

Solid State Reactions in Chalcogenide Systems.

VI. Ion Distribution Equilibria between $M\text{Cr}_2(\text{S}, \text{Se})_4$ Spinel Solid Solutions and $M(\text{S}, \text{Se})$ or $\text{Cr}_2(\text{S}, \text{Se})_3$ Solid Solutions

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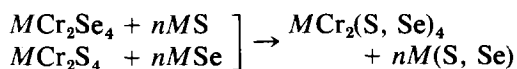
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The sulfur/selenium exchange equilibria between spinel solid solutions $M\text{Cr}_2(\text{S}, \text{Se})_4$ ($M = \text{Zn}$ and Cd) and $M(\text{S}, \text{Se})$ or $\text{Cr}_2(\text{S}, \text{Se})_3$ solid solutions with sphalerite, wurtzite, and defect NiAs structure have been determined by X-ray diffraction measurements of reaction mixtures quenched from 1073 and 1273 K, respectively. With the exception of the $\text{CdCr}_2\text{X}_4/\text{Cr}_2\text{X}_3$ system, there is a clear preference for incorporation of sulfur in the spinel structure, increasing in the series $\text{ZnCr}_2\text{X}_4/\text{Cr}_2\text{X}_3 < \text{ZnCr}_2\text{X}_4/\text{ZnX} < \text{CdCr}_2\text{X}_4/\text{CdX}$. Both equilibrium constants and reaction heats, including data on $M\text{Cr}_2\text{S}_4/M'S$ ($M, M' = \text{Mn}, \text{Co}, \text{Zn},$ and Cd) metal ion distribution equilibria, are given. Revised X-ray data on the solid solutions are also presented.

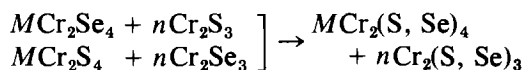
1. Introduction

Metal ion exchange equilibria between spinel solid solutions and binary oxides or sulfides have been studied in some examples (1-6). The obtained distribution equilibria show that the different preference of bivalent metal ions for incorporation into the spinel lattice can be correlated with site preference and size effects (4). But no thermodynamic or phase equilibrium measurements of spinel solid solutions of type $MM'_2(\text{S}, \text{Se})_4$ have been reported in literature.

In the present paper we have studied distribution equilibria of sulfide and selenide ions between zinc and cadmium chromium chalcogenide spinels and the binary zinc, cadmium, and chromium chalcogenides. We have analyzed the equilibria of the reactions



and



with $M = \text{Zn}$ or Cd at 1073 and 1273 K. These systems have been selected because both the spinels and the binary chalcogenides form complete solid solution series between corresponding sulfides and selenides (7-13).

Selenium sulfur ratio of the equilibrated chalcogenide phases has been determined with the help of X-ray powder photographs, using synthetic solid solutions as standards. For this purpose the unit cell dimensions of spinel type $M\text{Cr}_2(\text{S}, \text{Se})_4$, sphalerite type $\text{Zn}(\text{S}, \text{Se})$, and wurtzite type $\text{Cd}(\text{S}, \text{Se})$ solid solutions have been reinvestigated.

2. Experimental Methods

Fine powders of ZnS were supplied by

Riedel-De Haen, CdS by Schuchardt, and Cr_2S_3 by Alfa Products. ZnSe, CdSe, Cr_2Se_3 , and the sphalerite type ZnS–ZnSe solid solutions were prepared from the elements at 800°C. ZnCr_2S_4 , ZnCr_2Se_4 , CdCr_2S_4 , CdCr_2Se_4 —both the wurtzite type CdS–CdSe and the spinel type solid solutions of these systems were synthesized by firing mixtures of the binary chalcogenides. Two heating periods of 5 days are necessary.

The finely powdered and through a grinder intimately mixed components were pressed to pellets, pieces of which were heated in evacuated silica tubes in a Kanthal wound, horizontal furnace with a temperature constancy of $\pm 3^\circ\text{C}$. The samples were quenched with cold water to room temperature, ground, repellitized, and heat treated for another period to ensure the complete formation of the solid solutions.

The ion exchange equilibria were established in a similar manner by firing weighed quantities of the sulfide or selenide spinel and the conjugate binary selenide or sulfide for at least three heating periods. Equilibrium is obtained if the same Se/S ratio in the equilibrated phases is reached independently of starting materials, e.g., selenide spinels and binary sulfides or opposite.

The obtained solid solutions and equilibrated phase mixtures were analyzed with X-ray Guinier powder technique (Huber Guinier 600 system), using $\text{CrK}\alpha_1$ or $\text{CuK}\alpha_1$ radiation. Quartz was used as a standard. Unit cell dimensions of the equilibrated phases and the studied solid solutions have been calculated by least-squares method.

3. Results

3.1. Unit Cell Dimensions of ZnS–ZnSe, CdS–CdSe, ZnCr_2S_4 – ZnCr_2Se_4 , and CdCr_2S_4 – CdCr_2Se_4 Solid Solutions

Both the sphalerite type $\text{ZnS}_{1-x}\text{Se}_x$ and the wurtzite type $\text{CdS}_{1-x}\text{Se}_x$ mixed crystal series obey Vegard's law (see also (9–11)).

The obtained data fit the following equations

$$a_{\text{ZnS}_{1-x}\text{Se}_x} = 26.161x + 540.84 \text{ pm} \\ \Delta a = 0.32 \text{ pm}, \quad \Delta x = 0.012$$

with Δa = standard deviation in a , Δx = standard deviation in x

$$a_{\text{CdS}_{1-x}\text{Se}_x} = 16.436x + 413.60 \text{ pm} \\ \Delta a = 0.14 \text{ pm}, \quad \Delta x = 0.009$$

$$c_{\text{CdS}_{1-x}\text{Se}_x} = 30.115x + 671.70 \text{ pm} \\ \Delta c = 0.4 \text{ pm}, \quad \Delta x = 0.014.$$

The crystal data of $\text{Cr}_2\text{S}_{3-x}\text{Se}_x$ solid solutions (12) fit the equations

$$a_{\text{Cr}_2\text{S}_{3-x}\text{Se}_x} = 10.594x + 593.80 \text{ pm} \\ \Delta a = 0.22 \text{ pm}, \quad \Delta x = 0.02$$

$$c_{\text{Cr}_2\text{S}_{3-x}\text{Se}_x} = 25.587x + 1664.80 \text{ pm} \\ \Delta c = 0.14 \text{ pm}, \quad \Delta x = 0.055.$$

Both $\text{ZnCr}_2\text{S}_{4-x}\text{Se}_x$ and $\text{CdCr}_2\text{S}_{4-x}\text{Se}_x$ spinel solid solutions obey very exactly Vegard's law, as found by Riedel *et al.* (7). The lattice constants can be obtained from the following equations.

$$a_{\text{ZnCr}_2\text{S}_{4-x}\text{Se}_x} = 12.738x + 998.83 \text{ pm} \\ \Delta a = 0.26 \text{ pm}, \quad \Delta x = 0.019$$

$$a_{\text{CdCr}_2\text{S}_{4-x}\text{Se}_x} = 12.644x + 1023.51 \text{ pm} \\ \Delta a = 0.35 \text{ pm}, \quad \Delta x = 0.027.$$

3.2. Ion Distribution Equilibria

Because of material balance, as shown by the reaction equations given above, the ion distribution equilibria can be determined independently from the unit cell dimensions of the two equilibrated phases, i.e., the solid solutions of the spinel and the binary chalcogenide. Thus the accuracy of the obtained equilibrium data can be improved choosing mean values or the figures with the lower standard deviation. The un-

TABLE I
LATTICE PARAMETERS OF THE EQUILIBRATED CHALCOGENIDE PHASES (PM)

Starting composition <i>n</i>	Equilibrated phases after quenching from the given temperature					
	<i>M</i> Cr ₂ (S, Se) ₄ , spinel			<i>M</i> (S, Se) or Cr ₂ (S, Se) ₃		
	a 1073 K	1273 K	a 1073 K	1273 K	c 1073 K	1273 K
	ZnCr ₂ Se ₄ + <i>n</i> · ZnS			Zn(S, Se), sphalerite		
0.75	1043.05(8)		563.76(2)			
2	1029.01(9)		562.18(4)			
3	1021.2(1)	1022.39(3)	559.6(1)	559.24(1)		
4	1016.51(6)	1017.96(8)	557.29(3)	557.12(5)		
5	1012.09(9)	1013.82(9)	555.21(8)	555.08(4)		
6	1009.9(1)		553.80(7)			
7	1008.4(1)	1010.08(4)	552.3(1)	552.33(3)		
8	1007.4(1)		551.15(6)			
9	1006.56(9)	1007.56(8)	550.7(1)	550.37(2)		
20	1002.9(1)		550.02(3)			
	ZnCr ₂ Se ₄ + <i>n</i> · Cr ₂ S ₃			Cr ₂ (S, Se) ₃		
0.75	1029.56(9)		614.54(7)		1713.4(1)	
1.33	1021.43(3)	1022.45(9)	610.03(9)	610.6(2)	1703.6(9)	1705.9(3)
1.5	1019.3(1)	1019.56(3)	608.94(3)	608.97(6)	1702.2(1)	1702.1(2)
3	1010.76(8)	1009.69(4)	603.8(1)	601.83(5)	1691.7(2)	1686.7(1)
3.5	1009.00(7)		602.5(1)		1687.5(2)	
5	1006.4(1)	1004.87(2)	599.76(4)	602.82(3)	1683.1(1)	1684.3(2)
8	1003.49(5)		597.4(1)		1675.4(2)	
	ZnCr ₂ S ₄ + <i>n</i> · Cr ₂ Se ₃			Cr ₂ (S, Se) ₃		
1.33	1021.43(3)		610.03(9)		1703.6(9)	
3.5	1033.08(8)		618.3(1)		1717.6(6)	
8	1041.83(3)		620.9(2)		1719.9(3)	
	CdCr ₂ Se ₄ + <i>n</i> · CdS			Cd(S, Se), wurtzite		
0.75	1065.3(1)		429.21(5)		699.3(1)	
2	1050.30(9)		428.64(4)		700.16(8)	
3	1039.0(1)	1040.34(8)	427.10(9)	428.25(9)	701.2(2)	698.5(1)
4	1033.61(8)	1035.88(9)	425.80(8)	425.10(9)	694.1(1)	694.7(1)
5	1030.9(1)	1031.48(6)	424.84(8)	424.15(4)	691.6(1)	690.61(4)
6	1028.91(8)	1030.06(9)	423.25(9)	423.15(6)	688.9(1)	688.39(9)
7	1028.0(1)	1028.6(1)	422.2(1)	421.83(5)	687.0(1)	686.28(6)
8	1027.60(9)		421.54(9)		685.98(9)	
9	1027.31(5)		420.20(3)		683.65(5)	
20	1025.3(2)		416.7(1)		677.1(1)	
	CdCr ₂ Se ₄ + <i>n</i> · Cr ₂ S ₃			Cr ₂ (S, Se) ₃		
0.75	1056.19(9)		611.39(6)		1706.4(1)	
1.33	1050.10(3)	1049.55(2)	607.5(1)	607.89(4)	1700.1(1)	1700.04(9)
1.5	1047.57(8)	1046.65(9)	606.1(1)	606.3(1)	1695.7(1)	1700.2(2)
3	1039.46(9)		602.18(7)		1687.9(1)	
3.5	1037.97(8)		601.0(1)		1684.6(2)	
5	1034.75(9)	1034.58(8)	599.4(1)	599.04(5)	1681.2(3)	1680.34(8)
8	1029.7(1)		597.04(7)		1675.8(1)	
	CdCr ₂ S ₄ + <i>n</i> · Cr ₂ Se ₃			Cr ₂ (S, Se) ₃		
1.33	1050.10(3)		607.5(1)		1700.1(1)	
3.5	1063.80(9)		617.6(1)		1713.7(2)	
8	1069.38(8)		621.5(1)		1724.7(2)	

certainty in the composition of the equilibrated phases obtained by this method was less than 2%. Errors caused by losing chalcogen and forming nonstoichiometric compounds are negligible because of the chosen experimental procedure (closed system) and the weak tendency of the spinels under investigation to deviate from stoichiometry.

The unit cell dimensions and the Se/S ratios of the equilibrated, conjugate solid solutions are shown in Table I and Fig. 1. Excepting the $\text{CdCr}_2\text{X}_4/\text{Cr}_2\text{X}_3$ system there is a clear preference for incorporation of sulfur in the spinel structure, increasing in the series $\text{ZnCr}_2\text{X}_4/\text{Cr}_2\text{X}_3 < \text{ZnCr}_2\text{X}_4/\text{ZnX} < \text{CdCr}_2\text{X}_4/\text{CdX}$.

From the obtained experimental data equilibrium constants K_X have been calculated

$$K_X = \frac{X_{\text{Se}}(\text{spinel}) \cdot X_{\text{S}}(\text{MX or Cr}_2\text{X}_3)}{X_{\text{S}}(\text{spinel}) \cdot X_{\text{Se}}(\text{MX or Cr}_2\text{X}_3)}$$

with X_{Se} and X_{S} the mole fractions in the equilibrated solid solutions. The calculated equilibrium constants, $\ln K_X$ vs $X_{\text{Se}}(\text{spinel})$, are given in Fig. 2.

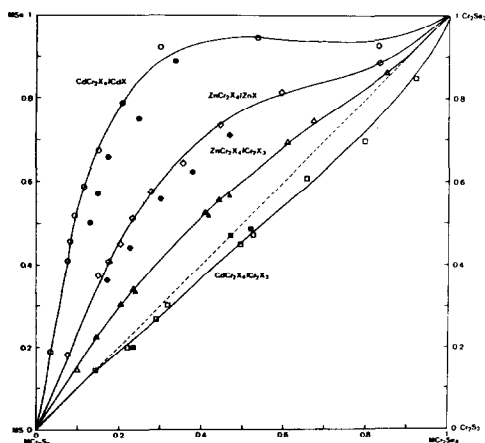


FIG. 1. Composition of the coexistent solid solutions $\text{MCr}_2(\text{S, Se})_4$ and $\text{M}(\text{S, Se})$ or $\text{Cr}_2(\text{S, Se})_3$ at 1073 K, open symbols, and at 1273 K, full symbols.

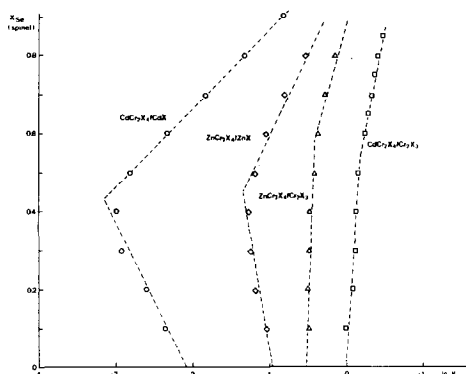


FIG. 2. Equilibrium constants K_X of the S/Se distribution equilibria in dependence of the mole fraction of selenium in the spinel phases at 1073 K, $\ln K_X$ vs $X_{\text{Se}}(\text{spinel})$.

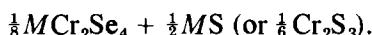
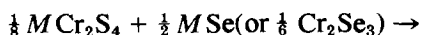
4. Discussion

Interpretation of the investigated ion distribution equilibria on the basis of size effects or site preference energies done for exchange of transition metal ions (4) is not straightforward in the present case. A full discussion of thermodynamics, e.g., use of Gibbs–Duhem relation for calculating deviation from Raoult's law in the solid solutions, is not possible since activity coefficients of both the spinel and the ternary solid solutions are not available in literature.

The dependence of the equilibrium constants K_X from mole fraction of selenium in the spinel phase, given in Fig. 2, indicates that deviation from ideal behavior is only slight in the systems $\text{ZnCr}_2\text{X}_4/\text{Cr}_2\text{X}_3$ and $\text{CdCr}_2\text{X}_4/\text{Cr}_2\text{X}_3$, but by no means negligible in the systems $\text{ZnCr}_2\text{X}_4/\text{ZnX}$ and $\text{CdCr}_2\text{X}_4/\text{CdX}$, possibly caused by strong deviation from Raoult's law in $\text{Zn}(\text{S, Se})$ and $\text{Cd}(\text{S, Se})$ solid solutions.

Disregarding the unknown excess enthalpies ΔH_{exc} and ΔG_{exc} , the tendency of incorporation of sulfide or selenide ions in the spinel structure is shown by free energies ΔG_T calculated from K_X : $\Delta G_T = -RT \ln K_X$ (see Table II). The ion preferences should also be represented by

reaction heats ΔH_r corresponding to the reaction



Data on heat of formation ΔH_f are well known in the case of zinc and cadmium chalcogenides and other chalcogenides of bivalent ions (14), but only a few, partly uncertain or only estimated values are available in the case of chromium chalcogenides (12, 14–16) and both sulfide and selenide spinels (16–19). Reaction heats ΔH_r calculated from the available data are included in Table II.

Exchange equilibria of bivalent metal ions between sulfospinels and the binary sulfides MnS, CoS, ZnS, and CdS, studied in a previous work (4), have been interpreted in the same manner as described above, and compared with the at that time unknown heats of formation of the sulfide spinels (see Table III).

The figures given in Tables II and III show that predicted and observed preferences of ion distribution between spinel type and binary chalcogenides are not in agreement in all systems studied, especially

TABLE II

REACTION HEATS ΔH_r AND FREE ENERGIES ΔG_r OF THE S/SE DISTRIBUTION EQUILIBRIA^a

	ΔH_r (kJ/mol)	ΔG_r (1073 K) (kJ/mol)
ZnCr ₂ X ₄ /ZnX	+9.5	+8(±3)
ZnCr ₂ X ₄ /Cr ₂ X ₃	+4.9(+18.6)	+3(±1)
CdCr ₂ X ₄ /CdX	+21.9	+20(±5)
CdCr ₂ X ₄ /Cr ₂ X ₃	-3.5(+10.3)	-2(±1)

^a Positive signs: preference for incorporation of sulfur in the spinel phase; heats of formation used for calculation of ΔH_r are: ZnS -205.0, ZnSe -158.9, CdS -149.4, CdSe -144.8 (14), ZnCr₂S₄ -574.5, ZnCr₂Se₄ -313.8, CdCr₂S₄ -512.9, CdCr₂Se₄ -319.2, Cr₂S₃ -341.0, and Cr₂Se₃ -174.9 kJ/mol (16), ΔH_r values in parentheses from ΔH_f (Cr₂Se₃) = -257.3 kJ/mol, obtained from dissolution experiments (15).

TABLE III

REACTION HEATS AND FREE ENERGIES OF THE M/M' ION DISTRIBUTION EQUILIBRIA^a

	ΔH_r (kJ/mol)		ΔG_r (1073 K) (kJ/mol)
	From ΔH_f	From temperature slope of $\ln K_x$	
MnCr ₂ S ₄ /CoS	-3.1	-6.9	-2.9
MnCr ₂ S ₄ /ZnS	-10.7	-5.4	-4.0
CoCr ₂ S ₄ /ZnS	+7.6	+15	+3.6
CoCr ₂ S ₄ /CdS	-4.7	+8.8	+5.1
MnCr ₂ S ₄ /CdS	-7.7	+24	+5.8
ZnCr ₂ S ₄ /CdS	+3.0	+37	+12.6

^a Positive signs: preference for ion distribution as given in the formulas; heats of formation used for calculation of ΔH_r are: MnS -213.4, CoS -89.5 (14), MnCr₂S₄ -561.5, and CoCr₂S₄ -443.9 kJ/mol (16) (see also Table II), $K_x = X_{M'}(\text{spinel})/X_M(\text{spinel})$ or $X_M(\text{spinel}) \cdot X_{M'}(\text{wurtzite})/X_M(\text{wurtzite}) \cdot X_{M'}(\text{spinel})$; experimental data from (4).

in the systems $M/M' = \text{Mn/Cd}$ and Co/Cd , as shown by different signs of ΔH_r and ΔG_r . It must be left open to question whether entropy and excess enthalpy effects reverse the equilibria or if the selected data on heat of formation of the involved chalcogenides are inaccurate, since small changes of ΔH_r lead to drastic alteration of the equilibria.

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References

1. K. T. JACOB AND C. B. ALCOCK, *J. Solid State Chem.* **20**, 79 (1977).
2. K. T. JACOB AND K. FITZNER, *J. Mater. Sci.* **12**, 481 (1977).
3. K. T. JACOB, K. FITZNER, AND C. B. ALCOCK, *Metall. Trans.* **8B**, 451 (1977).
4. H. D. LUTZ AND W. BECKER, *J. Solid State Chem.* **20**, 183 (1977).

5. M.-CH. TRINEL-DUFOUR, G. POUILLARD, AND P. PERROT, *Rev. Chim. Miner.* **15**, 513 (1978).
6. B. KNECHT, E. WOERMANN, AND A. EL GORESY, *Lunar Planet. Sci.* **10**, 670 (1979).
7. E. RIEDEL AND E. HORVÁTH, *Z. Anorg. Allg. Chem.* **371**, 248 (1969).
8. H. D. LUTZ AND H. HAEUSELER, *J. Solid State Chem.* **13**, 215 (1975).
9. S. LARACH, R. E. SCHRADER, AND C. F. STOCKER, *Phys. Rev.* **108**, 587 (1957).
10. H. J. YU AND T. H. WENG, *Solid State Electron.* **13**, 93 (1970).
11. P. CHERIN, CH. V. BIELAN, AND G. T. FEKETE, *Siemens Rev.* **48**, 9 (1976).
12. H. D. LUTZ, K.-H. BERTRAM, M. SREĆKOVIĆ, AND W. MOLLS, *Z. Naturforsch.* **28b**, 685 (1973).
13. K. R. PISHARODY, *J. Solid State Chem.* **30**, 149 (1979).
14. K. C. MILLS, "Data of Inorganic Sulfides, Selenides, and Tellurides." London (1974).
15. P.-G. GUNIA, Dissertation, Gesamthochschule Siegen, 1979.
16. YU. D. TRET'YAKOV, I. V. GORDEEV, AND YA. A. KESLER, *J. Solid State Chem.* **20**, 345 (1977).
17. YA. A. KESLER, V. A. SHCHELKOTUNOV, YU. D. TRET'YAKOV, V. K. KAMYSHOVA, I. V. GORDEEV, AND V. A. ALFEROV, *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **13**, 1189 (1977).
18. YA. A. KESLER, V. A. ALFEROV, I. V. GORDEEV, AND YU. D. TRET'YAKOV, *Conf. Int. Thermodyn. Chem.* **1975**, 1, 243.
19. A. S. ALIKHANYAN, A. V. STEBLEVSKII, V. T. KALINNIKOV, T. G. AMINOV, V. B. LAZAREV, YA. KH. GRINBERG, AND V. I. GORGORAKI, *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **13**, 1194 (1977).