Table V. $NaCuO_2$[a]

atom	x	y	z
Na	0	$^1/_2$	$^1/_2$
Cu	0	0	0
O	0.345	0	0.575

[a] Monoclinic unit cell, space group $I2/m$, $Z = 2$, $a = 6.160$ (4) Å, $b = 2.747$ (2) Å, $c = 6.105$ (4) Å, and $\beta = 117.62$ (3)°.

shorter Cu–Cu distances of roughly 2.8 Å alternate with one longer distance of 2.84 Å. The Cu–O distances are within the expected range and vary from 1.83 to 1.96 Å.

The variety of different superstuctures observed in $Ca_{1-x}CuO_2$[2] suggests structural phase transitions due to ordering of calcium atoms on cooling from the growth temperature. At high temperature, the calcium atoms are disordered in the channels parallel to the a axis, the symmetry of the lattice being orthorhombic. On cooling, ordering of the calcium atoms sets in, but different superstructures may develop, depending on calcium stoichiometry, cooling rate, temperature gradient, oxygen partial pressure, etc., accounting for the variety of observed superstructures. For instance, the preparation method clearly affects the stoichiometry, where flux grown crystals show a calcium to copper ratio of 0.8, whereas single-phase powders obtained in an oxygen atmosphere show a ratio of 0.829. The difference in growth temperatures and oxygen partial pressure may account for this.

Comparing $Ca_{1-x}CuO_2$ to $NaCuO_2$, one notices that the average copper valence is reduced from Cu^{3+} in $NaCuO_2$ to $Cu^{2.4+}$ in $Ca_{1-x}CuO_2$. To account for the insulating properties of $Ca_{1-x}CuO_2$, a mixed copper valence may be assumed, giving $Ca_4Cu^{2+}{}_3Cu^{3+}{}_2O_{10}$. The presence of Cu^{3+} is consistent with the fact that the phase becomes unstable at higher temperatures, although its stability range exceeds that of $NaCuO_2$. Appropriate doping to stabilize Cu^{2+} should extend the stability range even further.

The unit cell of $NaCuO_2$ as determined from Guinier powder X-ray patterns[5] was found to be triclinic with $a = 2.748$ Å, $b = 6.671$ Å, $c = 3.462$, $\alpha = 76.2°$, $\beta = 113.4°$, and $\gamma = 128.1°$. This triclinic cell is pseudoorthorhombic as given above, and an attempt to index the given powder pattern indicated line splittings consistent with monoclinic symmetry, resulting in an I-centered unit cell with $a = 6.160$ Å, $b = 2.748$ Å, $c = 6.105$ Å, and $\beta = 117.62°$ (see Figure 2). The powder pattern for $NaCuO_2$ calculated by using this monoclinic unit cell, space group $I2/m$, and transformed atom coordinates matches the observed intensities. It is therefore suggested that $NaCuO_2$ is monoclinic, and, similar to $Ca_{1-x}CuO_2$, undergoes a structural phase transition from monoclinic to orthorhombic at high temperature. The transformed unit-cell parameters and atom coordinates are given in Table V.

Summary

In summary, we have shown that the crystal structure of $Ca_{1-x}CuO_2$ is related to the $NaCuO_2$-type structure. Linear $[CuO_2]$ chains form channels with calcium atoms disordered at high temperatures and ordered at lower temperatures. Different superstructures caused by calcium ordering may develop, depending on the cooling rate, temperature gradient, stoichiometry, etc. Because of the close relation between $Ca_{1-x}CuO_2$ and $NaCuO_2$, sodium doping of $Ca_{1-x}CuO_2$ should be possible to obtain a conducting phase. Different superstructures, commensurate as well as incommensurate, are expected for different doping levels, and charge density wave behavior may occur.

Note Added in Proof. A recent neutron investigation of $NaCuO_2$ by N. E. Brese et al. (*J. Solid State Chem.* **1989**, *83*, 1) established the monoclinic symmetry of the unit cell.

Acknowledgment. We thank S. Bayrakci for the preparation of the single-phase powders and D. W. Murphy for stimulating discussions.

Registry No. $CaCuO_2$, 57348-56-8; $Ca_{0.8}CuO_2$, 125648-48-8; $NaCuO_2$, 12174-73-1.

Supplementary Material Available: Listings of distances and bond angles (6 pages); listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

Preparation and Characterization of $Cu_2ZnGeS_{4-y}Se_y$

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Received November 6, 1989

Cu_2ZnGeS_4 can be prepared in both tetragonal stannite and orthorhombic wurtz–stannite phases, whereas $Cu_2ZnGeSe_4$ exists only in the tetragonal phase. Selenium can be substituted for sulfur up to 100% in the tetragonal structure of $Cu_2ZnGeS_{4-y}Se_y$ prepared at 700 °C and up to 75% in the orthorhombic structure prepared at 900 °C. The temperature at which the phase transformation takes place was found to increase with higher selenium concentration. Iron was substituted into both forms of $Cu_2Zn_{1-x}Fe_xGeS_{4-y}Se_y$, and the resulting magnetic properties indicated that the Fe–Fe superexchange interactions are the same in both structures.

Introduction

In recent years, ternary chalcopyrites and quaternary chalcogenides have been studied to observe their semiconducting and optical properties. Some of them are promising for nonlinear optics.[1] Quaternary chalcogenides having the formula $Cu^{I}{}_2B^{II}C^{IV}X_4$, where B^{II} = Mn, Fe, Co, Ni, and Zn, have been prepared and characterized previously.[2-5]

These chalcogenides form a large class of structurally related compounds. Their structure is derived from the

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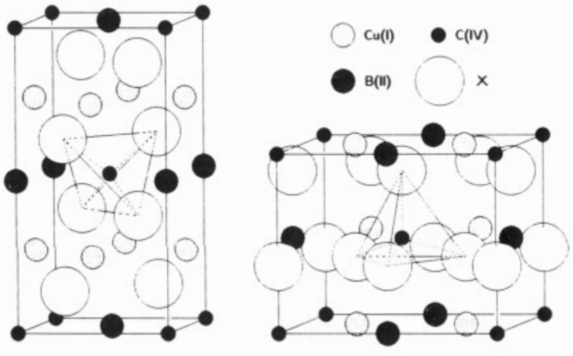

(a) Stannite (b) Wurtz–Stannite

Figure 1. Two possible structures of $Cu_2B^{II}C^{IV}X_4$.

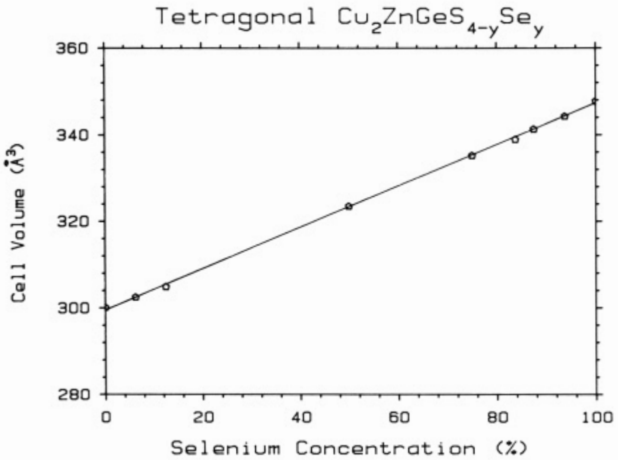

Figure 2. Vegards' law for tetragonal $Cu_2ZnGeS_{4-y}Se_y$.

zinc blende or wurtzite cell with an ordering of the metals on the cation sites. This leads to superstructures giving either a tetragonal or orthorhombic cell. The tetragonal stannite structure is derived from the zinc blende by doubling the lattice parameters in the *c* direction and has the space groups *I*42*m* (Figure 1). The orthorhombic wurtz–stannite cell is a superstructure of the wurtzite cell and has the space group $Pmn2_1$ (Figure 2). In both structures, there are two formula units per cell, each anion X is surrounded by two Cu(I), one B(II), and one C(IV), and every cation is tetrahedrally coordinated by X.

The compound Cu_2ZnGeS_4 crystallizes in the tetragonal stannite structure below 810 °C and the wurtz–stannite structure above 810 °C.[6] It is clear that the free energies of formation for these two structures are close in value. Schäfer and Nitsche[4] have indicated that the stannite and the wurtz–stannite structures are equally probable for compounds containing Ge(IV). However, the compound $Cu_2ZnGeSe_4$ crystallizes with the tetragonal stannite structure.[4] There have been no reports concerning studies of the system $Cu_2ZnGeS_{4-y}Se_y$. It is the purpose of this study to investigate the substitution of sulfur by selenium in the system $Cu_2ZnGeS_{4-y}Se_y$. Selenium will be substituted for sulfur in both the low-temperature and high-temperature phases to determine the solubility limits in each phase. The temperature at which the phase transformation occurs will also be studied as a function of selenium concentration.

The compound Cu_2FeGeS_4 crystallizes with the tetragonal stannite structure at all temperatures.[6] In this structure, the magnetic ions are never nearest neighbors. Nevertheless, antiferromagnetic Fe–Fe interactions yield a Weiss constant of −47 K.[5] Solid solutions between Cu_2ZnGeS_4 and Cu_2MnGeS_4 were shown to be interesting semimagnetic semiconductors.[7] It has been shown previously[6] that iron can be substituted for zinc in the tetragonal phase of $Cu_2Zn_{1-x}Fe_xGeS_4$ ($0 \le x \le 1$). More recently, it has also been observed that by quenching the samples, iron can be substituted in the high-temperature orthorhombic phase of $Cu_2Zn_{1-x}Fe_xGeS_4$ ($0 \le x \le 0.15$).[8] The magnetic properties of samples with the composition of $Cu_2Zn_{1-x}Fe_xGeS_4$ ($0 \le x \le 0.15$), crystallizing in the tetragonal phase (700 °C) or the orthorhombic phase (900 °C), were measured and showed the same Curie and Weiss constants. It would be interesting to attempt iron substitution into several thioselenides of $Cu_2Zn_{1-x}Fe_xGeS_{4-y}Se_y$, where both the tetragonal and orthorhombic phases can be obtained as single-phase materials. The magnetic properties would then be studied and compared to the magnetic properties of $Cu_2Zn_{1-x}Fe_xGeS_4$.

Experimental Section

Polycrystalline samples of $Cu_2Zn_{1-x}Fe_xGeS_{4-y}Se_y$ ($x = 0, 0.15, 0.20$; $0 \le y \le 4$) were prepared by combining stoichiometric weights of the elements. Prior to use, copper (Matthey 99.999%) and iron (Leico 99.999%) were reduced in an 85% Ar/15% H_2 atmosphere. Germanium (Cominco 7–9's, 40 Ω cm) and zinc (Gallard and Schlesinger 99.999%) were used after size reduction, while sulfur (Gallard and Schlesinger 99.999%) was sublimed before using. To each gram of charge, 5 mg of iodine was added (sublimed, Deepwater Chemical Co., Ltd., ACS reagent 99.9%).

The stoichiometric weights of the elements were introduced into a silica tube that was evacuated to 5×10^{-5} Torr. The tube was then sealed and enclosed in a tightly wound Kanthal coil to even out temperature gradients. The tube was then placed in a furnace and heated to 600 °C at the rate of 30 °C/h. The temperature was then raised to 650 °C for 24 h and then 700 °C for 72 h. the tube was then removed from the furnace and was opened, and the product was ground under a nitrogen atmosphere. The sample was then placed in another silica tube, evacuated, sealed, and placed back in the furnace for an additional 24 h at 700 °C. Since selenides are known to be toxic, it is advisable to use disposable gloves for these preparations.

Quenching Experiments. A portion of the tetragonal phase obtained at 700 °C was placed in a silica tube, evacuated, sealed, and then suspended by nichrome wire in a vertical furnace. The sample was heated to 900 °C, and after 24 h the wire was cut and the tube quenched into ice water.

Phase-Transformation Experiments. A portion of the tetragonal phase obtained at 700 °C for each of the three samples $Cu_2ZnGeS_{4-y}Se_y$ ($y = 0, 2.0, 3.0$) was placed in another silica tube and heated in the same furnace at each of the following temperatures for 24 h: 780, 790, 800, 820, 840, 875, and 900 °C. Each of the samples was then quenched immediately into ice water.

X-ray Analysis. Powder diffraction patterns of packed slides of these samples were obtained with a Philips diffractometer using high intensity Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å). For qualitative phase identification, patterns were taken with a scan rate of 1° 2θ/min, while cell parameters were determined from scans taken at 0.25° 2θ/min. Diffraction patterns were obtained over the range $12° \le 2\theta \le 72°$, and lattice parameters were determined by a least-squares refinement of the data using a computer program that corrected for the systematic errors in the measurement.

Magnetic Measurements. Magnetic measurements were made using the Faraday balance previously described,[9] which utilizes platinum as a standard. Magnetic susceptibilities were obtained as a function of temperature from 77 to 300 K in a field strength of 10.4 kOe. At both 77 and 300 K the field dependence from 6.22 to 10.4 kOe was also determined. The data were cor-

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Table I. Cell Constants for Tetragonal $Cu_2ZnGeS_{4-y}Se_y$ Prepared at 700 °C

y	cell vol, Å^3	a, Å	c, Å
0.00	300.1	5.342 (2)	10.516 (5)
0.25	302.5	5.357 (2)	10.540 (5)
0.50	304.9	5.373 (2)	10.561 (5)
2.00	323.5	5.479 (2)	10.776 (5)
3.00	335.2	5.541 (2)	10.919 (5)
3.35	338.9	5.563 (2)	10.951 (5)
3.50	341.3	5.578 (2)	10.970 (5)
3.75	344.3	5.592 (2)	11.009 (5)
4.00	347.7	5.610 (2)	11.049 (5)

Table II. Cell Constants for Orthorhombic $Cu_2ZnGeS_{4-y}Se_y$ Quenched from 900 °C

y	cell vol, Å^3	a, Å	b, Å	c, Å
0.00	301.2	7.509 (2)	6.479 (2)	6.192 (2)
0.50	306.0	7.549 (2)	6.514 (2)	6.222 (2)
0.75	308.6	7.572 (2)	6.532 (2)	6.239 (2)
1.00	312.3	7.604 (2)	6.558 (2)	6.263 (2)
2.00	323.7	7.694 (2)	6.638 (2)	6.338 (2)
2.50	328.9	7.737 (2)	6.673 (2)	6.371 (2)
3.00	335.7	7.794 (2)	6.717 (2)	6.412 (2)

rected for core diamagnetism by using the value for Cu_2ZnGeS_4 (1.305×10^{-4} emu/mol) previously reported.[10]

Results and Discussion

The compound Cu_2ZnFeS_4 crystallizes with the tetragonal stannite structure below 810 °C and transforms to the orthorhombic wurtz–stannite structure above this temperature (Figure 1). The selenium end member $Cu_2ZnGeSe_4$ crystallizes with the tetragonal stannite structure. In the present study, samples of $Cu_2ZnGeS_{4-y}Se_y$ with $0 \leq y \leq 4$ have been prepared at both 700 and 900 °C. At 700 °C a pure tetragonal stannite structure was obtained when selenium was substituted for sulfur in $Cu_2ZnGeS_{4-y}Se_y$ for $0 \leq y \leq 4$. There is an increase in the cell parameters as the larger selenium ion is substituted for the sulfur ion (Table I). The increase in the cell volume obeys Vegards' law as is illustrated in Figure 2. Therefore, in the low-temperature tetragonal phase, there is complete solid solution in $Cu_2ZnGeS_{4-y}Se_y$. When these samples were heated to 900 °C and quenched into ice water, a pure orthorhombic wurtz–stannite structure was obtained for $0 \leq y \leq 3$. By X-ray analysis, a multiphase region consisting of both the tetragonal and orthorhombic phases is found for $3 < y \leq 3.5$, but for samples with $3.5 < y \leq 4.0$ there is no sign of the orthorhombic phase. Higher temperatures could not be used because above 900 °C these samples begin to decompose. Hence, it has been shown that $Cu_2ZnGeSe_4$ remains tetragonal at temperatures up to the decomposition point. The cell parameters for the high-temperature orthorhombic phase are shown in Table II, while a Vegards' law plot for the orthorhombic phase is shown in Figure 3. There is a linear increase in the cell volume from $y = 0$ to $y = 3$ in $Cu_2ZnGeS_{4-y}Se_y$. Above $y = 3$, the cell volume no longer increases, which is consistent with the two-phase region identified by X-ray analysis. Therefore, a maximum of 75 at. % selenium can be substituted for sulfur in $Cu_2ZnGeS_{4-y}Se_y$ while still obtaining pure materials both below and above the transition temperature.

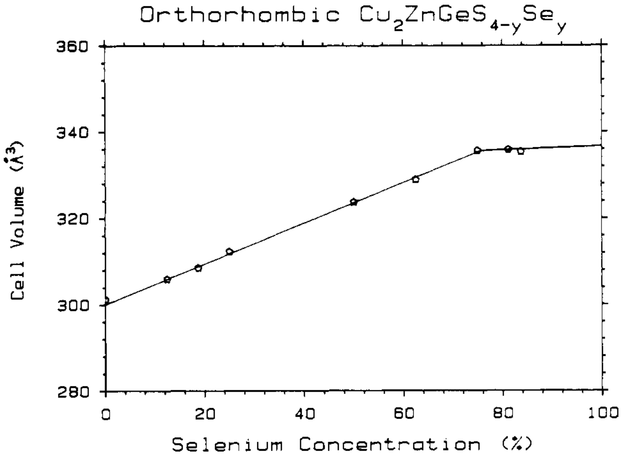

Figure 3. Vegards' law for orthorhombic $Cu_1ZnGeS_{4-y}Se_y$.

Table III. Phases[a] Adopted by $Cu_2ZnGeS_{4-y}Se_y$ at Various Temperatures

temp, °C	Cu_2ZnGeS_4	$Cu_2ZnGeS_2Se_2$	$Cu_2ZnGeSSe_3$
700	tet	tet	tet
780	tet + small amt orth	tet + trace orth	tet
790	orth	mixed	tet
800	orth	mixed	tet
820	orth	orth	mixed
840	orth	orth	mixed
875	orth	orth	mixed
900	orth	orth	orth

[a] tet = tetragonal; orth = orthorhombic.

The phase-transformation temperature from the low-temperature stannite structure to the high-temperature wurtz–stannite structure of $Cu_2ZnGeS_{4-y}Se_y$ (y = 0, 2.0, 3.0) was also investigated. It has been reported previously[6] that the phase-transformation temperature of Cu_2ZnGeS_4 was 810 °C. In the present study, samples of $Cu_2ZnGeS_{4-y}Se_y$ (y = 0, 2.0, 3.0) were heated at the temperatures listed in Table III for 24 h and were then quenched immediately into ice water to stabilize the high-temperature phase. The pure and member Cu_2ZnGeS_4 crystallizes with the tetragonal stannite structure at 700 °C, and as shown in Table III, at 790 °C the phase transition to the orthorhombic phase is complete. This transition temperature of 790 °C is slighly lower than reported by Ottenburgs.[6] When half the sulfur is replaced by selenium ($Cu_2ZnGeS_2Se_2$) the transition temperature is approximately 820 °C (Table III) which is 30 °C higher than the transition temperature in Cu_2ZnGeS_4. When there is a higher concentration of selenium present as in $Cu_2ZnGeSSe_3$, the transition temperature is raised further to 900 °C. Finally, the selenium end member $Cu_2ZnGeSe_4$ shows no phase transformation and crystallizes with the tetragonal stannite structure at all temperatures. Thus, as the selenium concentration in $Cu_2ZnGeS_{4-y}Se_y$ increases, the low-temperature tetragonal phase is stabilized with respect to the high-temperature orthorhombic phase. This can be seen in Figure 4, which shows three X-ray patterns of $Cu_2ZnGeS_{4-y}Se_y$ (y = 0, 2.0, 3.0) all heated to 790 °C for 24 h. For $y = 0$, only the high-temperature orthorhombic phase is present; for $y = 2.0$, there is a mixture of tetragonal and orthorhombic phases; the finally for $y = 3.0$, only the low-temperature tetragonal phase exists.

In previous studies,[6,8] iron was substituted for zinc in $Cu_2Zn_{1-x}Fe_xGeS_4$. The compound Cu_2FeGeS_4 crystallizes with the tetragonal stannite structure at all temperatures. It has been shown previously[6] that there was complete solid solution of $Cu_2Zn_{1-x}Fe_xGeS_4$ ($0 \leq x \leq 1$) in the low-temperature tetragonal phase. In the high-temperature orthorhombic phase of $Cu_2Zn_{1-x}Fe_xGeS_4$, single-phase materials with x = 0.05, 0.10, and 0.15 were made by quenching the samples into ice water from 900 °C.[8] The

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[10] Honig, E.; Shen, H.-S.; Yao, G.-Q.; Doverspike, K.; Kershaw, R.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1988**, *23*, 307.

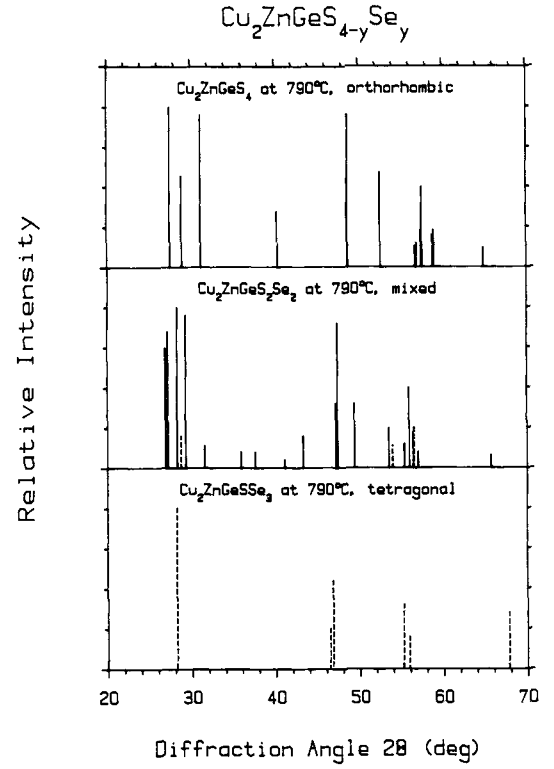

Figure 4. X-ray patterns for members of the system $Cu_2ZnGeS_{4-y}Se_y$.

magnetic properties of samples where $x = 0.05$, 0.10, and 0.15 in both the tetragonal and the orthorhombic phases with the same composition were measured and found to be similar in the two phases.[8]

It was reported by Schäfer and Nitsche[4] that the compound $Cu_2FeGeSe_4$ crystallizes with the tetragonal structure. In the present study, iron was substituted for zinc in the system $Cu_2Zn_{1-x}Fe_xGeS_{4-y}Se_y$ ($x = 0.15$, 0.20; $y = 2$, 2.5, 3.0, 4.0). These compounds have a much larger cell volume than Cu_2ZnGeS_4 due to the anion substitution (Tables I and II). The results of the iron substitution are that samples with $x = 0.15$ can be stabilized in the high-temperature orthorhombic phase of $Cu_2ZnGeS_2Se_2$ by quenching into ice water from 900 °C. By X-ray analysis, it is observed that a small amount of the tetragonal phase is also present in the $x = 0.20$ sample of $Cu_2Zn_{1-x}Fe_xGeS_2Se_2$. Therefore, 15 at. % Fe could be stabilized in both the tetragonal and the orthorhombic phases of $Cu_2Zn_{0.85}Fe_{0.15}GeS_{4-y}Se_y$ ($y = 0$, 2.0). When the selenium concentration is higher ($y = 2.5$, 3.0, 4.0), single-phase material where $x = 0.15$ could be obtained only in the low-temperature tetragonal phase. Since the end members Cu_2FeGeS_4 and $Cu_2FeGeSe_4$ both crystallize with the tetragonal cell at all temperatures, substituting iron and selenium into Cu_2ZnGeS_4 will stabilize the low-temperature stannite phase with respect to the high-temperature wurtz–stannite phase.

Magnetic susceptibility measurements were done on $Cu_2Zn_{1-x}Fe_xGeS_2Se_2$ ($x = 0.15$) in both the tetragonal and the orthorhombic phases. Field-independent behavior was observed, which indicated that there were not ferromagnetic phases present. The paramagnetic susceptibilities are shown in Figure 5 and obey the Curie–Weiss law. The observed Curie constants, Fe(II) magnetic moments, and Weiss constants are given in Table IV along with the magnetic data for both the tetragonal and orthorhombic phases of $Cu_2Zn_{0.85}Fe_{0.15}GeS_4$, and $Cu_2Zn_{0.85}Fe_{0.15}GeS_2Se_2$. The results indicate that the magnetic interactions of iron in both the tetragonal and orthorhombic phases of $Cu_2Zn_{1-x}Fe_xGeS_2Se_2$ ($x = 0.15$) are essentially equivalent. The results are similar to those observed for the system $Cu_2Zn_{1-x}Fe_xGeS_4$ ($x = 0.15$). The Weiss constants are small and negative in both systems for $x = 0.15$, indicating that weak net antiferromagnetic interactions predominate.

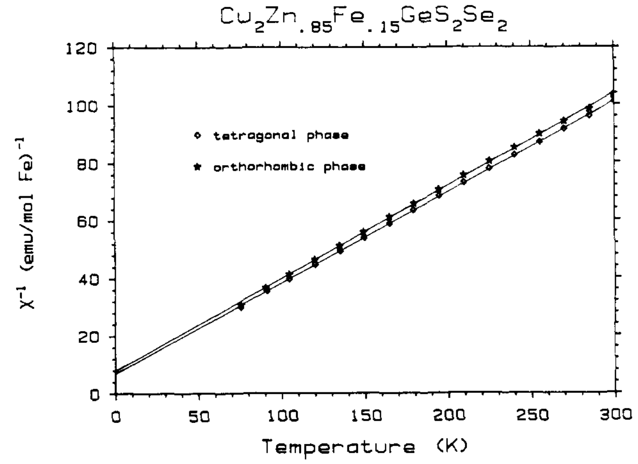

Figure 5. Magnetic susceptibility as a function of temperature for both phases of $Cu_2Zn_{0.85}Fe_{0.15}GeS_2Se_2$.

Table IV. Magnetic Data for $Cu_2Zn_{0.85}Fe_{0.15}GeS_{4-y}Se_y$

composition	phase	Curie constant	magnetic moment, μ_B	Weiss constant
$Cu_2Zn_{0.85}Fe_{0.15}$-GeS_4	tet (700 °C)	3.3	5.1	−20 (2)
$Cu_2Zn_{0.85}Fe_{0.15}$-GeS_4	orth (900 °C)	3.2	5.2	−22 (2)
$Cu_2Zn_{0.85}Fe_{0.15}$-GeS_2Se_2	tet (700 °C)	3.2	5.1	−22 (2)
$Cu_2Zn_{0.85}Fe_{0.15}$-GeS_2Se_2	orth (900 °C)	3.1	5.0	−25 (2)

Conclusions

The pure end member Cu_2ZnGeS_4 crystallizes in the tetragonal stannite structures below 790 °C, and the orthorhombic wurtz–stannite structure above 790 °C. The selenium end member crystallizes with the tetragonal stannite structure at all temperatures. Selenium can be substituted for sulfur up to 100% in the tetragonal structure of $Cu_2ZnGeS_{4-y}Se_y$ prepared at 700 °C and up to 75% in the orthorhombic structure prepared at 900 °C. The temperature at which the phase transformation takes place was found to increase with higher selenium concentration. Iron was substituted into both the low- and high-temperature forms of $Cu_2Zn_{0.85}Fe_{0.15}GeS_2Se_2$. Magnetic susceptibility measurements indicate no significant variation in the Curie or Weiss constants obtained from the tetragonal orthorhombic samples, which implies equality of the Fe–Fe superexchange interactions in both structures.

Acknowledgment. Thsi research was partially supported by the Office of Naval Research and by the National Science Foundation, DMR 890 1270, as well as the Exxon Education Foundation and Eastman Kodak Company.