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Preparation and Characterization of the System $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$

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Polycrystalline samples of the solid solution series $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ ($0 \leq x \leq 1.0$) have been prepared by direct combination of the elements. X-Ray diffraction analysis and density measurements have indicated that all members of the $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ system ($0 \leq x \leq 1.0$) crystallize with the chalcopyrite structure. Magnetic susceptibility data have shown that when $x = 0.025$, the observed moment for the iron approaches the spin-only values of $5.92 \mu_B$ calculated for high-spin iron (d^5). Deviations from the spin-only moment become appreciable when $x \geq 0.1$. Mossbauer spectra show at temperatures above 77°K the onset of antiferromagnetic order when $x \geq 0.5$.

Introduction

Chalcopyrite, CuFeS_2 , has been examined by many investigators¹⁻⁴ and found to crystallize in the space group $I\bar{4}2d$. Neutron diffraction studies on natural samples of CuFeS_2 have shown it to be antiferromagnetic.⁵ Mossbauer effect studies at 298°K have shown a six-line spectrum which indicates that the iron (d^5) is present in an ordered state.⁶⁻⁸ From susceptibility data, Teranishi reported a Neel temperature of 823°K for CuFeS_2 .⁶ Recently, it has been shown for CuFeS_2 that the Neel temperature is above the decomposition temperature of 663°K .⁴

CuGaS_2 has been reported to crystallize in the chalcopyrite structure.⁹ This material was found to be diamagnetic with a susceptibility of -20×10^{-6} emu/mole. In an attempt to investigate the nature of iron in CuFeS_2 , the solid solution series $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ ($0 \leq x \leq 1.0$) have been prepared. CuGaS_2 was chosen because it is isostructural with CuFeS_2 and is also a diamagnetic host. Magnetic susceptibility and Mossbauer measurements were made to study the onset of magnetic order with increasing iron content in the system $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$.

Experimental Section

Sample Preparation. Polycrystalline samples of $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ ($0 \leq x \leq 1.0$) were prepared by direct combination of the elements. Stoichiometric amounts of copper and iron (freshly reduced at elevated temperatures in a 15% H_2 -85% Ar gas flow) were combined with gallium and sulfur and placed in silica tubes, evacuated, sealed, and then heated from room temperature, at a rate of $15^\circ/\text{hr}$, to 600° where they were held for 1 day. [All elements, supplied by Gallard-Schlesinger, were at least 99.999% pure.] The tubes were then allowed to cool to room temperature over a period of 12 hr. The samples were shaken thoroughly and reheated at a rate of $25^\circ/\text{hr}$ to 900° , held at this temperature for 5 days, and allowed to cool to room temperature over a period of 24 hr. The sintered samples were then removed and ground in an agate mortar and pestle under an atmosphere of dry nitrogen. They were again sealed in evacuated silica tubes and heated at a rate of $75^\circ/\text{hr}$ to the temperatures listed in Table I, held at these temperatures for 6 days, and cooled at a rate

of $50^\circ/\text{hr}$ to room temperature. The samples were removed, ground under nitrogen, sealed in evacuated silica tubes, and then reheated at a rate of $75^\circ/\text{hr}$ to the temperatures listed in Table I. After 6 days at these temperatures, they were cooled at a rate of $50^\circ/\text{hr}$ to room temperature.

X-Ray Analysis. Samples prepared by the previously described procedure were analyzed by both fast ($1^\circ 2\theta/\text{min}$) and slow ($1/4^\circ 2\theta/\text{min}$) scan X-ray diffraction techniques using a Norelco diffractometer with monochromatic radiation (AMR-202 focusing monochromator) and a high-intensity copper source ($\lambda(\text{Cu } K\alpha_1) 1.5405 \text{ \AA}$). Lattice parameters were determined by a least-squares analysis of the data obtained from slow scan diffraction patterns with 2θ varying from 90 to 135° ; magnesium oxide ($a = 4.213 \text{ \AA}$) was used as an internal standard.

Density Measurements. Density determinations on several of the prepared polycrystalline samples were made by a hydrostatic technique¹⁰ using a Mettler Model H-54 analytical balance. Perfluoro(1-methyldecalin) (Pierce Chemical Co.) was used as the liquid medium and was first calibrated using a crystal of high-purity silicon (Gallard-Schlesinger, 99.9999%), $\rho = 2.328 \text{ g/cm}^3$. All measurements were conducted at $25 \pm 0.5^\circ$.

Magnetic Measurements. Magnetic susceptibility data were obtained using a Faraday balance¹¹ equipped with a Cahn RG electrobalance over the temperature range 77 - 500°K . The susceptibility was also measured as a function of field strength at 77 and at 298°K . The Honda-Owen technique¹² (plots of χ_M vs. $10^{-4}/H$) was used in order to ascertain the presence of ferromagnetic impurities. The effective magnetic moments were obtained from a least-squares analysis of the data which was corrected for diamagnetism. The values used for the diamagnetic corrections were -12×10^{-6} emu/mol for Cu^{2+} , -10×10^{-6} emu/mol for Fe^{3+} , -8×10^{-6} emu/mol for Ga^{3+} , and -38×10^{-6} emu/mol for S^{2-} .¹³

Mossbauer Measurements. The iron-57 Mossbauer spectra of $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ were measured with a Model NS-1 Mossbauer spectrometer (Nuclear Science and Engineering Corp.) operating in the constant-acceleration mode. The $14.4\text{-keV } \gamma$ radiation from a source of $20 \text{ mCi } ^{57}\text{Co}$ diffused into Pd was detected with a gas proportional counter and collected with a 400-channel analyzer (Nuclear Chicago Corp.) operating in time-sequence scaling mode. The source and drive were calibrated against a single crystal of sodium iron(II) nitropentacyanide dihydrate, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting was taken as 1.7048 mm/sec .¹⁴ Isomer shifts are reported with respect to the zero position of this standard. The sample cross sections were 28 mg/cm^2 , corresponding to 1 - 9 mg/cm^2 of total iron. The data were computer fit with a maximum likelihood regression analysis program to a product of lorentzian profiles superposed on a parabolic base line. All parameters, peaks positions, half-widths, and heights were allowed to vary independently. Cryogenic measurements were made in a variable-temperature dewar (Andonian Associates, Inc.). High-temperature measurements were made on compositions for which $x > 0.4$. The decomposition point of CuFeS_2 was determined to be 663°K by thermogravimetric analysis. There-

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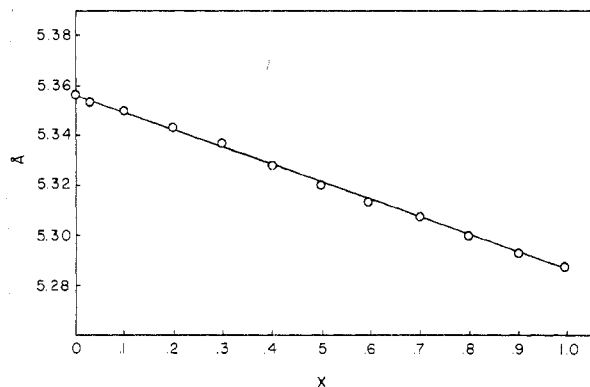
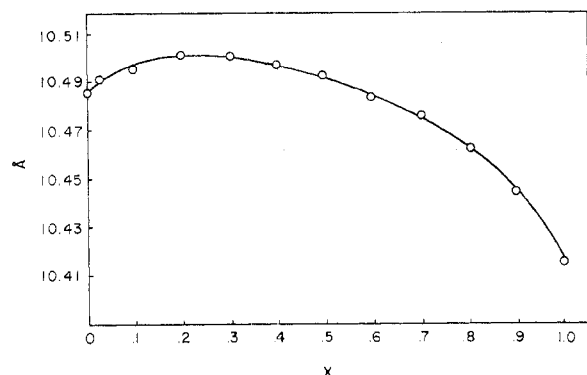
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Table I. Synthesis Temperatures for CuGa_{1-x}Fe_xS₂

Compn (x)	Third heating temp, °C	Final heating temp, °C	Compn (x)	Third heating temp, °C	Final heating temp, °C
0.0	800	800	0.5	600	600
0.025	775	775	0.6	700	550
0.1	750	750	0.7	700	550
0.2	750	750	0.8	700	700
0.3	700	700	0.9	750	750
0.4	650	650	1.0	800	800

Figure 1. *a* cell edge distance (Å) vs. composition (*x*) for CuGa_{1-x}Fe_xS₂.Figure 2. *c* cell edge distance (Å) vs. composition (*x*) for CuGa_{1-x}Fe_xS₂.

fore, no experimental data, for any of the compositions studied, were obtained above this decomposition temperature. Mossbauer data obtained at temperatures up to 663°K were fit by the method of least squares to a $J = 5/2$ reduced magnetization vs. reduced temperature curve. From these results accurate Neel temperatures were determined.

Results and Discussion

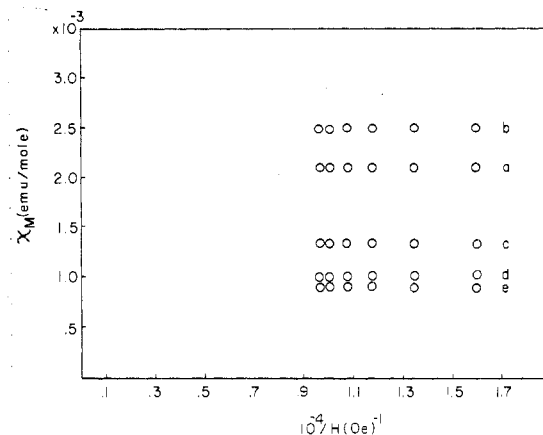
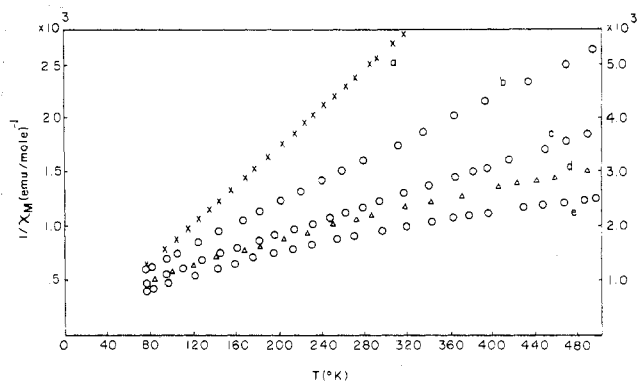
The powder X-ray diffraction data obtained for members of the system CuGa_{1-x}Fe_xS₂ are shown in Figures 1 and 2. The *a* axis was found to decrease linearly with increased iron content. This is consistent with the reported cell parameters for CuFeS₂ and CuGaS₂.^{9,15} However, the *c* axis initially increases, reaching a maximum at $x \approx 0.25$, and then decreases with continued increase in the iron content. This convex shape of the plot of the *c* axis vs. increasing iron content has been observed by Robbins, *et al.*, in similar systems of the type Cu_{1-x}Ag_xM^{III}X^{VI}₂ where M^{III} is In or Al and X^{VI} is S or Se.¹⁶ They have tentatively explained this behavior based on the formation of different cation-anion link-

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Table II. Lattice Parameters and Densities for CuGa_{1-x}Fe_xS₂

<i>x</i>	<i>a</i>	<i>c</i>	ρ_{calcd} , g/cm ³	ρ_{obsd} , g/cm ³
0.0	5.355 (1)	10.485 (1)	4.36	4.36 (2)
0.025	5.353 (2)	10.493 (2)		
0.1	5.349 (1)	10.496 (1)	4.33	4.33 (3)
0.2	5.344 (1)	10.501 (1)	4.31	
0.3	5.339 (1)	10.499 (1)	4.29	4.29 (2)
0.4	5.329 (2)	10.498 (3)	4.27	
0.5	5.321 (2)	10.494 (2)	4.26	4.26 (2)
0.6	5.313 (2)	10.483 (2)	4.24	
0.7	5.307 (1)	10.476 (2)	4.22	4.22 (1)
0.8	5.301 (2)	10.465 (1)	4.21	
0.9	5.295 (3)	10.446 (3)	4.19	4.19 (1)
1.0	5.291 (2)	10.415 (5)	4.18	4.13 (2)

Figure 3. Honda-Owen plots at 77°K for CuGa_{1-x}Fe_xS₂: a, $x = 0.2$; b, $x = 0.4$; c, $x = 0.6$; d, $x = 0.8$; e, $x = 1.0$.Figure 4. Inverse susceptibility vs. temperature for CuGa_{1-x}Fe_xS₂. For this composition (a, $x = 0.025$), use right ordinate axis: b, $x = 0.1$; c, $x = 0.2$; d, $x = 0.3$; e, $x = 0.4$.

ages along the *c* and *a* crystallographic directions. The lattice parameters for the CuGa_{1-x}Fe_xS₂ series, as well as experimental densities for several of these compositions, are listed in Table II.

Magnetic susceptibility data have been obtained between 77 and 500°K for CuGa_{1-x}Fe_xS₂. Field dependence measurements were made at 77 and 298°K and at fields ranging from 6.25 to 10.30 kOe. This was done in order to confirm the absence of ferromagnetic impurities. Figure 3 shows plots of susceptibility vs. inverse field for several compositions at 77°K. As can be seen, there are no ferromagnetic impurities present in the samples studied.

Plots of inverse susceptibility vs. temperature for the CuGa_{1-x}Fe_xS₂ series are shown in Figures 4 and 5. For compositions where $x \leq 0.2$, the inverse susceptibilities vary linearly with temperature. The magnetic moments and Weiss constants (μ_{eff} , Θ) for these compositions are listed in Table III. It can be seen that for $x = 0.025$ the magnetic

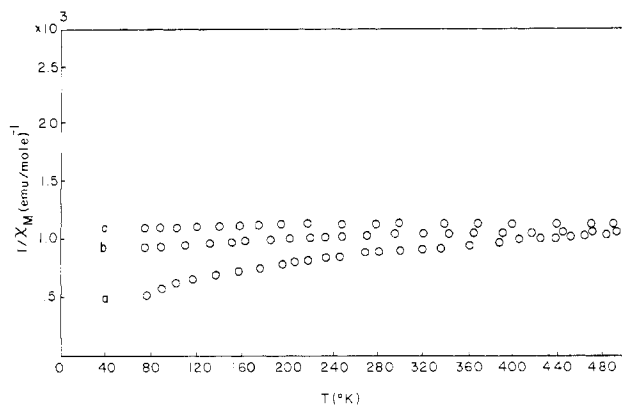


Figure 5. Inverse susceptibility vs. temperature for $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$: a, $x = 0.5$; b, $x = 0.7$; c, $x = 1.0$.

Table III. Magnetic Moments and Weiss Constants for $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$

x	μ_{eff} , BM	Θ , °K
0.025	5.49 (6)	-46 (3)
0.1	4.42 (1)	-70 (1)
0.2	3.90 (1)	-129 (2)

moment approaches the spin-only moment for Fe^{3+} of $5.92 \mu_B$. The magnetic moment decreases with increasing iron content and there is also a corresponding increase in the negative Weiss constant. The behavior exhibited by compositions of the system $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ is similar to that reported for the system $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$.¹⁷ In this mixed-oxide system, extrapolation of the moment for the Fe^{3+} ion to infinite dilution gave a value of $5.9 \mu_B$. Increased iron substitution, in both systems, results in a decrease in the magnetic moment. For low iron concentrations, the reduction in the magnetic moment per Fe^{3+} may reflect the formation of antiferromagnetically coupled Fe-Fe pairs.

Compositions in the system $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ with $x \geq 0.3$ do not follow Curie-Weiss behavior, Figures 4 and 5. These deviations may be due to the formation of a significant number of iron atom clusters which order antiferromagnetically relative to the number of isolated iron atoms present in these materials. This has been shown to be the case for manganese and iron substituted into ZnS .^{18,19} The presence of iron atom clusters in the $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$ system may be related to the absence of an observed Neel point in the susceptibility data and a reduction of the paramagnetic moments.

The inverse susceptibility for compositions with $x \geq 0.7$ approaches temperature independence, a behavior similar to the magnetic behavior of CuFeS_2 below the Neel point.^{4,6}

Mossbauer studies were made on the system $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$. Spectra obtained at 77 and at 298°K for several compositions are illustrated in Figures 6 and 7. Compositions with $x \leq 0.3$ appear to contain only iron (d^5) in the paramagnetic state above 77°K. A well-defined six-line hyperfine spectrum first appears at 77°K for the composition $x = 0.5$ and at 298°K for the composition $x = 0.6$. Spectra for compositions with $x > 0.7$ are similar to that for CuFeS_2 .²⁰ The internal fields at 77 and 298°K for compositions showing a hyperfine spectrum are listed in Table IV. The internal field

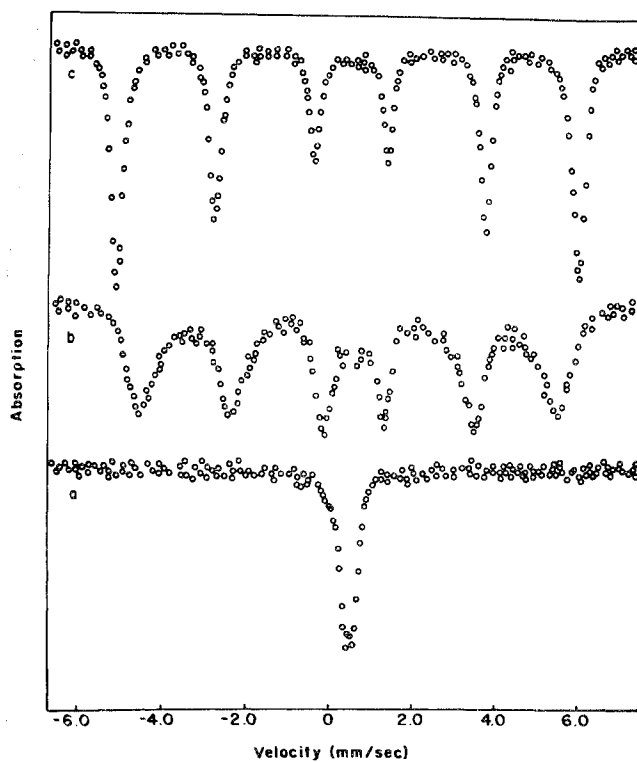


Figure 6. Mossbauer spectra at 77°K for $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$: a, $x = 0.2$; b, $x = 0.5$; c, $x = 0.9$.

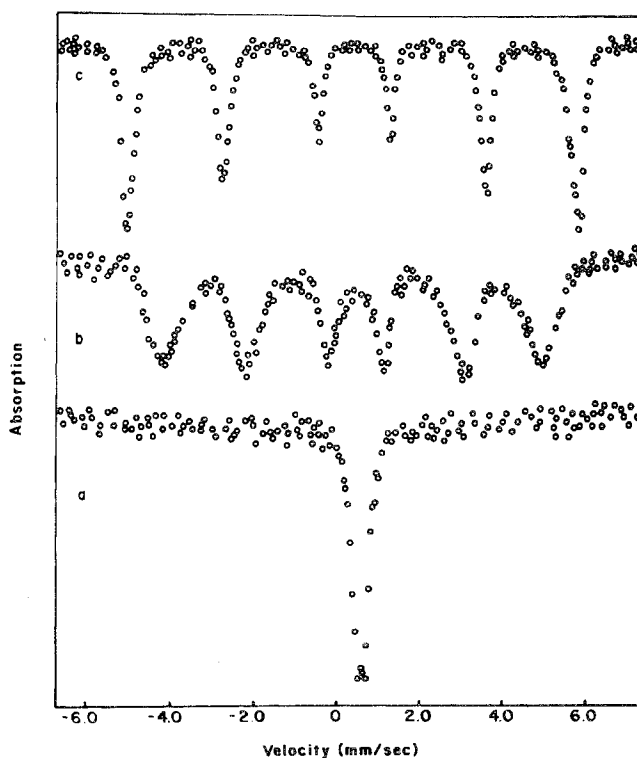


Figure 7. Mossbauer spectra at 298°K for $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$: a, $x = 0.3$; b, $x = 0.6$; c, $x = 0.9$.

Table IV. Internal Fields for $\text{CuGa}_{1-x}\text{Fe}_x\text{S}_2$

x	H , kOe		x	H , kOe	
	77°K	298°K		77°K	298°K
1.0	367 (3)	347 (3)	0.7	348 (3)	312 (3)
0.9	356 (3)	340 (3)	0.6	334 (3)	290 (3)
0.8	351 (3)	328 (3)	0.5	314 (3)	

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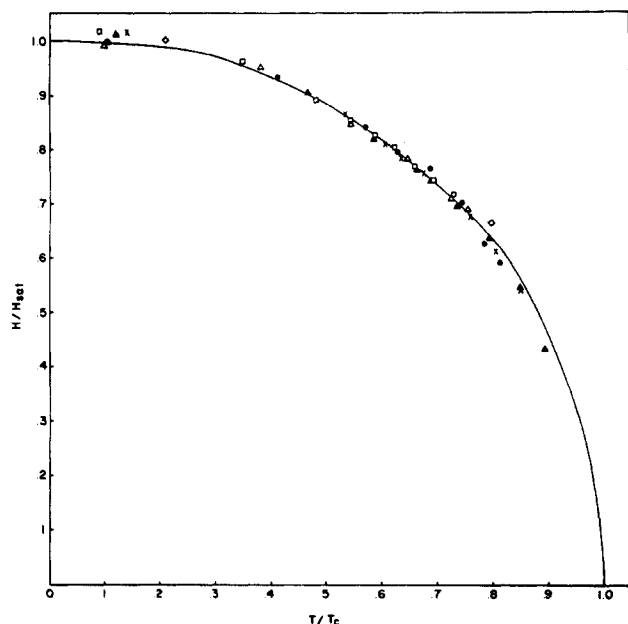


Figure 8. Reduced magnetization vs. reduced temperature for CuGa_{1-x}Fe_xS₂, 0.5 ≤ x ≤ 1.0: ○, x = 0.5; ×, x = 0.6; ▲, x = 0.7; ●, x = 0.8; △, x = 0.9; □, x = 1.0.

strengths increase at both temperatures with increased iron substitution, indicating a strengthening of the magnetic interactions. An isomer shift of 0.44 (5) mm/sec is observed at 298°K for all materials. These shifts are indicative of Fe³⁺ in a sulfur environment and are consistent with previously reported data.⁸ Spectra obtained in the paramagnetic state show a small quadrupole splitting. This is apparently due to a slight distortion from perfect tetrahedral symmetry and is consistent with the measured cell parameters which result in $c/a \neq 2$. Temperature-dependent Mossbauer data have been obtained for compositions where 0.5 ≤ x ≤ 1.0. For each of these compositions, the internal field strength decreases with increasing temperature. The collapse of the hyperfine splitting was observed for compositions where x = 0.5, 0.6, and 0.7. All the high-temperature data were fit to a plot of reduced magnetization vs. reduced temperature for $J = 5/2$, as illustrated in Figure 8. For compositions

Table V. Neel Temperatures for CuGa_{1-x}Fe_xS₂

x	T _N , °K	x	T _N , °K
1.0	853 (3)	0.7 ^a	635 (4)
0.9	777 (3)	0.6 ^a	553 (5)
0.8	723 (4)	0.5 ^a	440 (6)

^a For these compositions the complete collapse of the hyperfine spectrum was observed. For compositions where x > 0.7, the Neel temperatures were obtained by extrapolation.

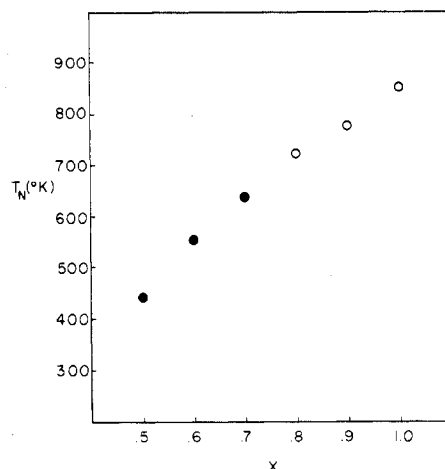


Figure 9. Neel temperatures for CuGa_{1-x}Fe_xS₂ vs. composition. The open circles indicate Neel temperatures obtained by extrapolation of data obtained below the decomposition temperature.

where x = 0.8, 0.9, and 1.0, the Neel temperatures were extrapolated from data obtained below their decomposition temperatures. The Neel temperatures are listed in Table V and Figure 9 illustrates their linear increase with increasing iron content.

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