X-ray Investigation of Copper Selenides $\text{Cu}_{2-x}\text{Se} (2.00 \geq 2 - x \geq 1.72)$

BY A. TONEJC, Z. OGORELEC AND B. MESTNIK

Institute of Physics, University of Zagreb, P.O.B. 304, 41001 Zagreb, Yugoslavia

(Received 25 July 1974; accepted 10 December 1974)

The lattice parameters and the linear coefficient of the lattice thermal expansion of f.c.c. $\beta$-$\text{Cu}_{2-x}\text{Se}$ ($1.86 \geq 2 - x \geq 1.72$) were determined by means of the Debye-Scherrer X-ray diffraction technique in the temperature range 25–336°C. The concentration and temperature dependence of the coefficient of thermal expansion are discussed. In addition the equilibrium phase diagram of the Cu-Se system in the region of a non-stoichiometric $\text{Cu}_{2-x}\text{Se}$ compound ($2.00 \geq 2 - x \geq 1.72$) was redetermined, with special consideration of the homogeneity range of the f.c.c. $\beta$-$\text{Cu}_{2-x}\text{Se}$, and compared with previously published results.

Introduction

The equilibrium diagram of the Cu-Se system in the region of non-stoichiometric $\text{Cu}_{2-x}\text{Se}$ has been determined by several authors but the principal data differ from author to author. For instance, considerable differences can be seen in the homogeneity range of $\beta$-$\text{Cu}_{2-x}\text{Se}$ and in the lattice parameter of $\beta$-$\text{Cu}_{1.80}\text{Se}$ at room temperature (see Table 1). Data about unit cell, structure and stoichiometry of cuprous selenide in the low-temperature phase $\alpha$-$\text{Cu}_{2-x}\text{Se}$ also vary (Borchert, 1945; Junod, 1959; Stevels, 1969; Asadov, Džabrailova & Nasirov, 1972; Ogorelec, Mestnik & Devčić, 1972). However, to date only Ogorelec et al. (1972) have obtained for the $\alpha$ phase a broad range of homogeneity at room temperature ($\alpha$-$\text{Cu}_{2-x}\text{Se}$), while all other authors give a very narrow homogeneity range ($\alpha$-$\text{Cu}_{2}\text{Se}$). The transition temperature as a function of stoichiometric deviations seems to depend on the experimental technique used (Fig. 1).

Table 1. Room-temperature homogeneity range of the $\beta$ phase and its lattice parameter $a$ for $2 - x = 1.80$ obtained by different authors

<table>
<thead>
<tr>
<th>Homogeneity range $a$ (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.80 \leq 2 - x \leq 1.86$</td>
<td>Borchert (1945)</td>
</tr>
<tr>
<td>$1.75 \leq 2 - x \leq 1.82$</td>
<td>Borchert &amp; Patzak (1955)</td>
</tr>
<tr>
<td>$1.65 \leq 2 - x \leq 1.84$</td>
<td>Heyding (1966)</td>
</tr>
<tr>
<td>$1.80 \leq 2 - x \leq 1.85$</td>
<td>Stevels (1969)</td>
</tr>
<tr>
<td>$1.75 \leq 2 - x \leq 1.79$</td>
<td>Ogorelec et al. (1972)</td>
</tr>
<tr>
<td>$1.69 \leq 2 - x \leq 1.82$</td>
<td>Konev &amp; Rudinova (1973)</td>
</tr>
<tr>
<td>$1.70 \leq 2 - x \leq 1.80$</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Special attention should be paid to the unusual changes of the lattice parameters with temperature in the high-temperature phase of cuprous selenide. Since detailed knowledge about these changes may help in understanding some important physical phenomena, we shall describe briefly some of the work done on the problem.

Borchert (1945) found that when a sample of $\text{Cu}_{1.80}\text{Se}$ (pure $\beta$ phase at room temperature) is heated, the unit-cell lattice parameter does not increase linearly but that its increase is most rapid at the beginning, slows down with increasing temperature (up to 250°C) and becomes linear at temperatures above 250°C. Borchert (1945) tried to explain this behaviour with a changed distribution of Cu atoms in the f.c.c. lattice. However, Stevels (1969) roughly confirmed Borchert's findings about the change in X-ray diffraction intensity going from low to high-temperature atomic distribution in the f.c.c. lattice. The low-temperature form, which has a temperature-dependent structure [hereinafter marked $\beta$-$\text{Cu}_{2-x}\text{Se}(T)$ or $\beta(T)$], is charac-
terized by a continual change of the intensity of certain diffraction lines as temperature increases from room temperature to about 250°C. Above 250°C the distribution of Cu atoms becomes stable, intensity no longer changes, and a high-temperature form emerges [herein-after marked \( \beta-Cu_{2-x}Se(h.T.) \) or \( \beta(h.T.) \)]. The most marked change in intensity going from \( \beta(T) \) to \( \beta(h.T.) \) is the disappearance of line 200 and the appearance of line 422 on X-ray diffraction patterns.

Because of the differences in the reported data we decided to reinvestigate this part of the Cu-Se system. Our aim was to establish lattice parameters, phase boundaries, and especially the linear coefficient of lattice thermal expansion. Knowledge of these properties may be of great help in future work on cuprous selenides and related compounds (e.g. on their peculiar magnetic behaviour).

### 2. Experimental

The samples were prepared by a modified method described previously (Mestnik, Ogorelec & Ambrožić, 1972). The samples were obtained by reaction from precisely weighed quantities of the respective elements (Cu and Se, both 99.999 % pure) in evacuated (up to \( 10^{-5} \text{Torr} \)) and sealed quartz tubes. The free volume in the preparation quartz tubes was reduced as much as possible. Synthesis was performed by keeping the tubes first at a temperature of 500 °C for one hour and then above the melting point of the sample for another five hours. The tubes were then slowly cooled to room temperature over a period of 24 hours. The inner walls of the quartz tubes remained clean after synthesis and no weight losses of the initial quantities could be observed. Thus the composition \( (2-x) \) was determined from the masses of the components used in the synthesis.

The samples obtained were powdered by grinding, and the powders placed in 0.3 mm evacuated and sealed quartz capillary tubes. The tubes with the powder were tightly sealed so that no free volume remained. X-ray powder photographs were taken at various temperatures up to 400°C with a Unicam 19 cm high-temperature powder camera using Cu Kα radiation from a Siemens X-ray unit. Exposure time was usually six hours with 40 kV and 30 mA. After the samples had been ground it was found necessary to anneal the powders for one hour at 200°C to obtain well-resolved sharp lines in the high-angle region. The annealing was designed to remove internal stresses introduced in the lattice by grinding. The presence of phases was examined at room temperature by means of a Nonius Guinier–de-Wolff quadruple focusing camera with crystal-monochromated radiation. The homogeneity of the samples was checked by taking X-ray photographs of different parts of each sample. No differences in the lattice parameters and in the phase composition of any of the parts of one particular sample were found.

Since electrical conductivity measurements (Ogorelec & Čelustka, 1969) had shown that when \( Cu_{2-x}Se \) samples are heated the equilibrium state at each temperature is easily established owing to the very fast diffusion of copper ions, we decided, before taking the X-ray photographs, to anneal the powders in a Unicam camera only for the time required for the stabilization of temperature within the camera (for about three to four hours at lower temperatures up to 250°C and for about two hours at temperatures above 250°C).

Aluminum, 99.998 % pure, was used as the internal standard for temperature calibration. Calibration was done at the beginning and checked at the end of the experiments. Temperature control was facilitated by the use of a voltage stabilizer, a Variac, and a precise ammeter. The precision of the temperature measurements was estimated to be about ±3°C which corresponds to the change of ±0.0002 Å in the lattice parameter of aluminum.

The lattice parameter of the \( \beta-Cu_{2-x}Se \) phases was first determined at room temperature and then at temperatures above 25°C. Each time the lattice parameter at temperatures above 25°C had been established, the powder was slowly cooled for 12 hours and the lattice parameter again measured at room temperature. Annealing for six hours (exposure time) at temperatures up to 336°C led to no changes in the lattice parameters found at room temperature, but after heating up to 365°C and above, the room-temperature lattice parameter slightly increased (about 0.03 % after annealing at 365°C). This was attributed to the evaporation of some selenium from samples above 336°C and was checked by an experiment in non-sealed quartz tubes (in the Unicam camera there was a vacuum of about

![Fig. 2. Lattice parameter \( a \) of the \( \beta \) phase as a function of temperature for samples with different Cu concentration:](image-url)
In this case the remeasured room-temperature lattice parameter noticeably increased (about 0.2 % after annealing at 365 °C). This is why we report the results obtained by heating the samples only up to 336 °C.

A computer was used to determine the best line fit to a plot of lattice parameters or linear coefficient of lattice thermal expansion vs. temperature or stoichiometric index (2 – x) (this procedure was not applied in case of Figs. 2 and 4 because the results of most samples presented in these figures were not obtained on single-phase samples at lower temperatures).

3. Results and discussion

3.1. Lattice parameter measurements of the β phase

The temperature dependence of the lattice parameter of β-Cu_{2-x}Se for different stoichiometric indices (1.86 ≥ 2 – x ≥ 1.72) is shown in Fig. 2. The errors in the lattice parameter lie within the indicated symbols. The figure does not include values for the lattice parameter for (1.86 ≤ 2 – x ≤ 2.00), because in this case the high-angle lines on Debye–Scherrer films were very diffuse and practically invisible and did not allow a precise determination of the lattice parameter.

The values presented in Fig. 2 were used to plot lattice parameters of pure β-phase samples against Cu concentration (2 – x). The result is shown in Fig. 3. It can be seen that the lattice parameter of the β phase increases linearly with increasing Cu content. The straight lines obtained for different temperatures run parallel indicating that the change in the lattice parameter of the β phase as a function of the Cu content is temperature-independent.

Comparison between the room-temperature lattice parameters given in Table 1 and those given in Fig. 3 shows very good agreement between Heyding's, Konev's, de Medicis's and our data. Besides, de Medicis gives also room-temperature parameters for two other Cu contents, and his values are very comparable with our data [2 – x = 1.785, 5.753a (de Medicis), 5.754a (our data); 2 – x = 1.765, 5.748a (de Medicis) 5.748a (our data)]. However, there is less good agreement with Stevels's value and practically none with Borchert's.

3.2. Determination of phase boundaries

In the examined range of concentrations (2.00 ≥ 2 – x ≥ 1.72) three kinds of phases (α-Cu_{2}Se, β-Cu_{2-x}Se and Cu_{5}Se_{3}) were detected, depending on Cu content, in the temperature range 25–140°C. At temperatures above 140°C only the β phase was present. Depending on temperature, we found the β(T) type or the β(h.T.) type. The change in diffraction intensity going from the low- to the high-temperature form of the β phase was the same as indicated by Borchert (1945).

On X-ray diffraction patterns, the β- and Cu_{5}Se_{3} phases could be easily identified using the known data (Landolt–Börnstein, 1971; Borchert, 1945). For the α-Cu_{2}Se phase 65 lines were detected on X-ray photographs. Eighteen of these had the same θ_{hkl} values as those given by Stevels (1969), but the rest could not be indexed by using either the orthorhombic cell proposed by Stevels, or the tetragonal cell proposed by Borchert (1945), Junod (1959) or Asadov et al. (1972). A detailed structure examination of the α-Cu_{2}Se phase is now in progress and the results will be reported later.

From the appearance and disappearance of the diffraction lines of different phases on the X-ray photographs with changing temperature and Cu content, and from the behaviour of the β-phase lattice parameter shown in Figs. 2 and 4 we concluded as follows:

- at room temperature, the homogeneity range of
378 COPPER SELENIDES \( \text{Cu}_{2-x}\text{Se} \) \((2 \geq 2 - x \geq 1.72)\)

\( \beta(T) \) exists in the composition range \(1.805 \geq 2 - x \geq 1.750\); this is in rough agreement with the results of Heyding (1966) and Ogorelec et al. (1972) (see Table 1):

- above \(140^\circ\text{C}\), only the \( \beta \) phase is found for all examined compositions. The \( \beta(\text{h.T.}) \) phase exists above \(250^\circ\text{C}\) for \(1.90 \geq 2 - x \geq 1.72\), above \(185^\circ\text{C}\) for \(2 - x = 1.96\) and above \(140^\circ\text{C}\) for \(2 - x = 2.00\);
- the less inclined curve for \(x = 1.72\) in Fig. 2 for temperatures from \(25^\circ\text{C}\) suggests that the \( \beta \) phase becomes richer in Se up to \(110^\circ\text{C}\). At \(140^\circ\text{C}\), the \( \text{Cu}_3\text{Se}_2 \) phase is completely dissolved, and above this temperature only the \( \beta \) phase exists. Thus it appears that the phase boundary \((\text{Cu}_3\text{Se}_2 + \beta) - \beta\) must lie between \(110^\circ\text{C}\) and \(140^\circ\text{C}\);
- curves for \(2 - x = 1.82, 1.84, 1.85\) and \(1.86\) are at first very steep (see Fig. 2) which is a sign that \( \beta(T) \) has become richer in Cu because of the dissolution of the \( \alpha \) phase with increasing temperature. When the \( \alpha \) phase completely dissolves, the increase of the lattice parameter is due exclusively to the thermal expansion of the \( \beta \) phase. The phase boundary \((\alpha + \beta) - \beta\) can be obtained by extrapolating as shown in Fig. 4. The temperatures obtained are \(56^\circ\text{C}\) for \(1.82, 74^\circ\text{C}\) for \(1.84, 90^\circ\text{C}\) for \(1.85\) and \(96^\circ\text{C}\) for \(1.86\), with an estimated error of \(\pm 5\%\);
- the \( \text{Cu}_1\text{.9Se} \) sample still contained large amounts of the \( \beta \) phase at room temperature, but on the X-ray diffraction pattern of the sample with the composition \( \text{Cu}_x\text{Se} \), apart from \( \text{Cu}_3\text{Se}_2 \) lines, even the strongest line (220) of the \( \beta \) phase was hardly visible. From this and from the fact that the \( \theta_{\text{BhI}} \) values of the \( \alpha \) phase did not vary in samples with different Cu content we conclude that the \( \alpha \) phase has a very narrow homogeneity range. We could not detect the broad single-phase region of the \( \alpha \) phase found by Ogorelec et al. (1972) from electrical conductivity measurements. At present we are not able to explain why electrical measurements suggest a broad homogeneity range.

The phase diagram of the Cu–Se system in the composition range \(2.00 \geq 2 - x \geq 1.70\), based on our present results, is shown in Fig. 5, together with the results of Heyding (1966) and part of a diagram of Ogorelec et al. (1972). There is very good agreement between our results and those of Ogorelec et al. as regards the boundary \((\alpha + \beta) - \beta\), and rough agreement between ours and Heyding’s as regards the boundary \((\text{Cu}_3\text{Se}_2 + \beta) - \beta\).

### 3.3. Lattice thermal expansion

The linear coefficient \( \alpha_T \) of the lattice thermal expansion of the \( \beta \)-phase, at constant pressure, was calculated using the expression

\[
\alpha_T = \frac{1}{a_0} \frac{Aa}{\Delta T}
\]

rather than (see Bucci, Robertson & James, 1972)

\[
\alpha_T = \frac{1}{a} \frac{Aa}{\Delta T}
\]

where \(Aa\) is the change in the lattice parameter (lattice parameter difference between experimental points in Fig. 2), \( \Delta T \) the corresponding temperature interval, and \(a_0\) the lattice parameter at reference temperature \(T_0\). We used the lattice parameter of \( \beta-\text{Cu}_1.72\text{Se} \) at \(25^\circ\text{C}\) as \(a_0\). The results are shown in Table 2. The linear coefficient \( \alpha_T \) of the lattice thermal expansion of the \( \beta \) phase in dependence on composition and temperature is shown in Fig. 6. Since the composition dependence of \( \alpha_T \) at \(147, 223\) and \(300^\circ\text{C}\) cannot be deduced from Fig. 6 with any certainty (cases \(40^\circ\text{C}\) and \(80^\circ\text{C}\) of Fig. 6 suggest a compositional dependence of \( \alpha_T \) but there are too few experimental points to support this claim), we calculated for each temperature the mean value of \( \alpha_T \) and the standard deviation of its arithmetic mean. The

![Fig. 5. Part of the phase diagram of the Cu–Se system based on our results ( ), together with the results of Heyding (•••) and Ogorelec et al. (—–).](image)

<table>
<thead>
<tr>
<th>(T) (°C)</th>
<th>(2 - x)</th>
<th>(1.72)</th>
<th>(1.75)</th>
<th>(1.755)</th>
<th>(1.77)</th>
<th>(1.805)</th>
<th>(1.82)</th>
<th>(1.84)</th>
<th>(1.85)</th>
<th>(1.86)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>32.6</td>
<td>32.6</td>
<td>32.6</td>
<td>32.6</td>
<td>34.2</td>
<td>33.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>83</td>
<td>31.3</td>
<td>29.4</td>
<td>28.9</td>
<td>32.8</td>
<td>30.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>147</td>
<td>23.6</td>
<td>25.0</td>
<td>25.0</td>
<td>28.6</td>
<td>26.1</td>
<td>24.4</td>
<td>24.2</td>
<td>26.5</td>
<td>25.5</td>
<td></td>
</tr>
<tr>
<td>223</td>
<td>22.6</td>
<td>26.4</td>
<td>24.9</td>
<td>23.6</td>
<td>24.6</td>
<td>25.0</td>
<td>25.1</td>
<td>24.8</td>
<td>22.2</td>
<td>24.6</td>
</tr>
<tr>
<td>300</td>
<td>24.7</td>
<td>22.0</td>
<td>20.3</td>
<td>19.3</td>
<td>24.6</td>
<td>21.2</td>
<td>24.3</td>
<td>21.4</td>
<td>23.6</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Table 2. Linear coefficient of the lattice thermal expansion of \( \beta-\text{Cu}_{1-x}\text{Se} \) calculated for different temperatures and different Cu concentrations.
results are presented in Fig. 7 which shows the temperature dependence of $\alpha_T$. The unusual decrease of $\alpha_T$ with increasing temperature indicates that besides the anharmonic effect which is responsible for normal thermal expansion, there must be some other process which influences the expansion coefficient $\alpha_T$.

We think that the unusual behaviour of $\alpha_T$ confirms Borchert's (1945) findings about the non-linear change of the lattice parameter of the $\beta$-phase vs. temperature and that structural changes in the low-temperature form of the $\beta$-phase are responsible for this behaviour [for details see Borchert (1945)]. In brief, the greatest contraction occurs near room temperature owing to the vacation of the 4(d) lattice position by the Cu atoms. This contraction is superimposed on normal thermal expansion and as a result the $\alpha_T$ curve has the most rapid decrease (Fig. 7). With further increase of temperature there are fewer Cu atoms in the 4(d) position and the contraction due to the departure of Cu atoms from the 4(d) position is supposed to have less influence on the expansion coefficient $\alpha_T$, which, as a result, diminishes more slowly as temperature increases. X-ray measurements indicate that a stable $\beta$ phase exists above 250°C. Above that temperature there are no more atoms in the 4(d) position, and $\alpha_T$ would probably be influenced only by normal thermal expansion; and the behaviour of the curve in Fig. 7 above 250°C seems to justify this claim. However we could not give the results for $\alpha_T$ above 300°C because our experiments could not be carried out at temperatures above 336°C.

Calculation of $\alpha_T$ with the aid of relation (1) and using de Medicis's data (he measured the lattice parameter of $\beta$-Cu$_{1.75}$Se between 21°C and 41.5°C) gives the following results: $\alpha_{22^\circ C}=69.5 \times 10^{-6} \mathrm{deg}^{-1}$, $\alpha_{30^\circ C}=50.9 \times 10^{-6} \mathrm{deg}^{-1}$, $\alpha_{85^\circ C}=42.4 \times 10^{-6} \mathrm{deg}^{-1}$. This confirms our finding that the value of $\alpha_T$ decreases rapidly as temperature increases near room temperature.

The value for $\alpha_T$ at 300°C for $\beta$-Cu$_{1.75}$-1.85Se, i.e. $(22.4 \pm 0.7) \times 10^{-6} \mathrm{deg}^{-1}$ is in excellent agreement with the value $22 \times 10^{-6} \mathrm{deg}^{-1}$ obtained by dilatometric examination of sample Cu$_{1.96}$Se in the temperature interval 230–400°C (Ogorelec & Celustka, 1966).

References