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Structural Properties of Layer $Cr_{0.87}Ga_{1.80}S_4$ Compound

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The crystal structure of $Cr_{0.87}Ga_{1.80}S_4$ ($a = 3.640(2)$ Å; $c = 12.037(4)$ Å; $Z = 1$; space group $P\bar{3}m1$) has been refined to a final $R = 0.085$ with 308 independent reflections. The sulfur stacking sequence is *hhhh* in type, with Cr atoms occupying the octahedral voids and Ga atoms the tetrahedral voids. Vacancies are distributed within all sheets of the lattice. The trigonal distortion ε of the octahedral sites has been determined by EPR investigations. © 1988 Academic Press, Inc.

Introduction

$ZnIn_2S_4$-type structures containing magnetic ions are good candidates for obtaining two-dimensional (2D) magnetic systems. Nevertheless, all attempts to observe a two-dimensional magnetic behavior failed in the cases of $MnAl_2X_4$ (*1*), α-$FeGa_2S_4$ (*2*), $Co_xZn_{1-x}In_2S_4$ (*3*), and $CoGaInS_4$ (*4*). Indeed, Mn^{2+}, Fe^{2+}, and Co^{2+} ions could not be completely localized in only one layer of the lattice and, therefore, their magnetic properties can be better understood in terms of short-range magnetic order (*5*).

During the study of the phase diagram of the system Cr_2S_3–Ga_2S_3 (*6*) we discovered the new layer compound $Cr_{0.87}Ga_{1.80}S_4$, which is isomorphous with α-$FeGa_2S_4$ (*7*). On the basis of the X-ray powder diagram, its magnetic behavior was explained assuming a two-dimensional model (*8*) with Cr^{3+} ions lying in a triangular planar sublattice.

This paper deals with a single-crystal structure refinement of $Cr_{0.87}Ga_{1.80}S_4$, which shows that chromium(III) is located only within the octahedral sheets and, therefore, confirms the previously suggested 2D model. Moreover, an EPR study allowed us to estimate the trigonal distortion of the sixfold coordinated sites.

Experimental

Single crystals of $Cr_{0.87}Ga_{1.80}S_4$ were obtained by a two-step process. A polycrystalline sample was first prepared by passing a stream of H_2S over a stoichiometric amount of Ga_2S_3 and Cr_2S_3 in a glassy carbon crucible at 750°C for 2 hr and at 1100°C for 5 min to eliminate possible impurities of oxygen; samples were then annealed 2 hr at 750°C to avoid possible sulfur vacancies. Single crystals were then obtained by heating the polycrystalline specimen in a small evacuated silica ampoule with 3 mg of I_2/1 g of sample, at 1000°C for 7 days. The single

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TABLE I

CRYSTAL DATA, ATOMIC PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$), AND ATOMIC OCCUPANCY FOR $Cr_{0.87}Ga_{1.80}S_4$

Atom	Occ.	x	y	z	$U_{11} = U_{22}$	U_{33}	$U_{23} = U_{13}$	U_{12}
Cr	0.43	0	0	0	76(10)	10(8)	0	38(5)
Ga	0.90	2/3	1/3	0.2947(1)	157(30)	16(10)	0	78(15)
S(1)	1.00	2/3	1/3	0.1054(2)	94(45)	28(20)	0	47(18)
S(2)	1.00	1/3	2/3	0.3675(2)	110(49)	35(17)	0	55(21)

Note. $Cr_{0.87}Ga_{1.80}S_4$; $M = 298.9$; space group $P\bar{3}m1$; $a = 3.640(2)$, $c = 12.037(4)$ Å; $V = 159.49$ Å^3; $Z = 1$; $F(000) = 141.80$.

crystals were obtained as thin black platelets.

Crystal data were collected on a Syntex P21 diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Three hundred eight independent reflections with $I > 3\sigma(I)$ were measured. The hkl, $\bar{h}kl$, and $h\bar{k}l$ reflections were collected up to $2\theta_{\max} = 85°$ and then the symmetry equivalent intensities were averaged. Lp and semiempirical absorption corrections, based on a 360° ψ scan around the scattering vector of selected reflections, were applied.

The structure was solved by means of three-dimensional Fourier synthesis and refined by full-matrix least-squares calculation using the SHELX 76 program system (*9*). The scattering factors and the corrections for the anomalous scattering were taken from the "International Tables for X-Ray Crystallography" (*20*). Final anisotropic refinement led to an R factor of 0.085; this relatively high value is due to the poor quality of the single crystals. Crystal data, final atomic coordinates, and anisotropic temperature factors are listed in Table I. Bond lengths and bond angles are reported in Table II.

Due to the extreme thinness of the samples, EPR spectra were recorded on crushed crystals at $\nu = 9115$ MHz in the temperature range $90 \leq T \leq 310$ K using a Varian E9 spectrometer. The field was measured with a Bruker NM-20 Gaussmeter and the frequency with a Sistron Donner (Model 6346A) counter.

Crystal Structure

As reported in Table I, $Cr_{0.87}Ga_{1.80}S_4$ crystallizes in the space group $P\bar{3}m1$ with cell parameters $a = 3.640(2)$ Å, $c = 12.037(4)$ Å. Referring to the widely studied $ZnIn_2S_4$ polytypes family (*10*), the structure can be described by a close packing of sulfur atoms following the sequence

$$\begin{array}{ccccccccccccccc} \mathrm{S} & \equiv & \mathrm{Ga} & — & \mathrm{S} & \equiv & \mathrm{Cr} & \equiv & \mathrm{S} & — & \mathrm{Ga} & \equiv & \mathrm{S} & \square & \mathrm{S} \\ B & & \gamma & & C & & a & & B & & \beta & & C & & B \end{array}$$

sulfur stacking of *hhhh* in type, where the full lines indicate the chemical bonds, the greek letters the layers of gallium atoms in tetrahedral voids, the small letters the chro-

TABLE II

BOND LENGTHS (Å) AND BOND ANGLES (°) FOR $Cr_{0.87}Ga_{1.80}S_4$ (ESTIMATED STANDARD DEVIATIONS ARE IN PARENTHESES)

$Cr–S_1$	2.455(1)	$S_1–Cr–S_1$	95.7(1)
$Ga–S_1$	2.279(3)	$S_1–Cr–S_1$	84.3(2)
$Ga–S_2$	2.277(1)	$S_2–Ga–S_2$	106.1(1)
$S_1–S_2$	3.791(3)	$S_1–Ga–S_2$	112.6(1)
		$Cr–S_1–Ga$	121.1(1)

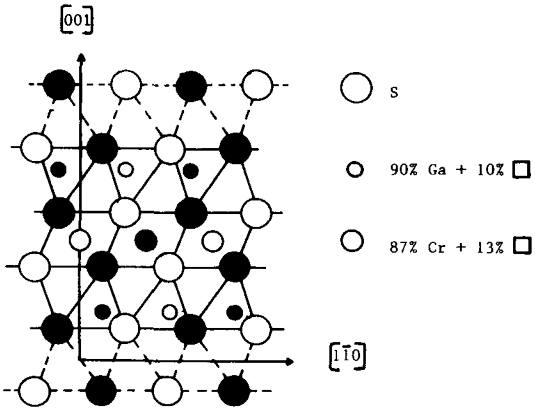

FIG. 1. (110) Section through the structure of $Cr_{0.87}Ga_{1.80}S_4$. Black circles are atoms at $\pm a/2$.

mium atoms in octahedral voids, and where the fourth layer is completely empty (□). All the layers are perpendicular to the c direction. The ratio $c/a \cdot n = 0.827$ ($n = 4$ is the number of sulfur layers in the unit cell) is close to the value $\sqrt{2/3} = 0.816$ for an ideal close packing of the anions.

With respect to the other $ZnIn_2S_4$-type structures (*1, 7, 10*), in $Cr_{0.87}Ga_{1.80}S_4$ vacancies are present also in γ, a, and β layers (Fig. 1), due to the fact that both chromium and gallium are present as trivalent ions. The octahedral sites Ω are occupied by Cr^{3+} ions and vacancies in the ratio 87 and 13%, respectively. The presence of a center of symmetry in the structure indicates that the tetrahedral voids τ (in γ position within the first sheet as well as in β within the third sulfur layer) are occupied by 90% Ga^{3+} and 10% vacancies. A random or ordered disposition of gallium atoms and vacancies cannot be inferred from present X-ray results.

The thickness of the different layers along the [001] axis (Fig. 1) is:

$$L(\tau) = 3.155\ \text{Å};\quad L(\square) = 3.190\ \text{Å};\quad L(\Omega) = 2.537\ \text{Å},$$

indicating a compression of the octahedral layer with respect to the tetrahedral ones, as found in α-$FeGa_2S_4$ ($L(\tau) = 3.159$ Å; $L(\square) = 3.149$ Å; $L(\Omega) = 2.587$ Å) (*7*).

The Ga–S and Cr–S bond lengths (Table II) are close to the sum of the ionic radii, 2.29 and 2.43 Å, respectively ($r_{Ga^{3+}} = 0.47$ Å, $r_{Cr^{3+}} = 0.61$ Å, $r_{S^{2-}} = 1.82$ Å) (*11*). These values are in agreement with those found in $MgGa_2S_4$ (2.26 Å), α-$FeGa_2S_4$ (2.25 Å), and α-Ga_2S_3 (2.27 Å) for Ga–S (*7, 12, 13*) and in $LaCrOS_2$ (2.45 Å) for Cr–S (*14*).

EPR Results

The octahedral sites have a trigonal symmetry in space group $P\bar{3}m1$, and the trigonal distortion ε, related to the zero-field splitting parameter D ($\varepsilon = D \cdot \Delta_0/8\lambda^2\kappa^2$) (*15*), can be calculated from the EPR linewidth. According to Anderson and Weiss's theory (*16*) the magnetic exchange integral J is related to the half-width at half-power ($\Delta H_{1/2}$) of an exchange narrowed EPR line by the expression:

$$\Delta H_{1/2} = M_2/H_e, \qquad (1)$$

where M_2 includes all the line-broadening mechanisms and $H_e = C \cdot J$ is the exchange field.

The EPR spectrum of $Cr_{0.87}Ga_{1.80}S_4$ consists of a single signal with a peak-to-peak linewidth ($\Delta H_{pp} = 410$ G) for $90 \leq T \leq 310$ K. The lineshape is strictly Lorentzian in the whole temperature range: the experimental reduced amplitude $|Y'/Y'_M|$ fits the theoretical curve very well (Fig. 2). Therefore, we conclude that an exchange mechanism is operating in our case and ΔH_{pp} is related to $\Delta H_{1/2}$ by the formula:

$$\Delta H_{1/2} = \sqrt{3}/2 \cdot \Delta H_{pp}. \qquad (2)$$

As far as the broadening mechanisms are concerned, the considerations reported for layer $ACrO_2$ compounds (*17*) are still valid and Eq. (1) is written in the final form:

$$\sqrt{3}/2 \cdot \Delta H_{pp} = \frac{10/3\ M_2^{d} = M_2^{cf}}{C \cdot J}. \qquad (3)$$

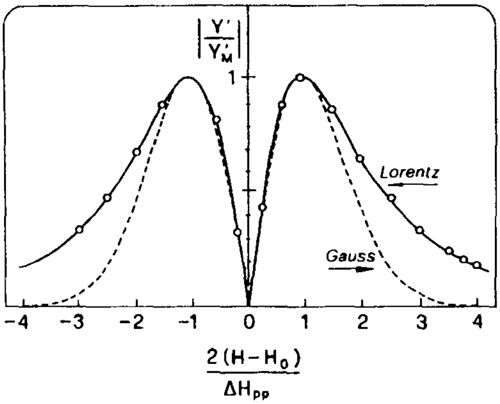

FIG. 2. Reduced amplitude $[Y'/Y'_M]$ vs $[2(H - H_0)/\Delta H_{pp}]$ at $T = 310$ K: ○, experimental points; Lorentzian (—) and Gaussian (- - -) curves.

M_2^d represents the dipolar broadening and can readily be calculated for a polycrystalline sample from the equation

$$M_2^d = 3/5g^2\beta^2S(S+1)\sum_k \frac{1}{r_{Jk}} \cdot x = 1.70 \times 10^6\text{G}^2, \quad (4)$$

where $x = 0.87$ is the chromium concentration; Σ_k is over the six nearest-neighbor Cr^{3+} ions at distance r_{Jk}, $S = 3/2$, β is the Bohr magneton, and $g = 1.98(5)$.

In Eq. (3) the factor 10/3 is included because the exchange integral ($J = 32{,}146$ G) determined from susceptibility data (*8*) is much higher than the resonant field ($H_0 = 3275$ G). As the coefficient C is related to the geometrical arrangement of the magnetic ions, it seems reasonable to assume that $C = 0.8$, which is the mean value determined for $ACrO_2$ systems (*17*), in which the magnetic ions lie in a triangular planar sublattice.

Consequently, the dipolar broadening due to the fine structure M_2^{cf} is calculated from Eq. (3) to be $M_2^{cf} = 3.46 \times 10^6$ G^2. Considering that M_2^{cf} is related to the trigonal distortion ε of the octahedral sites,

$$M_2^{cf} = \frac{64\lambda^4\kappa^4}{\Delta_0^2}\varepsilon^2[4S(S+1) - 3]/5, \quad (5)$$

where $\lambda = 92$ cm^{-1} (*18*), $\kappa = 0.61$, and $\Delta_0 = 13{,}800$ cm^{-1} (*6*), we obtain $\varepsilon = 0.061$ for our layer compound.

Conclusions

$Cr_{0.87}Ga_{1.80}S_4$ shows the same crystal structure as α-$FeGa_2S_4$ (*7*), with the magnetic Cr^{3+} ions lying in a triangular planar sublattice within the octahedral layer of the unit cell. This geometrical arrangement confirms the goodness of the two-dimensional model assumed in interpreting the magnetic behavior of the $Cr_xGa_{2.67-x}S_4$ ($0.87 \leq x \leq 1.00$) system (*8*). Any degree of inversion between gallium and chromium atoms, not revealed by X-ray analysis as a consequence of the similar scattering factors, would be definitively ruled out by the strong CFSE of Cr^{3+} ions in octahedral coordination (*19*).

The trigonal distortion $\varepsilon = 0.061$ is similar to that found for $ACrO_2$ (A = Li, Na, K) compounds ($\varepsilon = 0.051$), and this result is not unexpected considering the similarity in crystal structures between these oxides and $Cr_{0.87}Ga_{1.80}S_4$. The slightly higher value may be a consequence of the vacancies present in the octahedral layer of our compound.

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