Phase Relationships in the Systems MS–Cr_2S_3–In_2S_3 (M = Co, Cd, Hg)

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The phase diagrams of the quaternary systems MS–Cr_2S_3–In_2S_3, with M = Co, Cd, and Hg, were studied with the help of X-ray powder photographs of quenched samples, high-temperature X-ray diffraction patterns, DTA and TG measurements, and far-infrared spectra. Because indium sulfides do react with silica tubes, alumina crucibles must be used for annealing the samples. Complete series of mixed crystals are formed among the spinel-type compounds MCr_2S_4, MIn_2S_4 (M = Cd, Hg), and In_2S_3. $HgIn_2S_4$ is decomposed at temperatures above 300°C. In the sections $CoCr_2S_4$–$CoIn_2S_4$ and $CoCr_2S_4$–In_2S_3 relatively large miscibility gaps exist due to the change from normal to inverse spinel structure. But the interchangeability of both systems increases with increasing temperature, and at temperatures above 1000°C, complete series of solid solutions are formed, which can be quenched to ambient temperature. Superstructure ordering like that of ordered α-In_2S_3 has been found in the In-rich region of the MIn_2S_4–In_2S_3 solid solutions. The unit cell dimensions of all stoichiometric and phase boundary compounds, e.g., $Cd_{1.15}In_{1.9}S_4$, including the chromium spinels MCr_2S_4 (M = Mn, Zn) and $ZnCr_2Se_4$, are given and discussed in terms of possible deviations from stoichiometry.

Introduction

The phase diagrams of the three component systems MS–Cr_2S_3–In_2S_3, with M = Mn, Fe, Co, Cd, and Hg, exhibit as the only ternary compounds the sulfide spinels MCr_2S_4 and MIn_2S_4. The spinel phases crystallize partly in the normal structure, viz., MCr_2S_4 and $HgIn_2S_4$, and partly in the inverse structure, viz., $MnIn_2S_4$, $FeIn_2S_4$, and $CoIn_2S_4$ (*1*). Additionally it is known that solid solutions between the spinel-type ternary compounds and indium sulfide, which also crystallizes in spinel structure, are formed. But little work has been done with regard to the exact phase boundaries, the possible formation of superstructures due to cation ordering, and the transition from normal spinels to inverse structures.

Whereas the binary sulfides MS, Cr_2S_3, and In_2S_3, as well as the stoichiometric spinels, are well known in the literature, only the following quasi-binary sections of the ternary phase diagrams under discussion have been studied: Cr_2S_3–In_2S_3 (*2, 3*), MCr_2S_4–MIn_2S_4 with M = Mn (*4, 5*), Fe (*5–7*), Co (*5*), and Cd (*3, 8*), and MS–In_2S_3 with M = Fe (*9*), Co (*10, 11*), and Cd (*12, 13*). In the present work we report on the phase equilibria in the quasi-binary sections MS–In_2S_3, MCr_2S_4–MIn_2S_4, and MCr_2S_4–In_2S_3 (M = Co, Cd, Hg) and upon possible nonstoichiometry of chromium chalcide spinels.

Experimental Methods

Starting materials were cadmium sulfide (Schuchardt), mercury sulfide (cinnabar; Merck), chromium sulfide (Alfa Products),

and indium sulfide (Fluka). CoS, i.e., a mixture of Co_9S_8 and $Co_{1-x}S$ with a Co/S ratio of 1 : 1, was made from the elements cobalt (Merck) and sulfur (99.999%; Fluka). The ternary spinels MCr_2S_4 and MIn_2S_4 were obtained from stoichiometric amounts of the binary sulfides at 800°C.

The binary (or ternary) sulfides were equilibrated by the following procedure. Mixtures of the powdered sulfides in various molar ratios were homogenized in an oscillating mill and pressed into pellets. Coarse pieces of the pellets were heated in sealed evacuated silica ampoules or in alumina crucibles inserted in silica ampoules first at 600°C for 10 days, then twice at the equilibrium temperature, e.g., at 800°C, for 4 days. After each heat treatment the sintered material was ground and again pressed to pellets. Finally the samples were quenched to ambient temperature.

The obtained samples were analyzed with X-ray Guinier powder technique, using $CrK\alpha_1$ radiation. Quartz was used as a standard (SiO$_2$, $a_0 = 491.36$ and $c_0 = 540.54$

pm). Lattice constants were calculated by the least-squares method. High-temperature X-ray diffraction patterns were obtained using an Enraf–Nonius Guinier Simon camera.

From most samples the infrared spectra were recorded on Beckman Model FS 720 or Bruker Model IFS 114 Fourier-transform interferometers using Nujol mulls. The thermogravimetric (TG, DTG) and DTA measurements were made in a vacuum using a thermoanalyzer Linseis L 62 and a thermobalance L 81.

Results

System CdS–In_2S_3–Cr_2S_3

In the quaternary system CdS–In_2S_3–Cr_2S_3 complete series of spinel solid solutions are formed within the whole triangular region $CdCr_2S_4$–$CdIn_2S_4$–In_2S_3 of the ternary phase diagram (see Fig. 1). In the regions CdS–$CdCr_2S_4$–$CdIn_2S_4$ and $CdCr_2S_4$–In_2S_3–Cr_2S_3 the system is mostly
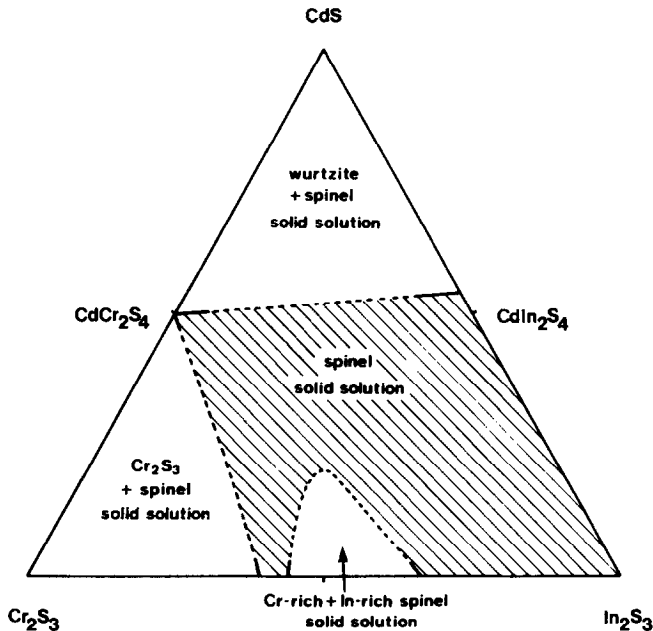

FIG. 1. Ternary phase diagram of the system CdS–In_2S_3–Cr_2S_3 at 800°C.

two-phase. In the former region wurtzite-type and spinel-type solid solutions, and in the latter region two kinds of spinel-type or spinel-type and Cr_2S_3 (2, 3, 8) mixed crystals coexist. These results were obtained from samples quenched from 800°C.

These studies, done some years ago, were complicated by the fact that indium sulfide spinels react with the wall of the silica tubes to form silicates of the metals present. This behavior, unknown in the literature so far, influenced the composition of the annealed samples. Therefore, the obtained results were not fully reproducible. After finding the reason for this trouble (see also Riedel and Karl (7), we reinvestigated the sections $CdS-In_2S_3$, $CdCr_2S_4-CdIn_2S_4$, and $CdCr_2S_4-In_2S_3$ using alumina crucibles, which do not react with indium chalcide spinels, inserted in silica ampoules as reacting capsules.

Our X-ray investigations indicate that Vegard's rule is obeyed in the section $CdCr_2S_4-CdIn_2S_4$, whereas in both the sections $CdCr_2S_4-In_2S_3$ and $CdS-In_2S_3$ Vegard's rule is not obeyed. This is also the case if the compositions of the solid solutions are taken as $Cd_{1-x}Cr_{2-2x}In_{8x/3}S_4$ and $Cd_{1-x}In_{2+2x/3}S_4$, respectively. In particular the unit cell dimensions of the In_2S_3-rich solid solutions remain nearly unaffected by small cadmium and chromium concentrations. In the system $CdS-In_2S_3$ the phase boundary of the spinel-type solid solutions has been found at a cadmium concentration which is larger than that given by the formula $CdIn_2S_4$. The obtained lattice constants are 1084.5(1) pm in the case of pure $CdIn_2S_4$ (1084.5 pm (13), 1081.8 (14)) and 1085.9(3) pm for the cadmium-richest mixed crystals of the approximate composition $Cd_{1.15}In_{1.9}S_4$ (samples quenched from 800°C, see also (12, 15)).
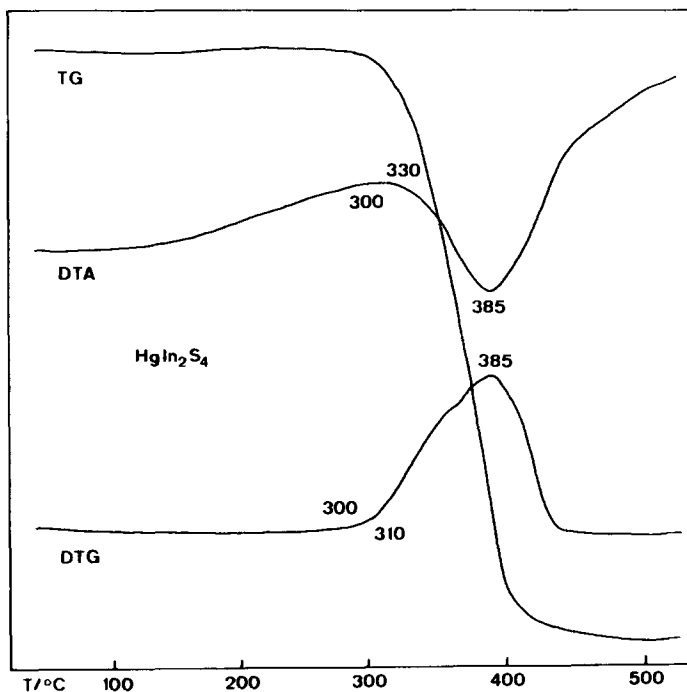
System $HgS-In_2S_3-Cr_2S_3$

The phase relationships found in the qua-

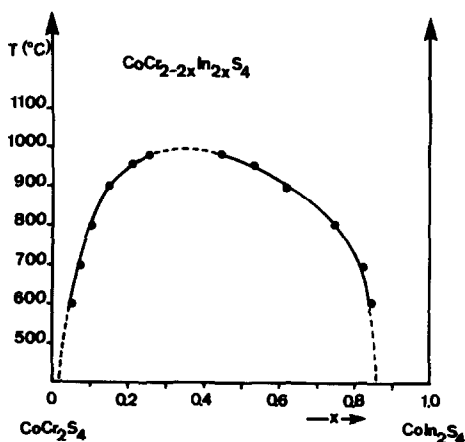FIG. 2. Thermogram of $HgIn_2S_4$ (vacuum, heating rate 1°C/min).

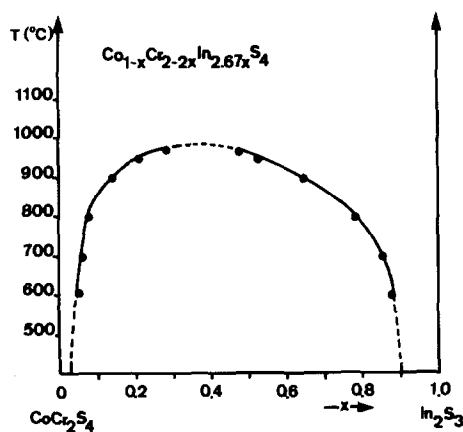FIG. 3. Phase diagram of the quasi-binary system CoCr$_2$S$_4$–CoIn$_2$S$_4$.

FIG. 4. Phase diagram of the system CoCr$_2$S$_4$–In$_2$S$_3$.

ternary system HgS–In$_2$S$_3$–Cr$_2$S$_3$ are nearly equal to those of the corresponding cadmium sulfide system discussed above, i.e., complete series of spinel solid solutions are formed in the whole triangular region HgCr$_2$S$_4$–HgIn$_2$S$_4$–In$_2$S$_3$ of the ternary phase diagram, but in the regions HgS–HgCr$_2$S$_4$–HgIn$_2$S$_4$ and HgIn$_2$S$_4$–In$_2$S$_3$–Cr$_2$S$_3$ the system is two-phase. In the section HgCr$_2$S$_4$–HgIn$_2$S$_4$ Vegard's rule is obeyed. The unit cell dimensions of the stoichiometric HgIn$_2$S$_4$ spinel have been

found to be 1085.3(1) pm (1083.3 pm (*14*)).

HgIn$_2$S$_4$ is thermally unstable. It decomposes at temperatures above 300°C, finally forming In$_2$S$_3$, HgS, mercury, and sulfur (see Fig. 2) (*16*). Therefore, samples of HgIn$_2$S$_4$ obtained by the usual procedure from silica ampoules are mostly not homogeneous. This is shown by the poor ir spectra of such samples (*16*), the occurrence of small amounts of elementary mercury, and the finding that the lattice constants of the remaining spinel-type compound are smaller than those given above.
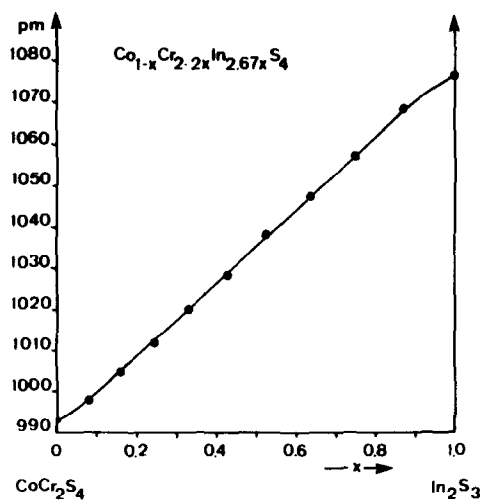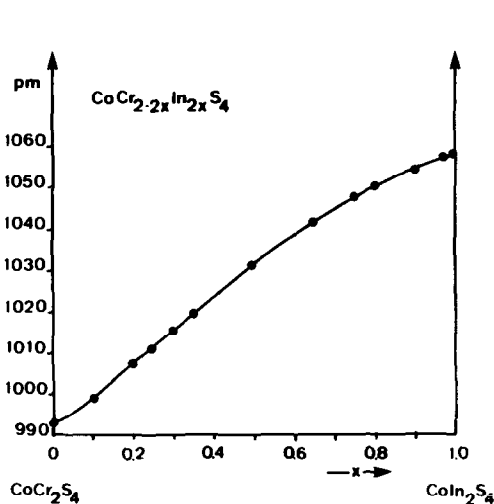

FIG. 5. Lattice constants of CoCr$_{2-2x}$In$_{2x}$S$_4$ and Co$_{1-x}$Cr$_{2-2x}$In$_{8x/3}$S$_4$ spinel-type solid solutions, quenched from 1050°C.

Systems $CoS-In_2S_3-Cr_2S_3$ and
$FeCr_2S_4-FeIn_2S_4$

The phase relationships of the quaternary system $CoS-In_2S_3-Cr_2S_3$ differ from those discussed above. Whereas in the section $CoIn_2S_4-In_2S_3$ a complete series of solid solutions has been found like in the corresponding systems with CdS and HgS, in both the systems $CoCr_2S_4-CoIn_2S_4$ and $CoCr_2S_4-In_2S_3$ relatively large miscibility gaps exist (see Figs. 3 and 4). The solubility limits of the Cr-rich solid solutions have been found to be $CoCr_{1.89}In_{0.11}S_4$ and $Co_{0.96}Cr_{1.92}In_{0.11}S_4$, respectively, and of the In-rich mixed crystals $CoCr_{0.33}In_{1.67}S_4$ and $Co_{0.11}Cr_{0.21}In_{2.38}S_4$, respectively, all at 600°C. But the mutual solid solubility of the two spinels increases with increasing temperature, as shown by high-temperature X-ray powder photographs. At temperatures above 1000°C complete series of mixed crystals are formed. The mixed crystals obtained at these temperatures can be quenched to ambient temperature without decomposition. We have some indications that the system $FeCr_2S_4-FeIn_2S_4$ also exhibits a small miscibility gap near the composition $FeCrInS_4$ at 600°C.

From the X-ray studies it is shown that Vegard's rule is not obeyed for all sections under investigation (see Fig. 5). Thus the curve, lattice constants vs composition of the $CoCr_2S_4-CoIn_2S_4$ solid solutions, is S-shaped with the steepest slope in the middle. The lattice constant of $CoIn_2S_4$ has been determined to be 1057.8(1) pm (1058.0 pm (*14*)). Smaller unit cell dimensions also found are due to sulfur deficiency. Contrary to the $CdS-In_2S_3$-system, $CoIn_2S_4$ is the Co-richest spinel in the section $CoS-In_2S_3$.

Sections $MS-Cr_2S_3$

In the systems $MS-Cr_2S_3$ the solubility limits of both Cr_2S_3 in MS and MS in Cr_2S_3 are small (*17*). The same is said for the phase width of the ternary spinel-type compounds MCr_2S_4. In this work we reinvestigated to what extent the composition of the spinels MCr_2S_4, with M = Mn, Zn, and Cd, and $ZnCr_2Se_4$ can vary. In the case of $MnCr_2S_4$ and $ZnCr_2S_4$ no deviations from stoichiometry were found with the help of X-ray Guinier technique, i.e., alterations of the unit cell dimensions of samples prepared in the presence of excess MS, Cr_2S_3, M, or S_8 are found to be ≦0.1 pm. The lattice constants obtained are 1010.94(5) pm (1011.0 pm (*14*)) and 998.79(3) pm (998.6 pm (*14*)), respectively. $CoCr_2S_4$, $CdCr_2S_4$, and $ZnCr_2Se_4$, however, show some amount of nonstoichiometry detectable from X-ray powder photographs. The unit cell dimensions of these spinels vary from 991.5(1) to 992.4(1), from 1023.7(1) to 1024.3(1) (see also (*18, 19*)), and from 1049.7(1) to 1050.2(2) pm, respectively, depending on the method of preparation.

Superstructure Ordering

The X-ray powder photographs of the obtained solid solutions do not show any superstructure reflections due to ordering of the vacancies or metal ions on the tetrahedral or octahedral sites of the spinel lattice (*20*). The fir-spectra of the spinel solid solutions (see Fig. 6 and 7), however, indicate that superstructure ordering occurs to some extent, at least in the case of In_2S_3-rich samples in the systems $MIn_2S_4-In_2S_3$ (see Fig. 6). The ordering of the vacancies seems to be like that of "ordered" α-In_2S_3 (*21*), which, however, is obviously due to ordering on the tetrahedral sites and not on the octahedral sites as claimed by Kambas *et al.* (*21*).

Discussion

The miscibility gaps in the $CoCr_2S_4-CoIn_2S_4$ and $CoCr_2S_4-In_2S_3$ (and $FeCr_2S_4-FeIn_2S_4$) spinel systems unknown so far in the literature (*5-7*), but not in contradiction with the data reported, are probably
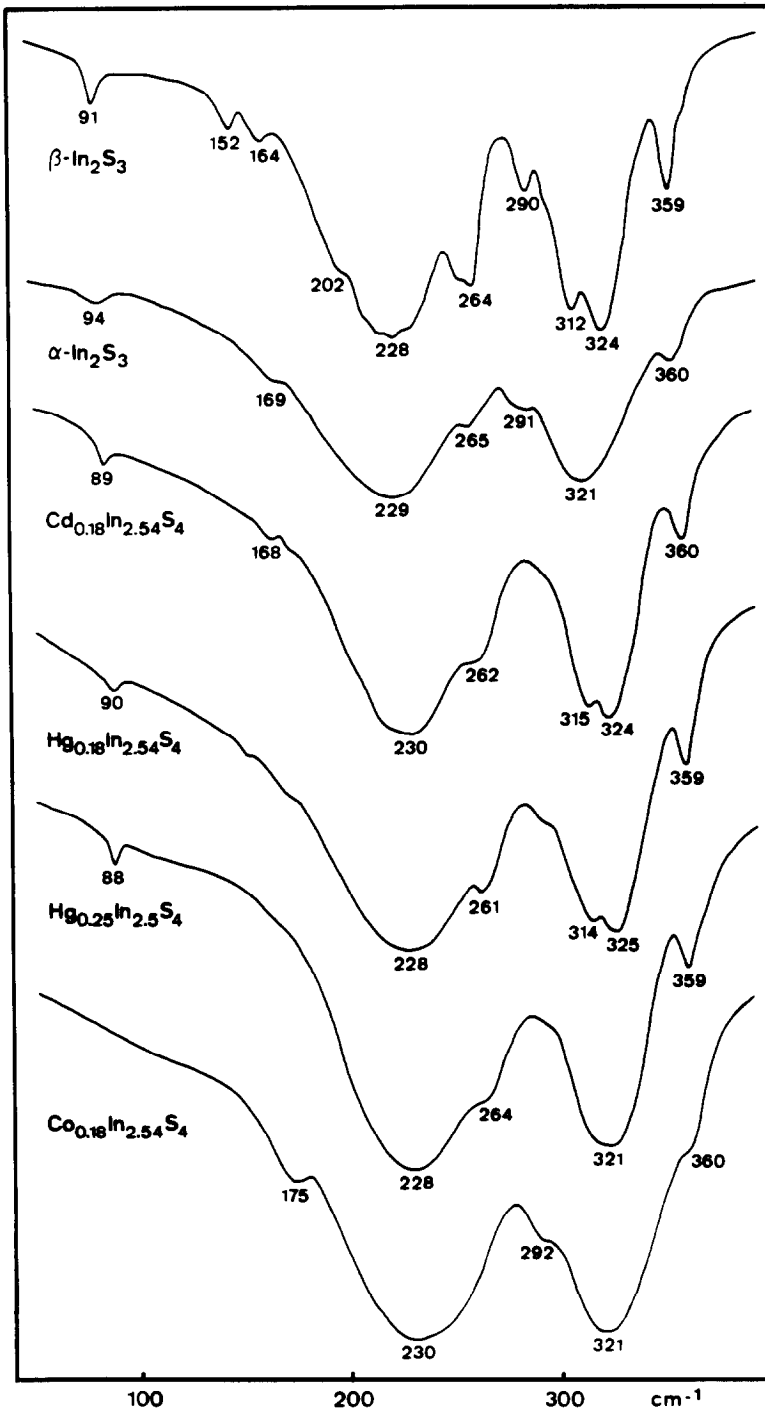
FIG. 6. Far-infrared spectra of β- and α-In_2S_3, i.e., with and without ordering of the vacancies, and of $Cd_{1-x}In_{2+2x/3}S_4$ and $Hg_{1-x}In_{2+2x/3}S_4$ solid solutions.
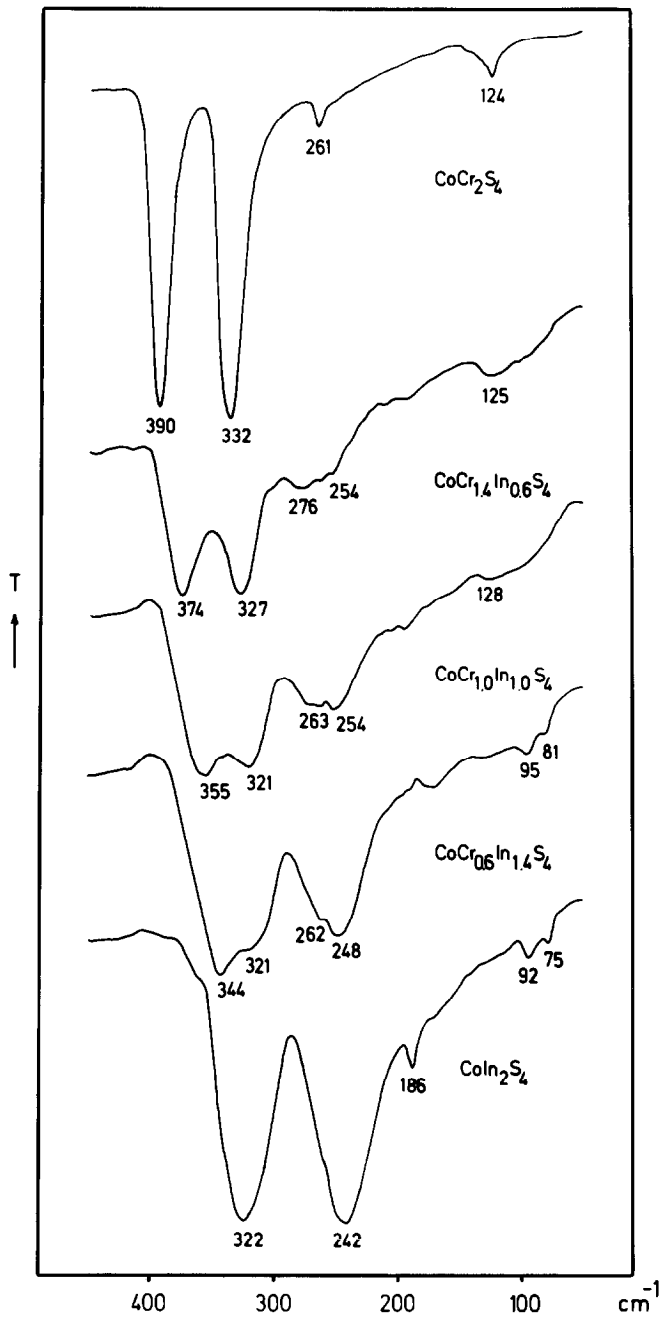
FIG. 7. Far-infrared spectra of $CoCr_2S_4$, $CoIn_2S_4$, and $CoCr_{2-x}In_{2x}S_4$ solid solutions.

due to the different cation ordering of the chromium and the indium spinels, viz., the normal spinel, $CoCr_2S_4$, and the inverse spinel, $CoIn_2S_4$. Thus in the case of the corresponding systems with cadmium and mercury complete series of spinel solid solutions also exist at lower temperatures because both the chromium and the indium

compounds are normal spinels. We there-
fore assume that in the system $MnCr_2S_4$–
$MnIn_2S_4$ (4, 5), structurally similar to the
$CoCr_2S_4-CoIn_2S_4$ system, a miscibility gap is
also present, at least at low temperatures.

The possible nonstoichiometry of some
chromium spinels, as found in this work,
must be borne in mind if using the unit cell
dimensions as an analytical tool in deter-
mining the composition of spinel solid solu-
tions.

Acknowledgments

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