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Phase Diagrams in the Quaternary Systems $M_{1-x}Cu_xCr_2X_4$ with M = Cd, Mn, and X = S, Se

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The phase diagrams of the spinel systems $Cd_{1-x}Cu_xCr_2S_4$, $Cd_{1-x}Cu_xCr_2Se_4$, and $Mn_{1-x}Cu_xCr_2S_4$ have been studied on the basis of X-ray powder photographs of quenched samples and high-temperature X-ray diffraction patterns. At room temperature the mutual solid solubilities of the metallic copper and the semiconducting cadmium and manganese spinels are only small ($x < 0.05$ and >0.95). The interchangeability, however, increases largely with increasing temperature. Complete series of mixed crystals, as in the $Zn_{1-x}Cu_xCr_2X_4$ (X = S, Se) systems, however, are not formed. The solid solutions with $x > 0.07$ and <0.95, $x > 0.095$ and <0.90, and $x > 0.36$ and <0.87, respectively, formed at higher temperatures cannot be quenched to room temperature without decomposition. The unit cell dimensions of the spinel solid solutions studied obviously do not obey Vegard's rule.

1. Introduction

Chromium chalcide spinels generally form complete series of solid solutions of the type $M_{1-x}M'_xCr_2X_4$ (*1–3*). In the systems with M' = copper, however, limited solid solubility has been found in the case of M = Zn (*1, 4, 5*), Cd (*1, 3, 6–8*), and Mn (*9*) and complete solid solubility in the case of M = Fe and Co (*10, 11*). The limited solid solubility of copper containing spinel systems has been attributed to the different band structure of the metallic $CuCr_2X_4$ and the semiconducting $ZnCr_2X_4$, $CdCr_2X_4$, and $MnCr_2S_4$ (*5, 12*). The complete solid solubility found in the system $Fe_{1-x}Cu_xCr_2S_4$ and $Co_{1-x}Cu_xCr_2S_4$ has been assumed to be due to valence states of the type (M^{III}, Cu^{I})Cr_2S_4, which are not possible for M = Zn, Cd, and Mn (*5, 9,12*).

In the systems with M = Zn (M' = Cu), we found that the relatively large miscibility gaps present at room temperature diminish at higher temperatures and that complete series of solid solutions are formed above 630°C for X = S (*5*) and above 400°C for X = Se (*4*). These mixed crystals are quenchable to ambient temperature in the case of the $Zn_{1-x}Cu_xCr_2Se_4$ system. To prove whether the miscibility gaps observed in the other spinel systems discussed above also vanish at higher temperatures, we studied the phase diagrams of the quaternary spinel system $Cd_{1-x}Cu_xCr_2S_4$, $Cd_{1-x}Cu_xCr_2Se_4$, and $Mn_{1-x}Cu_xCr_2S_4$.

2. Experimental Methods

The starting materials were the elements sulfur, 5 N (Fluka); selenium, 3 N (Ferak); copper, 3 N (Riedel-DeHaen); cadmium, 3

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N (Merck); chromium, 4 N (Fluka); and the binary sulfides CdS, puriss. (Fluka) and Cr_2S_3, 2 N (Ventron). Cr_2S_3 was also prepared by heating anhydrous $CrCl_3$ in an H_2S stream at 650°C; Cr_2Se_3 was obtained by firing the elements at 800°C, and MnS by precipitating from an aqueous solution of $MnCl_2 \cdot 4H_2O$ with gaseous H_2S and drying in an H_2S stream at 650°C.

The ternary spinels $CuCr_2S_4$, $CuCr_2Se_4$, $CdCr_2S_4$, $CdCr_2Se_4$, and $MnCr_2S_4$, and solid solutions with different Cu/Cd and Cu/Mn ratios, respectively, were prepared by firing stoichiometric mixtures of the starting materials in closed silica tubes at the elevated temperatures for 8–14 days and quenching with ice water to ambient temperature. Details of the procedure are given elsewhere (*13*).

The obtained solid solutions and equilibrated phase mixtures (quenched to ambient temperature) were analysed with X-ray Guinier powder technique (Huber Guinier 600 system), using Cr$K\alpha_1$ radiation. Unit cell dimensions of the spinels and the spinel solid solutions were calculated by least-squares method. Quartz was used as an internal standard (SiO_2, $a_0 = 491.36$ and $c_0 = 540.54$ pm). High-temperature X-ray diffraction patterns were obtained with an Enraf-Nonius Guinier Simon camera, using Cu$K\alpha_1$ radiation. Quartz capillaries were taken for sample holders.

3. Results

Both the high-temperature X-ray diffraction patterns and the Guinier powder photographs of quenched samples show that mutual solid solubility of the spinel systems under investigation enlarges with increasing temperature, but complete series of spinel solid solutions are not formed, at least at temperatures below 800°C (see Figs. 1–3). At temperatures above 700°C the reflections of the Cd- and Mn-rich solid solutions in the high-temperature X-ray diffraction patterns remain unchanged apart from normal thermal expansion; the reflections of the Cu-rich solid solutions become very weak or disappear. The miscibility gaps remaining at 700–800°C are relatively

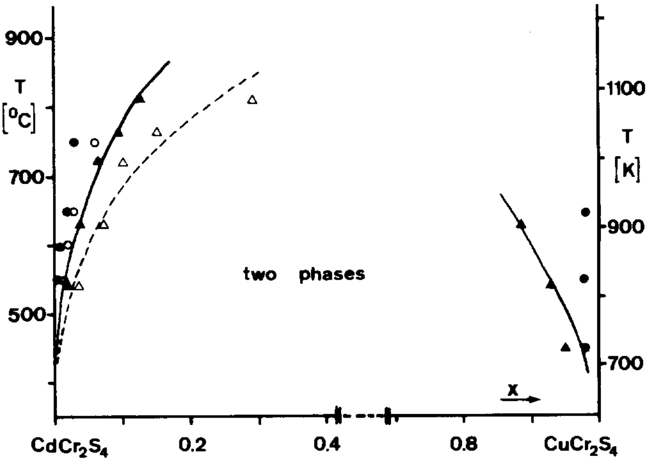

FIG. 1. Phase diagram of the spinel system $CdCr_2S_4$–$CuCr_2S_4$ ($Cd_{1-x}Cu_xCr_2S_4$). Composition of the equilibrated phases was determined from X-ray data of samples quenched to ambient temperature (●,O) and from high-temperature X-ray diffraction patterns (▲,△) under the assumption that Vegard's rule is obeyed (●,△,—) and that Vegard's rule is only obeyed to the hypothetical semiconducting $CuCr_2X_4$ (see Table I) (O,△,---), respectively.

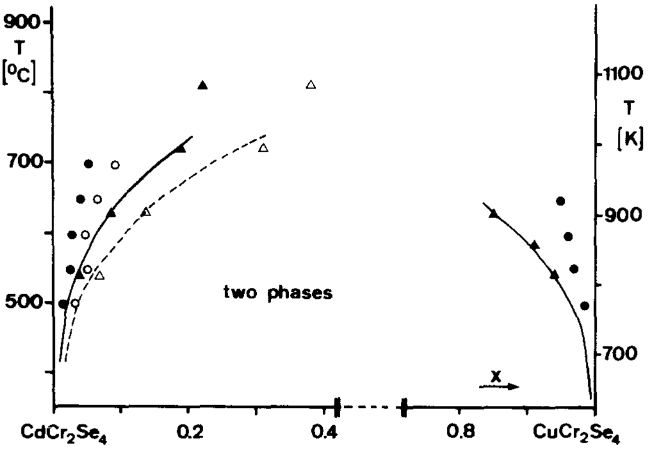

FIG. 2. Phase diagram of the spinel system $CdCr_2Se_4$–$CuCr_2Se_4$ ($Cd_{1-x}Cu_xCr_2Se_4$). Signs as for Fig. 1.

large, especially in the $Cd_{1-x}Cu_xCr_2S_4$ system. At temperatures below 400°C the mutual solid solubilities of all spinel systems studied are small, i.e., monophase solid solutions exist only, if $x < 0.02$ and $x > 0.97$ in the case of M = Cd, and $x < 0.05$ and $x > 0.97$ in the case of M = Mn.

The unit cell dimensions and tentative compositions of the two spinel solid solutions present in the equilibrated samples after quenching to ambient temperature are given in Table I. However, the lattice constants of samples quenched from temperatures above 500°C in the case of the Cu-rich solid solutions and above 600°C in the case of the Cd- or Mn-rich solid solutions do not reflect the phase relationships at the temperatures of equilibration, because decomposition takes place during quenching the samples, shown by relatively broad reflec-

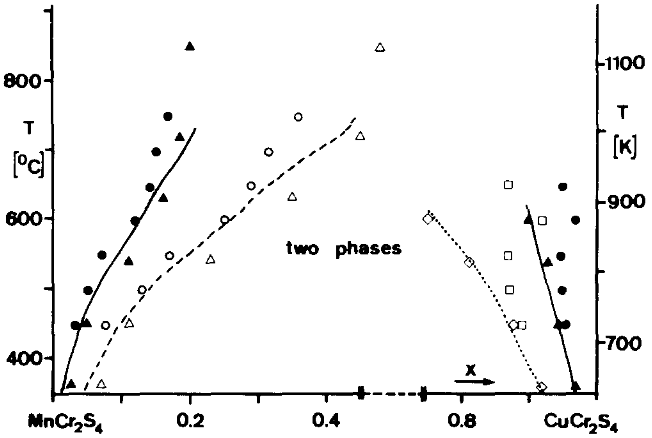

FIG. 3. Phase diagram of the spinel system $MnCr_2S_4$–$CuCr_2S_4$ ($Mn_{1-x}Cu_xCr_2S_4$). Signs as for Fig. 1. The composition of the Cu-rich solid solutions in the equilibrated phases was also calculated using experimental data of the unit cell dimensions of $Mn_{1-x}Cu_xCr_2S_4$ mixed crystals (see Fig. 4 and Table I) (□, quenched samples; ◇, ···, from high-temperature X-ray diffraction patterns).

TABLE I

EQUILIBRATED PHASES AFTER QUENCHING FROM THE GIVEN TEMPERATURE AND DATA FROM HIGH-TEMPERATURE X-RAY DIFFRACTION PATTERNS

Composition x of the reaction mixture	Temperature[a] (°C)	Lattice constants a (pm) Solid solution		Tentative composition x(b,c,d) Solid solution			
		M-rich	Cu-rich	M-rich		Cu-rich	
$Cd_{1-x}Cu_xCr_2S_4$				b	c	b	d
0.5	450	1023.8(1)	982.5(1)	<0.01	<0.02	>0.98	—
0.5	450[e]	1023.6(5)	984.7(5)	<0.01	<0.02	0.95	—
0.5	540[e]	1023.7(5)	984.9(5)	<0.01	<0.02	0.93	—
0.5	550	1023.6(1)	981.7(1)	<0.01	<0.02	>0.98	—
0.9	600	—	982.07(9)			>0.98	—
0.8	600	1023.6(3)	982.4(1)	<0.01	<0.02	>0.98	—
0.5	600	1023.69(3)	982.08(6)	<0.01	<0.02	>0.98	—
0.2	600	1023.3(1)	982.3(1)	0.025	0.35	>0.98	—
0.1	600	1023.3(1)	—	0.025	0.35	—	—
0.5	630[e]	1022.5(5)	986.9(5)	0.045	0.075	0.885	—
0.5	650	1023.5(1)	982.12(6)	0.02	0.03	>0.98	—
0.5	720[e]	1020.7(5)	—	0.065	0.10	—	—
0.5	750	1022.79(5)	982.2(1)	0.03	0.06	>0.98	—
0.5	800	1022.4(1)	982.3(1)	0.04	0.07	>0.98	—
0.5	810[e]	1019.1(5)	—	0.125	0.29	—	—
$Cd_{1-x}Cu_xCr_2Se_4$							
0.5	500	1073.78(7)	1034.8(1)	<0.02	<0.03	>0.98	—
0.5	540[e]	1072.8(5)	1036.2(4)	0.04	0.065	0.94	—
0.5	550	1073.4(1)	1035.0(1)	0.03	0.05	0.97	—
0.9	600	1073.3(2)	—	0.03	0.05	—	—
0.8	600	1073.4(2)	1035.7(2)	0.03	0.05	0.95	—
0.5	600	1073.6(1)	1035.2(1)	0.02	0.04	0.96	—
0.2	600	1073.3(1)	1035.5(2)	0.03	0.05	0.955	—
0.1	600	1073.3(2)	—	0.03	0.05	—	—
0.5	630[e]	1070.9(5)	1039.8(6)	0.09	0.14	0.85	—
0.5	650	1073.1(1)	1035.58(8)	0.04	0.065	0.95	—
0.5	700	1072.2(1)	1035.2(15)	0.055	0.095	0.96	—
0.5	720[e]	1066.9(5)	—	0.19	0.31	—	—
0.5	750	1072.0(11)	1036.2(3)	0.06	0.12	0.94	—
0.5	810[e]	1065.5(5)	—	0.22	0.36	—	—
$Mn_{1-x}Cu_xCr_2S_4$							
0.5	360[e]	1010.3(5)	982.4(5)	0.025	0.07	0.97	0.92
0.5	450	1010.0(1)	982.7(1)	0.03	0.075	0.955	0.89
0.5	450[e]	1009.3(5)	982.7(5)	0.05	0.135	0.955	0.89
0.5	500	1009.34(5)	982.9(1)	0.05	0.13	0.95	0.87
0.5	540[e]	1007.9(5)	983.5(5)	0.11	0.23	0.93	0.81
0.5	550	1008.9(1)	982.9(1)	0.07	0.17	0.95	0.87
0.9	600	—	982.3(1)	—	—	0.97	0.92
0.5	600	1007.6(2)	982.4(2)	0.12	0.25	0.97	0.92
0.1	600	1008.9(1)	—	0.07	0.17	—	—
0.5	600[e]	—	984.3(5)	—	—	0.90	0.75
0.5	630[e]	1006.4(5)	—	0.16	0.35	—	—
0.95	650	—	982.5(1)	—	—	0.965	0.91

TABLE I—*Continued*

Composition x of the reaction mixture	Temperature[a] (°C)	Lattice constants a (pm) Solid solution		Tentative composition $x^{(b,c,d)}$ Solid solution			
		M-rich	Cu-rich	M-rich		Cu-rich	
0.85	650	—	982.9(1)	—	—	0.95	0.87
0.75	650	1007.2(4)	982.7(2)	0.13	0.30	0.955	0.89
0.5	650	1007.0(1)	982.48(7)	0.14	0.32	0.97	0.91
0.35	650	1008.5(1)	982.5(11)	0.085	0.19	0.965	0.91
0.3	650	1008.8(1)	—	0.075	0.18	—	—
0.25	650	1008.8(1)	—	0.075	0.18	—	—
0.2	650	1009.3(1)	—	0.05	0.135	—	—
0.1	650	1010.30(6)	—	0.025	0.07	—	—
0.5	700	1006.7(1)	982.8(1)	0.15	0.34	0.96	0.88
0.5	720[e]	1005.5(5)	—	0.185	0.45	—	—
0.5	750	1006.1(1)	982.4(1)	0.17	0.36	0.97	0.92
0.5	800	1006.7(1)	982.4(1)	0.15	0.34	0.97	0.92
0.35	800	1008.2(2)	982.9(5)	0.095	0.21	0.95	0.87
0.25	800	1009.0(1)	983.3(4)	0.065	0.15	0.94	0.84
0.15	800	1009.4(1)	—	0.055	0.125	—	—
0.5	850[e]	1005.1(5)	—	0.20	0.48	—	—

[a] Accuracy of the given temperatures ±1°C, quenched samples, ±10°C, data of the high-temperature X-ray diffraction patterns.

[b] Under the assumption that Vegard's rule is obeyed.

[c] Under the assumption that the unit cell dimensions of the hypothetical semiconducting $CuCr_2X_4$ spinels are near those of $ZnCr_2S_4$ (998.79(3) pm (*14*)) and $ZnCr_2Se_4$ (1049.7–1050.2 pm (*14*)) and that the M-rich solid solutions obey Vegard's rule if these lattice constants are used instead of the unit cell dimensions of the real $CuCr_2X_4$.

[d] Using experimentally determined lattice constants of Cu-rich $Mn_{1-x}Cu_xCr_2S_4$ solid solutions (dotted line in Fig. 4).

[e] From high-temperature X-ray diffraction patterns, extrapolated to ambient temperature (see text).

tions in the Guinier powder photographs (see also Figs. 1–3). The data obtained from the high-temperature X-ray diffraction patterns are included in Table I. The unit cell dimensions of the two spinels extrapolated to ambient temperature are given. The following temperature coefficients of the lattice constants are used: 0.0075 ($CuCr_2S_4$), 0.0085 ($CuCr_2Se_4$), 0.0085 ($CdCr_2S_4$), 0.0095 ($CdCr_2Se_4$), and 0.0060 pm/°C ($MnCr_2S_4$).

Determination of the accurate composition of the spinel solid solutions from X-ray data suffers from the fact that the ternary spinels themselves exhibit some deviation from stoichiometry with phase widths detectable from X-ray measurements, at least in the case of $CdCr_2S_4$ (*14*) and $CdCr_2Se_4$ (*15*), and that it is unknown whether Vegard's rule is obeyed for the spinel solid solutions under investigation. Thus, Nogues *et al.* (*9*) found that in the $Mn_{1-x}Cu_xCr_2S_4$ system Vegard's rule is not obeyed. We can confirm this finding (see Fig. 4).

In the $Cd_{1-x}Cu_xCr_2X_4$ systems, however, investigations into whether Vegard's rule is obeyed or not are very difficult, because only small regions of monophase solid solutions are quenchable to ambient temperature. However, assuming that the lattice constants of the hypothetical semiconduct-

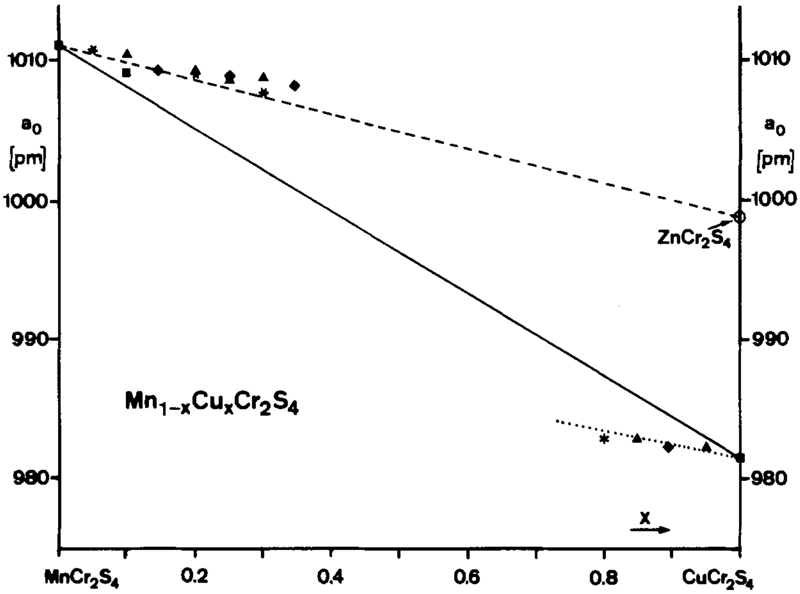

FIG. 4. Unit cell dimensions of monophase $Mn_{1-x}Cu_xCr_2S_4$ spinel solid solutions (see Table I). Samples quenched from 600 (■), 650 (▲), and 800°C (◆), respectively; data (600°C) given by Nogues *et al.* (*9*) (*); lattice constant of $ZnCr_2S_4$ (*14*) (○).

ing $CuCr_2X_4$ spinels (X = S, Se) are near those of $ZnCr_2X_4$ and that solid solutions between semiconducting $CuCr_2X_4$ and other chromium chalcide spinels obey Vegard's rule (which is obviously true in the case of the $Mn_{1-x}Cu_xCr_2S_4$ system (see Fig. 4)), the approximate composition of the Mn- and Cd-rich spinel solid solutions can be determined from the X-ray data (see Table I). This procedure, however, cannot be used for copper-rich mixed crystals, because not even estimated unit cell dimensions of the hypothetical metallic $CdCr_2X_4$ and $MnCr_2S_4$, respectively, are available. For the $Mn_{1-x}Cu_xCr_2S_4$ system, however, experimental data on the slope of the lattice constants could be obtained (see Fig. 4 and Table I).

In the phase diagrams (see Figs. 1–3) the data calculated assuming Vegard's rule, to be obeyed between MCr_2X_4 and $CuCr_2X_4$ spinels, and from the method discussed above are given. The differences between the results of the two methods of evaluation, however, are of larger weight only at temperatures above 600°C. The true values should be near those obtained assuming that Vegard's rule is not obeyed (dashed and dotted lines in Figs. 1–3). The solid solubility limits calculated under the assumption that Vegard's rule is obeyed (full lines in Figs. 1–3) should be considered as the lower limits.

Discussion

The limited mutual solid solubilities of the spinel systems $CdCr_2S_4$–$CuCr_2S_4$, $CdCr_2Se_4$–$CuCr_2Se_4$, and $MnCr_2S_4$–$CuCr_2S_4$ reported in the literature (*1*, *3–9*) are confirmed. The solid solubility limits of samples quenched to room temperature are somewhat smaller than given in the literature (see Table II).

The reason why complete series of solid solutions are not formed at elevated temperatures, as found for the $ZnCr_2X_4$–$CuCr_2X_4$ systems (*4*, *5*), may be the larger

TABLE II

SOLUBILITY LIMITS OF $M_{1-x}Cu_xCr_2X_4$ SOLID SOLUTIONS QUENCHABLE TO ROOM TEMPERATURE (SEE FIGS. 1–4)

M-rich solid solution		Cu-rich solution		
x	*a* (pm)	*x*	*a* (pm)	Ref.
$Cd_{1-x}Cu_xCr_2S_4$				
0.07	1022.4(1)	>0.95	982.5(1)	
0.2				(*6*)
$Cd_{1-x}Cu_xCr_2Se_4$				
0.095	1072.2(1)	>0.90	1036.2(3)	
0.07	1071.6(5)			(*3*)
$Mn_{1-x}Cu_xCr_2S_4$				
0.36	1006.1(1)	0.87	982.9(1)	
0.37	<1007.4	0.78	982.8	(*9*)

differences of the size of the corresponding metals, i.e., Cd and Cu and Mn and Cu, respectively. The so-called size factors Δr (= percent deviation of crystal radii) (*3*) are 32.3 and 14.2%, respectively, compared to 0.8% of Zn and Cu, if Shannon's sulfide radii (*16*) are used. The easier interchangeability of the selenides in both the $Cd_{1-x}Cu_xCr_2X_4$ and the $Zn_{1-x}Cu_xCr_2X_4$ systems is probably due to the larger unit cell dimensions of the selenides. As found by Nogues *et al.* (*9*), there is no evidence that M^{3+} ions appear in the $M_{1-x}Cu_xCr_2S_4$ mixed crystals under investigation contrary to the $FeCr_2S_4$–$CuCr_2S_4$ (*17*) and probably the $CoCr_2S_4$–$CuCr_2S_4$ systems.

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