JOURNAL OF SOLID STATE CHEMISTRY **93,** 146–153 (1991)

X-Ray and Neutron Diffraction Study of the Layered Compound $CoGaInS_4$

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Received March 6, 1991

The crystal of the title compound, trigonal ($P3m1$) with hexagonal parameters $a = 3.744(1)$ and $c = 12.149(3)$ Å, is isostructural with polytype I of $ZnIn_2S_4$, being formed by the stacking of hexagonal layers of S anions, with the cations occupying, in intermediate planes, voids of approximate O_h and T_d symmetry. Single-crystal X-ray and powder neutron diffraction intensities were used as the basis for the refinement of various models of cation distribution among three different crystallographic sites. Eventually the "best" model was found to be represented by the formula $(Co_{0.38}In_{0.62})_o(Co_{0.29}In_{0.38}Ga_{0.33})_{t1}(Co_{0.33}Ga_{0.67})_{t2}S_4$, where the subscript o refers to a pseudooctahedral site and subscripts $t1$ and $t2$ refer to two different sites of approximate T_d symmetry. Evidence is found for the fact that the center of gravity of the pseudooctahedral site, as determined by the neutron experiment, is different from that "observed" by X-ray diffraction and a possible explanation is presented for this fact.

Introduction

The quaternary layered title compound was originally prepared by Razzetti *et al.* (*1*). A preliminary X-ray diffraction study (*2*) indicated that $CoGaInS_4$ is isostructural with polytype I of $ZnIn_2S_4$ (*3*) and that therefore its structure may be described with reference to this "parent" ternary compound belonging to the widely studied Zn–In–S system (*4, 5*).

For layered compounds of this type the correlation of their properties and structures meets with many difficulties primarily due to their complex structures (*6*) formed by the stacking of hexagonal layers of anions with the cations occupying, in intermediate planes, voids of approximate O_h and T_d symmetry. One of every four cation planes is missing and therefore this type of structure can be described as resulting from the stacking of packets of four layers of anions with the cations distributed in three intermediate planes. Different polytypes are obtained as a consequence of differences in the stacking of anion layers and in the cation distribution among the various sites (*4*).

In the case of the title compound since the start of this work it was felt that in addition to the single-crystal X-ray analysis a powder neutron diffraction study could help in better defining the structure. Indeed, prelimi-

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0022-4596/91 $3.00

nary results of that analysis indicated that a possible disorder in the cation distribution could be represented by the general formula $(Co_xIn_{1-x})_o(Co_{1-x}In_x)_{t1}(Ga)_{t2}S_4$[1] without excluding a more complicated model of disorder involving also the Ga ions. Of course the X-ray data are not a good basis for refining such a model since the atomic numbers of Ga and Co differ by only four units. At a later stage of the refinement, when indeed we developed a model in which the Ga ions share tetrahedral sites with the other cations, we used the neutron powder pattern, thus taking advantage of the large difference between the neutron scattering lengths of Ga and Co.

A previous X-ray powder diffraction study (*7*) indicated the formula $(Co_{0.7}In_{0.3})_o$ $(Co_{0.3}In_{0.7}Ga)_tS_4$ for a possible model of disorder.

Experimental

Crystals suitable for X-ray analysis were prepared by a slight modification of the CVD method reported elsewhere (*8*). In our case, a stationary temperature profile was applied with source temperature T_s = 860°C and deposition temperature T_d = 800°C. This allowed us to obtain several small crystals after 1 day. Polycrystalline samples were prepared starting from a stoichiometric mixture of pure elements (5*N*) and firing them four times at 850°C under vacuum (2×10^{-5} Torr).

In both cases—single crystal and powders—the samples were cooled down slowly from reaction to room temperature.

In a first stage of our structural analysis X-ray powder diffraction was used for characterizing the polycrystalline samples, making reference to the previous diffraction study by Haeuseler (*7*). While the Bragg positions of the lines in all our patterns were in perfect agreement with those in the reference pattern by Haeuseler and no extra lines were ever observed, the relative intensity did not agree, showing very strong effects of preferred orientations with a definitive predominance by the 00l reflections. Apparently in Haeuseler's pattern this kind of effect is slightly different, 101 being the strongest reflection, but the importance of the effect in limiting the capability of X-ray powder diffraction in a study aimed at solving a problem of cation distribution was clearly recognized and stressed by this author. We also performed experiments of powder diffraction at the Stanford synchrotron facility by using two wavelengths (0.748 and 1.541 Å), but we met with even more serious problems of preferred orientations, thus coming to the conclusion that, by X-ray powder diffraction, it was not possible to have results better than those obtained by Haeuseler.

Many trials were necessary for finding a crystal of reasonable quality, due to the morphology of this layered compound. Eventually the chosen sample, in the shape of a hexagonal prism (with a basal edge of 108 μm and a thickness of 13 μm), showed reasonably small spots in all the preliminary precession photographs. The intensities of 2664 reflections ($\frac{1}{2}$ of reciprocal space) were measured ($MoK\alpha$ radiation) by a NONIUS four-circle diffractometer. Only 589 independent reflections were declared observed on the basis of the relation $I > 3\sigma(I)$ and were corrected for absorption and for the Lorentz and polarization factors by NONIUS standard programs. The crystal symmetry is trigonal with hexagonal parameters a = 3.744 (1) and c = 12.149 (3) Å. On the basis of the observed extinctions the possible space groups are $P321$, $P3m\bar{1}$ and $P3m1$. The structure was solved by direct methods by using the MULTAN program

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[1] Here and in what follows the symbols "o" and "t" refer to sites of approximate O_h and T_d symmetry, respectively, with "$t1$" and "$t2$" representing two different sites of type "t". Tables I and II give the coordinates of these sites.

of the NONIUS package. The first E map clearly showed the positions of the heavier atoms and established $P3m1$ as the space group. The other atoms appeared in various "difference" Fourier maps and the resulting structure was refined by least squares to a value of 0.053 for the conventional R factor ($R_w = 0.087$), using an anisotropic model for the thermal motion and a disordered model of cation distribution (see the following section). An extinction parameter was also refined and anomalous terms for the scattering factors were taken into account.

The neutron diffraction pattern of polycrystalline $CoGaInS_4$ ($0.6Å < d < 2.6$ Å) was obtained at the ISIS (Rutherford Appleton Laboratory) pulsed neutron source, by using the High-Resolution Powder Diffractometer (HRPD), with the sample (a loose powder having a volume of $4.5 \times 3.0 \times 1.0$ cm^3) positioned 2 m from the detectors, for a period of 20 hr. Disordered models of cation distribution have been derived and refined on the basis of the neutron data, according to the Rietveld method, by using the TFLSQ program developed at RAL. These models will be discussed and compared with the model based on the X-ray data in the following section. A total of 190 independent neutron structure factors were found at the end of the Rietveld refinement.

Tables of X-ray and neutron observed and calculated structure factors are available as supplementary material.

Derivation and Refinement of Disordered Models

At the start of this work the refinement, based on single-crystal X-ray intensities, of a model of cation distribution involving only Co and In atoms gave a disorder represented by the formula $(Co_{0.38}In_{0.62})_o(Co_{0.62}In_{0.38})_{t1}(Ga)_{t2}S_4$ (Model A), with an occupancy parameter of 0.624(1) for In in site $M(o)$, as derived from the multiplicity factor refined by the NONIUS least-squares program.

In view of the fact that this model is different from that represented by the formula $(Co_{0.7}In_{0.3})_o(Co_{0.3}In_{0.7})_{t1}(Ga)_{t2}S_4$ (Model B), derived from that suggested by Haeuseler (7) on the basis of conventional X-ray powder diffraction, it seemed proper to refine the two models by using both the single-crystal X-ray data and the neutron powder diffraction pattern. We also calculated a powder pattern for Model A and compared it with Haeuseler's measured pattern and with the pattern calculated on the basis of his model. The comparison shows that a slightly better agreement is obtained with Haeuseler's model, thus confirming our statement in the Experimental Section that by X-ray powder diffraction it was not possible to have results better than those obtained by Haeuseler.

Refinement of Model B on the basis of the single-crystal data brought to values of the occupancy parameters identical to those of Model A, thus clearly showing the inconsistency of Model B with this set of data. For the neutron refinement one has to consider that, with the Rietveld method, when the number N of profile points is large ($N = 7480$ in our case) and, due to high background corrections (See Fig. 1), the quality of the primary intensity data is not very good, the goodness-of-fit index (χ^2) ceases to be an efficient indicator of model errors (9). For this reason, we decided to test the significance of a possibly disordered model by considering first an ordered model of formula $(In)_o(Co)_{t1}(Ga)_{t2}S_4$ and by refining, according to the Rietveld method, the isotropic B factors of the various atoms in addition to the positional and profile parameters. At the end of this refinement, the isotropic B parameter of Co reached a strongly negative value (-3.7) while the Ga B value went up to an abnormal $+2.0$ and the B value for In converged to a rather high $+0.49$. This peculiar result can be easily rationalized if one considers the values of the neutron scattering factors of Ga ($0.72 \times$

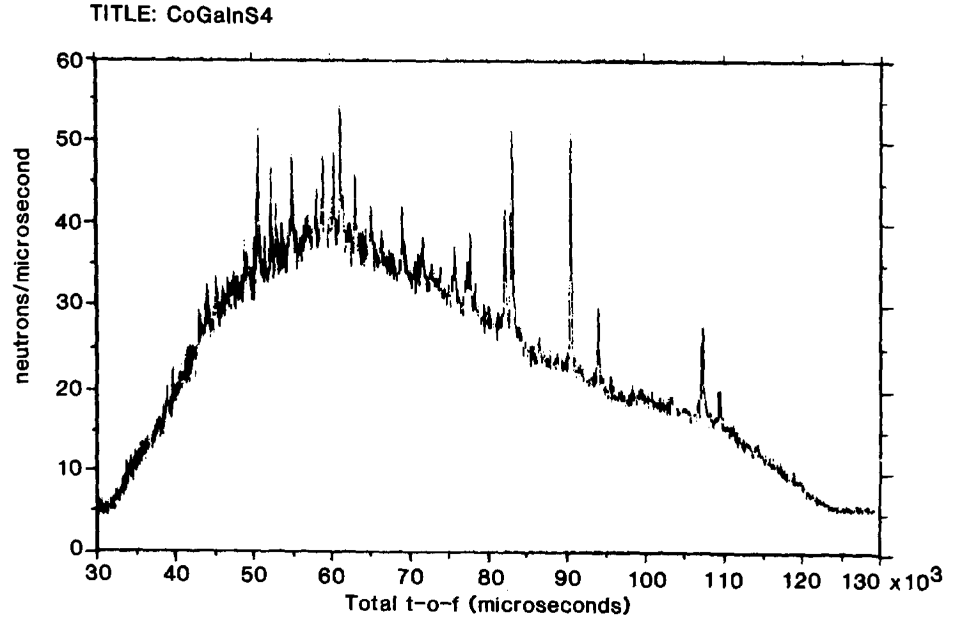

FIG. 1. Neutron diffraction time of flight powder diagram.

10^{-12} cm), Co (0.25×10^{-12} cm), and In (0.39×10^{-12} cm) and derives a disordered model in which Co shares site $M(o)$ with In, site $M(t1)$ with In and Ga and site $M(t2)$ with Ga only. Constrained refinement of this model, with a fixed isotropic temperature factor of 0.30 for all atoms, brought us to a χ^2 value of 1.053 ($R_w = 0.044$) and to the formula $(Co_{0.31}In_{0.69})_o(Co_{0.36}In_{0.31}Ga_{0.33})_{t1}(Co_{0.33}Ga_{0.67})_{t2}S_4$, with a value of 0.69(7) for the In occupancy of site $M(o)$ and a value of 0.67(4) for the Ga occupancy of site $M(t2)$. The coefficients representing the distribution of Co and In in $M(o)$ are very close to those of Model A and it seemed proper to refine another set of parameters with those coefficients kept fixed at the values determined on the basis of the X-ray diffraction experiment (see above). This refinement (the isotropic thermal factors were kept fixed at 0.30 as before) brought us to the same value of 0.67(4) for the Ga occupancy of site $M(t2)$, with the same final values of 1.053 and 0.044 for χ^2 and R_w, respectively. The formula representing the cation distribution for this model (Model C) is $(Co_{0.38}In_{0.62})_o(Co_{0.29}In_{0.38}Ga_{0.33})_{t1}(Co_{0.33}Ga_{0.67})_{t2}S_4$.

A further test of significance was performed by considering for refinement a model very different from Model C and defined by the formula $(Co_{0.98}In_{0.02})_o(Co_{0.01}In_{0.98}Ga_{0.01})_{t1}(Co_{0.01}Ga_{0.99})_{t2}S_4$. This model was refined taking as variables the positional and profile parameters as well as the occupancy factors of $M(o)$, $M(t1)$, and $M(t2)$, while keeping the proper constraints and fixed isotropic temperature factors of 0.30 (the same value used in the refinement of Model C). In fact the only occupancy parameters treated as independent variables were those of In in $M(o)$ and Ga in $M(t2)$ while the constraints were such as to satisfy the stoichiometric conditions. After nine cycles of refinement, the occupancy parameters shifted to values very close to those of

Model C, leading to a cation distribution represented by the formula $(Co_{0.34}In_{0.66})_o(Co_{0.32}In_{0.34}Ga_{0.33})_{t1}(Co_{0.33}Ga_{0.67})_{t2}S_4$.

Also Model B was considered as the basis for the refinement of a more complicated pattern of cation distribution with the Ga atoms in both sites $M(t1)$ and $M(t2)$. This refinement (final values of χ^2 and R_w were 1.063 and 0.044, respectively), with the occupancies of Co and In in $M(o)$ kept fixed at the values of the corresponding coefficients in the formula given by Haeuseler (*7*), gave a value of 0.70(4) for the Ga occupancy of $M(t2)$ and a formula (Model D) $(Co_{0.70}In_{0.30})_o(In_{0.70}Ga_{0.30})_{t1}(Co_{0.30}Ga_{0.70})_{t2}S_4$ in which no Co ions are present in site $M(t1)$.

Model D and the original Model B (*7*) are not in agreement with the results of the single-crystal X-ray refinement (Model A). Two interpretations are possible:

(i) Model D does not correctly represent the cation distribution;

(ii) the cation distribution in the powder samples is different from that in a single crystal. This is possible in view of the complex crystal growth characteristic of layered materials (see Introduction) and of the fact that different procedures have been used in the preparation of powder samples and of single crystals.

In the absence of more direct experimental evidence and/or of a convincing theoretical reasoning we adopt Model C as our best model.

Results and Discussion

The crystal of the title compound is isostructural with polytype I of $ZnIn_2S_4$ (see Fig. 2 and Introduction).

The complex pattern of cation distribution in Model C is consistent with the single-crystal X-ray results (Model A), if one considers the fact that the atomic numbers of Co and Ga differ by only four units (see previous section). For Model A the refined atomic positional and isotropic-equivalent thermal parameters are given in Table I while the atomic positional parameters and site occupancies of Model C, as obtained from the powder neutron experiment, are reported in Table II. Selected interatomic distances obtained from the single-crystal X-ray experiment are given in Table III and those derived from the elaboration of the neutron powder pattern are presented in Table IV.

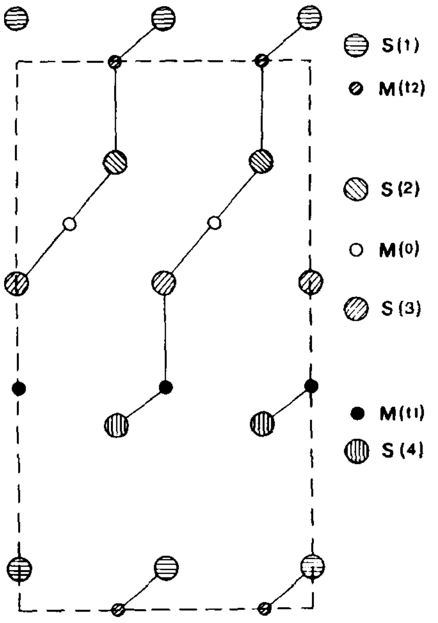

FIG. 2. Projection of the structure along the *a* axis of both the hexagonal and the orthohexagonal cell. The latter cell is obtained from the former by the transformation matrix

$$S_{H\text{-}O} = \begin{vmatrix} 1 & 0 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{vmatrix}.$$

The symbols of the ion sites are defined in Tables I and II and in the text.

Some of the Δz values (Δz is the difference between z coordinates of correspond-

TABLE I

ATOMIC POSITIONAL AND THERMAL PARAMETERS (MODEL A) OBTAINED FROM THE SINGLE-CRYSTAL EXPERIMENT

	x	y	z	B_{iso} (in Å^2)
$M(o)$	2/3	1/3	0.7019(4)	1.56(1)
$M(t1)$	0	0	0.4009(1)	1.26(1)
$M(t2)$	1/3	2/3	0	1.45(2)
S(1)	0	0	0.0742(4)	1.86(4)
S(2)	1/3	2/3	0.8094(3)	1.44(3)
S(3)	0	0	0.5890(3)	1.25(3)
S(4)	1/3	2/3	0.3309(3)	1.51(3)

Note. For the definition of Model A, see text. The symbol B_{iso} represents the isotropic-equivalent thermal parameters. The reported values are calculated from the refined anisotropic parameters (see text). Estimated standard deviations are given in parentheses.

TABLE II

ATOMIC POSITIONAL PARAMETERS (MODEL C) OBTAINED FROM THE POWDER NEUTRON EXPERIMENT

					Site occupancies		
	x	y	z	Δz	Ga	In	Co
$M(o)$	2/3	1/3	0.7169(15)	9σ		0.62	0.38
$M(t1)$	0	0	0.4018(10)	1σ	0.33	0.38	0.29
$M(t2)$	1/3	2/3	0	—	0.67		0.33
S(1)	0	0	0.0633(12)	8σ			
S(2)	1/3	2/3	0.8108(21)	1σ			
S(3)	0	0	0.5876(19)	1σ			
S(4)	1/3	2/3	0.3245(12)	5σ			

Note. For the definition of Model C, see text. Δz is the difference (in terms of σ) between z coordinates of corresponding atomic sites in Tables I and II. For the other symbols see Table I.

TABLE III

SELECTED INTERATOMIC DISTANCES OBTAINED FROM THE SINGLE-CRYSTAL EXPERIMENT

		Distance (Å)	Difference[a]	Average
$M(o)$	S(2)	2.527(4)	6.2σ	2.545
$M(o)$	S(3)	2.562(4)		
$M(t1)$	S(3)	2.288(7)	4.7σ	2.306
$M(t1)$	S(4)	2.324(3)		
$M(t2)$	S(1)	2.344(4)	2.2σ	2.331
$M(t2)$	S(2)	2.318(7)		
S(1)	S(2)	3.880(10)		
S(2)	S(3)	3.443(3)		
S(3)	S(4)	3.812(8)		
S(1)	S(4)	3.797(3)		

Note. Estimated standard deviations are given in parentheses.

[a] σ is the e.s.d. of the difference between the two distances.

TABLE IV

SELECTED INTERATOMIC DISTANCES OBTAINED FROM THE POWDER NEUTRON EXPERIMENT

		Distance (Å)	Difference[a]	Average
M(*o*)	S(2)	2.44(3)	5.4σ	2.56
M(*o*)	S(3)	2.67(3)		
M(*t*1)	S(3)	2.26(3)	3.1σ	2.31
M(*t*1)	S(4)	2.36(2)		
M(*t*2)	S(1)	2.29(2)	0.1σ	2.30
M(*t*2)	S(2)	2.30(3)		
S(1)	S(2)	3.75(3)		
S(2)	S(3)	3.47(3)		
S(3)	S(4)	3.86(3)		
S(1)	S(4)	3.84(2)		

Note. Estimated standard deviations are given in parentheses.

[a] σ is the e.s.d. of the difference between the two distances.

ing atomic sites as determined by X-ray and the neutron diffraction) reported in Table II are worthy of discussion, considering that the coordination tetrahedron of site $M(t_2)$ (for which $z = 0$) is quite regular and that, anyhow, no asymmetry in the electron distribution can be expected for high spin Co^{2+} and for Ga^{3+} sharing that site.

A high value of Δz (9σ) is reported for *M*(*o*) and this result may be indicative of the fact that the center of gravity of *M*(*o*), as determined by the neutron experiment, is different from that observed by X-ray diffraction. This difference may be attributed to asymmetric effects due to some covalency in the *M*(*o*)–S bonds. This asymmetry should generate a distortion of the coordination polyhedron of *M*(*o*) and, indeed, the differences between coordination distances of a given cation (see Tables III and IV) appear to be significant in the case of *M*(*o*), the true symmetry of its coordination polyhedron being C_{3v}. Since the ratio of the scattering factors of Co and In is different for neutrons and X-rays, the center of gravity of site *M*(*o*) shows, for the two sets of diffraction data, two different *z* coordinates and thus the two cations in *M*(*o*) behave as if they had two slightly different positions in this site.

The high Δz values observed for S(1) and S(4) may possibly be generated by some asymmetry in the electron distribution of these anions limiting the four-layer packets characteristic of this structure.

Note

When the final version of this paper was ready, the referee drew our attention to a second paper by Haeuseler *et al.*(*10*) on the same subject. While their single-crystal X-ray diffraction results are in agreement with our own results for the cation distribution in the pseudooctahedral sites, they write that "there is no evidence that the occupation of the two tetrahedral sites is different." This is at variance with the conclusions reported above, since, on the basis of our X-ray and neutron results, we adopt Model C as our best model. While we cannot offer an explanation for this difference, we wish to stress the fact that our choice was based on the convergence of considerations coming from two independent sets of measurements (X-ray and neutron data) and that it seems difficult, on the basis of X-ray data only, to be sure about a cation distribution involving atoms (Ga and Co) differing by only four units in atomic number, as pointed out in the Introduction.

Acknowledgments

We thank Prof. F. De Martin for helpful suggestions in planning the single-crystal X-ray experiment and Dr. M. Bellotto for assistance in the implementation of computer programs for the elaboration of experimental data. One of us (M.Z.) thanks the Consiglio Nazionale delle Ricerche, Roma, for financial support of this research.

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