than $\alpha$-Cu$_{1.98}$Se, has relatively small quasi-elastic component increasing in intensity with temperature.

![Figure 7: Quasi-elastic neutron scattering spectra of (a) Cu$_{1.98}$Se (b) Cu$_{1.75}$Se at 430K](image)

The experimental $Q$-dependence of the width of the quasi-elastic peaks calculated assuming one Lorentzian quasi-elastic component and elastic term is shown in Figure 8. At low momentum transfers $Q$ ($Q^2 < 0.5 \text{ Å}^{-2}$) the quasi-elastic broadening shows the linear dependence on $Q^2$: $\Gamma(Q) = \hbar D_s Q^2$. This regime corresponds to the macroscopic diffusion because the details of jump diffusion mechanism are averaged over distances in the range of 20 Å in the current experiment ($0.3 < Q < 0.7 \text{ Å}^{-1}$).

The coefficient of self-diffusion determined from the slope of the $\Gamma(Q)$ versus $Q^2$ dependence at low $Q$ decreases with the deviation from the stoichiometry (Table 2) [21]. The absolute value of $D_s$ is in reasonably good agreement with value reported by Korzhuev et al. for Cu$_{1.90}$Se compound at 430K ($D_s = 4\times10^{-5} \text{ cm}^2 \text{ s}^{-1}$) [8]. However the slowing down of Cu diffusion with deviation from the stoichiometry observed in QENS experiment contradicts to results reported in papers [7, 8] where the coefficient of self-diffusion normalized to the number of mobile ions does not depend on composition. Probably, this discrepancy is related to the model used in studies [7, 8] for calculation of $D_s$ from the chemical diffusion coefficient $D_{chem}$, which does not take into account the blocking and mobility correlation factors. Note that the quasi-elastic broadening observed in the QENS experiments is related to the mobile ions only [4].
Figure 8: Q-dependence of quasi-elastic broadening in Cu$_{2-\delta}$Se compounds.

Table 2: Diffusion parameter in α-Cu$_{2-\delta}$Se compounds at T=430K. $D_s$ is the coefficient of self-diffusion; $\tau$ is the residence time and $l$ is the jump length.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$D_s \times 10^{-5}$ cm$^2$ s$^{-1}$</th>
<th>$\tau$, ps</th>
<th>$l$, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{1.75}$Se</td>
<td>3.4±0.2</td>
<td>3.7±0.3</td>
<td>3.9±0.4</td>
</tr>
<tr>
<td>Cu$_{1.90}$Se</td>
<td>5.2±0.2</td>
<td>1.7±0.1</td>
<td>3.6±0.2</td>
</tr>
<tr>
<td>Cu$_{1.98}$Se</td>
<td>6.1±0.2</td>
<td>1.0±0.1</td>
<td>3.2±0.2</td>
</tr>
</tbody>
</table>

Analysis in frame of Chudley-Elliott model provides insight into the macroscopic mechanism of diffusion. Fitting of Eq. 11 to the experimental data shows that the residence time has the clear tendency for an increase with deviation from stoichiometry (Table 2) [21]. This indicates that mobile atoms remain in the interstitial site for the longer time and the jumps to another site in the lattice occur rarely. According to the Einstein - Smoluchowski relation, $D_s = \frac{l^2}{6\tau}$, it will cause the diffusion coefficient to drop with decreasing Cu content. It is significant that the similar trend for a decrease of self-diffusion coefficient was found in the continuous diffusion model (coefficient $D_s$ in Table 2).

Values of the jump length, $l$, are in the range of distances between the nearest and next nearest 8c sites. These distances have values of 2.9 Å and 4.1 Å for Cu$_{2-\delta}$Se samples at 430K as derived from the structural model. Taken into account that Cu ions occupy both 8c and 32f sites, this indicates that the Cu atoms rather go to the nearest 8c site through the closest 32f sites: 8c $\rightarrow$ 32f $\rightarrow$ 32f $\rightarrow$ 8c $\rightarrow$ 8c, or pass the longer path among the second nearest 32f neighbours as shown in Figure 4.

The diffusion through the 32f sites can explain the relatively strong thermal correlations between Se↔Cu(32f) and Cu(8c)↔Cu(32f) pairs found in diffuse scattering experiment. Furthermore, the occupation of 32f sites by Cu atoms in the average structural model is consistent with elongation of the electron density of the Cu atoms in direction $<111>$ toward the octahedral site previously reported based on X-ray diffraction data [14]. The QENS data also correlate well with the results of crystallochemical modelling of the conduction channels [22] which show that “mobile ion from the tetrahedral positions moves...
first in the <111> direction, then along the periphery of the octahedral hole in <100> direction, thereafter toward the empty tetrahedral position again in <111> direction”.

5. CONCLUSION I (Elastic & Quasi-elastic Scattering)

Neutron diffraction and QENS methods give detail information on crystal structure, short-range order and diffusion in Cu$_2$Se compounds. The crystallographic model of $\alpha$-Cu$_2$Se compounds shows the occupation of both 8c and 32f sites by Cu atoms. In the superionic $\alpha$-phase the broad peaks of diffuse scattering are observed. Theoretical calculations show that the diffuse intensity is related to contributions from correlated thermal vibrations of Se and Cu atoms, with Se$\leftrightarrow$Cu(8c,32f) and Cu(8c)$\leftrightarrow$Cu(8c) correlations being strongest.

The value of self-diffusion coefficient determined from QENS experiment is in reasonably good agreement with previously published data, but decreases with the deviation from the stoichiometry in contrast with results from the literature [6, 7]. This dependence arises from the longer residence time of mobile atoms. The jump distance determined from the experimental data indicates that the Cu atoms most probably diffuse between the nearest 8c site through the 32f sites. Simultaneous occupation of the 8c and 32f sites in the average structure model and strong correlations between thermal displacements of Se-Cu and Cu-Cu atoms found in simulation of diffuse scattering add considerable support for the this conclusion.

INELASTIC SCATTERING

1. One-phonon scattering

Energy of thermal neutrons is in the range of 1 – 100 meV, which is appropriate for studying of dynamical phenomena in solids and liquids such as lattice vibrational excitations (phonons) and spin waves (magnons). The inelastic scattering process with creation (annihilation) of phonon is defined by coherent differential cross section (Eq. 3) with dynamic structure factor represented by the following formula [3]:

$$\frac{d\sigma^{coh}(\bar{Q},\omega)}{d\Omega d\omega} \propto \sigma^{coh} \frac{k_f}{k_i} n(\omega, T) \sum_{\bar{G},\bar{q}} \delta(\bar{Q} - \bar{q} - \bar{G}) \sum_{s} \left| \frac{F(\bar{Q})}{\omega_{q,s}} \delta(\omega - \omega_{q,s}) - \delta(\omega + \omega_{q,s}) \right|^2$$

where $\omega_{q,s}$ is the frequency of phonon with wavevector $q$ and polarization vector $\xi_s$; $n(\omega, T)$ is the Bose factor and $F(\bar{Q})$ is dynamic structure factor involving dot product of momentum transfer and phonon polarization vectors ($\bar{Q}\xi$).

Equation (12) contains two $\delta$-functions, that give the energy and moment conservation relationships:

$$\bar{Q} = \bar{G} + \bar{q} = k_f - k_i$$

$$E_f - E_i = h^2 / 2m(k_f^2 - k_i^2) = \pm \hbar \omega_{q,s}$$

where $\omega_{q,s}$ is the frequency of phonon with wavevector $q$ and polarization vector $\xi_s$; $n(\omega, T)$ is the Bose factor and $F(\bar{Q})$ is dynamic structure factor involving dot product of momentum transfer and phonon polarization vectors ($\bar{Q}\xi$).
The scattering diagram of one-phonon scattering differs from the Bragg scattering case, shown in Figure 2 and includes phonon wave vector (Figure 9).

Figure 9: Scattering diagram of inelastic one-phonon scattering.

Phonon wavevector is in direction [0-10]. Corresponds to phonon with polarisation vector in [100] direction due to \((Q \cdot \xi)\) factor in the cross section.

2. Ordering in Cu-Se

The characteristic features of copper selenide are the ordering of Cu atoms in the low-temperature phase and a random distribution of Cu over interstitial sites in high-temperature superionic phase [9, 10, 13, 14]. However the superstructure reflections have been also observed in the \(\alpha\)-Cu\(_{1.8}\)Se compound at ambient temperature at the \(Q = G \pm q\) positions of reciprocal space with \(q = 1/2 (\pm 1, 1, 1)\) and \(q = 1/3 (0, 2, 2)\) [23]. The appearance of superstructure is essential for the understanding the specific behaviour of phonon dispersion curves therefore the measurements of the elastic scattering intensity in the \(\alpha\)-Cu\(_{1.8}\)Se single crystal will be discussed more closely. The experiment was carried out as a series of one dimensional \(Q\)– scans covering the area of \((2, 0, 0), (3, 1, 1)\) and \((1, 1, 1)\) Bragg reflections. These peaks are seen in Figure 10 as saturated white colour spots because of enlarged intensity scale. The intense superstructural reflections could be seen at the \(q = 1/2 (\pm 1, 1, 1)\); \(1/3 (0, 2, 2)\) and \(1/2 (2, 0, 0)\) positions of reciprocal space. The lower intensity peaks at \(q = 1/4 (\pm 1, 1, 1)\) positions in \((200)\) and \((311)\) Brillouin zones (BZ) and \(q = 1/2 (2, 0, 0)\) in \((200)\) BZ are observed. As will readily be seen the strongest superstructural reflections are located at the BZ boundaries or close to them as in case of \(q = 1/3 (0, 2, 2)\) and \((2H-1)/2, 1/2, 1/2)\) spots. This causes effects similar to folding of the BZ due to the doubling of the lattice parameter. Note that we observed ordering in the Cu\(_{1.8}\)Se compound which is described as “disordered” \(\alpha\)-phase in the literature [8]. On heating the intensity of superstructural peaks disappear gradually and peaks vanish at ~365 K.
Figure 10: Contour plot of scattering intensity in (0, -1, 1) reciprocal plane of Cu$_{1.8}$Se determined from a series of one-dimensional Q-scans.

3. Phonon Softening

Phonon dispersion curves in Cu$_{1.8}$Se single crystal sample were measured in [1, 0, 0], [1, 1, 0] and [1, 1, 1] directions with triple-axis spectrometer TAIPAN [24]. Due to strong broadening of phonon peaks data are limited to low energy modes [25]. The onset of the broadening is rapid and takes place at phonon wave vectors $q/q_m \approx 0.5$ for all measured phonon branches. Phonons with wave vectors $q/q_m \leq 0.5$ are narrow and show a fast decrease in intensity with increasing wave vector which is characteristic for acoustic phonons (Figure 11).

Figure 11: Surface and contour plots of inelastic scattering intensity in Cu$_{1.8}$Se determined from a series of constant – Q scans along direction [2-q, 2+q, 0] in (2, 0, 0) reciprocal plane. Corresponds to TA$_2$ branch with wave vector, q, along [110] and polarization vector [1-10].
At higher wave vectors \( q/q_m \geq 0.5 \) a change-over from strong \( q \)-dependence to broad phonon peaks with minor modifications in peak shape and intensity takes place. At the same time the low intensity soft phonons with tendency to condense at \( X \) point (\( q/q_m = 1 \)) could be seen (Figure 11). The elastic peaks (\( \hbar \omega = 0 \)) at \( q/q_m \approx 0.66 \) and 1.0 correspond to superstructure with wave vectors \( q = 1/3 \ (2, 2, 0) \) and \( 1/2 \ (2, 0, 0) \) observed in Figure 10. The dispersion curves are shown in Figure 12 where the frequencies of phonon peaks at \( q/q_m \geq 0.5 \) relate to centre of broad peaks.

![Figure 12: Phonon dispersion curves in Cu\(_2\)Se.](image)

Dots – experiment, lines – calculations. Hexagon symbols show the position of superstructural reflections.

It is seen that the TA\(_1\) [110] branch with the polarization vector along [1-10] direction (Figure 12) and TA phonons in [100] direction demonstrate a decrease in frequency at \( q/q_m \geq 0.5 \) rather than the flattening observed previously. The transverse acoustic branch with wave vector in the [111] direction shows a considerably greater decrease for \( q/q_m \geq 0.25 \). In contrast, the \( q \)-dependence of frequency of TA\(_2\) [110] phonons polarized in [001] direction and longitudinal modes is almost linear.

Phonon dispersion curves were calculated with density functional theoretical (DFT) approach and the lattice-dynamics program PHONON 4.2.4 [26, 27]. Results are shown in Figure 12 together with experimental data. The initial slope which is a measure of the sound velocity is in very good agreement with the DFT calculations. The most remarkable features of calculated acoustic modes are the low frequencies and the instability over a large area of reciprocal space. Acoustic modes TA [100], TA [111], TA\(_1\) [110] and LA [110] are unstable and go to negative values in vicinity of BZ centre and at \( q \geq 0.3 – 0.4 \) in case of transverse modes and at \( K \) – point for LA [110] mode. This indicates that the stoichiometric compound is dynamically unstable and antifluorite structure is not true low-temperature one. Indeed, a phase transition to low-temperature \( \beta \)-phase takes place at 414 K for stoichiometric Cu\(_2\)Se [8, 9].

The instability of acoustic modes is directly related to the order – disorder transformations observed in copper-selenide. The intensity of the superstructure reflections is quite large. As noted the appearance of strong reflections at the edge of the BZ in this direction can cause effects similar to the folding of the Brillouin zone. Indeed, Figs. 11 and 12 shows that TA phonon branches to soften at the boundary of BZ, although phonon intensities at “new” BZ centres are weak. In Figure 12 the positions of superstructural
reflections are shown by hexagons at $L$-point and at $q=0.66$ in direction $[110]$ which is close to $K$-point. These points are in the area of pronounced instability of acoustic modes indicating that ordering process is actually driven by a soft mode.

Acoustic phonon peaks at $q \geq 0.5$ are very broad in all directions that were studied. The width of the peaks is comparable with the energy of phonons, which can be an effect of coupling of phonons with displacements of mobile ions. Notice that “softened” transverse branches have a polarization vector in the direction $<110>$, orthogonal to the $<111>$; the $<111>$ directions which is assumed to be diffusion path for Cu atoms. Such vibrational modes can promote the diffusion of mobile ions.

4. CONCLUSION II (Inelastic Scattering)

Diffraction experiments on $\alpha$-Cu$_{1.8}$Se single crystal have revealed an ordered structure with superstructure reflections at the $q = 1/2 (\pm 1, 1, 1); 1/3 (0, 2, 2)$ and $1/2 (2, 0, 0)$ positions of reciprocal space at room temperature.

Inelastic neutron scattering measurements show that transverse acoustic phonons with wave vectors in $[100], [111]$ and TA$_1 [110]$ directions have tendency to soften at BZ boundary. DFT calculations show that these modes are unstable over the large area in $Q$ space. This directly correlates with the ordering in Cu sub-lattice in the $\alpha$-phase at ambient temperature. The superstructure arising from the ordering causes effects similar to the folding of the BZ, when new phonon branches arise from new BZ centres. The coupling of low-energy phonon modes with displacement of mobile ions is particularly relevant to the superionic conductivity and this may explain the strong damping of phonons at $q > 0.5$ observed in experiment.

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