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Preparation and Structural Study of a New Ternary Gold Chromium Sulfide, $AuCrS_2$

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A new ternary chromium sulfide, $AuCrS_2$, was prepared from a mixture of Au, Cr, and S powder. It crystallized in the trigonal space group $R3m$ with $a = 3.4814(1)$ Å and $c = 21.451(8)$ Å. Single crystal study showed that $AuCrS_2$ was a layered compound composed of CrS_2 layers and Au ions which reside in the interlayer regions. It was also revealed that the structure of $AuCrS_2$ was different from those of the other ACrS$_2$-type layered compounds (A = Ag, Cu, Li, and Na) in the stacking sequence of CrS_2 layers. Each Au atom is coordinated with two sulfide atoms. The magnetic susceptibility of $AuCrS_2$ followed the Curie–Weiss law above 150 K, and it became antiferromagnetic with Néel temperature (T_N) at 55 K. © 1999 Academic Press

INTRODUCTION

Gold is known to have outstanding sulfidation resistance and only a few gold sulfides have been discovered. In the binary system, two metastable phases (Au_2S and Au_2S_3) were reported (1, 2). In the ternary system, alkali metal–gold sulfides such as KAuS, $K_4Au_6S_5$, and Na_3AuS_2 (3, 4, 6, 7, 8), solid solutions of AgS–AuS (9, 10, 11, 12), and $AuTa_5S$ (13) were obtained.

Although studies for gold sulfides are still scarce, we thought that there was a possibility of forming new ternary or multinary gold sulfides if reactants and reaction conditions were chosen properly. We tried to prepare a new gold-transition metal sulfide and paid attention to chromium as a third component because chromium is known to form sulfides with many different kinds of monovalent cations.

Most of the ternary chromium chalcogenides with monovalent cations have layered crystal structures. For example, ternary chromium chalcogenides ACrS$_2$ (A = Li, Na, Ag, and Cu; X = S, Se) have a layered structure based on a cubic closed packing of X atoms (14, 15, 16). The Cr^{3+} ions occupy the octahedral sites in every other interval of X sheets to form CrS_2 single layers. Monovalent cations are sandwiched between these layers.

In the present paper, we describe a preparation and single crystal structure analysis of a new ternary gold chromium sulfide $AuCrS_2$. It has a layered structure composed of CrS_2 layers and Au^+ ions, but the stacking patterns of S atoms is different from those of the other layer-type ACrS$_2$ compounds.

EXPERIMENTAL

Preparation

Gold chromium sulfide $AuCrS_2$ was prepared from a mixture of Au powder (Niraco Co., LTD, 99.95% 300 mesh), Cr powder (Rare Metallic Co., LTD, 99.9%), and S powder (Rare Metallic Co., LTD, 99.9%) in a mole ratio of Au : Cr : S = 1 : 1 : 3. An excess of sulfur was necessary to obtain a pure sample without chromium sulfide or unreacted Au powder. The mixture was pelletized and sealed in a silica ampoule. The ampoule was heated in an electric furnace at 1000°C for 2 days. Unreacted sulfur was removed by using a temperature gradient furnace, and a single phase of $AuCrS_2$ was obtained.

Single crystals of $AuCrS_2$ were prepared from the same mixture mentioned above. The mixture sealed in an evacuated silica ampoule was heated at 1000°C for 3 weeks. The products contained a lot of tiny black single crystals.

Characterization

The products were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). Powder XRD data were collected on an M18XHF-SRA diffractometer (MAC SCIENCE) using monochromatized Cu$K\alpha$ radiation. Lattice constants were calculated using 23 reflections ranging from $2\theta = 45 \sim 100°$. All reflections used here were well separated into Kα1 and Kα2 peaks, and only Kα1 peaks were used in the calculation. SEM observations were performed on the powder sample supported by silver paste using JSM-6320F (JEOL).

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A single crystal with a dimension of 0.05 × 0.05 × 0.02 mm was selected for the structure analysis. The crystal was mounted on the top of a glass capillary and its diffraction intensities were collected on a CCD X-ray diffractometer SMART1000 (BRUKER) equipped with monochromatized Mo$K\alpha$ radiation. Atomic parameters were determined by the direct method (SHELXS86 (18)) and Fourier techniques (Rigaku TEXSAN program). A full-matrix least-squares program ANYBLK (19) was used for the final refinement.

Measurement of Magnetic Susceptibility

Magnetic susceptibility measurements were carried out on powder samples by using a SQUID magnetometer MPMS (QUANTUM DESIGN). The temperature dependence of the susceptibility was measured from 4 K up to 300 K under 5000 Oe.

RESULTS AND DISCUSSION

Crystal Structure

The powder XRD pattern of $AuCrS_2$ was similar to those of the other layer-type $ACrX_2$ compounds. All reflections were indexed on a rhombohedral unit cell with $a = 3.4814(1)$ Å, $c = 21.451(8)$ Å. A SEM picture in Fig. 1 shows that the morphology of $AuCrS_2$ is trigonal prismatic, which corresponds to the structural symmetry. Layer lines on the side of the crystals indicate the existence of stacking faults or twinning in the crystals. The observed intensities and d values of $AuCrS_2$ are given in Table 1. The gold chromium sulfide seemed to be isotypic with other layer-type $ACrS_2$ compounds. We calculated the diffraction intensities of $AuCrS_2$ by using the atomic parameters of $AgCrS_2$. The calculated intensities for some indices were, however, very different from the observed values. It was, therefore, considered that $AuCrS_2$ has some differences in structure compared with the other layered chromium sulfides. To confirm the differences, single crystal analysis was performed. It was very difficult to obtain single crystals of $AuCrS_2$ suitable for the single crystal analysis because the obtained crystals often showed twinning or stacking faults. We could not obtain a perfectly good single crystal but finally selected a relatively good crystal with a dimension of 0.05 × 0.05 × 0.02 mm for the intensity data collection.

TABLE 1
X-Ray Diffraction Pattern of $AuCrS_2$

h	k	l	d_{obsd}	d_{calcd}	I_{obsd}
0	0	3	7.16	7.15	59
0	0	6	3.576	3.575	51
1	0	1	2.988	2.986	47
− 1	0	2	2.904	2.903	100
1	0	4	2.630	2.628	27
− 1	0	5	2.468	2.467	5
0	0	9	2.384	2.383	19
1	0	7	2.150	2.149	12
− 1	0	8	2.0039	2.0037	34
0	0	12	1.7878	1.7876	12
1	0	10	1.7480	1.7479	43
1	1	0	1.7409	1.7407	14
1	1	3	1.6917	1.6913	4
0	1	11	1.6377	1.6375	7
1	1	6	1.5654	1.5651	14
0	2	1	1.5041	1.5038	5
2	0	2	1.4929	1.4928	6
0	2	4	1.4513	1.4513	4
1	1	9	1.4059	1.4057	12
− 1	0	14	1.3661	1.3660	6
− 2	0	7	1.3525	1.3527	4
2	0	8	1.3139	1.3141	8
1	1	12	1.2472	1.2471	6
− 2	0	10	1.2334	1.2334	8
1	0	16	1.2251	1.2251	9
0	0	18	1.1917	1.1918	7
− 1	0	17	1.1640	1.1640	6

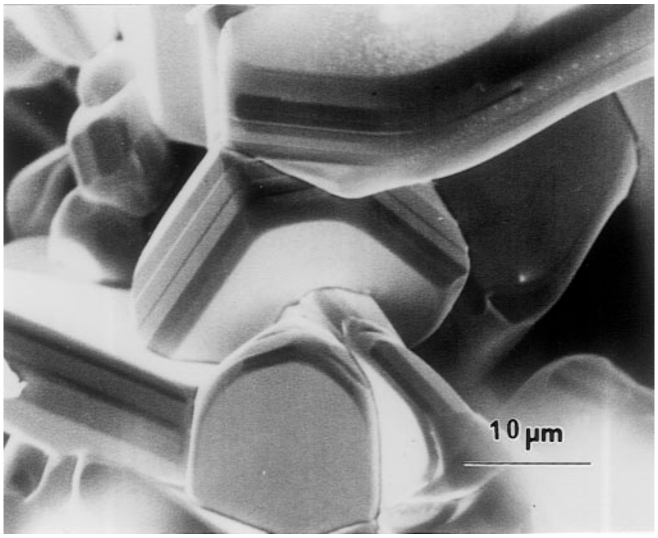

FIG. 1. A SEM picture of $AuCrS_2$.

The space group and crystal structure of $AuCrS_2$ were determined by using this crystal. Laue group $\bar{3}m$ and the extinction condition $-h + k + l = 3n$ indicated that the space group of $AuCrS_2$ was $R3m$ or $R\bar{3}m$. Structural refinement was performed according to the two space groups. Final refinement converged into $R = 8.65\%$ and $R_W = 10.76\%$ for $R\bar{3}m$ and $R = 4.76\%$ and $R_W = 5.39\%$ for $R3m$. The centrosymmetric model used here was Au at (1/3, 2/3, 1/6), Cr at (0, 0, 0), S at (1/3, 2/3, 0.2737). In this refinement of $R\bar{3}m$, anisotropic thermal parameters for the sulfur atom did not converged on appropriate values. In fact, the sulfur atom became a nonpositive definite atom. The space group of $AuCrS_2$ was, therefore, determined to be

TABLE 2
Crystallographic Data for $AuCrS_2$

Space group	$R3m$ (No. 160)
a (Å)	3.4823(4)
c (Å)	21.463(3)
V (Å^3)	225.40(5)
Z	3
T (K) of data collection	299
Crystal size (mm)	$0.05 \times 0.05 \times 0.02$
Diffractometer	SMART1000 CCD System (BURUKER)
Radiation (graphite monochromated)	Mo$K\alpha$ 0.7107 Å
Collection region	$-4 \leq h \leq 4$ $-3 \leq k \leq 4$ $-30 \leq l \leq 26$
2θ limit	$5.7^\circ \leq 2\theta \leq 60^\circ$
No. of measured reflections	3219
No. of unique reflections with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	206
No. of variable parameters	12
R, R_w[a]	0.0476, 0.0539

[a] $R = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$, $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2]^{1/2}$ $(w = 1/\sigma(F_o)^2)$.

noncentrosymmetric $R3m$. The crystallographic data for $AuCrS_2$ are shown in Table 2. The refined atomic parameters and thermal vibrational parameters are listed in Table 3. Selected bond distances and angles are shown in Table 4.

The obtained crystal structure of $AuCrS_2$ is shown in Figs. 2 and 3a. It is closely related to the structure of $AgCrO_2$ (20). The Cr atoms are coordinated with six sulfur atoms in the distances of 2.38 and 2.39 Å. Bond angles for S1–Cr–S1, S2–Cr–S2, and S2–Cr–S1 are 93.8, 94.1, and 86.0°, respectively. The resulted CrS_6 octahedra are almost regular. They share their edges with each other to form CrS_2 layers. Au atoms are situated in two-coordinated sites between the layers. The Au site is slightly displaced from the midpoint of the interlayer region. The bond distances of Au–S are 2.31 and 2.29 Å. The calculated value for the Au^+ radius in $AuCrS_2$ is 0.60 Å using Shanon's S^{2-} radius of 1.7 Å (21). This is in good agreement with the Shanon's crystal radius of Au^+ ions (0.58 Å for coordination number II) in sulfides.

The structure of $AuCrS_2$ is different from those of the other layer-type $ACrS_2$ compounds in terms of the stacking sequence of sulfur layers. The arrangements of sulfur atoms along the c-axis in $AuCrS_2$ and $AgCrS_2$ are shown in Fig. 3. In the $AgCrS_2$ structure, the stacking sequence of sulfur atoms is AB–CA–BC. Using this sequence, two types of holes are presented between the CrS_2 layers. One is the octahedral hole and the other is the tetahedral hole. The

TABLE 3
Atomic Parameters and Anisotropic Thermal Vibration Parameters for $AuCrS_2$, with Standard Deviations in Parentheses

Atom	x	y	z	U_{iso}
Au	1/3	2/3	0.4994(14)	0.0197(6)
Cr	0	0	1/3	0.005(7)
S1	1/3	2/3	0.607(3)	0.021(10)
S2	1/3	2/3	0.392(2)	0.01(2)

			$U_{ij} \times 100$			
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au	2.59(6)	2.59(6)	0.74(6)	0.13(3)	0.0	0.0
Cr	1.28(15)	1.28(15)	0.7(3)	0.64(8)	0.0	0.0
S1	2.5(9)	2.5(9)	1.4(13)	1.3(4)	0.0	0.0
S2	0.5(6)	0.5(6)	0.4(9)	0.2(3)	0.0	0.0

TABLE 4
Bond Distances and Angles in $AuCrS_2$

Au–S1	2.31(3) Å
–S2	2.29(2) Å
Cr–S1 × 3	2.38(3) Å
–S2 × 3	2.38(3) Å
S1–Cr–S1	93.8(14)°
S2–Cr–S2	94.1(12)°
S1–Cr–S2	86.0(2)°

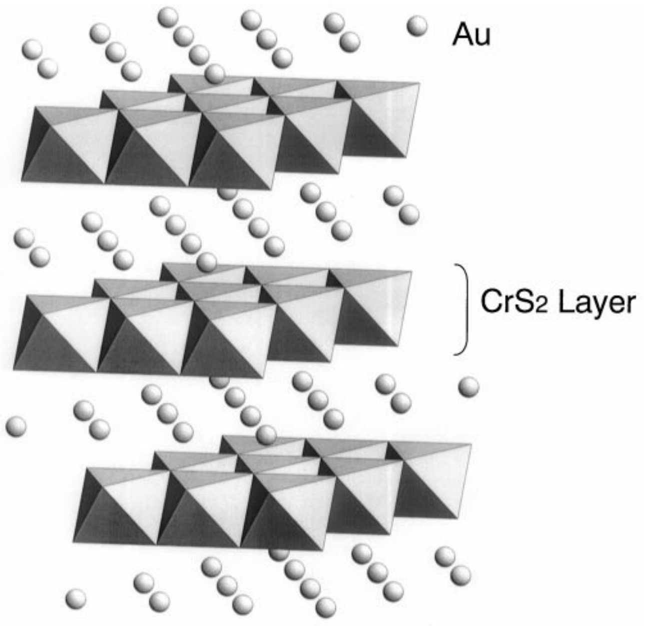

FIG. 2. The crystal structure of $AuCrS_2$. Small circles indicate Au^+ ions, and edge-shared octahedra are CrS_6 units.

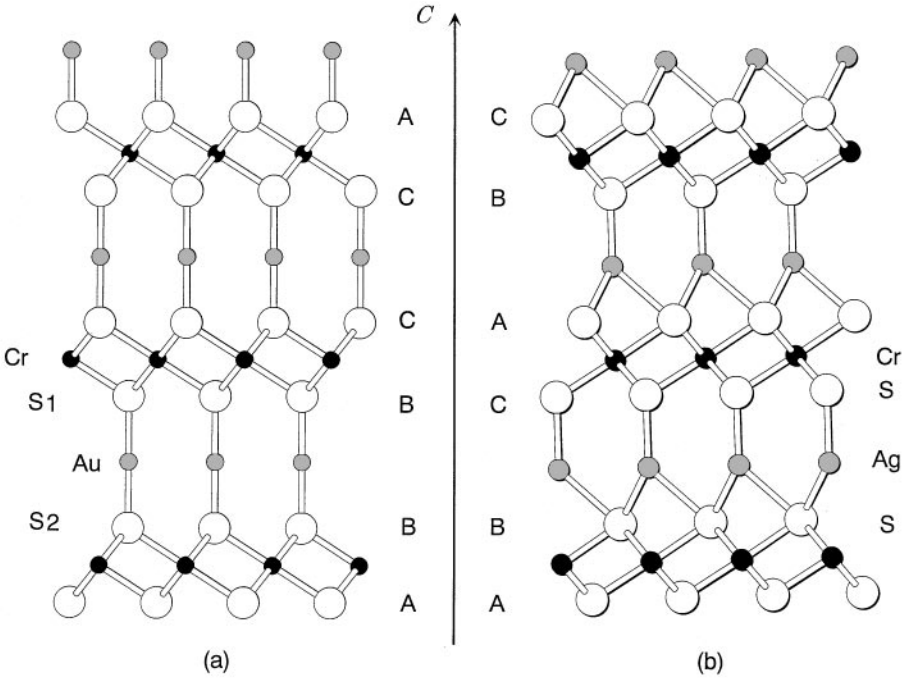

FIG. 3. The stacking patterns of sulfur atoms along the *c* axis in $AuCrS_2$ (a) and $AgCrS_2$ (b). Large open and small filled circles are sulfur and chromium atoms, respectively. Half-filled circles are Au and Ag ions.

Ag^+ ions are situated in the tetrahedral holes (14). On the other hand, sulfur atoms in $AuCrS_2$ are stacked in an AB–BC–CA type sequence. Trigonal prismatic and two-coordinated sites are presented in an interlayer regions by this sequence. Only the two-coordinated sites in the $AuCrS_2$ structure are occupied by the Au^+ ions.

This structural difference is explained in terms of the site preferences of Au and Ag ions. Au^+ ions prefer two-coordinated sites in sulfides. In fact, all Au^+ ions in the known gold sulfides except for $AuTa_5S$ occupy two-coordinated sites (3, 4, 6, 7, 8). On the other hand, the Ag^+ ions can occupy two (in Na_3AgS_2 (22)), four (in Ag_3AuS_2 (12), $Ag_4K_2S_3$ (23), $Ag_{0.62}NbS_2$ (24), etc.), and six (in $Ag_{0.35}TiS_2$ (25), etc.) coordinated sites in sulfides. The Ag^+ ions prefer the tetrahedral and octahedral sites to the two-coordinated site. The sequence of sulfur atoms will be influenced by the site preferences of these ions.

Magnetic Properties

Figure 4 shows the χ^{-1}–T curve for $AuCrS_2$. The layered compounds $ACrX_2$ (A = Li, Na, Ag, and Cu) are reported to be antiferromagnetic at low temperatures (14, 15, 16, 17). $AuCrS_2$ also became antiferromagnetic with Néel temperature (T_N) at 55 K. Above 150 K the susceptibility follows the Curie–Weiss law with a value for Weiss temperature $\Theta = -116$ K. Large deviations from the Curie–Weiss law were observed above T_N up to $2T_N$.

The magnetic properties and lattice constants of the *a*-axis for layered chromium compounds are summarized in Table 5. Engelsman *et al.* mentioned an interesting correlation between the length of cell edge *a*, which corresponds to the Cr–Cr distance, and Weiss temperatures (16). As the length of cell edge *a* becomes longer, the Θ value becomes larger. From this observation, they assumed that the interactions between moments of Cr ions in different layers were very weak, and the Weiss temperatures Θ could mainly be determined by the intralayer interactions of moments.

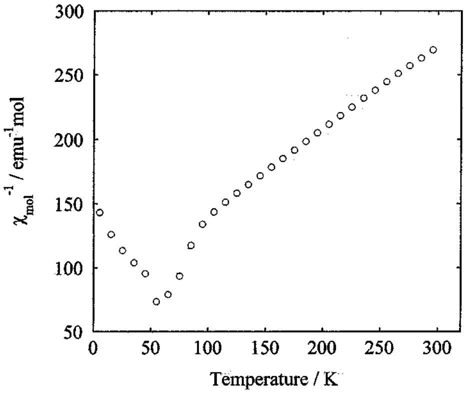

FIG. 4. The temperature dependence of magnetic susceptibility measured on a powder sample of $AuCrS_2$.

TABLE 5
Néel Temperature T_N, Weiss Temperature Θ, Molar Curie Constant C_M, and Lattice Constant a of the Compounds $ACrS_2$[a]

	T_N (K)	Θ (K)	C_M (emu mol^{-1} K)	a (Å)[b]	
$LiCrS_2$	55	− 276	1.84	3.4637	Ref. (15)
$CuCrS_2$	39	− 90	1.78	3.4812	Ref. (14, 16)
$AuCrS_2$	55	− 116	1.52	3.4814	This work
$AgCrS_2$	40	− 55	1.71	3.4974	Ref. (14, 16)
$NaCrS_2$	19	30	1.79	3.5544	Ref. (14, 16)

[a] A = Li, Na, K, Cu, Ag, and Au.
[b] Room temperature.

Although the gold chromium sulfide $AuCrS_2$ has a different stacking sequence for sulfur atoms from the other layered sulfides listed in Table 5, the structure of CrS_2 layers in $AuCrS_2$ is same as those in the other sulfides. The values of Θ and the lattice constant a for $AuCrS_2$ are similar to those for $CuCrS_2$. They are larger than the values for $LiCrS_2$ and smaller than those for $AgCrS_2$. This observation shows that the interlayer interactions of moments do not play an important role in the whole magnetic character in these $ACrS_2$ type compounds. Our observation for $AuCrS_2$ is in good agreement with Engelsman's assumptions.

CONCLUDING REMARKS

The new gold chromium sulfide $AuCrS_2$ had a layered structure composed of CrS_2 layers and Au^+ ions. The structure is different from the other layer-type chromium sulfides in the stacking sequence of CrS_2 layers. The Au ions are situated in the two-coordinated sites in the interlayer regions, and chromium atoms are coordinated by six sulfur atoms to form CrS_6 octahedra which compose the CrS_2 layers by sharing their edges. The gold chromium sulfide showed antiferromagnetic transition as did the other layer-type chromium sulfides.

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