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X-Ray Diffraction Study on $\alpha \leftrightarrow \beta$ Phase Transition of Cu_2Se

The phase transition of a superionic Cu_2Se conductor was investigated by X-ray diffraction methods. In the experiment the Debye line intensity variation with temperature showed a behavior usually expected for the second-order transition. However, the transition was found to be of the first order. The anomalous behavior is explained.

A fair amount of theoretical and experimental work has been done to study the dynamics of the diffusion process in various inorganic solids possessing the common feature of at least one high-temperature phase with exceptionally high ionic conductivity. These materials are called superionic conductors (e.g., AgI, Ag_2Se, Ag_2S, CuBr, Cu_2S, Ag_3SI, $RbAg_4I_5$, Cu_2Se). The transitions to the superionic phase are of the typical first order with a considerable change of the lattice structure (e.g., AgI, Ag_2Se, Ag_2S, CuBr, Cu_2S; (*1*)). However the transition may also be of the second order (e.g., $RbAg_4I_5$ (*1*)) or of mixed behavior (e.g., Ag_3SI (*2*)). Cu_2Se has not yet been definitely classified (*1*), but the transition from a low-temperature α phase to a high-temperature superionic β phase is known to be complex (*3*). The fact that, on heating, the equilibrium state at each temperature can be easily established (*4*, *5*) makes this system very interesting for investigation.

According to Murray and Heyding (*3*) α phase has a large monoclinic unit cell, which transforms to the cubic β phase at about 136°C. They also performed DTA measurements. From their results it can be concluded that the $\alpha \leftrightarrow \beta$ phase transition of Cu_2Se should be of the first order.

The polycrystalline samples of nominal Cu_2Se used in our experiments were prepared as described previously (*5*). The intensities of Debye reflections of Cu_2Se were recorded using powder samples in an Anton Paar high-temperature vacuum furnace mounted on a Siemens X-ray diffractometer. Ni-filtered Cu$K\alpha$ radiation was used. In addition, a Nonius Guinier–de Wolf quadruple-focusing camera was used for the structure analysis at room temperature.

As can be seen from the diffraction patterns shown in Fig. 1, only one Bragg reflection (030), occurs clearly resolved in the low-temperature phase (Fig. 1b), and this peak was used for the examination of the temperature dependence of the peak intensity. However, in the 2θ range shown in Fig. 1b, there exist about 40 additional peaks of α phase of very low intensity, not recorded by the diffractometer, but clearly detected on the film of Guinier–de Wolf focusing camera.

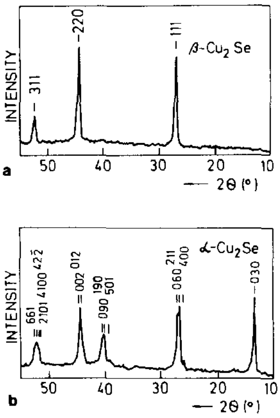

FIG. 1. X-Ray powder diffraction patterns of Cu_2Se at (a) 146°C and (b) room temperature.

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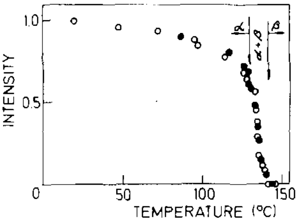

FIG. 2. Temperature dependence of intensity (normalized to room temperature intensity) for the $2\theta \approx 13°$ peak of α-Cu_2Se in Fig. 1b. ○, values for heating; ●, values for cooling.

The temperature in the temperature camera could be varied very quickly, but the transformation of α to β and vice versa was faster than the fastest temperature change attainable in the camera. Figure 2 shows the temperature dependence of the peak intensity of the (030) Bragg reflection. The intensity decreases as the temperature was raised, and vice versa. The peak disappears completely at about 142°C.

It may be mentioned that neither the form of the (030) line profile nor the temperature of the disappearance or appearance of the (030) line were altered by repeated heating and cooling runs. The measurements were repeatable and showed no hysteresis effects. The (030) peak appeared to change intensity to a new equilibrium value as soon as the temperature was changed. Annealing for up to 2 hr did not affect the behavior. When the temperature was changed, peak intensity developed in the usual way. Hence the phenomenon is not time dependent, but only temperature dependent. This means that, with changing temperature, atoms take up almost instantaneously the position appropriate to the new structure.

In view of the continual variation of diffraction intensity (without any jump at the transition point) and the absence of hysteresis about the transition point, the transition $\alpha \leftrightarrow \beta$ should be of the second order. But if the structure changes are taken into account, the transition should be of the first order. In order to clear up this point, further information was needed. It was found that line (030) disappeared without notable broadening, which could indicate that the transformation is probably not monophase. Careful X-ray examination confirmed this point. There exists a two-phase ($\alpha + \beta$) field, the lower end of which coincides with the rapid drop of intensity (about 130°C, Fig. 2). The upper end is determined by the disappearance of line (030), which vanishes at about 142°C.

Is the two-phase field an intrinsic or only an apparent phenomenon for the phase transition of Cu_2Se? At least two possibilities must be taken into consideration:

(a) If the diffractometer samples were slightly richer in Se than Cu_2Se, then the gradual disappearance of the (030) reflection for α-Cu_2Se with inreasing temperature would be expected because of the shift of the $Cu_{2-x}Se$ boundary to compositions richer in copper.

We examined several $Cu_{2-x}Se$ samples of different copper content in the range $2.01 \geq 2 - x \geq 1.99$. The samples with stoichiometric index $2.00 > 2 - x \geq 1.99$ were two-phase alloys with α and β as constituents, α was naturally the main phase. In these samples the disappearance of the (030) α reflection proceeds throughout the temperature interval from room temperature up to $(\alpha + \beta)$–β phase boundary.

Samples with index $2.01 \geq 2 - x > 2.00$ also proved to be two-phase alloys (α + Cu), but with α phase as the main constituent and with minor quantities of pure Cu. For these samples the disappearance of the (030) line of α-phase was always between 130 and 142°C.

(b) The inhomogeneity of a sample with various nonstoichiometric compositions could also have caused that the transition temperature could be altered from part to part in the sample, and consequently the mixed-phase region would be observed. Therefore the syntheses were prepared very carefully. Some parts of each bulk sample were examined by means of X rays and no difference in the phase composition of any of the parts of one particular sample was found on X-ray powder photographs. Moreover, samples obtained in different syntheses but of equal compositions showed the same behavior when heated in the X-ray camera and when the disappearance of the (030) reflection was examined.

We may conclude that the intermediate two-phase ($\alpha + \beta$) field is an intrinsic phenomenon for the phase transition of Cu_2Se.

Why is there no hysteresis? It is obvious that in this system diffusion is fast enough at these temperatures to bring the specimen into equilibrium immediately after the temperature is changed. In view of this and of the existence of the two-phase field near the transition point, the temperature variation of the (030) line can be understood even for the first-order transition. All these facts allow us to conclude that the $\alpha \leftrightarrow \beta$ transition on Cu_2Se is of the first order.

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