JOURNAL OF MATERIALS SCIENCE 15 (1980) 3090–3094

Phase diagram and some properties of $Cu_{2-x}Se$ ($2.01 \geq 2-x \geq 1.75$)

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The temperatures of phase transformation from low-temperature α-phase to high-temperature β-phase were measured for copper selenide $Cu_{2-x}Se$ in the composition range $2.01 \geq 2-x \geq 1.75$. The α-phase was found to be unstable in air, and further experiments should be performed in a good vacuum. The phase diagram of $Cu_{2-x}Se$ was redetermined by the X-ray parametric method and the possible reasons why the phase diagrams reported by several authors do not coincide with each other are discussed.

1. Introduction

Superionic conductors have been intensively investigated during the last few years, e.g. [1]. An example of this type of ionic conductor is copper selenide. It has a wide range of stoichiometric deviation which distinguishes it from all other superionic conductors. There exists a large two-phase region ($\alpha + \beta$), where α is a monoclinic phase [2] and β is cubic [3]. However, recent publications [2, 4, 5] have not resolved where the phase boundary $(\alpha + \beta) - \beta$ is situated exactly in the phase diagram (Fig. 1). The phase diagram given by Murray and Heyding [2] is very uncertain in the concentration range $2.00 \geq 2-x \geq 1.75$ and for temperatures from 20 to 200° C. Takahashi *et al.* [5] used the change in ionic conductivity to locate the $(\alpha + \beta) - \beta$ phase boundary, and Tonejc *et al.* [4] tried to locate the phase boundary mainly with the aid of the disappearing-phase X-ray method which is very approximative in most cases.

In this work it was decided to reinvestigate the problem and to locate the $(\alpha + \beta) - \beta$ phase boundary as accurately and precisely as possible using the experimental technique described below.

2. Experimental procedure

Samples of different compositions were prepared as described in [4]. X-ray powder diffraction patterns above room temperature were obtained by means of an "Anton Paar kg" high temperature camera mounted on a Siemens X-ray diffractometer. The construction of the heating element allowed very quick variations in temperature (from 20 to 200° C within a minute). The samples for X-ray diffractometer examination were prepared by spreading the powders mixed with a binder onto the platinum sample holder, onto which a thermocouple was spot-welded. The thermocouple was calibrated with the aid of the known values of the Al and Ag lattice thermal expansion coefficients. CuKα radiation was used and the values $\lambda(\alpha_1) = 1.54051$ Å, $\lambda(\alpha_2) = 1.54433$ Å and $\lambda(\alpha) = 1.54178$ Å were used in the calculations.

The fact, found by Ogorelec and Čelustka [6], that at each temperature the equilibrium state for copper selenide is easily established, was confirmed at the beginning of our experiments. A few preliminary measurements showed that the transformation of α- to β-phase and vice versa was faster than the fastest temperature change attainable in the X-ray camera. The structures could be neither overheated nor undercooled in heating or cooling runs. As a result no annealing time was needed, which made it possible to take a great number of measurements to determine the phase boundary. Practically the only time needed was the time required for recording the diffraction pattern with the diffractometer.

In order to locate the $(\alpha + \beta) - \beta$ phase boundary the parametric method [7] was used and "kinetic" X-ray diffraction patterns obtained by the following procedure. The lattice parameter a_T of the cubic β-phase was measured at temperatures from 20 to 250° C for a given sample concentration. In the two-phase region ($\alpha + \beta$) the lattice

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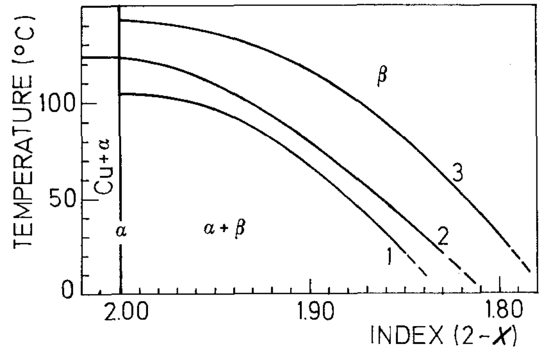

Figure 1 Phase diagram of the $Cu_{2-x}Se$ ($2.01 \geqslant 2-x \geqslant 1.79$) obtained by different authors: 1. Takahashi *et al.* [5], 2. Murray and Heyding [2], 3. Tonejc *et al.* [4].

parameter changed not only due to thermal expansion, but also as a result of the change in composition because of the $\alpha \rightarrow \beta$ transformation. In the single-phase region (β-phase) only thermal expansion influenced the lattice parameter. Accordingly the slope of the curve, $a_T = f(T)$, was different both in the two-phase field and in the single-phase field. The intercept gave the temperature of the $(\alpha + \beta) - \beta$ phase boundary. With the aid of a series of curves $a_T = f(T)$ for different compositions, we were able to construct the $(\alpha + \beta) - \beta$ phase boundary in the phase diagram. However, to be able to apply this procedure two conditions had to be fulfilled. The change in the sample composition had to produce a parameter change large enough to be measured, and secondly, we had to be able to measure the lattice parameter. The first condition was well fulfilled but the second caused some difficulties because most of the high-angle lines on the diffraction pattern were practically invisible in samples with compositions within the composition range $200 \geqslant 2-x \geqslant 1.86$. It was, however, found that the line (4 2 2) was strong enough at all temperatures and sample concentrations to be of use in our experiments.

It was decided to use a relative method for the determination of the lattice parameter at different temperatures. First the room-temperature lattice parameter a_0 of the β-phase for $Cu_{1.850}Se$, $Cu_{1.870}Se$, $Cu_{1.936}Se$ and $Cu_{1.960}Se$ samples were determined using Debye–Sherrer powder patterns and Straumanis film loading. The result obtained was $a_0 = (5.7600 \pm 0.0003)$ Å. Then measurements on the diffractometer were made. The temperature was increased at different intervals and the position of the (4 2 2) line was recorded at each temperature. Changes of only 3° C in temperature gave measurable changes in the (4 2 2) line position. As mentioned before, the temperature could be changed very quickly, and at each temperature level the temperature remained stable within ± 1° C for about 10 min, which was long enough to record the (4 2 2) line several times. The lattice parameter at each temperature was obtained by the simple relation $a_T = a_0 \sin v_0 / \sin v_T$. The method proved very good for the purpose of this work.

At room temperature the presence of phases was examined also by means of a Nonius Guinier–de Wolff quadruple focusing camera with crystal monochromated radiation.

3. Room temperature structures

We did not succeed in obtaining a pure α-phase sample at room temperature. Samples with a nominal concentration of Cu_2Se showed themselves to be two-phase alloys with the α-phase as the main constituent and with minor quantities of pure Cu. However, samples close to Cu_2Se with a relatively high Se concentration were also two-phase alloys with but minor quantities of β-phase in place of copper. We concluded that if α-phase exists as the single phase, its concentration must be about $Cu_{1.997}Se$.

4. Oxidation

Preliminary results with $Cu_{1.99}Se$ samples revealed that there is no reproducibility with respect to the values of the lattice parameter in successive heating and cooling runs. The samples behaved as if they were changing their composition to samples with higher Se contents during heating. This behaviour was explained when it was found that the primary vacuum obtained with the aid of a rotary pump connected to the high-temperature camera was not good enough to prevent the samples from oxidizing. When an oil-diffusion pump was added, the oxidation was prevented and the results became reproducible. However, it was decided to look in greater detail into the oxidizing process in the $Cu_{2-x}Se$ samples. For this purpose $Cu_{2-x}Se$ powders were annealed in air for different periods of time at different temperatures and then checked for phases with the Nonius focusing camera at room temperature.

It was found that samples with nominal Cu_2Se concentrations were unstable during annealing in air. The X-ray diffraction patterns showed that during annealing lines of β-$Cu_{1.80}Se$ began to appear and those of Cu became stronger, which indicated that the α-phase had decomposed into β-$Cu_{1.80}Se$ and Cu. During further annealing, the lines of the α-phase gradually disappeared but Cu began to oxidize as shown by the appearance of CuO lines on the diffraction patterns when samples were annealed below 370° C, or of Cu_2O lines when the samples were annealed above 370° C. However, annealing the samples with nominal composition $Cu_{1.75}Se$ (pure β-phase sample) showed that the lattice parameter changed progressively to the value of the $Cu_{1.80}Se$ sample, while on further annealing the lines of the α-phase appeared. This means that sublimation of Se from the cubic β-phase is very intensive. On further annealing, α-phase which had appeared began to decompose, and Cu, which appeared during this process, started to oxidize. In brief, the samples with nominal concentrations close to Cu_2Se changed their concentrations to a lower content of Cu owing to the decomposition of α-phase, and the samples with concentrations of about $Cu_{1.75}Se$ changed their concentrations to a higher Cu content owing to the sublimation of Se. From our experiments it was concluded that, in the samples with nominal composition $Cu_{1.90 \pm 0.02}Se$, both processes (decomposition of the α-phase and sublimation of Se from the β-phase) are in equilibrium.

Annealing for 15 h at only 60° C or for 10 min at 200° C was long enough for the decomposition of α-phase or the sublimation of Se from the β-phase to be seen on the X-ray diffraction patterns.

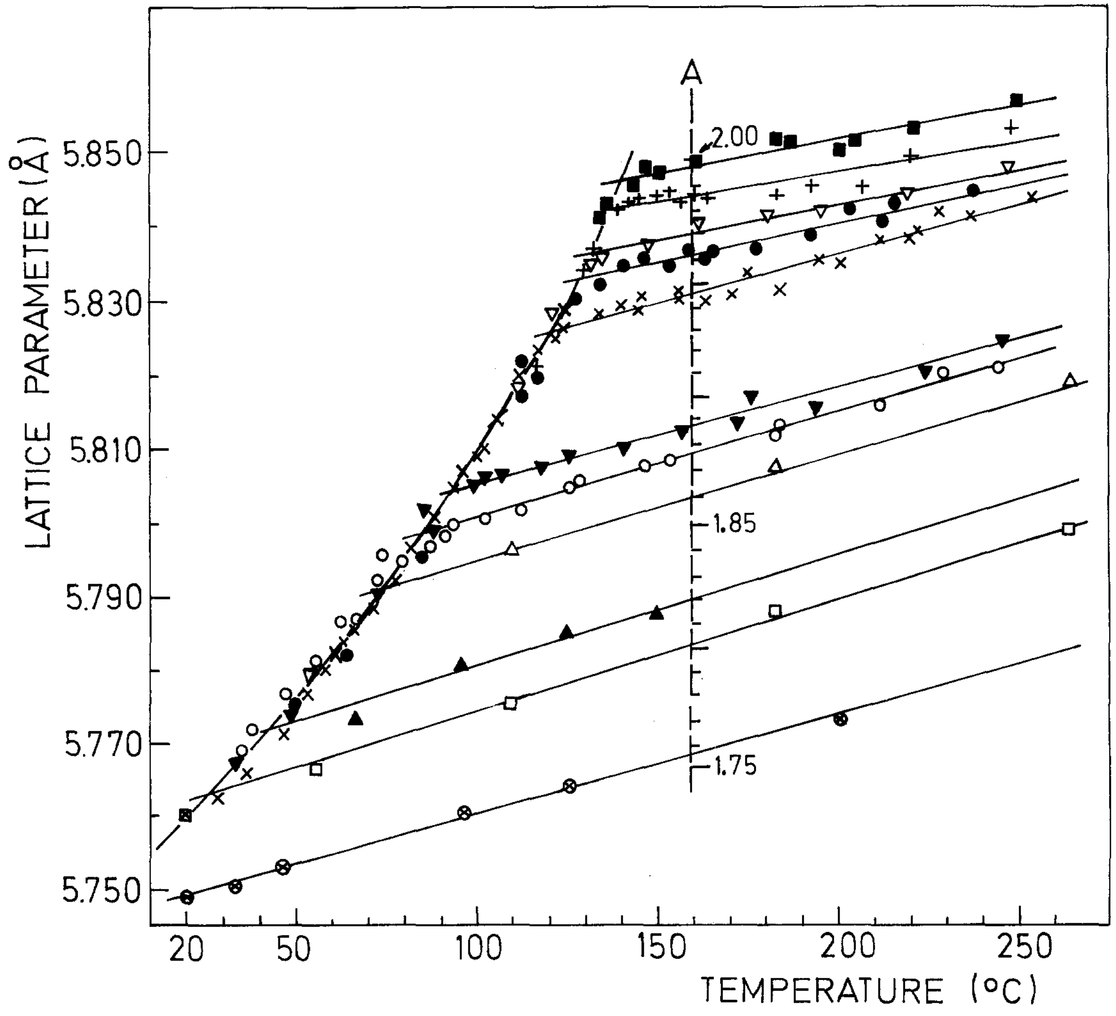

Figure 2 Lattice parameters of the $Cu_{2-x}Se$ β-phase as a function of temperature for nominal concentrations: $2-x =$ {⊗ 1.750, □ 1.805, ▲ 1.820, △ 1.860, ○ 1.870 (two samples), ▼ 1.905 (two samples), × 1.936 (three samples), ● 1.955, ▽ 1.960, + 1.990, ■ 2.000 (two samples)}.

5. $(\alpha + \beta) - \beta$ phase boundary determination

The variation of the cubic lattice parameters of β-$Cu_{2-x}Se$ $(2.00 \geqslant 2-x \geqslant 1.75)$ as a function of temperature is shown in Fig. 2. For certain concentrations, independent measurements were made (two or three powder samples were prepared from different parts of the bulk sample). A least-square fit of the experimental data was used to draw the straight lines and the curve in Fig. 2. The intercepts of the straight lines with the curve give us the temperatures of the $(\alpha+\beta)-\beta$ transition points for different concentrations. Interpolated lattice parameter data for a temperature of 160° C were used to show that the lattice parameter is a function of composition (Fig. 3). The relationship was shown to be linear. This fact enabled us to construct a vertical line (dotted line A in Fig. 2) with composition marks. With the aid of line A we were able to find the temperatures of the $(\alpha+\beta)-\beta$ transition for any concentration in the composition range $2.00 \geqslant 2-x \geqslant 1.80$ and to construct the $(\alpha+\beta)-\beta$ phase boundary practically point by point. The result is shown in Fig. 4. From the data presented in Fig. 2 it was estimated that the maximal error in the transition temperature was ± 3° C, which is indicated in Fig. 4 by dotted lines on both sides of the main line.

On the diffractograms of the samples with nominal concentrations of Cu_2Se and $Cu_{2.01}Se$, which were without β-phase at room temperature, β-phase lines appeared above 130° C, together with the already existing lines of α-phase. Above 141° C the samples contained only β-phase. Obviously, the transition $\alpha \rightarrow \beta$ always occurs through the $(\alpha+\beta)$ two-phase region. This behaviour is included in Fig. 4.

Using the relationship $\alpha_T = 1/a_0 \cdot \Delta a/\Delta T$ [8] and the value $a_0 = 5.7600$ Å, the linear coefficient

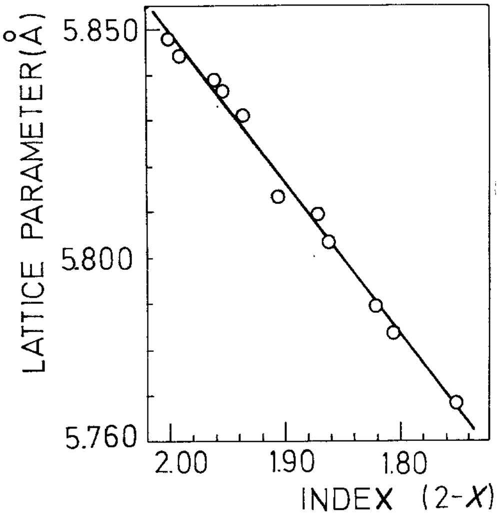

Figure 3 Lattice parameters of $Cu_{2-x}Se$ β-phase as a function of the stoichiometric index $2-x$ for a temperature of 160° C.

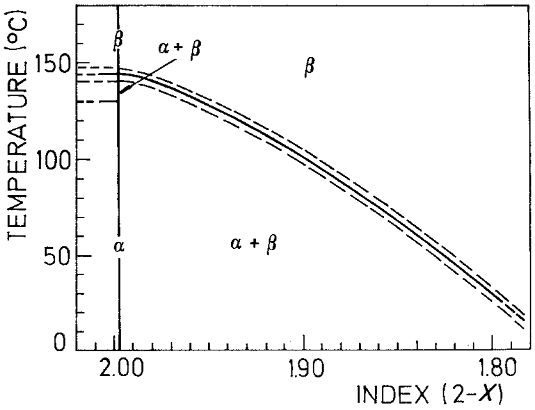

Figure 4 Phase diagram of the $Cu_{2-x}Se$ $(2.01 \geqslant 2-x \geqslant 1.97)$ based on present measurements.

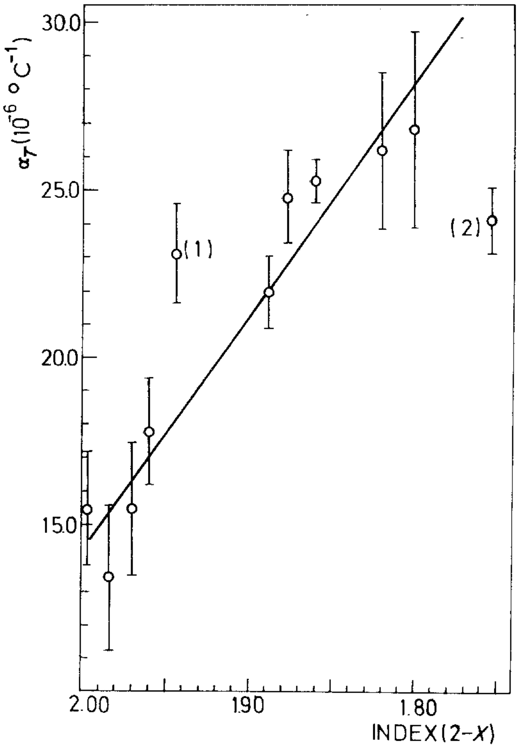

Figure 5 Linear coefficients of lattice thermal expansion α_T for $Cu_{2-x}Se$ β-phase as a function of the stoichiometric index $2-x$ (experimental points (1) and (2) were not used in the least-square fit).

α_T of the lattice thermal expansion of the β-phase was calculated, and the results are presented in Fig. 5 (points marked (1) and (2) in Fig. 5 were not used in the least-square fit). It is evident that α_T is composition dependent and that it decreases with increasing Cu content.

6. Conclusions

Low-temperature α-phase is highly unstable in air above room temperature and decomposes into β-$Cu_{1.80}Se$ and Cu, which in its turn oxidizes. However, in good vacuum conditions α-phase appears very stable. Therefore experiments should be performed in good vacuum.

Low-temperature α-phase always transforms to high-temperature β-phase over an equilibrium two-phase $(\alpha + \beta)$ region, even for a nominal concentration of Cu_2Se.

We suppose that the apparently great differences between authors in the determination of the $(\alpha + \beta) - \beta$ phase boundary derive from different experimental conditions. As shown in this paper, experiments performed in air or in bad vacuum conditions are incompatible with those in good vacuum. The results of Takahaski *et al.* [5] and our own differ appreciably. However, we prepared the samples by direct reaction (constituents heated above the melting points), while Takahashi *et al.* used a sintering method at 400° C. It is possible that a comparison of the published results is rendered more difficult by the uncertainty regarding the composition of the samples for which the data are given.

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Received 14 April and accepted 8 May 1980.