JOURNAL OF SOLID STATE CHEMISTRY **118**, 176–179 (1995)

Phase Transition of $CuS_{1-x}Se_x$ ($0 \le x \le 1$) Studied by Powder X-Ray Diffractometry

Hiroshi Nozaki, Kenji Shibata, Motohiko Ishii, and Ken Yukino

National Institute for Research in Inorganic Materials 1-1 Namiki, Tsukuba, Ibaraki, 305, Japan

Received September 19, 1994; in revised form February 8, 1995; accepted February 20, 1995

The temperature dependence of lattice parameters for $CuS_{1-x}Se_x$ ($0 \le x \le 1$) is presented by powder X-ray diffractometry. A hexagonal/orthorhombic transition was observed in the whole range of x. The high temperature hexagonal c/a of the compound increases with increasing x until $x = 0.6$ and decreases above $x = 0.6$. This composition dependence of c/a is due to the preferential occupation of Se at S2 sites in the Cu_2S_2 sheet which is previously reported by a Raman spectroscopic study of the system. The transition temperature increases from 55 K for $x = 0$ to 398 K for $x = 1$ with increasing x and is closely related to the occupancy of Se at the S2 sites.

INTRODUCTION

The compound CuSe undergoes two phase transitions upon cooling (1–3). The structure above about 398 K is hexagonal ($a_h = 3.9887(13)$ Å and $c_h = 17.263(7)$ Å at 407 K) and probably isotypic with the structure of CuS (covellite) (2, 3). Below about 398 K, the structure is orthorhombic ($a = 3.9472(12)$ Å, $b = 6.9601(44)$ Å, and $c = 17.244(6)$ Å at 325 K) (2, 3). This phase transition is (or is close to) second-order. Below 323 K, a hexagonal superlattice $a_h'\sqrt{13} \times a_h'\sqrt{13} \times c_h'(a_h' \approx a_h$ and $c_h' \approx c_h)$ appears (klockmannite) (4). This phase transition is first-order (2, 3). Upon heating above 323 K, the hexagonal superlattice phase changes to a metastable pseudo-hexagonal phase (monoclinic, $A \approx a_h'\sqrt{13}, B = c_h', C \approx a_h'\sqrt{13}$ and $\beta \approx 120°$), where superlattice reflections similar to those of klockmannite are maintained (3). Above about 398 K, the superlattice reflections disappear and the lattice becomes hexagonal as mentioned above.

The crystal structure of CuS (covelite) is hexagonal (space group $p6_3/mmc$) at room temperature and consists of alternate layers of CuS sheet and Cu_2S_2 sheet along the c axis. In the CuS sheet, the Cu atom (Cu1) is triangularly coordinated by S atoms (S1) (5). The S1 atom links to two Cu atoms (Cu2) which are in the Cu_2S_2 sheets above and below along the c axis. In the Cu_2S_2 sheet, two S atoms (S2) form S–S bonds along the c axis with a short distance 2.071(4) Å (5). The S–S pair is antiprismatically coordinated by Cu2 atoms. Upon cooling below 55 K, the hexagonal structure changes to an orthorhombic one (space group *Cmcm*) (6). This phase transition is (or is close to) second-order, judging from the temperature variation of lattice parameters reported previously (6). The existence of the phase transition in CuS has been observed in some changes of heat capacity and some other physical properties at 55 K as well as lattice parameters (6–8).

The hexagonal-to-orthorhombic distortion of CuS may be similar to that of CuSe at 398 K, although the orthorhombic structure of CuSe has not been studied in detail at present. It is thus expected that the transition temperature of the solid solution $CuS_{1-x}Se_x$ ($0 \le x \le 1$) continuously increases from 55 K for CuS to 398 K for CuSe with increasing x.

Anion distribution and phase transition in the system $CuS_{1-x}Se_x$ ($0 \le x \le 1$) were recently studied by Raman spectroscopy (9). It has been revealed that the Se atoms preferentially occupy the S2 site of the structure below about $x = \frac{2}{3}$ and then occupy the S1 site with the further increase of x. The frequency of the lowest frequency Raman peak pronouncedly decreases with decreasing temperature and has a minimum with temperature. The temperatures at the frequency minima are 125, 170, and 230 K for $x = 0.17, 0.33$, and 0.5 of $CuS_{1-x}Se_x$, respectively. The temperatures at the minima are suggested to be around the transition temperatures. The temperature dependence of the lowest frequency has been considered to be due to soft-mode behavior, which should be related to the hexagonal/orthorhombic phase transition of $CuS_{1-x}Se_x$.

This paper reports the temperature dependence of lattice parameters of $CuS_{1-x}Se_x$ ($0 \le x \le 1$) by powder X-ray diffractometry and intends to determine the transition temperature of $CuS_{1-x}Se_x$. The temperature dependence makes the phase relations of the system clear and confirms the hexagonal/orthorhombic phase transition in the whole range of x. The composition dependence of lattice parameters supports the result of anion distribution by the previ-

0022-4596/95 $12.00

ous Raman study. The composition dependence of the transition temperature is correlated with the anion distribution.

EXPERIMENTAL

The specimens of the end members CuS and CuSe were prepared by reacting the elements in evacuated silica tubes. Specimens $CuS_{1-x}Se_x$ ($x = \frac{1}{6}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$, and $\frac{5}{6}$) were also prepared by reaction of the elements. The details have been reported in a previous paper (9). Some specimens with intermediate compositions were synthesized by heating mixtures of appropriate amounts of CuS and CuSe in evacuated silica tubes at 300°C for 4–8 days. Powder X-ray diffractometry showed that the specimen was homogenous and had no other phases. X-ray diffraction patterns at various temperatures were collected by the same equipment as reported in a previous study for CuSe (3). A thermocouple of Au–0.07% Fe versus chromel was used for a temperature measurement below 297 K. The transition temperature was determined by not only the temperature dependence of lattice parameters but also the temperature dependence of the half-width of 116 reflection (hexagonal), or the half-width of a peak profile consisting of 206 and 136 (orthorhombic). A specimen set on the equipment was covered by aluminum foil so as to obtain a homogeneous temperature of the specimen during a measurement (3). The transition temperature was determined within an accuracy ±5 K.

RESULTS AND DISCUSSION

The temperature variations of lattice parameters of $CuS_{1-x}Se_x$ ($0 \leq x \leq 1$) are shown in Figs. 1a, 1b, and 1c, where the cell volume (Fig. 1c) corresponds to the hexagonal cell volume and therefore is half of the orthorhombic cell volume. The splitting between a and $b/\sqrt{3}$ (Fig. 1a) indicates that the hexagonal/orthorhombic transition exists in the whole range of x. The splitting between a and $b/\sqrt{3}$ dimensions continuously increases with decreasing temperature below the transition temperature. On the contrary, the temperature dependence of c_h (or c) and the cell volume for any x in $CuS_{1-x}Se_x$ changes little at the transition temperature (Figs. 1b and 1c). The transition temperature is indicated by open arrows in the figure and increases from 55 K for CuS ($x = 0$) to 398 K for CuSe ($x = 1$). A discontinuous change at 323 K for CuSe (solid arrows in Figs. 1a and 1c) corresponds to another phase transition from the orthorhombic phase to a hexagonal phase with a large superlattice $a'_h\sqrt{13} \times a'_h\sqrt{13} \times c'_h$ upon cooling (2, 3). This orthorhombic/hexagonal phase transition of CuSe has already been discussed in a previous paper (3). The temperature dependence of the lattice parameters of $CuS_{1-x}Se_x$ suggests that the hexagonal/orthorhombic transition is (or is close to) second-order.

The result of the temperature dependence of lattice parameters shows that the system at 297 K consists of three phases: the hexagonal phase, which is probably isotypic with CuS in the range between $x = 0$ and $x = \frac{3}{6}$, an orthorhombic phase with $a < b/\sqrt{3}$ for $x = \frac{4}{6}$ and $\frac{5}{6}$, and another hexagonal phase for $x = 1$ with the large superlattice of $a'_h\sqrt{13} \times a'_h\sqrt{13} \times c_h$.

The ratio c_h/a_h does not vary monotonically with increasing x (Fig. 2), where data are taken for the isotypic hexagonal lattice; i. e., data between $x = 0$ and $x = \frac{1}{2}$ are taken at 298 K but those between $x = \frac{2}{3}$ and $x = 1$ are taken at temperatures just above the hexagonal/orthorhombic transition temperatures. It should be noted that the changes of lattice dimensions on compositional variation are far larger than those on temperature variation. The ratio c_h/a_h increases with increasing x below about $x = 0.6$ and then decreases above it (Fig. 2). This variation of c_h/a_h suggests the preferential occupation of Se at S2 site, as discussed in the following.

The compound $CuS_{1-x}Se_x$ has a layered structure and two types of anion sites, S1 and S2. The substitution of Se for S at each site is thus expected to expand the lattice anisotropically. One can assume that the substitution of Se for S at the S2 site increases c_h/a_h and the substitution at the S1 site decreases c_h/a_h. This assumption is considered reasonable from the viewpoint of the geometric configuration of neighbors at the S1 and S2 sites. It is therefore expected that the preferential occupation of Se at the S2 site increases c_h/a_h with increasing x from 0 to $\frac{2}{3}$ and then decreases with x above $\frac{2}{3}$, which almost agrees with the present experimental result. The previous Raman study has revealed the anion distribution in $CuS_{1-x}Se_x$ and given a relation between the occupancy of Se at each site and x (9). The present result on the variation of c_h/a_h provides further evidence of the anion distribution proposed by the Raman study.

In spite of the anisotropic expansion of the unit lattice by the substitution of Se for S, the cell volume of the high-temperature hexagonal lattice shows an excellent linear dependence on composition x and obeys the Vegard law (Fig. 2, inset). This means that the respective volumes of S and Se averaged in the unit lattice of $CuS_{1-x}Se_x$ are constant over the whole range of x.

The transition temperature T_t increases from 55 K for $x = 0$ to 361 K for $x = \frac{2}{3}$ with increasing x and saturates to be 398 K above $x = \frac{5}{6}$ (Fig. 3, inset). This composition dependence correlates to the preferential occupancy of Se at the S2 site. The correlation is clearly shown by plotting T_t versus the occupancy of Se at the S2 site, α (Fig. 3), where the occupancy determined by the previous Raman study is used (9). The dotted line in the figure is a quadratic line obtained by the least-squares method.

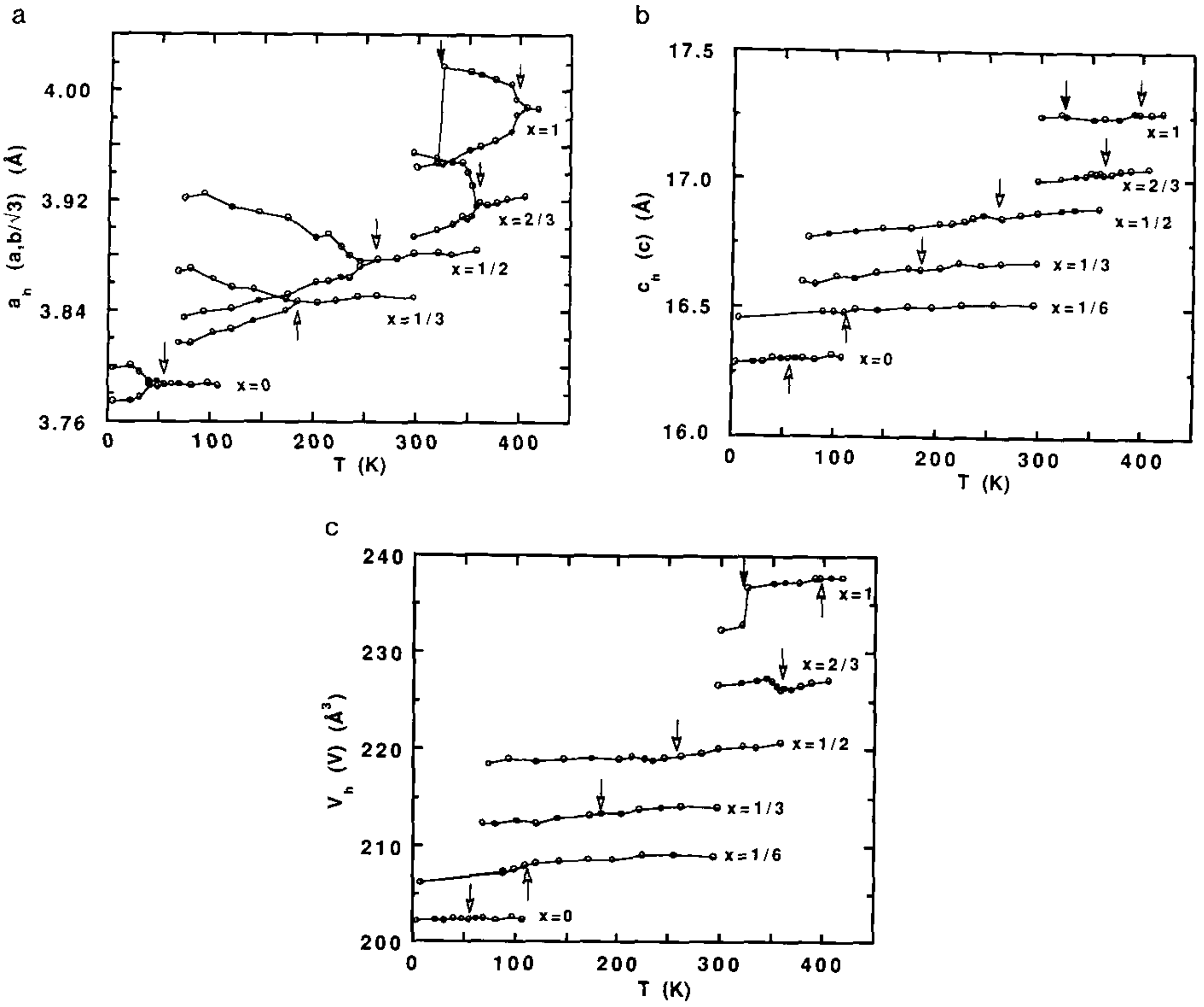

FIG. 1. Temperature dependence of lattice parameters in $CuS_{1-x}Se_x$ ($0 \leq x \leq 1$). (a), (b), and (c) show a_h (a and $b/\sqrt{3}$), c_h (c) and V_h ($V/2$), respectively. Open arrows show the hexagonal/orthorhombic transition temperature. A solid arrow shows another transition temperature at 323 K for CuSe.

The transition temperature is thus expressed by the quadratic equation

$$T_t = 404.8\alpha^2 + 131 \times 2\alpha(1 - \alpha) + 56.7(1 - \alpha)^2,$$

where α^2, $2\alpha(1 - \alpha)$, and $(1 - \alpha)^2$ mean the abundance ratios of Se–Se, Se–S, and S–S pairs in the Cu_2S_2 sheet, respectively, assuming that Se atoms randomly occupy S2 sites. The full occupation of the Se–Se pair ($\alpha = 1$) at the S2 site gives the transition temperature of 405 K for CuSe and that of the S–S pair ($\alpha = 0$) the transition temperature of 57 K for CuS according to the equation. The coefficient of the second term, 131, gives the degree of contribution of the Se–S pair to the transition temperature. The present composition dependence of transition temperature can thus be expressed by the sum of contributions from the S–S, S–Se, and Se–Se bonding pairs, which suggests that the transition temperature of $CuS_{1-x}Se_x$ is closely related to the bonding characteristics of the anion pair in the Cu_2S_2 sheet.

The hexagonal-to-orthorhombic crystal distortion in CuS is essentially a shift of the CuS sheets relative to the Cu_2S_2 sheets along the orthorhombic b axis (6). It has been suggested that the formation of metal–metal bonds between Cu1 and Cu2 is the driving force for the hexagonal-to-orthorhombic transition (6). On the other hand, Liang and Whangbo have proposed that the slipping of the CuS and Cu_2S_2 sheets, associated with the phase tran-

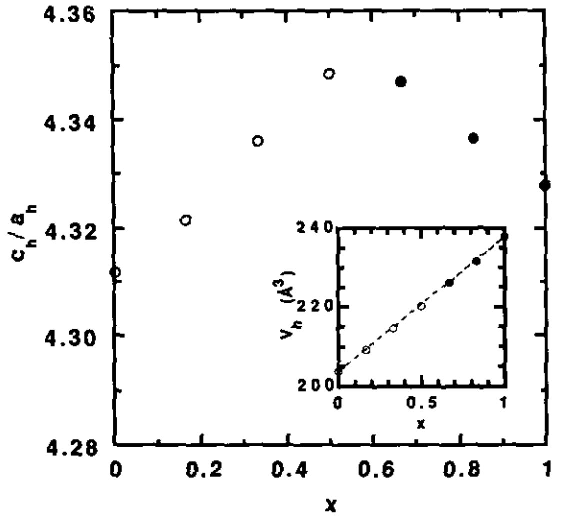

FIG. 2. Composition dependence of high-temperature hexagonal c_h/a_h in $CuS_{1-x}Se_x$ ($0 \leq x \leq 1$) and that of hexagonal cell volume (inset). Data marked by open circles were taken at 298 K and those by solid circles were taken just above the transition temperatures which are 358, 404, and 407 K for $x = \frac{2}{3}$, $\frac{5}{6}$, and 1, respectively.

sition, is more likely caused by van der Waals interactions of the interlayer S···S contacts than by the interlayer Cu^+–Cu^+ bonding interactions (10). The present result indicates that the substitution of Se at the S2 sites strongly increases the transition temperature but the substitution of Se at the S1 sites does not change the transition temperature much.

The bond strength of the Se–Se pair is weaker than that of the S–S pair, as indicated by the values of the anion–anion stretching bond force constants calculated from their Raman frequencies (9). The weak bond strength of the Se–Se pair may be appropriate for the slipping of the CuS and Cu_2S_2 sheet and may decrease the strength of stability of the high-temperature hexagonal lattice, which *may increase the transition temperature with increasing* x until $x = \frac{2}{3}$.

Another possibility is that a change in the bonding nature of the anion–anion pair on varying temperature may be the driving force of the hexagonal-to-orthorhombic distortion. Really, the bond distance of the S–S pair in the orthorhombic CuS is 2.03(2) Å at 8 K, which is shorter than that of the hexagonal CuS, 2.071(4) Å at 295 K by about 2% (6). The change in the bond distance seems to be too large for a change due to its thermal dilatation. The shortening of the bond distance on temperature may give an effect on the bonding between Cu2 and S1 ions as well as on the bonding between S2 ions, as seen in a cooperative change in the distances of S2–S2 and Cu2–S1 bondings reported in a study for the crystal structure of CuS under applied hydrostatic pressure up to 33 kbar (11). The effect on the Cu2–S1 bonding may cause the slipping of the CuS and Cu_2S_2 sheets. The change of the bond distance on temperature variation is probably dependent on anions occupying the S2 sites. If this driving force increases with increasing x until $\frac{2}{3}$, the transition temperature should also increase with increasing x. The hypotheses must be confirmed by further investigations, especially, a Raman spectroscopic study using single crystals and a crystallographic study of the high-temperature hexagonal and orthorhombic structures of the system.

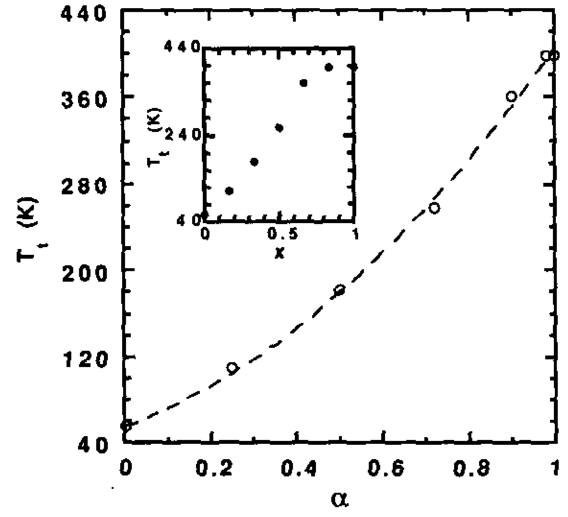

FIG. 3. Hexagonal/orthorhombic transition temperature versus occupancy of Se at S2 sites. A dotted line is fitted to a quadratic equation by the least-squares method. The inset shows the composition dependence of transition temperature.

ACKNOWLEDGMENT

The authors thank Dr. H. Nakazawa in NIRIM for his comments on the manuscript.

REFERENCES

1. R. D. Heyding, *Can. J. Chem.* **44,** 1233 (1966).
2. A. L. N. Stevels and F. Jellinek, *Recueil* **111,** 273 (1971).
3. H. Nozaki, K. Shibata, M. Onoda, K. Yukino, and M. Ishii, *Mater. Res. Bull.* **29,** 203 (1994).
4. C. A. Taylor and F. A. Underwood, *Acta Crystallogr.* **13,** 361 (1960).
5. H. T. Evans, Jr., and J. A. Konnert, *Am. Mineral.* **61,** 996 (1976).
6. H. Fjellvåg, F. Grønvold, S. Stølen, A. F. Andresen, R. Muller-Kafer, and A. Simon, *Z. Kristallogr.* **184,** 111 (1988).
7. E. F. Westrum, Jr., S. Stølen, and F. Grønvold, *J. Chem. Thermodyn.* **19,** 1199 (1987).
8. H. Nozaki, K. Shibata, and N. Ohhashi, *J. Solid State Chem.* **91,** 306 (1991).
9. M. Ishii, K. Shibata, and H. Nozaki, *J. Solid State Chem.* **105,** 504 (1993).
10. W. Liang and M.-H. Whangbo, *Solid State Commun.* **85,** 405 (1993).
11. Y. Takeuchi, Y. Kudoh, and G. Sato, *Z. Kristallogr.* **173,** 119 (1985).