SHORT STRUCTURAL PAPERS

Structure of a Non-Stoichiometric Chromium Silver Sulphide

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Abstract. $Ag_{0.37}Cr_{1.21}S_2$, rhombohedral, $R\bar{3}m$, $a = 3.4325$ (1), $c = 37.190$ (1) Å (in hexagonal setting), $Z = 6$. The structure was determined using single-crystal X-ray data from 908 independent reflections; the least-squares refinement of the positional and thermal parameters and the population parameters of Ag and Cr led to a final $R_F = 0.102$. It is a layer compound with hexagonal layers of atoms. Layers of S form a close packing of the type $(hcch)_3$, forming CrS_2 sandwiches with Cr in octahedral coordination. The gaps between these sandwiches are alternately occupied by Cr (2 × 0.21 Cr per site), also in octahedral coordination, and by Ag in tetrahedral holes. Both tetrahedral holes are partly occupied by 0.37 Ag; Ag is distributed over several sites within the S tetrahedra.

Introduction. Stoichiometric compounds $MCrX_2$ ($M = $ Ag, Cu; $X = $ S, Se) have been known for many years. Their structures are based on cubic close packing of the anion with Cr in half of the octahedral holes so that CrX_2 sandwiches are formed; Ag and Cu occupy half of the tetrahedral holes between CrX_2 sandwiches. The compounds undergo reversible phase transitions to structures with Ag and Cu randomly distributed over all tetrahedral holes. They are semiconductors and the magnetic moments of Cr^{3+} order antiferromagnetically at low temperature (Engelsman, Wiegers, Jellinek & van Laar, 1973). The electrochemical properties of $AgCrS_2$ and $AgCrSe_2$ have been investigated (Murphy & Chen, 1977; Hibma, 1980).

Non-stoichiometric compounds M_xTX_2 (T is a $3d$ transition element) are known, *e.g.* $Cu_{0.7}TiS_2$ (Le Nagard, Gorochov & Collin, 1975), isostructural with $CuCrS_2$ with a statistical distribution of Cu atoms over all tetrahedral holes, $Cu_{0.75}VS_2$ (Le Nagard, Collin & Gorochov, 1977) and $Cu_{0.65}VS_2$ (Le Nagard, Collin &

Gorochov, 1979a), both with structures related to the $Cd(OH)_2$ type with Cu in some of the tetrahedral holes. These non-stoichiometric compounds are metallic; in the case of $Cu_{0.75}VS_2$ localization of the $3d$ electrons occurs at low temperature.

In the search for non-stoichiometric Cr compounds M_xCrX_2, we found a compound $Ag_{0.37}Cr_{1.21}S_2$ with a structure related to that of $AgCrS_2$; its structure determination is described in this paper.

Experimental. Samples of composition Ag_xCrS_2 ($x = 0.1, 0.2, \ldots, 1.0$) were prepared by a direct combination of the elements in evacuated quartz ampoules. The ampoules were heated at 1273 K for several weeks. The products were studied by X-ray diffraction. The powder lines of a sample with $x = 0.3$ could be indexed rhombohedrally with $a = 3.4325$ (1) and $c = 37.190$ (1) Å (hexagonal setting). This indexing was confirmed by Weissenberg photographs of single crystals. We observed that the samples were contaminated by rhombohedral (rh.) Cr_2S_3; even some 'single' crystals turned out to be intergrowths with rh. Cr_2S_3.

Samples were prepared for several starting compositions. We found that samples with $x > 0.3$ always contained $AgCrS_2$; for $x < 0.3$ the amount of rh. Cr_2S_3 increased considerably. Good single crystals were present when an excess of about 25% S was used. The density measured by dilatometry on a powder sample was 4.18 Mg m^{-3}.

A chemical analysis carried out on some large crystals (10 mg sample) yielded an atomic ratio of $0.25:1.17:2.00$ for Ag:Cr:S.

An X-ray microanalysis with $AgCrS_2$ crystals as a reference resulted in an atomic ratio $0.38:1.22:2.00$.

The approximate structure was found from powder data by trial and error. The space group is $R\bar{3}m$ and

there are six formula units in the cell. The structure is related to that of the so-called second-stage alkali-metal intercalates of transition-metal dichalcogenides, like $Na_{0.3}TiS_2$ (Tigchelaar, Haange, Wiegers & van Bruggen, 1981; Wiegers, 1980). These compounds have a transition metal to chalcogen ratio of $1:2$. In our compound this ratio is smaller than $1:2$ (from chemical analysis). The density corresponding to six units of $Ag_{0.25}Cr_{1.17}S_2$ per cell is 3.98 Mg m^{-3}, which is about 5% lower than the experimental density; the density corresponding to six units of $Ag_{0.21}CrS_{1.71}$ (also in agreement with the chemical analysis) is 3.40 Mg m^{-3}, 19% lower than the experimental density. We therefore assumed that the deviation from the ratio $1:2$ for Cr to S is due to some extra Cr in the crystal, the S framework being essentially complete. The occupancies of Ag and Cr sites were taken as variables in the structure investigations.

Intensity measurements were made on a single-crystal platelet about 0.27 mm in diameter and about 0.06 mm thick (the crystal consisted of two parts with a difference of about $0.5°$ in the direction of their c axes); the ω-scan technique was used.

4438 reflections were measured with $2\theta_{max} = 136°$ ($-8 \leq h \leq 0$; $-8 \leq k \leq 8$; $0 \leq l \leq 74$) and Mo $K\alpha$ radiation; Lorentz, polarization and absorption corrections were made. Scattering factors were from Cromer & Mann (1968) and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography*, 1974). Reflections with $I > 0$ were used in the refinements. All calculations were carried out on a CDC Cyber 170/760 computer using the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Possible space groups were: $R3$, $R\bar{3}$, belonging to Laue class $\bar{3}$, and $R32$, $R3m$ and $R\bar{3}m$, belonging to Laue class $\bar{3}m1$ (no extinctions). From the powder data we found that the atoms are on the trigonal axes. This leaves the space groups $R32$, $R3m$ and $R\bar{3}m$. From experience with other Ag-containing chalcogenides, *e.g.* AgCrS$_2$, however, the possibility of an off-axis position of Ag could not be excluded. The 4438 measured reflections reduced in Laue class $\bar{3}$ to 1464 independent

structure factors of which 196 were extinct. Inspection of the reflection symmetry showed that the Laue class is probably $\bar{3}m1$; this indicated that the deviation from a structure with all atoms on the trigonal axes must be small.

Refinements were carried out in space groups $R3$, $R\bar{3}$ and $R3m$. In $R3$ the Cr and S atoms were placed at positions $3(a)$ $00z$; the origin was taken at one of the fully occupied Cr sites. There are two tetrahedral holes between neighbouring layers of S. The agreement between observed and calculated structure factors improved considerably by distributing Ag in equal amounts over both tetrahedral sites. The electron density of Ag was smeared out over a relatively large area in the ab plane. This indicates an off-axis position of Ag. A calculation of the distances between the atoms showed that a centre of symmetry is present. We therefore adopted space group $R\bar{3}$, taking Cr(2), the partly filled Cr site, as origin. Refinement in $R\bar{3}$ (with about half the number of variables) yielded an R_F of 0.109.

For refinement in space group $R\bar{3}m$ the 1464 independent reflections in Laue class $\bar{3}$ reduced to 908 in Laue class $\bar{3}m1$; 90 were extinct. The index R_F decreased to 0.102. The atomic parameters are given in Table 1.*

The thermal parameters of Ag also reflect the distribution of Ag around the trigonal axes: U_{33}, along the trigonal axis, is about the same as for Cr and S but the in-plane parameters are much larger. There is, of course, a large correlation between the in-plane thermal parameters of Ag with the occupancy of the Ag sites and the x parameter of Ag(2). The composition, deduced from the refinement, is $Ag_{0.37}Cr_{1.21}S_2$. The difference Fourier map shows some spurious density along the threefold axes; this is probably due to the occurrence of stacking faults in the crystal.

Table 1. *Atomic parameters of* $Ag_{0.37}Cr_{1.21}S_2$

Standard deviations in the last decimal place are given in parentheses. U_{ij} (Å^2) are defined by the formula $\exp[-(2\pi^2 \sum_i \sum_j U_{ij} \times h_i h_j a_i^* a_j^*)]$; for the atoms in position $6(c)$ and $3(a)$: $U_{11} = U_{22} = \frac{1}{2}U_{12}$, $U_{13} = U_{23} = 0$; for Ag(2) in position $18(h)$: $U_{11} = U_{22}$; $U_{12} = 0.12$ (3); $U_{13} = U_{23} = -0.008$ (4).

	Position	x	y	z	Occupancy	U_{11}	U_{33}
Ag(1)	$6(c)$	0	0	0.1589 (3)	0.22 (3)	0.072 (8)	0.001 (2)
Ag(2)	$18(h)$	0.080 (8)	−0.080	0.1635 (3)	0.05 (1)	0.16 (3)	0.004 (4)
Cr(1)	$6(c)$	0	0	0.07510 (1)	1.00 (1)	0.0087 (2)	0.0128 (4)
Cr(2)	$3(a)$	0	0	0	0.43 (1)	0.0080 (6)	0.007 (1)
S(1)	$6(c)$	0	0	0.37118 (5)	1.0	0.0065 (4)	0.0101 (6)
S(2)	$6(c)$	0	0	0.22301 (5)	1.0	0.0109 (4)	0.0093 (6)

Discussion. The compound has a layered structure with the atoms in hexagonal layers. The layers of anions are in a close packing of the type $(hcch)_3$, forming CrS_2 sandwiches with Cr in trigonally distorted octahedra ($3m$ symmetry). The gaps between these sandwiches are alternately occupied by extra Cr in octahedra of $\bar{3}2/m$ symmetry between adjacent h layers and Ag in tetrahedral coordination between adjacent c layers. There is a close relationship with the structure of $AgCrS_2$ and isotypes. The structure is also related to that of the so-called second-stage alkali-metal intercalates of the transition-metal dichalcogenides, viz $Na_{0.3}TiS_2$ (Tigchelaar et al., 1981; Wiegers, 1980). In these compounds the anions are no longer close-packed; the space between the TiS_2 sandwiches is alternately empty (for $Na_{0.3}TiS_2$) or occupied by extra transition metal (for $Na_{0.34}Cr_{1.15}Se_2$), and occupied by the alkali metal in trigonal-prismatic coordination. These relationships are demonstrated in Fig. 1.

The behaviour of Ag in the lattice is quite analogous to that observed in other Ag- and Cu-containing chalcogenides. The Ag (Cu) atoms are not at the centre of the tetrahedron but distributed statistically over several sites within the tetrahedron as found in $AgCrS_2$, $CuCrS_2$ and $AgCrSe_2$ (Engelsman et al., 1973). The same was found in a single-crystal X-ray study of $CuCrS_2$ (Le Nagard, Collin & Gorochov, 1979b). In $CuCrS_2$, $AgCrS_2$ and $AgCrSe_2$ (and probably also in $CuCrSe_2$) only half of the tetrahedral holes between the CrX_2 sandwiches are occupied at lower temperature. There is a transition to a structure with all tetrahedral holes statistically occupied by 0·5 Ag or Cu. The high-temperature form of $AgCrS_2$ shows superionic conduction of Ag (Murphy & Chen, 1977; Hibma, 1980). In $Ag_{0.37}Cr_{1.21}S_2$ both tetrahedral holes are statistically occupied by 0·37 Ag (from refinement).
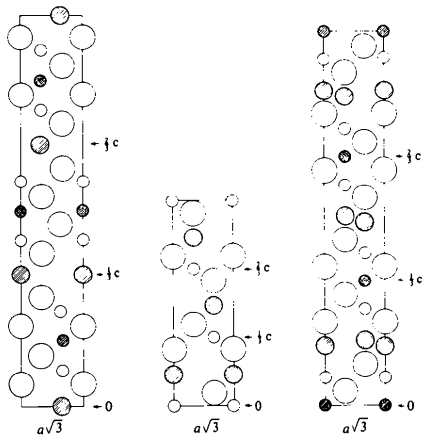

Fig. 1. The $(11\bar{2}0)$ section of the structures of (a) $Na_{0.34}Cr_{1.15}Se_2$, (b) $AgCrS_2$, low-temperature modification, and (c) $Ag_{0.37}Cr_{1.21}S_2$. The anions are large open circles; large hatched circles are Na atoms (a) or Ag (b,c); small open circles are Cr atoms in the fully occupied layers; small cross-hatched circles are Cr atoms in the partly filled layers.
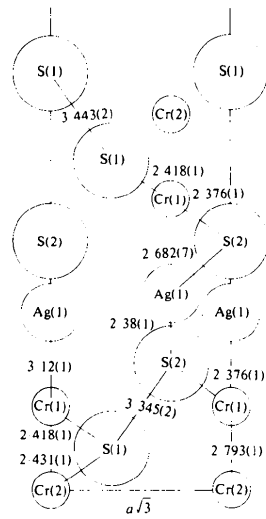

Fig. 2. Important distances (Å) between the atoms of $Ag_{0.37}Cr_{1.21}S_2$. Standard deviations, given in the last decimal place, are in parentheses.

The tetrahedra of S are elongated along the trigonal axes (S···S $= 3·4325$ and $4·636$ Å). The distribution of 0·37 Ag within a tetrahedron is represented by 0·22 Ag at the trigonal axes at distances of 2·38 Å (1×) and 2·68 Å (3×) from sulphur and 3 × 0·05 Ag at a distance of 0·5 Å from the trigonal axis. The distance between the two planes of Ag atoms in the van der Waals gap amounts to 0·5 Å. In the Fourier map also some density is seen at the octahedral site with $z \simeq 0·17$, but refinement failed to yield occupancy of that site.

Both types of Cr in the crystal are in octahedral coordination; these distances agree with those in $AgCrS_2$ and $CuCrS_2$ (Le Nagard et al., 1979b). The distances are summarized in Fig. 2.

In some aspects, there is a relationship with the binary sulphides Cr_2S_3. The distances between the atoms in the hexagonal planes of $Ag_{0.37}Cr_{1.21}S_2$ ($a = 3·4325$ Å) are shorter than those in $AgCrS_2$ ($a = 3·4974$ Å) and almost equal to those in trigonal and rhombohedral Cr_2S_3 (3·430 and 3·428 Å, respectively; Jellinek, 1957). This explains why intergrowths of rh. Cr_2S_3 and $Ag_{0.37}Cr_{1.21}S_2$ are often found.

There is a discrepancy between the formula $Ag_{0.37}Cr_{1.21}S_2$ from our refinement and the composition from chemical analysis. We consider this to be due to a contamination of the phase by mainly Cr_2S_3; this impurity strongly affects the Ag content. The formula is in good agreement with the X-ray microanalysis. A neutron powder diffraction diagram also showed a considerable amount of rh. Cr_2S_3 to be present (about 15%). A profile refinement with the occupation parameters also as variables yielded the

same composition $Ag_{0.37}Cr_{1.21}S_2$. We therefore accept the formula $Ag_{0.37}Cr_{1.21}S_2$. From the ionic description: $Ag_{0.37}^+Cr_{1.21}^{3+}S_2^{2-}$ it follows that $Cr^{3+}(d^3)$ only is present.

Preliminary measurements of the magnetic properties of $Ag_{0.37}Cr_{1.21}S_2$ show Curie–Weiss behaviour and antiferromagnetic order at low temperature. The asymptotic Curie temperature θ is about -750 K, also more in agreement with those of the two modifications of Cr_2S_3 [trigonal Cr_2S_3 -585 K, rh. Cr_2S_3 -670 K (van Bruggen, 1969)] than with that of $AgCrS_2$, -55 K (Engelsman et al., 1973).

Recently, we obtained a compound $Ag_xCr_ySe_2$ ($x \simeq 0.3$, $y \simeq 1.2$) with a hexagonal unit cell: $a = 3.628$, $c = 12.40$ Å; the compound was always contaminated by Cr_2Se_3. The structure, as derived from the powder intensities, consists of the same entities as found in $Ag_{0.37}Cr_{1.21}S_2$, but with hexagonal instead of rhombohedral stacking of the entities; the stacking of the Se layers is hexagonal.

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μ-Hyperoxo-bis[pentaamminecobalt(III)] Hydrogensulfate Bissulfate Trihydrate*

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Abstract. $[Co_2(NH_3)_{10}(O_2)](HSO_4)(SO_4)_2.3H_2O$, monoclinic, $P2_1/c$, $a = 13.392$ (3), $b = 9.742$ (3), $c = 17.709$ (7) Å, $\beta = 100.98$ (2)°, $Z = 4$, $D_c = 1.943$ g cm^{-3}, $R = 0.109$ for 3640 reflections with $I > 0$. The dicobalt pentacations are centrosymmetric with O–O bond lengths of 1.271 (7) Å, characteristic of a hyperoxo species. The sulfate, hydrogensulfate, and water moieties show various degrees of disorder.

Introduction. The dark-green, binuclear cation $[Co_2(NH_3)_{10}(O_2)]^{5+}$ crystallizes from 2 M H_2SO_4 in the form of orthorhombic crystals as a monosulfate tris(hydrogensulfate) salt. Both the structure (Schaefer

& Marsh, 1966; Schaefer, Ealick & Marsh, 1981; SEM hereafter) of this compound and its electronic spectrum (Lever & Gray, 1978) are consistent with the bridging group being hyperoxide, O_2^-. If this compound is recrystallized from 1 M H_2SO_4, monoclinic crystals form which contain only one hydrogensulfate and two sulfate groups per dicobalt cation. We have carried out X-ray diffraction studies of these monoclinic crystals; while crystal decay and disorder of the sulfate and hydrogensulfate groups have limited the accuracy of the studies, the dimensions of the cation are again consistent with a bridging hyperoxide group.

μ-Hyperoxo-bis[pentaamminecobalt(III)] monosulfate tris(hydrogensulfate) was prepared as described previously (Schaefer & Marsh, 1966). It was added to saturation to 50 ml of 1 M sulfuric acid at 373 K and