

Anion Distributions and Phase Transitions in $\text{CuS}_{1-x}\text{Se}_x$ ($x = 0-1$) Studied by Raman Spectroscopy

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Anion distributions and phase transitions in $\text{CuS}_{1-x}\text{Se}_x$ ($x = 0-1$), which are isostructural with CuS (covellite), have been studied through the Raman spectroscopic measurements. In hexagonal CuS type structure, there exist two different anion sites (2c and 4e sites of the hexagonal space group $P6_3/mmc$), and it has been shown that the selenium atoms occupy the 4e sites preferentially in these solid solutions. The temperature dependences of the frequencies of the Raman peaks have also been measured for the seven samples of $\text{CuS}_{1-x}\text{Se}_x$ in the temperature range from 300 to 80 K. For each sample except for CuSe, the lowest frequency Raman peak has shown the soft mode behavior, which is considered to be related to the structural phase transition. These results have been discussed referring to those obtained by the X-ray diffraction method. In these solid solutions, the phase transition temperatures rise with increasing selenium contents. © 1993 Academic Press, Inc.

Introduction

The solid solutions $\text{CuS}_{1-x}\text{Se}_x$, which are isostructural with CuS (covellite), exist in the composition range from $x = 0$ to $x = 1$ (1). At 300 K, CuS crystallizes in the hexagonal space group $P6_3/mmc$, and there exist two crystallographic sites of sulfur atoms: one third of the sulfur atoms are at the 2c sites and are triangularly coordinated to Cu(1) atoms in the c plane and linked to two Cu(2) atoms along c axis, while two thirds of the sulfur atoms are at the 4e sites and form sulfur-sulfur bonding with short bond length of 2.071 Å (2) (see Fig. 1). The X-ray photoelectron spectroscopic studies (3-5) and the studies on the electrical and magnetic properties (6, 7) have suggested that the bonding of CuS can be described as either $(\text{Cu}^{1+})_3\text{S}_2^{2-}\text{S}^{1-}$ or $(\text{Cu}^{1+})_3\text{S}_2^{1-}\text{S}^{2-}$ (S_2 : S-S pair of sulfur atoms at 4e sites, S: sulfur atoms at 2c sites) in terms of the ionic model. In the solid solution $\text{CuS}_{1-x}\text{Se}_x$, a part of sulfur atoms in these two sites is substituted by the selenium atoms. Therefore, in order

to analyze several physical properties of these solid solutions and to discuss their bonding nature, the information on the anion distributions to these two chalcogen sites in $\text{CuS}_{1-x}\text{Se}_x$ is valuable. The first aim of the present paper is to elucidate the anion distributions in these solid solutions on the basis of the Raman spectroscopic measurements.

The structure of CuS, one of the end members of these solid solutions, is distorted slightly at 55 K, and a second order phase transition takes place (2). For CuSe, the other end member of these solid solutions, the similar type phase transitions were also reported to take place (8, 9). On the basis of these experimental results, it is expected that the structural phase transitions similar to those of the end member compounds also take place in these solid solutions of the intermediate compositions. The second aim of this paper is to report the results of the Raman spectroscopic investigations on the structural phase transitions of these solid solutions.

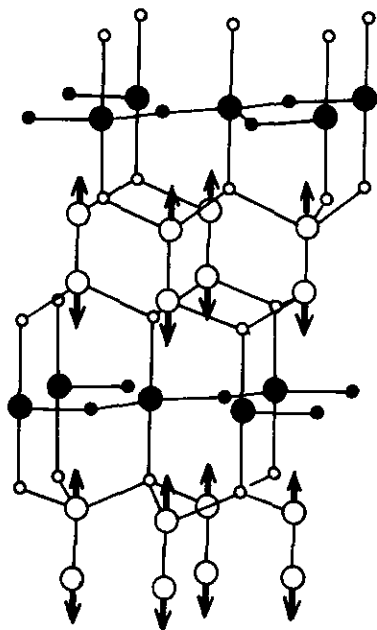


FIG. 1. Crystal structure of hexagonal CuS (covellite). Displacement of each atom for the Raman active S-S stretching mode (A_{1g}) is also shown schematically by arrows. Large solid circles, S at $2c$ sites; large open circles, S at $4e$ sites; small solid circles, Cu(1); small open circles, Cu(2).

Experimental

Samples used in this experiment were synthesized from thin plates of copper (99.999 mass% pure), granular sulfur (99.999 mass% pure), and granular selenium (99.999 mass% pure) according to the following procedures. (i) CuS: The weighted amounts of copper and sulfur were sealed in an evacuated vitreous silica tube and were synthesized by heating at 250°C for 2 weeks. (ii) CuSe: The weighted amounts of copper and selenium were sealed in an evacuated vitreous silica tube and were synthesized by heating at 235°C for 3 weeks. (iii) $\text{CuS}_{1-x}\text{Se}_x$ ($x = 0.17\text{--}0.83$): The weighted amounts of copper, sulfur, and selenium were sealed in an evacuated vitreous silica tube and were synthesized by heating at 250°C for 2 or 3 weeks. The synthesized samples were identified by the X-ray powder diffraction

method. Details of the synthesis will be reported elsewhere (1).

Raman spectra were obtained from the seven polycrystalline samples of $\text{CuS}_{1-x}\text{Se}_x$ with $x = 0.00, 0.17, 0.33, 0.50, 0.67, 0.83,$ and 1.00 . A Spex 1403 double monochromator and a photon counting system were used with 514.5 nm excitation of an argon ion laser. Observed spectra of CuS and CuSe in the frequency region below 600 cm^{-1} are reproduced in Fig. 2. In Figs. 4 and 6, observed spectra of seven samples in the frequency region from 550 to 200 cm^{-1} and in the frequency region below 80 cm^{-1} are reproduced, respectively.

Results and Discussion

1. Raman Active Modes in CuS and CuSe

CuS crystallizes in the hexagonal space group $P6_3/mmc(D_{6h}^4)$ above 55 K and a primitive unit cell contains twelve atoms ($6(\text{CuS})$). By the group theoretical analysis, we obtain the symmetries of the zone-center optical phonon modes as follows: $2A_{1g} + 4B_{2g} + 2E_{1g} + 4E_{2g} + 3A_{2u} + 2B_{1u} + 3E_{1u} + 2E_{2u}$, where eight modes of $2A_{1g} + 2E_{1g} + 4E_{2g}$ are active in Raman spectra. On the basis of the structural peculiarities of CuS as described in the previous section, it is reasonable to consider that the chalcogen atoms at $4e$ sites form the diatomic chalcogen-chalcogen ions in this compound. There exist two chalcogen-chalcogen bond stretching modes of these diatomic ions and these are distributed in A_{1g} and B_{2g} symmetries at the zone-center. Of these, that of A_{1g} symmetry is active in Raman spectra. Below 55 K , CuS crystallizes in the orthorhombic space group $Cmcm(D_{2h}^{17})$, and a primitive unit cell also contains 12 atoms ($6(\text{CuS})$). The zone-center optical phonon modes are classified as $6A_g + 4B_{1g} + 2B_{2g} + 6B_{3g} + 2A_u + 5B_{1u} + 5B_{2u} + 3B_{3u}$, where 18 modes of $6A_g + 4B_{1g} + 2B_{2g} + 6B_{3g}$ are active in Raman spectra. In the low temperature orthorhombic structure, the diatomic chalcogen-chalcogen ions can also be considered to exist (2), and two Raman

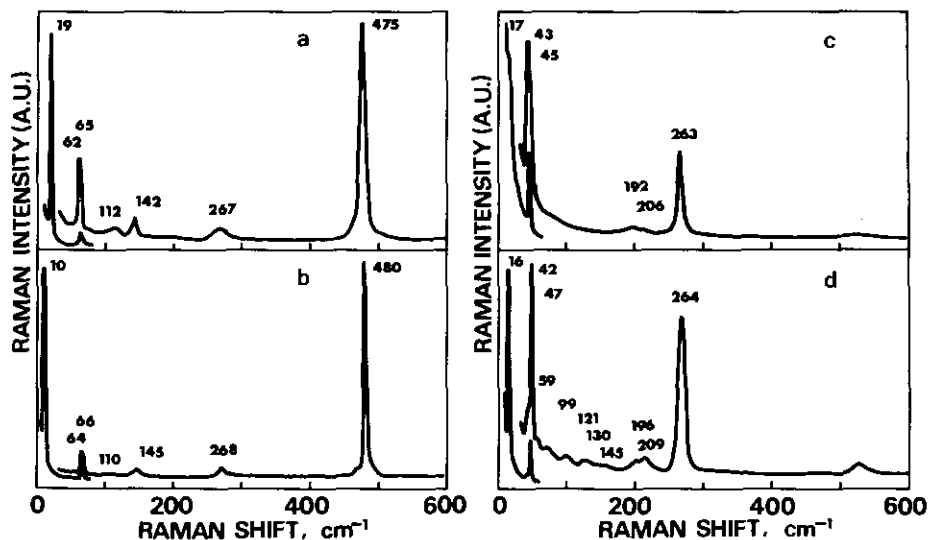


FIG. 2. Raman spectra of CuS and CuSe. (a), CuS (300 K); (b), CuS (80 K); (c), CuSe (300 K); (d), CuSe (80 K).

active chalcogen–chalcogen bond stretching modes of A_g and B_{3g} symmetries are expected. CuSe possesses the hexagonal CuS type structure above 390 K, the orthorhombic one between 390 and 320 K, while a hexagonal superstructure, the details of which are not yet known, is stable below 320 K (8).

In the Raman spectra of CuS at 300 and 80 K shown in Fig. 2, about seven peaks are observed in the frequency region below 500 cm^{-1} . Of these peaks, a strong peak at 475 cm^{-1} observed at 300 K can be assigned to the S–S stretching mode of S_2 ions at $4e$ sites. This assignment is consistent with the results reported for the metal sulfides of pyrite type structure, in which S–S pairs of rather short atomic distances exist (10). Lattice dynamical calculations based on the valence force field model were made for the hexagonal CuS (11), and the displacement of each atom for the Raman active S–S stretching mode of A_{1g} symmetry is shown schematically in Fig. 1 on the results of this calculation. As shown in this figure, the S–S stretching mode is almost completely localized on S_2 ions at $4e$ sites.

As is seen in Fig. 2, each peak observed

at 475 , 267 , 142 , 65 , and 62 cm^{-1} in the spectra of CuS at 300 K shifts to higher frequencies with the amount less than 5 cm^{-1} at 80 K. On the contrary, the lowest frequency peak observed at 19 cm^{-1} in the spectra at 300 K shifts to the lower frequencies with decreasing temperature and is observed at 10 cm^{-1} in the spectra at 80 K. This observation suggests that the anomalous behavior of this lowest frequency peak is related to the phase transition in CuS. The details of the temperature dependences of this peak will be discussed in the later section.

In the spectra of CuSe at 300 K, about six peaks are observed in the frequency region below 300 cm^{-1} (Fig. 2). Of these, a rather strong one at 263 cm^{-1} can be assigned to the Se–Se stretching mode of Se_2 ions. This assignment is also consistent with the results reported for the metal selenides of pyrite type structure, in which Se–Se pairs of rather short atomic distances exist (12–14). The results of the lattice dynamical calculations on CuSe of the hexagonal CuS type structure have also shown that the Se–Se stretching mode of CuSe is almost completely localized on Se_2 ions (11). Though

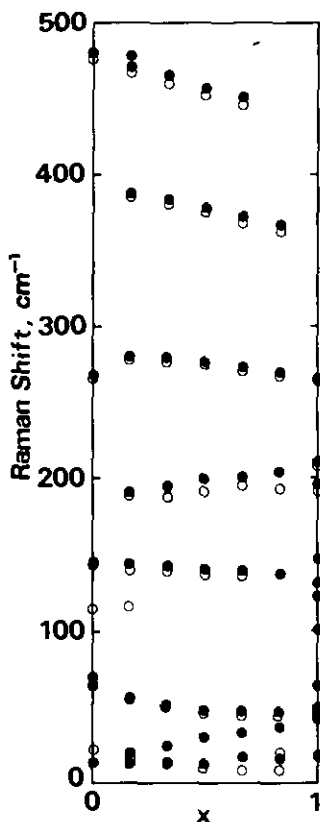


FIG. 3. Frequencies (cm^{-1}) of the observed Raman peaks of $\text{CuS}_{1-x}\text{Se}_x$ plotted against the composition x . Open circles, 300 K; solid circles, 80 K.

CuSe is reported to possess the hexagonal superstructure at 300 K as mentioned above (8), the splittings of the Raman peaks due to the lowering of the symmetry from the hexagonal CuS type structure have not been observed in the spectra at 300 K (Fig. 2c). At 80 K, however, the width of the Se–Se stretching peak increases, and about 11 peaks are observed in the frequency region below 300 cm^{-1} as is seen in Fig. 2d. These observations clearly show that the structure of CuSe is distorted from the hexagonal CuS type structure at 80 K.

2. Chalcogen–Chalcogen Stretching Modes and Anion Distributions in $\text{CuS}_{1-x}\text{Se}_x$

In Fig. 3, the frequencies of the observed Raman peaks of $\text{CuS}_{1-x}\text{Se}_x$ are plotted

against the composition. As is seen in this figure, except for the lowest frequency figure, almost all of the observed Raman frequencies at 300 K shift monotonously with the variation of the compositions and no splitting of the peak is observed. The lattice constants of the four compounds of $\text{CuS}_{1-x}\text{Se}_x$ ($x = 0.00, 0.33, 0.67, 1.00$) in the hexagonal CuS structures shift almost linearly with the variation of the compositions as well (9). These results suggest that the observed Raman spectra of $\text{CuS}_{1-x}\text{Se}_x$ of the intermediate compositions are able to be interpreted based on the hexagonal CuS type structure. Accordingly, the chalcogen–chalcogen stretching modes of the diatomic chalcogen–chalcogen ions in these solid solutions are also considered to be localized on the diatomic ions. These stretching modes are expected to be observed in the frequency region from 500 to 250 cm^{-1} , and actually, as shown in Fig. 4, one, two, or three peaks are observed in the spectrum of each compound at 300 K. Of these peaks, those observed in the frequency region from 480 to 440 cm^{-1} are due to S–S stretching modes and these peaks become weaker in intensity with increasing selenium content (A in Fig. 4). The peaks observed in the frequency region from 280 to 260 cm^{-1} are due to Se–Se stretching modes and these peaks become stronger in intensity with increasing selenium content (C in Fig. 4). In addition to these peaks, in the spectra of $\text{CuS}_{1-x}\text{Se}_x$ ($x = 0.17$ – 0.83), the peaks due to S–Se stretching modes of SSe ions, i.e., one of the chalcogen–chalcogen pair sites ($4e$ sites of the space group $P6_3/mmc$) is occupied by a sulfur atom and the other is occupied by a selenium atom, are observed in the frequency region from 390 to 360 cm^{-1} (B in Fig. 4). These peaks become weaker in intensity with increasing selenium content. As described later, the structures of $\text{CuS}_{1-x}\text{Se}_x$ with $x = 0.67, 0.83,$ and 1.00 are considered to be distorted from the hexagonal CuS type one at 300 K. However, as shown in Fig. 4, the splittings of the chalcogen–chalcogen stretching peaks due to the

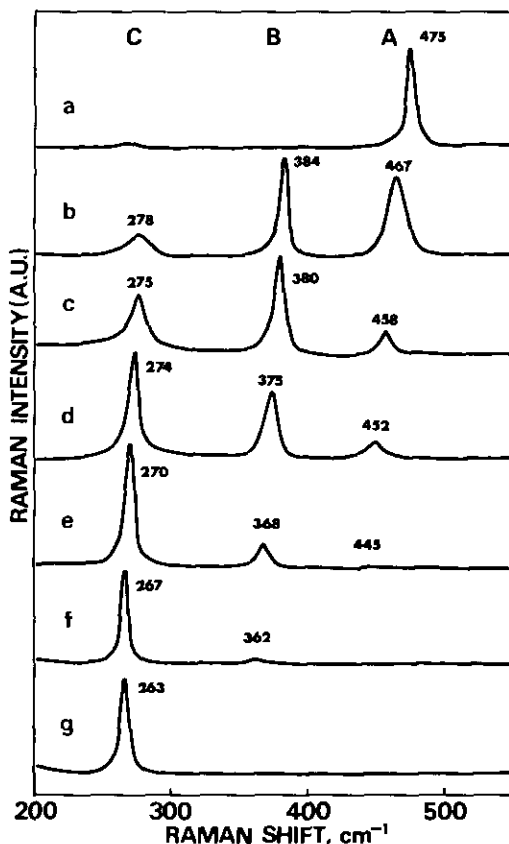


FIG. 4. Raman spectra of $\text{CuS}_{1-x}\text{Se}_x$ in the frequency region from 550 to 200 cm^{-1} observed at 300 K. (a), $x = 0.00$; (b), $x = 0.17$; (c), $x = 0.33$; (d), $x = 0.50$; (e), $x = 0.67$; (f), $x = 0.83$; (g), $x = 1.00$. A, B, and C denote the peaks due to S-S, S-Se, and Se-Se stretching modes, respectively.

lowering of the symmetries were not observed. As in Fig. 4, though a very weak peak due to the other lattice modes is observed at about 260 cm^{-1} in the spectrum of CuS, its intensity is so weak that the existence of this peak is negligible in the following discussions.

On the basis of these results, it is reasonable to consider that the relative intensities of the three peaks described above provide the information on the anion distribution at the chalcogen-chalcogen pair sites for each solid solution. Therefore, in order to elucidate the anion distributions in $\text{CuS}_{1-x}\text{Se}_x$, the occupancies of sulfur or selenium atoms

at these sites were estimated for each solid solution based on the assumption that the relative intensities of the three peaks due to S-S, S-Se, and Se-Se stretching modes are proportional to the ratio of the amount of S-S, S-Se, and Se-Se diatomic ions which occupy the chalcogen-chalcogen pair sites, respectively. The results are shown in Fig. 5 schematically, and as is seen in this figure, the selenium atoms show nearly complete preferential occupancy to the chalcogen-chalcogen pair sites. As compared to sulfur, selenium has less electronegative character (15), and it is considered that the selenium atoms have a stronger tendency to form the chalcogen-chalcogen pairs than the sulfur atoms in these solid solutions.

3. Phase Transitions and Softenings of the Raman Active Modes in $\text{CuS}_{1-x}\text{Se}_x$

As mentioned in the previous section, in the Raman spectra of CuS at 300 K, a strong

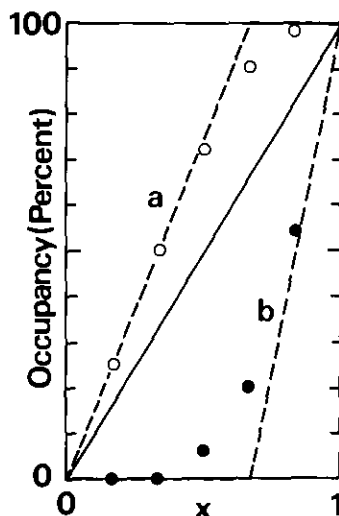


FIG. 5. Occupancies (%) of selenium atoms at $4e$ (chalcogen-chalcogen pair) and $2c$ sites in $\text{CuS}_{1-x}\text{Se}_x$ plotted against the composition x ($\text{CuS}_{1-x}\text{Se}_x$). Open and solid circles denote the occupancies of selenium atoms at $4e$ and $2c$ sites, respectively. Solid line denotes the occupancies of selenium atoms at $4e$ and $2c$ sites in the case of the random distribution. Broken lines a and b denote the occupancies of selenium atoms at $4e$ sites in the case of the complete preferential occupancies of selenium atoms at $4e$ sites, respectively.

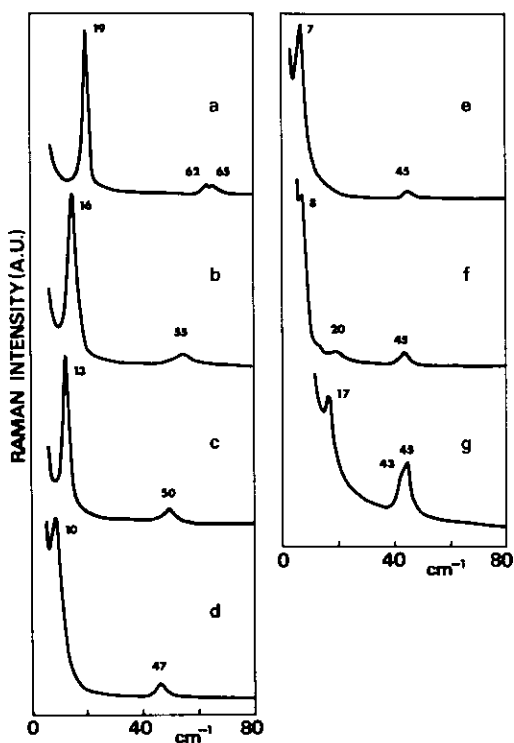


FIG. 6. Raman spectra of $\text{CuS}_{1-x}\text{Se}_x$ at 300 K in the frequency region below 80 cm^{-1} . (a), $x = 0.00$; (b), $x = 0.17$; (c), $x = 0.33$; (d), $x = 0.50$; (e), $x = 0.67$; (f), $x = 0.83$; (g), $x = 1.00$.

peak is observed at 19 cm^{-1} (Fig. 6a), and as is seen in Fig. 7a, this peak shifts to lower frequencies with decreasing temperature anomalously. For CuS, the phase transition due to the slight distortion from the high temperature hexagonal structure to the low temperature orthorhombic one is reported to take place at 55 K (2, 7, 16). The structural distortion is essentially a shift of the BN-like layers formed by Cu(1) and S(2c site) relative to the slabs including Cu(2) and S-S pairs (4e site), as shown in schematically in Fig. 8 (2). This phase transition is known to be second order and the number of atoms in a primitive unit cell does not change through the transition (2). These experimental results suggest that the some optical phonon modes at the zone-center are expected to soften at the phase transition (17). As is seen in Fig. 8, the features of the displacements

of atoms at the phase transition correspond to those of a Raman active E_{2g} mode of hexagonal CuS. Therefore, the observed 19 cm^{-1} Raman peak at 300 K mentioned above is considered to be due to a mode of E_{2g} symmetry, and this mode softens as the temperature is lowered to the transition temperature (55 K) (Fig. 7a).

As for $\text{CuS}_{1-x}\text{Se}_x$ with $x = 0.00, 0.33, 0.67,$ and 1.00 , the temperature dependences of the crystal structures were investigated by means of the X-ray powder diffraction method (9). The results suggest that the structural distortions from the high temperature hexagonal phases to the low temperature orthorhombic ones take place for $x = 0.33, 0.67,$ and 1.00 as well as $x = 0.00$. The transition temperatures estimated by this method for $x = 0.00, 0.33, 0.67,$ and 1.00 of $\text{CuS}_{1-x}\text{Se}_x$ are 55, 182, 361, and 396 K, respectively. In the Raman spectrum of each solid solution, a rather strong peak has also been observed in the frequency region below 20 cm^{-1} as reproduced in Fig. 6, and as is seen in Fig. 7, the temperature dependences of the frequencies of these peaks show anomalous behavior for all of the compounds except for CuSe. Of these, in the spectra of $\text{CuS}_{1-x}\text{Se}_x$ with $x = 0.17, 0.33,$ and 0.50 , the minimum of the frequency is observed in the frequency-temperature curve for each compound. The temperatures at the frequency minima are about 125, 170, and 230 K for $x = 0.17, 0.33,$ and 0.50 of $\text{CuS}_{1-x}\text{Se}_x$, respectively. The temperature for $x = 0.33$ approximately corresponds to that of the phase transition obtained by the X-ray powder diffraction method as mentioned above. As for the temperature dependences of the soft modes, Scott reviewed those in various compounds, and it was suggested that, for the several cases, the frequencies of the soft modes do not decrease to 0 cm^{-1} at the phase transition (17). Therefore, it may be reasonable to consider that the anomalous behavior of the temperature dependences of the observed frequencies in these solid solutions are also due to the softenings of the E_{2g} type

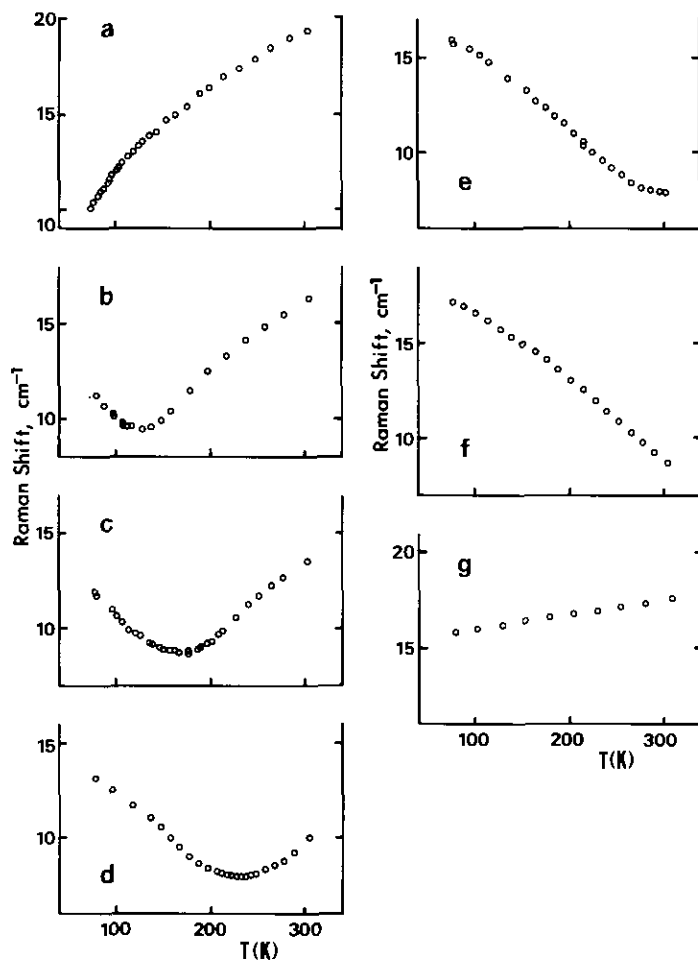


FIG. 7. Temperature dependences of the observed frequencies (cm^{-1}) of the lowest frequency Raman active modes in $\text{CuS}_{1-x}\text{Se}_x$. (a), $x = 0.00$; (b), $x = 0.17$; (c), $x = 0.33$; (d), $x = 0.50$; (e), $x = 0.67$; (f), $x = 0.83$; (g), $x = 1.00$.

modes at the phase transition. However, for the detailed investigation on the behavior of the soft modes in these solid solutions, the data obtained for the single crystal samples will be necessary. In the spectra of $x = 0.67$ and 0.83 of $\text{CuS}_{1-x}\text{Se}_x$, the observed frequencies decrease with increasing temperature in the temperature range below 300 K, suggesting that the phase transition temperatures are higher than 300 K (Fig. 7), and actually the phase transition temperature for $\text{CuS}_{1-x}\text{Se}_x$ with $x = 0.67$ obtained by the X-ray powder diffraction method is 361 K (9). For $\text{CuS}_{1-x}\text{Se}_x$ with $x = 0.17, 0.50,$ and

0.83 , the investigations on the temperature dependences of the crystal structures by the X-ray powder diffraction method are also in progress (9), and their preliminary results for $x = 0.17$ and 0.50 seem to be consistent with those of the Raman spectroscopic measurements. As for CuSe , the frequency of the lowest Raman active mode is not sensitive to temperature in the temperature range from 300 to 80 K (Fig. 7). The crystal structure of CuSe at 300 K is reported to be a hexagonal superstructure, and at 320 K, the structure changes to an orthorhombic one as mentioned in the previous section (8).

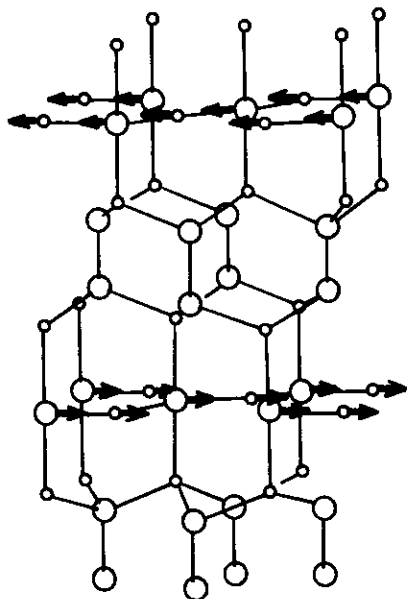


FIG. 8. Approximate displacements of atoms in hexagonal CuS at the phase transition of 55 K. Large and small open circles denote S and Cu atoms, respectively.

This phase transition is reported to be the first order one, and no Raman active mode may soften at this transition.

On the basis of the results of the Raman spectroscopic measurements together with those of the X-ray powder diffraction method (9), it is concluded that the structural phase transition similar to that reported for CuS takes place and the lowest frequency E_{2g} type Raman active mode softens at the phase transition for each solid solution $\text{CuS}_{1-x}\text{Se}_x$ ($x = 0.00-0.83$). These

results also suggest that the transition temperatures rise with increasing selenium contents from 55 K of CuS to 396 K of CuSe. It seems that the composition dependences of the transition temperatures are related to the anion distributions in $\text{CuS}_{1-x}\text{Se}_x$. To elucidate these relations in detail, further investigations are being made by means of the X-ray diffraction method (9).

References

1. K. SHIBATA, to be published.
2. H. FJELLVÅG, F. GRØNVOLD, S. STØLEN, A. F. ANDRESEN, R. MÜLLER-KÄFER, AND A. SIMON, *Z. Kristallogr.* **184**, 111 (1988).
3. I. NAKAI, Y. SUGITANI, K. NAGASHIMA, AND Y. NIWA, *J. Inorg. Nucl. Chem.* **40**, 789 (1978).
4. D. L. PERRY AND J. A. TAYLOR, *J. Mater. Sci. Lett.* **5**, 384 (1986).
5. J. C. W. FOLMER AND F. JELLINEK, *J. Less-Common Met.* **76**, 153 (1980).
6. K. OKAMOTO, S. KAWAI, AND R. KIRIYAMA, *Jpn. J. Appl. Phys.* **8**, 718 (1969).
7. H. NOZAKI, K. SHIBATA, AND N. OHASHI, *J. Solid State Chem.* **91**, 306 (1991).
8. A. L. N. STEVELS AND F. JELLINEK, *Recueil* **111**, 273 (1971).
9. H. NOZAKI, to be published.
10. C. SOURISSEAU, R. CAVAGNAT, AND M. FOUSSIER, *J. Phys. Chem. Solids* **52**, 537 (1991).
11. M. ISHII, unpublished work.
12. E. ANASTASSAKIS, *Solid State Commun.* **13**, 1297 (1973).
13. B. MÜLLER AND H. D. LUTZ, *Solid State Commun.* **78**, 469 (1991).
14. B. MÜLLER AND H. D. LUTZ, *Phys. Chem. Miner.* **17**, 716 (1991).
15. L. PAULING, "The Nature of the Chemical Bond," Chap. 3, Cornell Univer. Press, New York (1960).
16. E. F. WESTRUM, JR., S. STØLEN, AND F. GRØNVOLD, *J. Chem. Thermodyn.* **19**, 1199 (1987).
17. J. F. SCOTT, *Rev. Mod. Phys.* **46**, 83 (1974).