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The Preparation and Characterization of the Solid Solution Series $CuFe_xGe_{1-x}S_2$ ($0.5 < x < 1.0$)

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Single crystals of the solid solution series $CuFe_xGe_{1-x}S_2$ ($0.5 < x < 1.0$) have been prepared by the chemical vapor transport technique. X-ray diffraction analysis and density measurements have indicated that all members of this system crystallize with the chalcopyrite structure. Mössbauer spectra show that these crystals contain both iron(II) and iron(III) on tetrahedral sites and that the iron concentration agrees with that determined by chemical analysis. Magnetic susceptibilities for $x = 0.53$ display antiferromagnetic behavior. The Néel temperature of 12°K and an effective moment of 5.0 BM is observed, which approaches the calculated spin-only moment of 4.92 BM. As x increases, deviations from spin-only behavior occur, indicating complex magnetic interactions.

Introduction

Chalcopyrite, $CuFeS_2$, crystallizes with an ordered zincblende structure, space group $I\bar{4}2d$, in which all the atoms occupy slightly distorted tetrahedral sites (*1*). The metal atoms are located at the centers of sulfur tetrahedra, each corner of which is shared by two neighboring tetrahedra (Fig. 1). Both Mössbauer (*2, 3*) and neutron diffraction (*4*) studies indicate that chalcopyrite is antiferromagnetic with a Néel temperature of 853°K. These studies also confirm that iron is present in the high spin d^5 electron configuration (Fe^{III}).[1]

Briartite, $CuFe_{0.5}Ge_{0.5}S_2$, has been reported to crystallize with a stannite-related structure in the space group $I\bar{4}2m$ (Fig. 2) (*5*). Wintenberger *et al.* (*6, 7*) have shown that briartite orders antiferromagnetically at 12°K and contains iron in the high spin d^6 state (Fe^{II}). It would be of interest to see if it is possible to prepare members of the intermediate solid solution series $CuFe_xGe_{1-x}S_2$ ($0.5 < x < 1.0$) either as polycrystalline powders or, preferably as single crystals. The members of this solution series would contain both Fe^{III} and Fe^{II} according to the stoichiometry $CuFe_xGe_{1-x}S_2 = CuFe^{II}_{1-x}Fe^{III}_{2x-1}Ge_{1-x}S_2$ ($0.5 < x < 1.0$). The growth, crystallographic, and magnetic properties of crystals which contain d^5 and d^6 iron on tetrahedral sites are reported.

Experimental

Single crystals of the solid solution series $CuFe_xGe_{1-x}S_2$ ($0.5 < x < 1.0$) were grown by the chemical vapor transport technique (*8*). The elements were purified before use. High purity copper (Matthey–Johnson 99.999%) was reduced in a 15% H_2/85% Ar atmosphere at 600°C for 4 hr. High purity iron (Leico 99.9999%) was reduced in a similar atmosphere at 950°C for 20 hr. Sulfur (Atomergic 99.9999%) was vacuum sublimed at 120°C and iodine (Baker 99.95%) at 50° to remove trace impurities. Electronic grade germanium (Gal-

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[1] In this paper, Fe^{II} and Fe^{III} will be used to denote the d^6 and d^5 electron configurations of iron, respectively.

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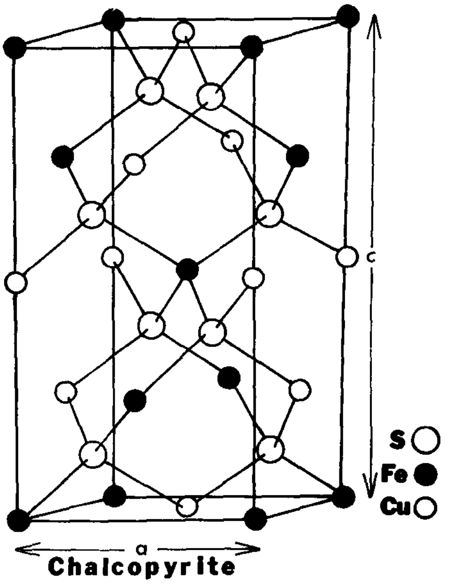


FIG. 1. The structure of chalcopyrite, space group $I\bar{4}2d$.

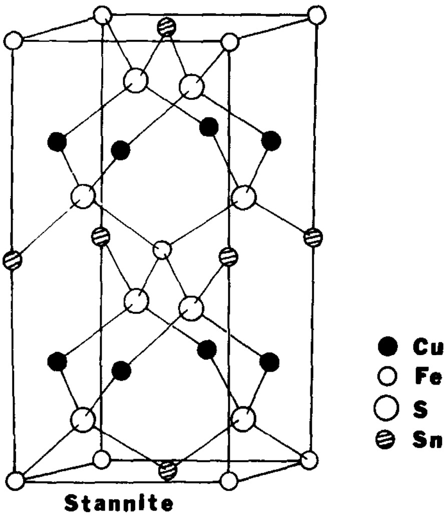


FIG. 2. The stannite structure, space group $I\bar{4}2m$. Note the ordering of the iron and tin atoms.

lard–Schlesinger 99.9999%) was used without further treatment.

Nominal stoichiometries of Cu, Fe, Ge, and S were introduced into an 11-mm i.d. silica tube and evacuated to 1 μmHg. After iodine (5 mg/cm^3) was sublimed inside (*9*), the silica tube was sealed. The sealed tube was wrapped with a tightly wound Kanthal wire (0.057-in. diam.) coil to even out extraneous temperature gradients within the transport furnace. The tube was heated for 12 hr, during which the growth zone was held 100°C higher than the charge zone. This process back-transported all nucleation sites from the growth zone. After thermal equilibration of the growth and charge zones, the temperature of the growth zone was then reduced over a period of 5 days to the values given in Table I. After the growth period, the tube was cooled slowly to room temperature. The crystals were removed and washed with absolute ethanol in order to extract the iodine. Using this method, crystals were produced with dimensions 10 × 4 × 1 mm and weights up to 60 mg. The crystals grew as platelets, with colors varying from black, for those with low iron content, to gold, for those with high iron content.

TABLE I

CONDITIONS OF PREPARATION OF $CuFe_xGe_{1-x}S_2$

Charge stoichiometry	Growth stoichiometry	Transport agent	Temperature gradient (charge zone–growth zone) (°C)	Duration (weeks)
$CuFe_{0.5}Ge_{0.5}S_2$	$CuFe_{0.53}Ge_{0.47}S_2$	I_2	850–790	3
$CuFe_{0.6}Ge_{0.4}S_2$	$CuFe_{0.65}Ge_{0.35}S_2$	I_2	840–780	3
$CuFe_{0.7}Ge_{0.3}S_2$	$CuFe_{0.75}Ge_{0.25}S_2$	I_2	825–750	3½
$CuFe_{0.8}Ge_{0.2}S_2$	$CuFe_{0.84}Ge_{0.16}S_2$	I_2	830–770	3
$CuFe_{0.9}Ge_{0.1}S_2$	$CuFe_{0.95}Ge_{0.05}S_2$	I_2	850–790	3

Chemical Analysis

In chemical vapor transport reactions of mixed solution series there is the possibility that the crystal growth stoichiometry differs from the charge (nominal) stoichiometry. To determine the true stoichiometry of the single crystals, iron analysis was performed using the photometric thiocyanate method (*10*, *11*). Known weights of the unknowns were dissolved in 50 ml of aqua regia. Oxides of nitrogen and sulfur were dispelled from the solution by boiling. Precipitated sulfur was removed by filtration. After 400 ml of water and 25 ml of 0.5 *M* potassium thiocyanate were added, the solution was diluted volumetrically to 500 ml with water. The absorbance at 480 μm of the red $(Fe(H_2O)_5SCN)^{2+}$ complex was measured at once on a Cary 14 spectrophotometer. Weighed amounts of freshly reduced high-purity iron were dissolved and used as references. A 0.025 *M* potassium thiocyanate solution was used as the blank. The charge and growth stoichiometries are listed in Table I.

Mössbauer Measurements

The iron-57 Mössbauer spectra of ground single crystals of $CuFe_xGe_{1-x}S_2$ $(0.5 < x < 1.0)$ were measured with a model NS-1 Mössbauer spectrometer (Nuclear Science and Engineering Corp.) operating in the constant acceleration mode. The 14.4-keV radiation emitted from 20 mCi of ^{57}Co diffused into Pd was detected with a gas proportional counter and collected with a 400-channel analyzer (Nuclear Chicago Corp.). Isomer shifts are reported with respect to the zero position of a crystal of sodium iron(II) nitropentacyanide dihydrate, $Na_2(Fe(CN)_5NO)\cdot 2H_2O$ (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting of the standard was taken as 1.7048 mm/sec (*12*).

Results, X-Ray Measurements, and Densities

X-ray powder diffraction patterns were obtained for ground single crystals of the members of the solution series $CuFe_xGe_{1-x}S_2$ $(0.5 < x < 1.0)$ with a Norelco diffractometer using monochromatic radiation (AMR Focusing Monochromator) and a high-intensity copper source ($CuK\alpha_1 = 1.5405$ Å). Scanning rates of 1° 2θ/min and $\frac{1}{4}$° 2θ/min were used. High purity silicon ($a_0 = 5.4301$ Å) was added as an internal standard in order to obtain precise lattice dimensions. Both stepcounting on ground crystals and long-exposure precession techniques on single crystals were used to search for reflections caused by the ordering of the iron and germanium atoms. Observation of the (101) reflection and the absence of the (110) and (002) reflections for all members of this series shows that the members adopt the $I\bar{4}2d$ chalcopyrite space group in which the Fe^{II}, Fe^{III}, and Ge atoms are distributed randomly upon the Fe sites of chalcopyrite. The precision lattice constants for the members of this series are given in Table II. The introduction of iron into briartite, $CuFe_{0.5}Ge_{0.5}S_2$, replaces germanium with the larger Fe^{III} atoms. In order to maintain electroneutrality, some of the Fe^{II} is converted into

TABLE II

CRYSTALLOGRAPHIC PARAMETERS AND DENSITIES FOR $CuFe_xGe_{1-x}S_2$

x	a (Å)	c (Å)	V (Å^3)	ρ_{obs}	ρ_{calc}
0.53	5.332(1)	10.531(1)	299.4	4.25(1)	4.25
0.65	5.334(1)	10.536(1)	299.7	4.20(1)	4.20
0.75	5.327(1)	10.531(1)	298.8	4.18(1)	4.17
0.84	5.304(1)	10.517(1)	295.8	4.19(1)	4.18
0.95	5.287(1)	10.488(1)	293.2	4.17(1)	4.17
1.0	5.280(1)	10.409(1)	290.2	4.18(1)	4.18

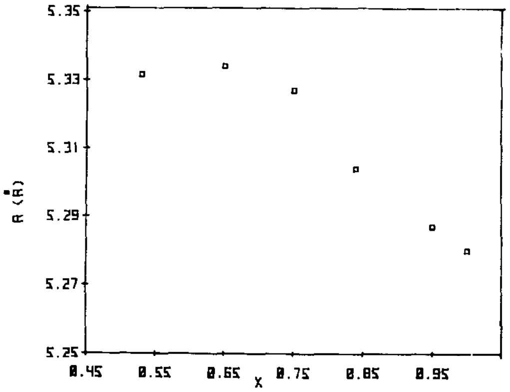


FIG. 3. The variation of the a_0 parameter with composition.

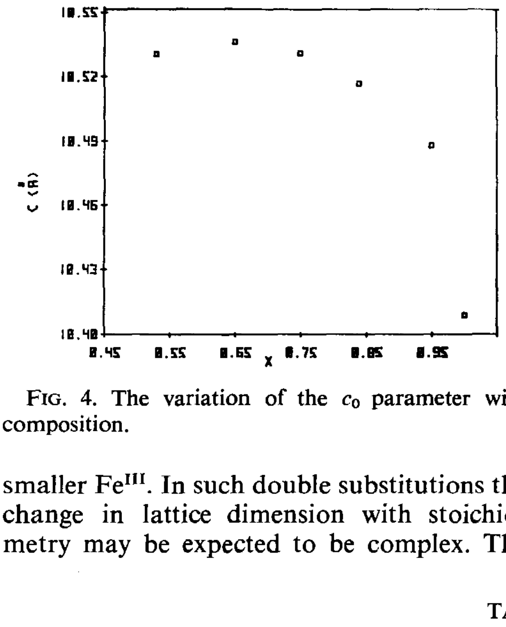


FIG. 4. The variation of the c_0 parameter with composition.

smaller Fe^{III}. In such double substitutions the change in lattice dimension with stoichiometry may be expected to be complex. The changes in the a_0- and c_0-axes with stoichiometry are shown in Figs. 3 and 4 and display a nonlinear behavior.

Densities of single crystals of the solid solution series $CuFe_xGe_{1-x}S_2$ $(0.5 < x < 1.0)$ were obtained by the hydrostatic technique (*13*) using perfluoro-(1-methyldecalin) as the fluid medium. Prior to each measurement, the fluid was calibrated against a single crystal of silicon with a density of 2.328 g/cm^3. All measurements were made at 24 ± 0.2°C and 31 ± 3% relative humidity. The observed densities are given in Table II with the values calculated from the analyzed stoichiometries and observed lattice constants.

Mössbauer Spectra

Mössbauer spectra of the members of the solid solution series $CuFe_xGe_{1-x}S_2$ where $x = 0.53$, 0.65, and 0.84 have been obtained. The spectra display two quadrupole split absorptions. From the quadrupole splittings it was possible to assign one of the doublets to Fe^{II} (QS 2.52–2.57 mm/sec) and the other doublet to Fe^{III} (QS 0.46–0.56 mm/sec). The ratio of the area under the Fe^{III} doublet to the area under the $Fe^{III} + Fe^{II}$ doublets (Fe^{III}/Fe_{total}) is presented in Table III, together with the ratios calculated from chemical analysis. Observation of the two distinct doublets displays the presence of both Fe^{II} and Fe^{III} in the chalcopyrite structure. Furthermore, the agreement between observed and calculated Fe^{III}/Fe_{total} ratios shows the concentrations of Fe^{II} and Fe^{III} to be consistent with chemical

TABLE III

THE ISOMER SHIFTS (IS) AND QUADRUPOLE SPLITTINGS (QS) FOR MEMBERS OF THE SERIES $CuFe_xGe_{1-x}S_2$ WHERE $x = 0.53$, 0.65, AND 0.84[a]

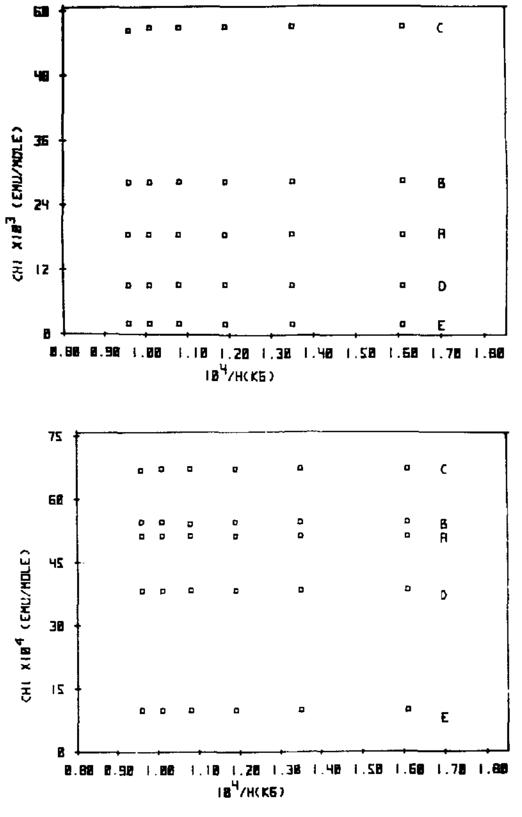
	Inner peaks (Fe^{III})		Outer peaks (Fe^{II})		Ratio of Fe^{III}/Fe_{total}	
x	IS	QS	IS	QS	Mössbauer	Analysis
0.53	0.568	0.55	0.884	2.52	0.13	0.11
0.65	0.546	0.47	0.857	2.57	0.42	0.46
0.84	0.567	0.49	0.858	2.48	0.70	0.81

[a] All spectra were recorded at 22 ± 2°C.

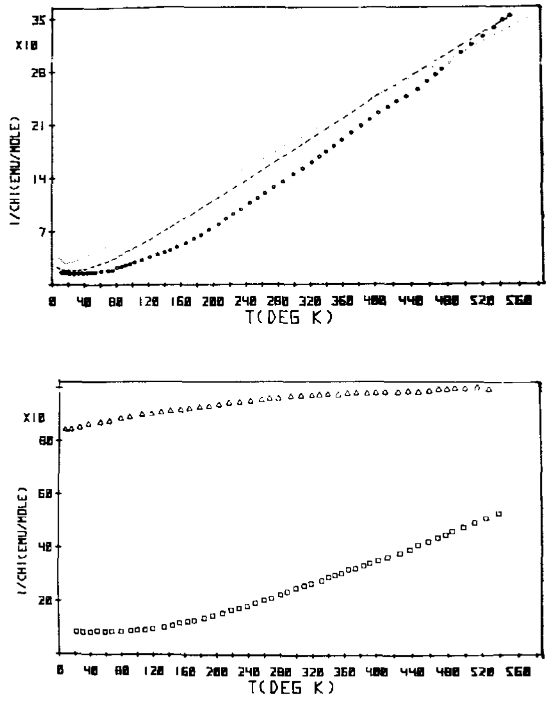
analysis. For members of the solution series with $x \geqslant 0.84$, a six-line magnetic hyperfine spectrum is seen; however, the lack of resolution of the peaks in this spectrum prevents an accurate determination of the area ratios and the Fe^{II} and Fe^{III} assignments.

Magnetic Measurements

Magnetic measurements were made using the Faraday balance described by Morris and Wold (*14*). For every sample the bulk magnetic susceptibility was measured as a function of field strength at 300 and 77°K (Honda–Owens method; *15*, *16*). The results are shown in Figs. 5 and 6. The lack of any field dependence indicates the absence of ferromagnetic impurities or bulk ferromagnetic order in these samples. The susceptibility was also measured as a function of temperature from 3 to 575°K. The plot of inverse susceptibility vs temperature for $CuFe_{0.53}Ge_{0.47}S_2$ is shown in Fig. 7. This material shows antiferromagnetic order with a Néel temperature of 12°K and a paramagnetic moment of 5.0 BM, which is consistent with a spin-only moment due to iron in the high spin d^6 configuration. For materials with a greater Fe concentration, complex magnetic behavior involving Fe^{II} and Fe^{III} situated randomly in a chalcopyrite structure appears. In the inverse susceptibility vs temperature curves (Figs. 7 and 8), this complex magnetic behavior is observed by a broadening of the Néel points as well as a reduction of the paramagnetic moment from the spin-only values. The magnetic parameters for these materials are summarized in Table IV.



FIGS. 5 and 6. The variation of the molar susceptibility with field strength at 300°K (Fig. 5) and at 77°K (Fig. 6) for $Cu(Fe_xGe_{1-x})S_2$. (A) $x = 0.53$; (B) $x = 0.65$; (C) $x = 0.75$; (D) $x = 0.84$; (E) $x = 0.95$.



FIGS. 7 and 8. χ_m^{-1} versus temperature for members of the solution series $Cu(Fe_xGe_{1-x})S_2$. ●●●, $Cu(Fe_{0.53}Ge_{0.47})S_2$; ---, $Cu(Fe_{0.65}Ge_{0.35})S_2$; ○○○, $Cu(Fe_{0.75}Ge_{0.25})S_2$; □□□, $Cu(Fe_{0.84}Ge_{0.16})S_2$; △△△, $Cu(Fe_{0.95}Ge_{0.05})S_2$.

TABLE IV

MAGNETIC PARAMETERS OF $CuFe_xGe_{1-x}S_2$

x	θ (°K)	T_N (°K)	$P_{eff(obs)}$ (BM)	$P_{eff(calc)}$ (BM)	Temperature of paramagnetic behavior (°K)
0.53	−12	12	4.99(2)	5.00	40–575
0.65	33	16	4.30(2)	5.36	100–575
0.75	80	16	3.56(2)	5.57	185–575
0.84	112	35	2.81(2)	5.72	300–575
0.95	Néel temperature and paramagnetic region				
1.0	above decomposition temperature 853 (*3*, *18*)				

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