

## The Quaternary Systems $MS-Cr_2S_3-In_2S_3$ ( $M = Mn, Fe, Co$ )

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The phase diagrams of the quaternary systems  $MCr_2S_4-MIn_2S_4-Cr_2S_3-In_2S_3$  ( $M = Mn, Fe, Co, (Cd, Hg)$ ) have been studied by X-ray phase analyses and FIR spectra of quenched samples. At temperatures above 1200, 1200, and 1330 K, spinel-type solid solutions  $(1 - y)Cr_{2-2x}In_{2x}S_3-yMS$  are formed in a large range of compositions. Two-phase regions are only the regions near  $Cr_2S_3$  and between  $MS$  and  $M(Cr, In)_2S_4$ . At lower temperatures, the spinel-type solid solutions (except  $M = Cd$  and  $Hg$ ) decompose to Cr-rich and In-rich compounds. The sections with constant  $y$  show more or less nonquasibinary behavior. Thus, cobalt is enriched in the Cr-rich solid solutions. The phase width of  $Cr_2S_3$  with respect to  $M$  content is 2.5 mole% for  $M = Co$ , but it is negligible for  $M = Mn$  and  $Fe$ . © 1992 Academic Press, Inc.

### Introduction

In the quaternary systems  $MS-Cr_2S_3-In_2S_3$  with  $M = Mn, Fe, Co, Cd,$  and  $Hg$ , hitherto only the ternary borderlines  $MS-In_2S_3$  (1–8),  $Cr_2S_3-In_2S_3$  (7, 8), and the quasibinary sections  $MCr_2S_4-MIn_2S_4$  (5, 6, 9–13) have been studied. Whereas in the case of  $Cr_2S_3-In_2S_3$  incomplete mutual solid solubility has been observed, complete series of spinel-type solid solutions are formed in the sections  $MIn_2S_4-In_2S_3$  and  $MCr_2S_4-MIn_2S_4$ . In the latter case (as well as in the case of  $Cr_2S_3-In_2S_3$ ), the spinel-type solid solutions obtained at elevated temperatures, however, decompose to Cr-rich and In-rich compounds at lower temperatures (5, 6, 8). This decomposition is kinetically retarded and probably spinoidal in nature (5, 14).

In the case of the systems  $(1 - y)$

$Cr_{2-2x}In_{2x}S_3-yMS$  with  $0 < y < 0.5$ , it is expected (and already established for  $NiS-Cr_2S_3-In_2S_3$  (8)) that spinel-type mixed crystals are formed within large ranges of  $x$  and  $y$ . However, the question arises whether decomposition to Cr-rich and In-rich compounds at lower temperatures occurs quasibinarly, i.e., within sections of constant  $M$  content, or whether the compatible phases have different contents of bivalent metals  $M$ . In this paper, we present the phase relationships of the systems  $MnS-Cr_2S_3-In_2S_3$ ,  $FeS-Cr_2S_3-In_2S_3$ , and  $CoS-Cr_2S_3-In_2S_3$  at temperatures above and below decomposition of the spinel-type solid solutions. The phase diagrams were established by X-ray phase analyses of equilibrated samples quenched to ambient temperature. Furthermore, FIR spectra of the spinel-type solid solutions have been recorded.

## Experimental

The ternary and quaternary sulfides under discussion have been prepared by firing appropriate mixtures of the binary sulfides in evacuated closed silica tubes at elevated temperatures. The binary sulfides CoS (mixtures of  $Co_{1-x}S$  and  $Co_9S_8$  (15)) and FeS were obtained from the elements,  $Cr_2S_3$  from anhydrous  $CrCl_3$  and  $H_2S$ , and  $\alpha$ -MnS by precipitation from an aqueous solution of  $MnCl_2$  with gaseous  $H_2S$ . Details are given elsewhere (6, 8). Starting materials were  $In_2S_3$  (Fluka), anhydrous  $CrCl_3$  (Fluka),  $MnCl_2 \cdot 4H_2O$  (Riedel de Hen), and the elements iron, 5 N (Ventron), cobalt, 3 N (Ventron), and sulfur, 5 N (Fluka). Both starting materials and ternary and quaternary sulfides were checked with respect to oxygen content and other impurities by X-ray and IR methods.

The samples were equilibrated at the respective temperatures and quenched with ice water to ambient temperature. The number of heating periods (1–3) and annealing times (1–50 weeks) necessary for equilibration depends strongly on the nature of  $M$  and the temperatures chosen (5).

The monophasic and two-phase sulfides obtained were analyzed by the X-ray Guinier powder technique (Huber Guinier 600 system) using  $CuK\alpha_1$  radiation;  $\alpha$ -quartz was used as an internal standard ( $a = 491.36$  and  $c = 540.54$  pm). Unit-cell dimensions were calculated by the least-squares method. Far-infrared spectra were recorded on a Bruker Model IFS 114 Fourier transform interferometer (paraffin mulls).

## Results

### 1. Sections $MS-Cr_2S_3$ ( $M = Mn, Fe, Co$ )

In the ternary systems  $MS-Cr_2S_3$ , four compounds are formed, viz,  $MS$ , spinel-type  $MCr_2S_4$ ,  $Cr_2S_3$  hP20, and  $Cr_2S_3$  hR10. The binary sulfides  $MS$  are polymorphous

(16). Possible solid solubility of  $Cr_2S_3$  in  $MS$  has not been studied in this work (but see, for example, (17)). Contrary to  $Fe_3Se_4$ -type  $NiCr_2S_4$  (8), the phase widths of ternary  $MCr_2S_4$  with respect to an excess and a deficiency of  $Cr_2S_3$  are very small (6). However, solid solutions are formed by incorporation of CoS in NiAs defect-type  $Cr_2S_3$ . The phase widths of samples quenched from 1270 K are 2.5 mole%. As found for the system  $NiS-Cr_2S_3$  (8), the trigonal polymorph  $Cr_2S_3$  hP20 is stabilized by formation of mixed crystals. The unit-cell dimensions of  $Cr_2S_3$  hP20 increase with an increase in CoS content up to  $a = 594.0$  and  $c = 1112.8$  pm compared to  $a = 593.3$  and  $c = 1110.5$  pm at negligible CoS contents. No mutual solid solubilities have been established for the systems  $MS-(MCr_2S_4)-Cr_2S_3$  with  $M = Mn$  and  $Fe$ .

### 2. Phase Diagrams of Quaternary $MS-Cr_2S_3-In_2S_3$ ( $M = Mn, Fe, Co$ ) at Temperatures above Decomposition to Cr- and In-Rich Spinel-Type Solid Solutions

The phase diagrams of the quaternary systems  $MS-Cr_2S_3-In_2S_3$  ( $M = Mn, Fe, Co$ ) at 1270, 1270, and 1340 K, respectively, are given in Figs. 1–3. The phase relationships shown have been established by X-ray phase analyses of samples quenched to ambient temperature. Like the quasibinary sections  $Cr_2S_3-In_2S_3$  (7, 8) and  $MCr_2S_4-MIn_2S_4$  (5, 6, 9–13), there are large regions of spinel-type  $(1 - y)Cr_{2-2x}In_{2x}S_{3-y}MS$  solid solutions. Only at the Cr-rich parts are the systems two phase; i.e., spinel-type solid solutions are in equilibrium with  $Cr_2S_3$ . The solubility of  $In_2S_3$  in NiAs defect-structure  $Cr_2S_3$  is negligible. The same is true for the solubility of  $In_2S_3$  in MnS, FeS, and CoS (1–6).

The unit-cell dimensions of the quaternary spinel-type solid solutions are included in Figs. 1–3 (see also (15, 18)). In all systems studied, the lattice constants of binary  $In_2S_3$  are largest while those of ternary  $MCr_2S_4$

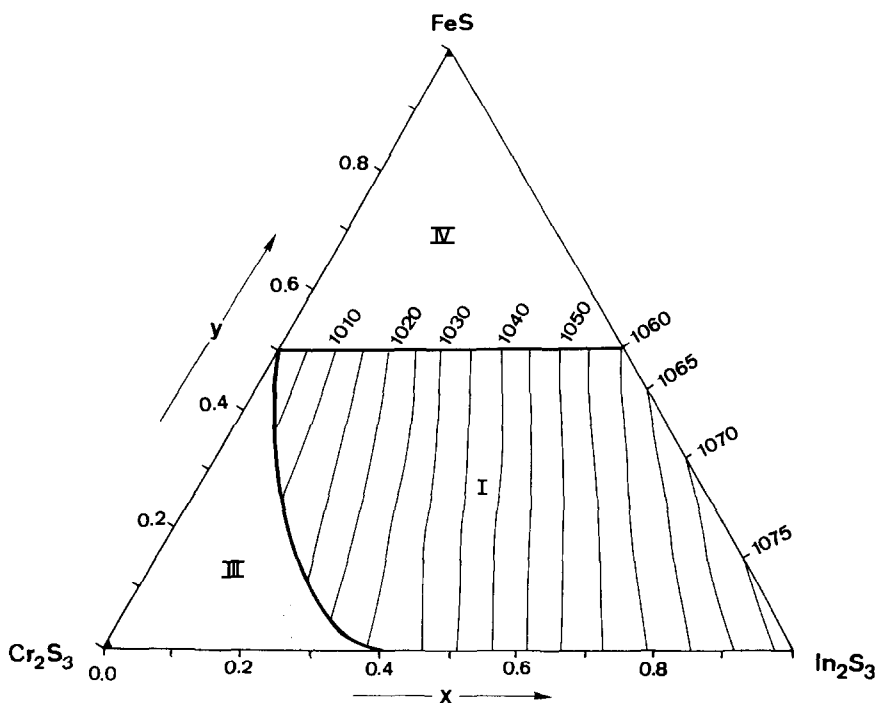


FIG. 1. Phase diagram of the quaternary system FeS-Cr<sub>2</sub>S<sub>3</sub>-In<sub>2</sub>S<sub>3</sub> at 1270 K: I, spinel-type solid solutions; II, Cr<sub>2</sub>S<sub>3</sub>-type solid solutions; III, two-phase, spinel type and Cr<sub>2</sub>S<sub>3</sub> type; IV, two-phase, spinel-type solid and MnS; (—) samples of equal lattice parameters (pm).

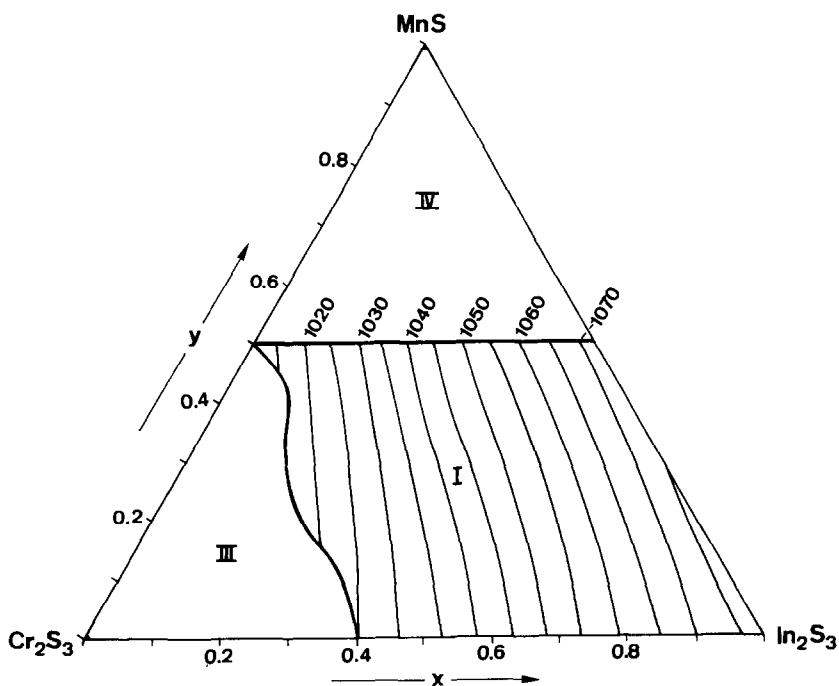


FIG. 2. Phase diagram of the quaternary system MnS-Cr<sub>2</sub>S<sub>3</sub>-In<sub>2</sub>S<sub>3</sub> at 1270 K (for further explanation see Fig. 1).

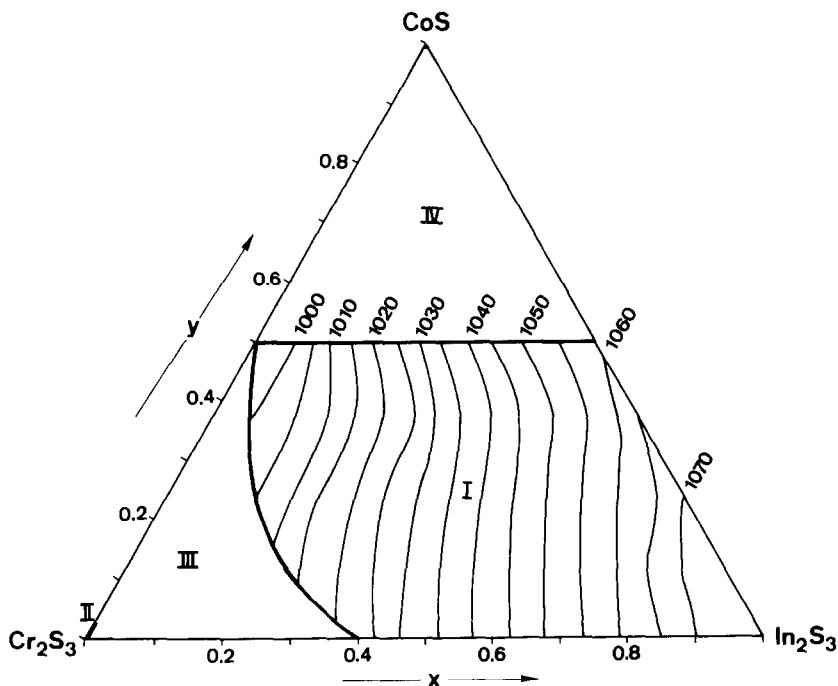


FIG. 3. Phase diagram of the quaternary system  $CoS-Cr_2S_3-In_2S_3$  at 1340 K (for further explanation see Fig. 1).

are smallest. However, the contour lines of equal lattice parameters are inclined differently owing to the larger ionic radius of manganese compared to those of iron and cobalt. The lattice constants of quaternary  $(1 - y)Cr_{2-2x}In_{2x}S_3-yMS$  do not fully obey Vegard's rule for both sections, i.e., those with a constant content of  $M$  ( $y = \text{const}$ ) and those with constant Cr/In ratios ( $x = \text{const}$ ). For details see (8, 15, 18).

The FIR spectra of spinel-type  $(1 - y)Cr_{2-2x}In_{2x}S_3-yMS$  (see Figs. 4–6 and (15, 18)) differ greatly with respect to the Cr/In ratios, owing to the different degree of inversion of the chromium (normal spinels) and indium sulfides (inverse spinels) (see the discussion given in (8, 15, 18)). Thus, the bandwidths increase and the band frequencies decrease with an increase in indium content. The influence of the bivalent metals is less important with respect to both the content and the nature of  $M$ .

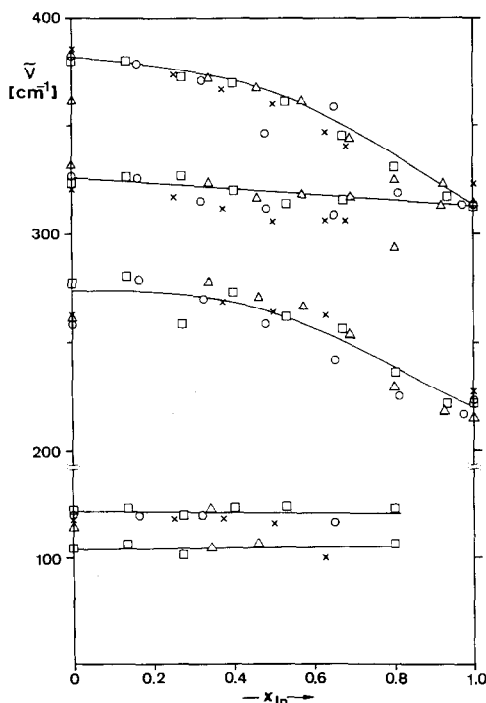


FIG. 4. IR bands ( $cm^{-1}$ ) of  $(1 - y)Cr_{2-2x}In_{2x}S_3-yMnS$  spinel-type solid solutions:  $y = (\times) 0.5, (O) 0.38, (\square) 0.25, (\diamond) 0.13$ .

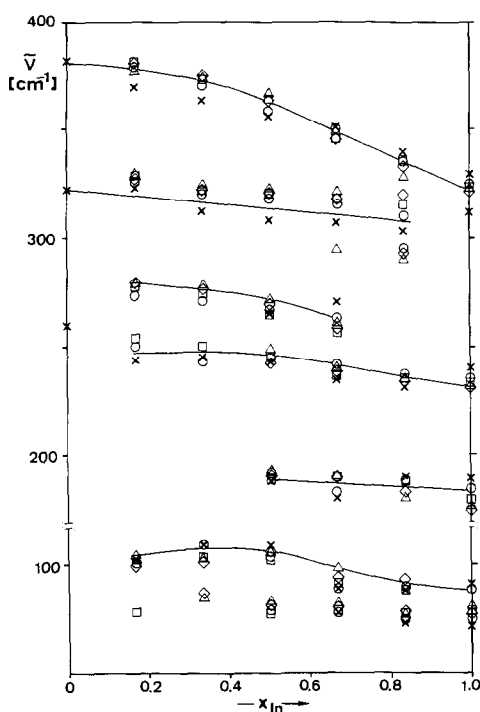


FIG. 5. IR bands ( $\text{cm}^{-1}$ ) of  $(1-y)\text{Cr}_{2-2x}\text{In}_{2x}\text{S}_3-y\text{FeS}$  spinel-type solid solutions:  $y = (\times) 0.5, (\text{O}) 0.4, (\square) 0.3, (\diamond) 0.2, (\Delta) 0.1$ .

### 3. Decomposition of $(1-y)\text{Cr}_{2-2x}\text{In}_{2x}\text{S}_3-y\text{MS}$ ( $M = \text{Mn}, \text{Fe}, \text{Co}, (\text{Cd}, \text{Hg})$ ) Spinel-Type Solid Solutions at Temperatures below 1200–1330 K

At temperatures below 1200 ( $M = \text{Mn}$ ), 1200 ( $M = \text{Fe}$ ), and 1330 ( $M = \text{Co}$ ) K, the quaternary spinel-type chromium indium sulfides decompose into Cr-rich and In-rich mixed crystals as do ternary  $\text{Cr}_{2-2x}\text{In}_{2x}\text{S}_3$  (8) and quasibinary  $M\text{Cr}_{2-2x}\text{In}_{2x}\text{S}_4$  (5, 6). The phase relationships in the systems  $\text{FeS}-\text{Cr}_2\text{S}_3-\text{In}_2\text{S}_3$  at 870, 1020, and 1170 K and those of  $\text{CoS}-\text{Cr}_2\text{S}_3-\text{In}_2\text{S}_3$  at 870 and 1070 K are given in Figs. 7 and 8. As shown in the figures, the miscibility gaps increase with decreasing temperature.

In the case of the system  $\text{MnS}-\text{Cr}_2\text{S}_3-\text{In}_2\text{S}_3$ , decomposition takes place extremely slowly (see the discussion

given in (5)). Thus, the respective phase diagrams could not be completely established. In the case of the systems  $M\text{S}-\text{Cr}_2\text{S}_3-\text{In}_2\text{S}_3$  with  $M = \text{Cd}$  and  $\text{Hg}$ , no decomposition of the spinel-type solid solutions occurs, even with reaction times of more than 1 year.

The true composition of the compatible spinel phases cannot be determined from the unit-cell dimensions (see Table I) alone because there are two unknown factors, viz,  $x$  and  $y$ . However, it is revealed from the lattice parameters that the iron-containing spinel-type mixed crystals behave nearly quasibinarily on decomposition; i.e., the iron contents of the compatible phases are nearly equal. In the case of the ternary cobalt sulfides, cobalt is enriched in the Cr-rich spinel-type solid solutions and depleted in the In-rich ones (see Fig. 8).

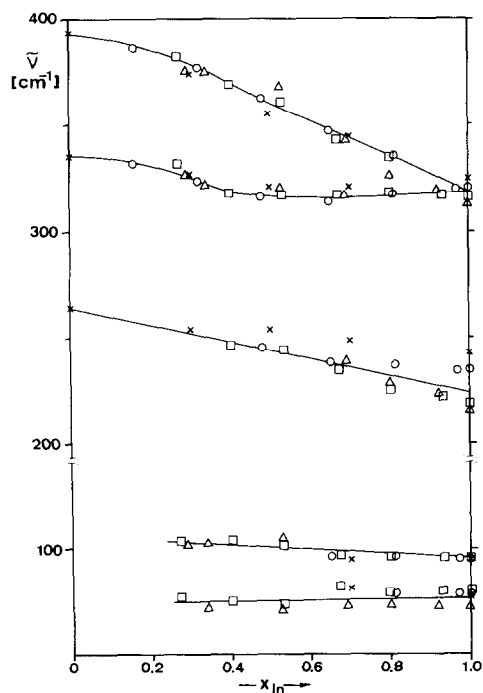


FIG. 6. IR bands ( $\text{cm}^{-1}$ ) of  $(1-y)\text{Cr}_{2-2x}\text{In}_{2x}\text{S}_3-y\text{CoS}$  spinel-type solid solutions (for further explanation see Fig. 4).

TABLE I

UNIT-CELL DIMENSIONS (pm) OF SPINEL-TYPE CHROMIUM INDIUM SULFIDE SOLID SOLUTIONS  $(1 - y)\text{Cr}_{2-2x}\text{In}_{2x}\text{S}_3-y\text{MS}$  ( $M = \text{Fe}, \text{Co}$ )<sup>a</sup> BEFORE AND AFTER DECOMPOSITION AT TEMPERATURES BELOW 1200 K

Compositions		Starting material	Temperature (K)	Time (days)	Resultants	
y	x				Cr-rich	In-rich
FeS-Cr <sub>2</sub> S <sub>3</sub> -In <sub>2</sub> S <sub>3</sub>						
0.1	0.500	1033.5(2)	1170	112	1023.8(9)	1060.3(3)
	0.667	1048.9(2)			1025.7(9)	1060.5(6)
0.2	0.500	1033.3(2)			1021.6(1)	1058.6(7)
	0.667	1047.2(2)			1043.1(7) <sup>b</sup>	1059.9(9)
0.3	0.500	1032.4(2)			1021.8(2)	1053.3(3)
0.1	0.500	1033.5(2)	1020	112	1016.8(2)	1073.2(9)
	0.667	1048.9(2)			1017.5(9)	1072.8(9)
0.2	0.500	1033.3(2)			1013.9(9)	1067.1(7)
	0.667	1047.2(2)			1017.5(9)	1066.0(4)
0.3	0.500	1032.4(2)			1022.9(2)	1040.9(3)
0.4	0.500	1032.2(2)			1016.8(9)	1041.2(7)
0.1	0.333	1020.8(4)	870	90	1017.5(2)	1066.6(8)
	0.500	1033.5(2)			1017.7(2)	1068.1(3)
	0.667	1048.9(2)			1016.2(2)	1067.0(3)
	0.833	1061.8(2)			1016.7(9)	1067.6(3)
0.2	0.333	1020.2(2)			1014.8(3)	1062.6(8)
	0.500	1033.3(2)			1015.4(5)	1062.0(3)
	0.667	1047.2(2)			1014.8(3)	1061.8(2)
	0.833	1060.0(2)			1014.3(6)	1061.5(1)
0.3	0.333	1020.4(2)			1012.5(4)	1056.7(9)
	0.500	1032.4(2)			1012.9(2)	1057.0(3)
	0.667	1045.2(2)			1013.0(3)	1056.4(5)
0.4	0.333	1020.7(2)			1008.0(4)	1055.3(9)
	0.500	1032.2(2)			1007.2(3)	1053.8(4)
	0.667	1043.1(2)			1007.0(4)	1053.8(4)
	0.833	1055.0(2)			1007.1(3)	1053.7(4)
CoS-Cr <sub>2</sub> S <sub>3</sub> -In <sub>2</sub> S <sub>3</sub>						
0.13	0.46	1028.6(1)	1070	4	1017.7(1)	1058.3(2)
	0.57	1039.4(1)			1015.3(3)	1058.8(1)
0.25	0.40	1022.8(1)			1001.1(1)	1061.9(1)
	0.53	1033.4(1)			1001.3(8)	1058.4(3)
	0.67	1044.8(1)			1000.4(2)	1058.0(2)
0.38	0.48	1025.9(2)			1001.6(1)	1054.2(3)
	0.65	1039.2(1)			1000.5(1)	1049.3(1)
0.13	0.34	1019.3(1)	870	4	1013.7(1)	1070.2(3)
	0.46	1028.6(1)			1012.1(1)	1069.5(1)
	0.57	1039.4(1)			1010.1(1)	1068.9(1)
	0.69	1048.1(1)			1007.7(1)	1068.5(1)
0.25	0.27	1011.6(1)			996.1(1)	1069.5(8)
	0.40	1022.8(1)			996.5(2)	1070.3(4)
	0.53	1033.4(1)			996.1(3)	1070.3(4)
	0.67	1044.8(1)			995.1(2)	1070.5(1)
0.38	0.32	1014.1(1)			995.7(9)	1066.9(3)
	0.48	1025.9(2)			996.3(3)	1063.1(4)
	0.65	1039.2(1)			997.3(1)	1064.6(1)
	0.81	1049.9(1)			996.3(1)	1959.0(1) <sup>b</sup>

<sup>a</sup> The composition of other samples given in Table I of (8) is related to the formula  $\text{Ni}_y(\text{In}_x\text{Cr}_{1-x-y})\text{S}_{3-2y}$ , not to  $(1 - y)\text{Cr}_{2-2x}\text{In}_{2x}\text{In}_{2y}\text{S}_3-y\text{NiS}$  as reported in (8).

<sup>b</sup> Incomplete decomposition.

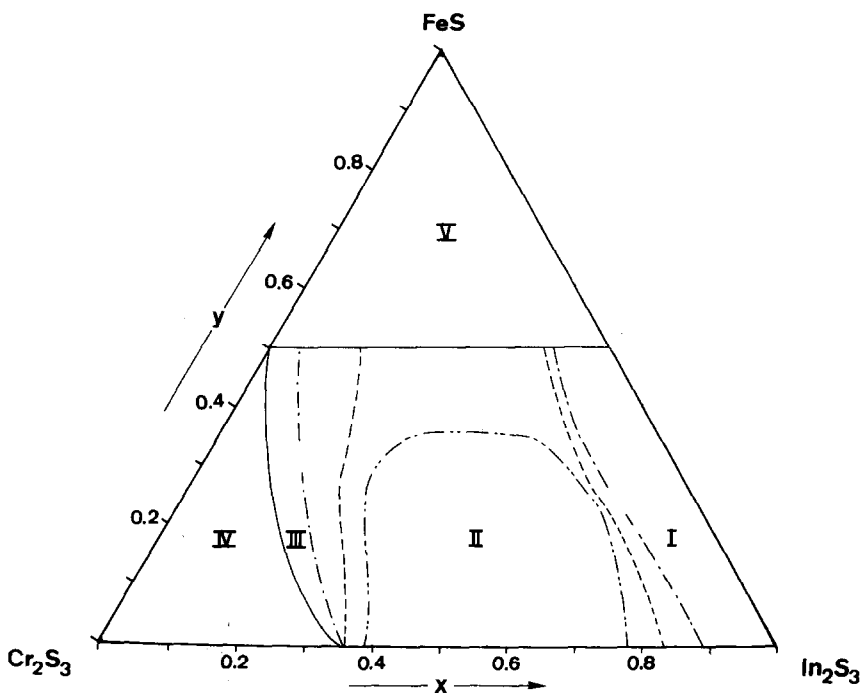


FIG. 7. Phase relationships of the system  $\text{FeS}-\text{Cr}_2\text{S}_3-\text{In}_2\text{S}_3$  at 870 (—), 1020 (---) and 1170 (— · —) K, respectively: I, In-rich spinel-type solid solutions; II, two-phase, Cr-rich and In-rich spinel-type solid solutions; III, Cr-rich spinel-type solid solutions; IV, two-phase, spinel type and  $\text{Cr}_2\text{S}_3$  type; V, multiphase, Cr-rich and In-rich spinel-type solid solutions and FeS ( $\text{Fe}_9\text{S}_8$  and  $\text{Fe}_{1-x}\text{S}$ ).

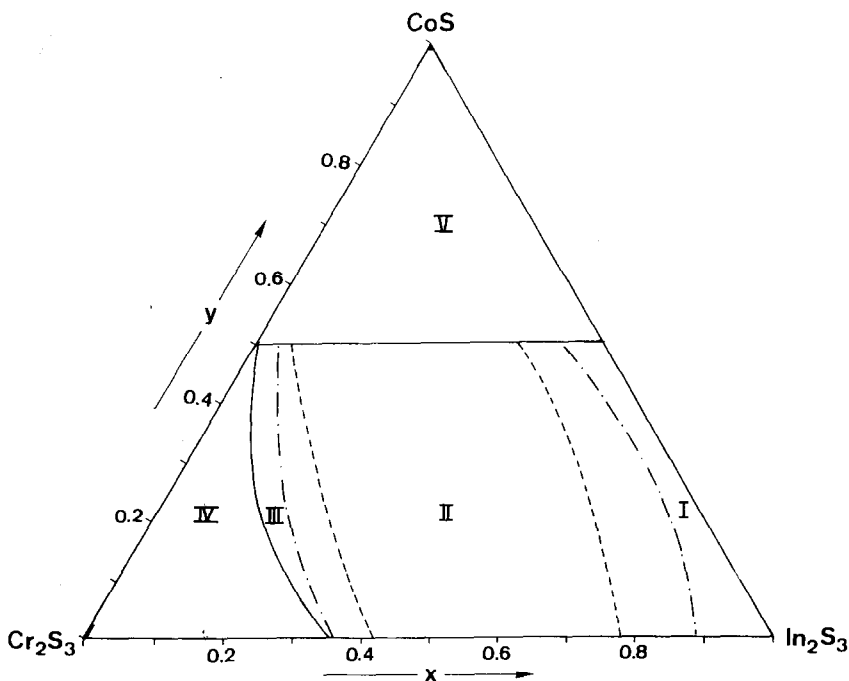


FIG. 8. Phase relationships of the quaternary system  $\text{CoS}-\text{Cr}_2\text{S}_3-\text{In}_2\text{S}_3$  at 870 (---) and 1070 (— · —) K, respectively (for further explanations see Fig. 7).

## Discussion

The results obtained reveal and confirm that binary and ternary chromium and indium sulfides form spinel-type solid solutions in large ranges of composition. In the case of  $M = Mn, Fe, Co$ , and  $Ni$  (8) (but not  $M = Cd$  and  $Hg$ ), the solid solutions formed decompose into Cr-rich and In-rich mixed crystals at temperatures below 1200, 1200, 1330, and 1200 K, respectively. This decomposition is kinetically retarded as discussed in (5) and probably spinoidal in nature (14). According to high-resolution transmission electron microscope studies (14) the decomposition starts by migration of metal ions in the tetrahedral  $8a$  sites of the spinel structure to the  $16c$  interstitial sites, forming lamellar domains of the NaCl structure and NaCl superstructure ( $Li_2MnBr_4$ ,  $cF56$  type (19)), respectively.

The change in the unit-cell dimensions of quaternary spinel-type solid solutions as a function of composition is caused by the different size of the metal ions involved as well as by the alteration in the cation distribution on going from Cr-rich to In-rich compounds with different degrees of inversion (8). Thus, the cation distribution with respect to the formula  $(M, In, \square)_4[M, Cr, In]_2S_4$  can be obtained from the lattice constants, to a certain extent (18). For determination of the exact cation distribution, however, X-ray structure studies are necessary (see, for example, (20, 21)). X-ray structure determination is also required to establish the accurate composition of the compatible spinel phases after decomposition (18). The FIR spectra of quaternary spinel-type chromium indium sulfides, especially in view of the degree of inversion and metal ion distribution on tetrahedral and octahedral sites, have been discussed elsewhere (8, 15, 18).

The octahedral site preferences in sulfides of the metal ions under discussion rank  $Mn^{2+} < In^{3+} < Co^{2+} < Fe^{2+} < Ni^{2+} < Cr^{3+}$ . This sequence reflects the metal ion

distribution in spinel-type chromium and indium sulfides. We assume that deviation from the quasibinary behavior of sections with a constant  $M$  content is also due to the relative site preferences of the metal ions involved. Thus, the relatively low octahedral site preference of  $Co^{2+}$  obviously causes the enrichment of cobalt in the Cr-rich spinel-type solid solutions mentioned above. For a more detailed analysis, however, the true composition of the compatible spinel phases must be established by X-ray structure determination.

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