Investigation of Some Chalcogenides with Spinel Structure*

YU. D. TRETYAKOV, I. V. GORDEEV, AND YA. A. KESLER

Moscow State University, Moscow, U.S.S.R.

The unusual combination of magnetic, semiconducting, and optical properties of the chalco-chromites and other chalcogenide phases with spinel structure AB_2X_4 has attracted considerable attention for researchers (1–3). Although the physics of magnetic semiconductors is based on highly developed theoretical models and numerous experiments, the physical chemistry of these materials has many gaps. Knowledge of the thermal stability of the chalcogenide spinels, of the equilibrium conditions of their formation, and of their thermodynamics is lacking, although extremely important for the synthesis and thermal processing of single crystals and polycrystalline materials of the AB_2X_4 type. This paper presents the results of a study of the thermal stability and thermochemical, thermodynamic, and crystallochemical properties of the chalcochromites $MeCr_2X_4$ (Me = Cd, Co, Zn, Fe, Cu; X = S, Se, Te), thiocobaltites $MeCo_2S_4$ (Me = Cu, Co), thiorhodites $Me_xRh_{3-x}S_4$ (Me = Cu, Co, Fe), thioaluminates $MeAl_2S_4$ (Me = Zn, Cr), and solid solutions based on these. An attempt is made to show how much the investigated properties influence the magnetic and electrical properties of the chalcogenide spinels. This work is a continuation of the systematic investigation of chalcospinels, including, in particular, nonstoichiometry and defect formation in the chalcochromites (4–7) homo- and heterovalent replacement in the chalcochromites (6, 8), and compound chalcochromites with replacement in the cation sublattice (9–11).

I. Thermal Stability of Chalcogenide Spinels

Reports in the literature on the stability of chalcogenide spinels have been limited to the study of several chalcochromites (12–14) and thiocobaltites (13). We have expanded these studies in order to determine the regularity of change in the thermal stability of the series chalcochromites, thiocobaltites, thiorhodites. DTA (differential thermal analysis) and DTG (differential thermal gravimetry) as well as X-ray and chemical analyses have been used for the study of the thermal stability. Table I presents the results of the study of the behavior of chalcochromites when they are heated in air (15). As seen in Table I, stable oxide phases are formed as a result of oxidation of $CuCr_2X_4$ (X = S, Se), $CdCr_2S_4$, $FeCr_2S_4$, $CoCr_2S_4$ and their solid solutions.

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This has permitted use of the oxidation processes for a thermodynamic study.

It has been established that the resistance of selenochromites to oxidation is less than that of the corresponding thiochromites. $CdCr_2S_4$ and $CuCr_2Te_4$ are the most resistant to oxidation, the resistance of the former being an obvious anomaly. The other thiochromites $CuCr_2S_4$, $CoCr_2S_4$, and $FeCr_2S_4$ oxidize completely even at 700°C, whereas for $CdCr_2S_4$ complete oxidation is observed only at temperatures above 850°C. The behavior of $CdCr_2Se_4$ when heated in air differs from that of $CdCr_2S_4$. $CdCr_2O_4$ and Cr_2O_3 are always present among the final oxidation products. In inert atmosphere the stability of chalcochromites is higher than in air; dissociation begins at ≥600°C, and $FeCr_2S_4$ begins to lose weight only at 800°C. Qualitative experiments showed that in a closed system under excess pressure of chalcogen vapor, thermal stability of the chalcogenide phases is signifi-

TABLE I

OXIDATION OF CHALCOCHROMITES

Compound	Temperature of the beginning of the oxidation (°C)	Final phases
$CuCr_2S_4$	600	CuO, Cr_2O_3
$CoCr_2S_4$	600	$CoCr_2O_4$
$FeCr_2S_4$	550	Fe_2O_3, Cr_2O_3
$Fe_{1.2}Cr_{1.8}S_4$	400	Fe_2O_3, Cr_2O_3
$Cu_{0.2}Fe_{0.8}Cr_2S_5$	410	CuO, Fe_2O_3, Cr_2O_3
$CdCr_2S_4$	720	$CdCr_2O_4$
$CuCr_2Se_4$	500	CuO, Cr_2O_3
$CdCr_2Se_4$	350	$CdCr_2O_4$, Cr_2O_3
$CuCr_2Te_4$	700	not established

cantly greater than in an open system. The behavior of thiocobaltites and thiorhodites when heated in air is shown in Table II.

From the DTA, DTG, X-ray, and chemical analyses, it follows that, for the thiospinels $CuCo_2S_4$ and $Cu_{0.5}Co_{2.5}S_4$, a breakdown to individual sulfides precedes oxidation in the temperature range 420–600°C. The sulfides formed oxidize further with an increase in weight; according to the chemical analysis, sulfates are the primary products of oxidation. When the temperature rises further decomposition of the latter leads to the final mixture of oxides. In the case of iron and cobalt thiorhodites, decomposition into the sulfides occurs prior to formation of sulfates and decomposition to the oxide phases indicated in Table II.

When heated in air, copper thiorhodite behaves differently. At a temperature of 460°C, breakdown of the spinel into the sulfides takes place, and the sulfides oxidize further with loss of weight, bypassing the sulfate-formation stage. At 720°, an oxide phase of composition $CuRh_2O_4$ is formed. The gaseous products of the oxidation of thiochromites, thiocobaltites, and thioaluminates in air are SO_2 and SO_3, whereas during the oxidation of thiorhodites practically pure SO_3 is formed.

By comparing data on thermal stability, one can draw the conclusion that stability decreases in the sequence thiochromite–thiorhodite–thiocobaltite. It may be noted that spinel oxide is always formed on oxidation

TABLE II

OXIDATION OF THIOCOBALTITES AND THIORHODITES

Compound	Temperature of the beginning of the oxidation (°C)	Final phases
Co_3S_4	370	Co_3O_4
$CuCo_2S_4$	420	CuO, Co_3O_4
$Cu_{0.5}Co_{2.5}S_4$	430	CuO, Co_3O_4
$CuRh_2S_4$	460	$CuRh_2O_4$
$FeRh_2S_4$	500	Fe_2O_3, Rh_2O_3
Fe_2RhS_4	500	Fe_2O_3, Rh_2O_3
$CoRh_2S_4$	440	$Co_2Rh_2O_4$
Co_2RhS_4	500	$CoRh_2O_4$, Co_3O_4

of cobalt-containing thiospinels ($CoB_2S_4 \rightarrow CoB_2O_4$), whereas during oxidation of iron-containing thiospinels, a mechanical mixture of oxides is formed ($FeB_2S_4 \rightarrow Fe_2O_3 + B_2O_3$).

II. Thermodynamic Properties of Chalcospinels

1. Enthalpies of Formation of Chalcogenide Spinels

The standard enthalpies of formation of many chalcospinels were estimated from experimental determination of the oxidation heats for the thiospinels and the dissolution heats of the selenochromites. The double Calvé microcalorimeter (16) was used in all the calorimetric experiments. The method of determining oxidation heats and the means of calculating standard enthalpies of formation are described in (16). The correctness of the calorimetric method has been verified for the compounds Co_3S_4 and Rh_2S_3, for which there are sufficiently reliable thermochemical data.

	Experiment	Reference (17)
$-\Delta H^{\circ}_{f298}$ (Co_3S_4) kcal/mole	75.9 ± 2.5	78 ± 3
$-\Delta H^{\circ}_{f298}$ oxidation of Rh_2S_3 kcal/mole	315.2 ± 1.0	312 ± 5

(The magnitude of ΔH°_f of the oxidation of Rh_2S_3 corresponds to that of the reaction $Rh_2S_3 + 6O_2 = Rh_2O_3 + 3SO_3$.) The enthalpy of formation of the thiospinels as obtained from experimentally measured oxidation heats according to the method described in (16), taking into account the necessary data from the literature (17–20), is presented in Table III. For all the thiochromites studied (Table III), it is established that there is a correlation between the enthalpy of formation of $MeCr_2S_4$ and that of MeS ($Me = $ Cu, Co, Fe), as expressed by the equation

$$\Delta H^{\circ}_{f298} MeCr_2S_4 = (0.975 \pm 0.025)$$
$$\times \Delta H^{\circ}_{f298} MeS - (86 \pm 2.0) \text{ kcal/mole.}$$

Assuming this equation is also correct for other thiochromites with spinel structure, we have estimated the enthalpy of formation

for the thiochromites of mercury, manganese, and cadmium. The results are also given in Table III.

From a comparison of the enthalpy of formation of copper thiocobaltites with the additive sum of the formation enthalpy of the corresponding binary sulfides $\Sigma[m\Delta H^{\circ}_{f298} (MeX) + n\Delta H^{\circ}_{f298}(B_2X_3)]$, it follows that the enthalpy change for the reaction $\frac{1}{2}CuS + \frac{1}{2}Cos + Co_2S_3 = Cu_{0.5}Co_{2.5}S_4$ and $CuS + Co_2S_3 = CuCo_2S_4$ is positive. This explains the failure of attempts to obtain these spinels from the binary compounds. Moreover, it is observed that the thiocobaltites, if kept a long time, disintegrate spontaneously, which also indicates the great thermodynamic stability of the binary sulfides compared to their products of interaction.

Using the enthalpy of formation of $CoRh_2S_4$ and $FeRh_2S_4$ (Table III), of Rh_2S_3 (according to our data), and of CoS and FeS (17), we have shown that for the reaction $MeS + Rh_2S_3 = MeRh_2S_4$ ($Me = $ Co, Fe), $\Delta H^{\circ}_{f298} = -6 \pm 3$ kcal/mole. Assuming this value is correct for all thiorhodites, the formation enthalpies of thiorhodites of zinc, manganese, and nickel have been estimated (see Table III).

The standard formation enthalpies of the selenochromites of cadmium and copper have also been determined in the Calvé microcalorimeter as the difference of the dissolution heats for the selenochromites $MeCr_2Se_4$ ($Me = $ Cd, Cu) and the mechanical mixtures $MeSe + 2Cr + 3Se$ (21) in concentrated sulfuric acid ($d = 1.84$) at 475°K. Preliminary experiments showed the identity of the dissolution products with that of the corresponding mechanical mixtures. To calculate the standard enthalpies of formation of the selenochromites of cadmium and copper, besides experimental data on the dissolution heats and C_p for $CdCr_2Se_4$ and $CuCr_2Se_4$, data for ΔH°_{f298} CuSe (19) and ΔH°_{f298} CdSe (19), as well as measurements of high-temperature heat capacity of the elements (18) and of CdSe (22), were used. Because of lack of data on the heat capacity of CuSe, we have assumed ΔH_{f475} CuSe $= \Delta H_{f298}$ CuSe ± 0.5 kcal/mole. The results of the calculation are presented in Table III. The standard enthalpy

TABLE III

Compound	$-\Delta H_{f298}^{\circ}$ kcal/mole	Compound	$-\Delta H_{f298}^{\circ}$ kcal/mole
$CoCr_2S_4$	106.1 ± 1.6^a	$CuCr_2Se_4$	50.0 ± 3.6^b
$CuCr_2S_4$	98.5 ± 1.9^a	$CdCr_2Se_4$	76.3 ± 3.7^b
$FeCr_2S_4$	109.3 ± 2.0^a	$MnCr_2Se_4$	78.8 ± 5.7^d
$ZnCr_2S_4$	137.3 ± 1.4^a	$FeCr_2Se_4$	59.8 ± 5.0^d
$Fe_{1.2}Cr_{1.8}S_4$	119.0 ± 2.1^a	$CoCr_2Se_4$	51.8 ± 5.6^d
$CdCr_2S_4$	122.6 ± 3.0^c	$NiCr_2Se_4$	51.8 ± 5.7^d
$MnCr_2S_4$	134.2 ± 3.3^c	$ZnCr_2Se_4$	75.0 ± 5.7^c
$HgCr_2S_4$	97.1 ± 2.3^c	$HgCr_2Se_4$	55.8 ± 5.1^c
$NiCr_2S_4$	104 ± 5^d	Cr_2Se_3	41.8 ± 4.7^c
Cr_2S_3	81.5 ± 1.5^d	$FeRh_2S_4$	83.6 ± 2.6^a
Cr_3S_4	126 ± 5^d	Fe_2RhS_4	89.5 ± 2.3^a
$CuCr_2Te_4$	26 ± 5^c	$CoRh_2S_4$	75.8 ± 2.9^a
Co_3S_4	75.9 ± 2.5^a	Co_2RhS_4	82.3 ± 2.7^a
$Cu_{0.5}Co_{2.5}S_4$	57.2 ± 2.5^a	$CuRh_2S_4$	75.2 ± 2.5^a
$CuCo_2S_4$	36.7 ± 2.0^a	$ZnRh_2S_4$	107 ± 4^c
$ZnAl_2S_4$	230.2 ± 1.9^a	$NiRh_2S_4$	77 ± 4^c
$CrAl_2S_4$	222.8 ± 0.9^a	$MnRh_2S_4$	100 ± 4^c

^{a} Experimental values obtained from oxidation experiments.

^{b} Experimental values obtained from dissolution experiments.

^{c} Results of estimating from empirical equations.

^{d} Results of estimating without taking into account the enthalpy of the structural transition of the spinel-type Cr_3S_4.

of formation values for $MeCr_2Se_4$ as shown in the same table were derived under the assumption that for the reaction $MeSe + Cr_2Se_3 = MeCr_2Se_4$ ($Me = $ Zn, Cd, Hg, Fe, Co, Ni, Mn, Cu) $\Delta H_{f298} = 0 \pm 3$ kcal/mole. The presence of structural transformations in the selenochromites of manganese, iron, cobalt, and nickel and uncertainty in the enthalpy value of this transition explains the great error in the estimate of ΔH_{f298}° for these compounds.

The enthalpy of copper tellurochromite $CuCr_2Te_4$ was estimated from the approximation expressed by the relation

$$\frac{\Delta H_{f298}^{\circ} CuCr_2S_4 - \Delta H_{f298}^{\circ} CuCr_2Se_4}{\Delta H_{f298}^{\circ} CuCr_2Se_4 - \Delta H_{f298}^{\circ} CuCr_2Te_4}$$
$$= \frac{\Delta H_{f298}^{\circ} CuS - \Delta H_{f298}^{\circ} CuSe}{\Delta H_{f298}^{\circ} CuSe - \Delta H_{f298}^{\circ} CuTe}$$

with use of the experimentally determined values for ΔH_{f298}° $CuCr_2X_4$ ($X = $ S, Se) and data in Refs. (19, 23).

It is interesting to compare formation enthalpies for the oxo- (24, 25), thio-, and seleno-

chromites of the transition metals. As seen in Fig. 1, the character of the change in magnitude of ΔH_{f298}° on the nature of the transition metal occupying the A sites in the spinel structure is similar in the oxides, sulfides, and selenides. The anomalously high values of the formation enthalpy for compounds of cadmium and zinc are apparently explained by sharp changes in the character of the MeX bond ($X = $ O, S, Se) on transition from ions
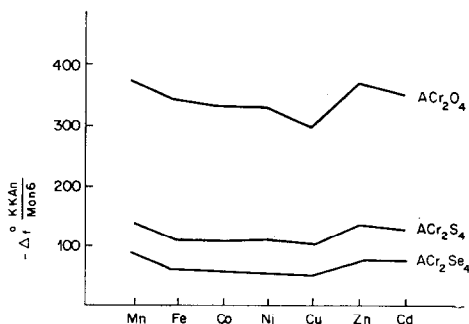

FIG. 1. Standard enthalpies of formation of oxide, sulfide, and selenide chromites from elements. Abscissa, metal with a valency of +2; ordinate, the value of $-\Delta H_{f298}^{\circ}$ (kcal/mole).

with an empty d level (Fe^{2+}, Co^{2+}, Ni^{2+}) to ions having filled d levels (Zn^{2+}, Cd^{2+}).

The magnitudes of the standard enthalpies of formation for the selenochromites of copper and cadmium are calculated using handbook data. Table III presents the standard enthalpies of formation from the elements for the chalcochromites, thiocobaltites, thiorhodites, and thioaluminates.

2. Heat Capacity of AB_2X_4 Compounds

There is in the literature a series of works on the determination of the actual heat capacity and the character of the phase transitions in compounds of the type $MeCr_2X_4$ (26–31). Using our own experimental data for the actual heat capacity, the change of heat content, and the coefficient of linear thermal expansion along with data from the literature, we have carried out a calculation and analysis of the thermodynamic parameters for a large group of AB_2X_4 compounds. We have succeeded in making a most complete calculation of the thermodynamic parameters for cadmium thiochromite.

Thermodynamic parameters of $CdCr_2S_4$. The heat capacity of cadmium thiochromite as studied by Borukhovich et al. (27) in the temperature range 50–300°K and our data in the temperature range 173–673°K coincide in

the interval 173–300°K with an accuracy of $\pm 0.3\%$. Our data on the change of heat content of $CdCr_2S_4$ over the temperature interval 298–750°K (15) is described by the equation $(H_t - H_{298}) = (42.29 \pm 0.03) + (0.463 \pm 0.001) \times 10^{-3} \cdot T^2 + (3.988 \pm 0.003) \times 10^5 \cdot T^{-1} - 13.985$. The three series of data coincide within the error limits of the experiment.

In Ref. (27), the character and thermodynamic parameters are determined for the ferromagnetic–paramagnetic transition at the Curie point ($85 \pm 2°K$); the magnetic and lattice components of the heat capacity C_p (specific heat at constant pressure) were estimated over the temperature range studied. We have computed the contributions to the heat capacity of cadmium thiochromite over the temperature range 173–673°K. Using the well-known value of the Debye temperature $\theta_D = 415 \pm 5°K$ (27), we have calculated the lattice component of the heat capacity according to the Debye law as well as the contribution to the thermal expansion to the heat capacity according to the formula $C_p = C_v + C_m + C_d + C_{el}$. [For the semiconductor $CdCr_2S_4$ in a temperature range higher that the Curie temperature $C_m \simeq 0$, $C_{el} \simeq 0$.] The components of the heat capacity of $CdCr_2S_4$ are presented in Table IV. The contribution of the thermal expansion, as is known from

TABLE IV

COMPONENTS OF THE HEAT CAPACITY OF $CdCr_2S_4$

T (°K)	C_p (cal mol^{-1} degree^{-1})	C_v (cal mol^{-1} degree^{-1})	C_d (cal mol^{-1} degree^{-1})
200	34.15	33.97	
223	35.59	35.32	
248	36.80	36.48	
273	37.71	37.34	
298.15	38.17	37.96	
323	38.78	38.50	0.28
273	39.70	39.28	0.42
423	40.50	39.95	0.55
473	40.90	40.24	0.66
523	41.27	40.48	0.79
573	41.57	40.67	0.90
623	41.84	40.84	1.00
673	42.04	40.95	1.09

(32), is expressed by the ratio $C_d = (9\alpha^2 VT)/K$, where α is the coefficient of linear expansion; K is the isothermal coefficient of compressibility; V is the molar volume; T is the absolute temperature. If K does not depend on temperature, then Grüneisen's ratio is fulfilled; $C_d = 3\alpha \Gamma C_v T$, where $\Gamma =$ Grüneisen constant. From the values of C_d determined above and from the experimentally measured magnitudes of α, we have calculated the value of the Grüneisen constant Γ over the temperature range 373–673°K at each interval of 25°. It turned out that the Grüneisen constant $\Gamma = 1.69 \pm 0.05$ throughout the entire temperature range, i.e., Grüneisen's ratio is valid for cadmium thiochromite. Having determined the Grüneisen constant, we could calculate the compressibility coefficient K for any given temperature including 298°K.

$$K = \frac{3 \cdot \alpha \cdot v}{\Gamma \cdot C_v} = 5.63 \times 10^{-12}\,\text{Pa}^{-1}.$$

The values obtained for the Grüneisen constant and for the isothermal coefficient of compressibility are close to those for magnetite *(33)* and copper thiochromite *(26)*, which also have spinel structure. This allows us to recommend the following values for the constants for calculation of the lattice energy and of the components of the heat capacity for crystals with spinel structure: $\Gamma = 1.7 \pm 0.1$; $K = (5.5 \pm 0.1) \times 10^{-12}\,\text{Pa}^{-1}$.

Debye temperatures, enthalpies, and entropies of the magnetic transformation of several chalcochromites. In the temperature range 173–673°K we have obtained actual heat capacity values for the compounds $CuCr_2X_4$ ($X = S$, Se, Te), $CoCr_2S_4$, $Cd_{1-x}Co_xCr_2S_4$,

$FeCr_2S_4$, $Cu_{0.2}Fe_{0.8}Cr_2S_4$, Co_3S_4, $Fe_{1.2}Cr_{1.8}S_4$. Using the above suggested values for the Grüneisen constant and the isothermal coefficient of compressibility as well as data from the literature we have calculated for all the compounds studied the lattice component C_v, the contribution of thermal expansion C_d to the heat capacity, and the Debye temperature θ_D, as well as the change in enthalpy and entropy for the magnetic transition of those compounds which have one in the temperature range studied. These values are presented in Table V.

3. Calculation of Excess Entropy Contributions of the Chalcogenide Chromites

According to the model of Neél *(1)*, the ferro- and ferrimagnetism of the chalcochromites is explained by spin ordering on the A and B sublattices of the spinel structure. If the cations of the A and B sublattices have unpaired electrons, then magnetic transition at the Curie point is determined chiefly by the disordering of spins on both sublattices, or at least one of them. The process of spin ordering represents a phase transition of second order *(1)*. There are data suggesting that the anomaly in the heat capacity within range of the Curie point, for example, for $CdCr_2S_4$ *(27)* and $CuCr_2Se_4$ *(30)*, includes as well a first-order phase transition, which is determined by a magnetostrictive transition, although the entropy of such a structural transformation is small and amounts to 0.05–0.18 e.u. *(27, 30)*.

For the sulfochromites of copper and cobalt which we have studied *(34)*, the basic contribution to the magnitude of ΔS_{exc} is

TABLE V

VALUES FOR DEBYE TEMPERATURE, ENTHALPY, AND ENTROPY OF MAGNETIC TRANSITION

Compound	$\theta_D \pm 10$ (°K)	ΔH magnetic $\pm$ 20 (cal/mole)	ΔS magnetic ± 0.10 (e.u.)
$CuCr_2S_4$	400	500	1.36
$CoCr_2S_4$	405	530	2.62
$CuCr_2Se_4$	280	780	1.87
$CuCr_2Te_4$	260	970	3.27
$Cu_{0.2}Fe_{0.8}Cr_2S_4$	425	720	2.85
$Fe_{1.2}Cr_{1.8}S_4$	395	550	2.51

spin disordering on the A sublattice, the entropy of which is $\Delta S_{spin} = R \ln (2S + 1)$, where $S = n/2$ and $n =$ the number of unpaired electrons. For $CoCr_2S_4$, $\Delta S_{spin} = R \ln 4 = 2.79$ e.u. and for $CuCr_2S_4$ $\Delta S_{spin} = R \ln 2 = 1.37$ e.u. If our supposition is correct, then for $CdCr_2S_4$ (Cd^{2+}, configuration $3d^{10}$) $\Delta S_{spin} = 0$ and for $FeCr_2S_4$ (Fe^{2+}, configuration $3d^6$) $\Delta S_{spin} = R \ln 5 = 3.22$ e.u.

It is known that the majority of magnetic chromium spinels, with the exception of $CuCr_2X_4$, are p-type semiconductors with specific electrical resistance of 10^2–10^9 ohm-cm (*1*). Therefore, the electronic contribution to the heat capacity of these compounds is in the first approximation, negligible. For $CuCr_2X_4$, which has p-type metallic conductivity, the contribution of conduction electrons to the entropy is determined by $\Delta S_{el} = -nR \ln n$, where n is the concentration of electrons per formula unit. From experimental data on the Hall effect of single crystals of $CuCr_2Se_4$ (*35*), $n = 0.10 \pm 0.05$; the corresponding entropy change is $\Delta S_{el}(CuCr_2Se_4) = 0.46$ e.u. Thus, the calculated excess entropy of copper selenochromite $\Delta S_{exc}^{calc} = \Delta S_{spin} + \Delta S_{magn} + \Delta S_{el} = 1.37 + 0.18 + 0.46 = 2.01$ e.u., which is in correspondence with our experimentally determined value $\Delta S_{exc}^{exp} = 1.87$ e.u. (the difference in the values of ΔS_{exc}^{calc} and ΔS_{exc}^{exp} corresponds to a low temperature contribution to the excess entropy from 0 to 170°K, i.e., the lower range of the C_p measurements). For copper sulfochromite $CuCr_2S_4$ there are no data on the Hall effect. Therefore, assuming that the mobility of the current carriers in copper sulfo- and selenochromites is the same, from the approximate relation $\sigma(CuCr_2S_4)/\sigma(CuCr_2Se_4) \simeq n(CuCr_2S_4)/n(CuCr_2Se_4)$, where $\sigma^{298}(CuCr_2Se_4) = 1.11 \times 10^3$ ohm^{-1} cm^{-1} and $\sigma^{298}(CuCr_2Se_4) = 2.62 \times 10^{-3}$ ohm^{-1} cm^{-1} (*35*), it follows that $n(CuCr_2S_4) \simeq 0.04$; the corresponding entropy change is $\Delta S_{el} = -0.04\, R \ln 0.04 = 0.20$ e.u. The excess entropy of copper sulfochromite is then $\Delta S_{exc} = 1.37 + 0.05 + 0.20 = 1.62$ e.u. The magnetostriction contribution amounts to 0.05 e.u., as in $CdCr_2S_4$.

The results of a C_p investigation for solid solutions of $Fe_{1.2}Cr_{1.8}S_4$ and $Cu_{0.2}Fe_{0.8}Cr_2S_4$ can serve as proof of the correctness of the

analysis carried out on the heat capacity anomaly. According to the data of (*10*), both compounds are semiconductors and consequently the electronic component is negligibly small. From neutron diffraction data (*10*), it follows that the distribution of cations may be expressed by the formulas $Fe_{0.8}^{2+}Fe_{0.2}^{3+}[Fe_{0.2}^{2+}Cr_{1.8}^{3+}]S_4$ and $Fe_{0.8}^{2+}Cu_{0.2}^{2+}[Cr_2^{3+}]S_4$. Consequently, the excess entropy can be characterized only as a contribution of the spin interaction of the cations which are found on the A sites of the spinel lattice, i.e.,

$$\Delta S_{exc}(Cu_{0.2}Fe_{0.8}Cr_2S_4) = R(0.2 \ln 2 + 0.8 \ln 5)$$
$$= 2.83 \text{ e.u.}$$

and

$$\Delta S_{exc}(Fe_{1.2}Cr_{1.8}S_4) = R(0.8 \ln 5 + 0.2 \ln 6)$$
$$- 0.2\, R \ln 2 = 2.64 \text{ e.u.,}$$

in agreement with the experimentally found values presented in Table VI.

As can be seen from the cation distribution in the spinel $Fe_{1.2}Cr_{1.8}S_4$, part of the Cr^{3+} is replaced by Fe^{2+}. This fact deserves attention. It is known that the Cr^{3+} ion has a strong preference for an octahedral environment, as is related to configuration $3d^3$. The Fe^{2+} ion in a high-spin state has the configuration $3d^6$; therefore, one might expect an additional contribution to the entropy arising from the disordering of the Fe^{2+} spins. However, this is not observed, in obvious relation to the transition of Fe^{2+} into a low-spin state, which gives three filled $3d$ orbitals and does not change the symmetry from that of Cr^{3+} in an octahedral field. Our experimental data on the enthalpy of formation of $Fe_{1.2}Cr_{1.8}S_4$ from simple materials, which comes out to be equal to $\Delta H_{f298}Fe_{1.2}Cr_{1.8}S_4 = -119.0 \pm 2.1$ kcal/mole, are evidence in favor of a similar model. Considering $Fe_{1.2}Cr_{1.8}S_4$ as a solid solution of 90% $FeCr_2S_4$ and 10% Fe_3S_4 and noting both that the enthalpy of formation of $FeCr_2S_4$ is $\Delta H_{f298}^\circ = -109.3 \pm 1.9$ kcal/mole and the enthalpy of formation of Fe_3S_4 is less than the latter, one might expect that $-\Delta H_f$ of formation of $Fe_{1.2}Cr_{1.8}S_4$ would be less than 109 kcal/mole. The observed energy gain, which corresponds to the difference in

TABLE VI

CONTRIBUTIONS TO EXCESS ENTROPY OF THE CHALCOGEN CHROMITES (in e.u.)

Compound	ΔS_{spin}	ΔS_{magn}	$\Delta S_{cond\ el}$	ΔS_{orb}	ΔS_{exc}^{calc}	$\Delta S_{exc}^{exp} \pm 0.10$
$CuCr_2S_4$	1.37	0.05[a]	0.20	—	1.62	1.36
$CdCr_2S_4$	0	0.05	—	—	0.05	0.05
$CoCr_2S_4$	2.79	—	—	—	2.79	2.51
$Cu_{1.2}Fe_{0.8}Cr_2S_4$	2.85	—	—	—	2.85	2.80
$FeCr_2S_4$	3.22	—	—	—	3.22	3.22[b]
$Fe_{1.2}Cr_{1.8}S_4$	2.63	—	—	—	2.63	2.51
$CuCr_2Se_4$	1.37	0.18	0.46	—	2.01	1.87
$CdCr_2Se_4$	0	0.41	—	—	—	0.41
$CuCr_2Te_4$	1.37	0	0.3–0.5[a]	2.18	3.8–4.0	3.27

[a] Estimate.

[b] $\Delta S_{exc}(FeCr_2S_4) = [\Delta S_{exc}Cu_{0.2}Fe_{0.8}Cr_2S_4) - 0.2\Delta S_{exc}(CuCr_2S_4)]/0.8.$

experimental and calculated values of ΔH, apparently comes from transition of the Fe^{2+} ions on the octahedral sublattice from a high- to a low-spin state.

The change of saturation magnetic moment of $Fe_{1.2}Cr_{1.8}S_4$ (10) indicated that for the solid solution under examination, the magnetic moment on the B sublattice is $\mu(B) = 2.65\mu_B$, which practically coincides with that calcu- lated for an Fe^{2+} ion in a low-spin state

$$\mu(B) = (0.9)(3) + (0.1)(0) = 2.7\ \mu_B.$$

It is noticeably lower than the value of the Fe^{2+} ion in a high-spin state, which also is evidence in favor of the suggested model. In Table VI the results of the calculation of pos- sible contributions to the excess entropy for the compounds examined are shown.

We have assumed to this point that the orbital moment is quenched and the entropy change corresponding to it equals zero, which apparently is correct for the thio- and selenochromites. Tests conducted by Kano- mata (36) have shown that the Weiss constant characterizing the crystal field increases in the series $CuCr_2S_4 \rightarrow CuCr_2Se_4 \rightarrow CuCr_2Te_4$. Consequently, one can expect a splitting of the degenerate t_{2g} levels of the chromium ion in the octahedral ligand field at higher tem- peratures. From the dependence on tempera- ture of the lattice constant of $CuCr_2Te_4$ according to the data of (26), the coefficient of thermal expansion α undergoes a break at

a temperature 100°K higher than the Curie point, while the slope $\partial\alpha/\partial T$ becomes less, which is evidence of a distortion of the spinel structure and of a possible structural change. The contribution of the t_{2g} orbitals to the excess entropy of $CuCr_2Te_4$ is determined by the formula $\Delta S_{orb} = R\ln 3 = 2.18$ e.u., which gives an excess entropy of 3.8–4.0 e.u. (taking into account a possible contribution of con- duction electrons. The experimentally found magnitude in the range 173–673°K is 3.27 e.u.

The analysis we have carried out on the heat capacity of chromite chalcogenides dis- closes a quantitative connection between thermodynamic and physical properties of this class of compounds.

III. Crystallochemical Properties of the Chalco- spinels

Because of the strong preference of Cr^{3+} ion for an octahedral environment, practically all the chalcochromites have a normal spinel structure. Therefore, one can expect that the change in magnetic, electric, and thermo- dynamic properties in going from one chalco- chromite to another is determined to a signifi- cant degree by the nature of the cations oc- cupying the tetrahedral positions. From this point of view it was useful to accept the principle of invariability of Poix (37). Des- cribing the spinel lattice by two characteristic

TABLE VII

Me–S DISTANCES IN THE THIOCHROMITES

Compound	a(Å)	u	β (Å)	α (Å)	Reference
$MnCr_2S_4$	10.110	0.3863[a]	2.419	2.387	38, 39
		0.3876	2.407	2.409	
$FeCr_2S_4$	9.995	0.3850[a]	2.403	2.338	38, 39
		0.3840	2.412	2.321	
$CoCr_2S_4$	9.923	0.3821[a]	2.412	2.270	38, 39
		0.3830	2.404	2.286	
$CuCr_2S_4$	9.814	0.3841	2.367	2.279	38, 39
$ZnCr_2S_4$	9.986	0.3842	2.408	2.321	38, 39
$CdCr_2S_4$	10.240	0.390	2.417	2.484	40
$HgCr_2S_4$	10.237	0.390	2.416	2.486	40

[a] Obtained by neutron diffraction.

parameters, α and β, for the cations occupying tetrahedral and octahedral positions, respectively, it is easy to show that $\alpha = a3^{1/2}(\frac{1}{8} + \delta)$ and $\beta = a(\frac{1}{16} + 3\delta^2 - \delta/2)^{1/2}$, where a = the lattice constant and $\delta = u - \frac{3}{8}$, the deviation of the observed position parameter of the anion from ideal. As seen in Table VII, the magnitude of β, which represents a characteristic distance for the Cr^{3+} ion, is within limits of error actually constant for all the thiochromites except $CuCr_2S_4$; it amounts to 2.41 ± 0.006 Å. Moreover, this value practically coincides with the Cr^{3+}–S^{2-} distance in lithium thiochromite $LiCrS_2$, which has the α-$NaFeO_2$ hexagonal structure (β = 2.415 ± 0.008 Å). Assuming for all thiochromites $\beta_{Cr^{3+}}$ = 2.411 Å and using thiospinel lattice constants as well as anion parameters from the literature, one can calculate (41) the characteristic distance for cations (CR) in the tetrahedral and octahedral sites (Table VIII) formed by the sulfide ions. Comparison of the CR in oxo- and thio-compounds of the transition metals indicates that there is a correlation (Fig. 2). The value of CR for ions in the tetrahedral field decreases in the series Mn^{2+}–Fe^{2+}–Co^{2+}–Ni^{2+}–Cu^{2+}, indicating an increase in the ionic contribution and, correspondingly, a decrease in the covalent contribution to the Me^{2+}–X^{2-} bond formation in a series of spinels with a given B cation (for example, Cr). On the other hand, the change in CR of ions on octa-
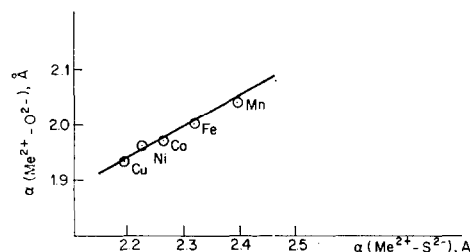

FIG. 2. Relation between CR of divalent cations of the transition elements in tetrahedral sites for the oxo- and thiospinels. Abscissa, the value of $\alpha(Me^{2+}$–$S^{2-})$ in angstroms; ordinate, the value of $\alpha(Me^{2+}$–$O^{2-})$ in angstroms.

hedral sites in oxo- and thiospinels of the transition metals is irregular, apparently because of extremely different stabilization energies for these cations in the octahedral field of the oxygen and sulfur ions. This fact is confirmed by lack of success in attempts to synthesize thioferrites and thiomanganites with a spinel structure (Fe_3S_4 is an exception).

Based on the equations[1]

$$\alpha = \Sigma n_i \alpha_i / \Sigma n_i, \qquad (1)$$

and

$$\beta = \Sigma n_i \beta_i / \Sigma n_i, \qquad (2)$$

[1] α and β are characteristic parameters that describe the cations occupying the tetrahedral and octahedral positions, respectively; n = the mole fraction of cation.

and using known (37, 41, 42) values of the CR for cations in the field of the oxygen ions and values of the lattice parameters for γ-Al_2O_3 ($Al_{2/3}\square_{1/3}[Al_2]O_4$) and γ-Fe_2O_3($Fe[Fe_{5/3}\square_{1/3}]$ O_4) as well as the results of investigations on the γ-Fe_2O_3–Cr_2O_3 system (43), one can show that the characteristic distances for the "oxygen vacancy" is given by $\alpha_\square = 1.947 \pm 0.005$ Å and $\beta_\square = 2.248 \pm 0.005$ Å. The ratio

$$\alpha_\square/\beta_\square = 3^{1/2}/2 \tag{3}$$

corresponds to ideal cubic packing with $\delta = u - \frac{3}{8} = 0$. One can assume that the hypothetical packing of anions with parameters $\alpha = \alpha_\square$ and $\beta = \beta_\square$, and not containing cations, requires the least stabilization energy by the cation field, and $\alpha_\square$ and $\beta_\square$ are constants which characterize the anion ionic radius. We have made an attempt to calculate possible distances in the octahedral and tetrahedral sites of spinel using the values of $\alpha_\square$ and $\beta_\square$ indicated above. We postulate that the pushing apart of the anions by the cations, the CR of which exceed the CR of the vacancies, leads in the limit to an increase in the number of nearest neighbors of the cation, i.e., to an increase in coordination number and to a break in close packing. If in the center of the vacant site there is placed a fictitious cation with charge q_k, then the stabilization energy (not taking into account the anion–anion interaction) is determined by the relation

$$E_n = -nq_kq_{an}/r_n, \tag{4}$$

where n is the coordination number and r_n is the CR of the vacancy. To raise the coordination number one unit it is necessary to lose ΔE, which equals

$$\Delta E = E_{n+1} - E_n = -\frac{(n+1)q_kq_{an}}{r_{n+1}} + \frac{nq_kq_{an}}{r_n}, \tag{5}$$

where r_i is the independent variable. The minimum value of ΔE is determined by the condition

$$\frac{d\Delta E}{dr_i} = \frac{(n+1)q_kq_{an}}{r_{n+1}^2} - \frac{nq_kq_{an}}{r_n^2} = 0 \tag{6}$$

from which it follows that

$$(r_n + 1)/r_n = [(n+1)/n]^{1/2} \tag{7}$$

with r_{n+1} being the limiting value of the CR.

If $r_n = a_\square$, then $r_{n+1} = (5^{1/2}/2)\alpha_\square = \alpha_{max}.$
$$\tag{8}$$

If $r_n = \beta_\square$, then $r_{n+1} = (7/6)^{1/2}\beta_\square = \beta_{max}.$
$$\tag{9}$$

Let us verify this model for the oxospinels. According to Eq. (8), $\alpha_{max} = (5^{1/2}/2)\alpha_\square = (5^{1/2}/2) \times 1.947 = 2.177 \pm 0.005$ Å, whereas the maximum value of CR found experimentally in the oxospinels for Cd^{2+} equals 2.169 ± 0.005 Å. According to Eq. (9), $\beta_{max} = (7/6)^{1/2}\beta_\square = (7/6)^{1/2} \times 2.248 = 2.428 \pm 0.005$ Å, whereas the maximum magnitude of β found experimentally is $\beta_{Ag^+} = 2.420 \pm 0.005$ Å. From the known value of $\alpha_\square = 2.230 \pm 0.004$ (44) and using relation (3), we have found for thiospinels $\beta_\square = 2\alpha_\square/3^{1/2} = 2.575 \pm 0.005$ Å. According to Eq. (8), $\alpha_{max} = 2.493 \pm 0.010$ Å whereas the value found experimentally in the spinels is $\alpha_{max}(In^{3+}) = 2.500 \pm 0.010$ Å. From Eq. (9) it follows that $\beta_{max} = 2.781 \pm 0.010$ Å; the value found experimentally is $\beta_{max}(Y^{3+}) = 2.756 \pm 0.010$ Å. It is interesting to note that in the rare earth spinel series MeR_2X_4, only compounds with REE of the gadolinium subgroup, for which $\beta \leqslant \beta_{max}$, have been synthesized. Moreover, spinels with REE in which $\beta > \beta_{max}$ have not been detected (45). The proposed model, unlike an ionic spheres model, satisfactorily explains the existence of spinels containing Cd^{2+} and In^{3+} and the impossibility of forming stable oxo- and thiospinels with ions Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+}, U^{4+}, and Th^{4+} for which the values of α and β exceed the limiting α_{max} and β_{max}. Maximum lattice constants are determined by the relation $a_{max} = 2.0995\alpha_{max} + (5.8182\beta_{max}^2 - 1.4107\alpha_{max}^2)^{1/2}$ (10); they are equal to 9.824 ± 0.014 Å and 11.253 ± 0.014 Å for the oxo- and thiospinels, respectively, in agreement with experimental data (46).

IV. Interconnection of Thermodynamic and Crystallochemical Properties of Chalcospinels

Existence of a correlation between the thermodynamic and crystallochemical pro-

TABLE VIII

CHARACTERISTIC DISTANCES OF α AND β CATIONS IN TETRAHEDRAL AND OCTAHEDRAL ENVIRONMENTS, RESPECTIVELY, IN THE SULFIDES

Cation	α (Å)	β (Å)	Cation	α (Å)	β (Å)
Li^+	2.319	2.597	Fe^{2+}	2.323	2.526
Cu^+	2.279	—	Ni^{2+}	2.225	2.396
Ag^+	2.445	—	Cu^{2+}	2.200	2.328
Be^{2+}	2.087	—	Al^{3+}	2.301	2.416
Mg^{2+}	2.425	2.596	Ga^{3+}	2.296	2.450
Zn^{2+}	2.322	—	In^{3+}	2.506	2.630
Cd^{2+}	2.487	—	Fe^{3+}	2.148	2.342
Hg^{2+}	2.497	—	Co^{3+}	2.039	2.292
Mn^{2+}	2.402	2.610	Ni^{3+}	2.066	2.313
Co^{2+}	2.272	2.408	Rh^{3+}	—	2.350
Vacancy	2.230	2.575	Cr^{3+}	—	2.411
Ti^{3+}	—	2.470	V^{3+}	—	2.404
Sc^{3+}	—	2.587	Lu^{3+}	—	2.709
Yb^{3+}	—	2.719	Tb^{3+}	—	2.730
Er^{3+}	—	2.754	Y^{3+}	—	2.756
Ti^{4+}	—	2.390	Zr^{4+}	—	2.577
Hf^{4+}	—	2.596	V^{4+}	—	2.327
Cr^{4+}	—	2.324	Sn^{4+}	—	2.596

perties of the chalcochromites and thiocobaltites has already been mentioned in preceding sections. Below, the thermochemical and crystallochemical properties of the thiorhodites are compared. Table IX and Fig. 3 show the dependence of lattice constant on composition for $Me_xRh_{3-x}S_4$ (Me = Co, Fe). It is evident that Vegard's law is followed in the Fe_3S_4–$FeRh_2S_4$ system, but the Co_3S_4–$CoRh_2S_4$ system is characterized by a significant positive deviation, which can be explained on the basis of the principle of invariability.

Considering the preference of the Rh^{3+} ion for octahedral positions, one may expect that the spinels $FeRh_2S_4$ and $CoRh_2S_4$ would have a normal structure. Using experimentally determined values for the lattice constants and the previously found value for αCo^{2+} = 2.272 Å and αFe^{2+} = 2.323 Å, we have shown that βRh^{3+} = 2.350 ± 0.005 Å for both spinels.

Keeping in mind the values αCo^{3+} = 2.039 Å, βCo^{2+} = 2.414 Å, and βCo^{3+} = 2.292 Å, as found earlier, it is easy to show that the cation and valence distribution in the spinel Co_2RhS_4 corresponds to the formula $Co^{2+}[Co^{3+}Rh^{3+}]S_4$. Thus, the replacement of Co by Rh in $Co_{1+x}Rh_{2-x}S_4$ takes place with preservation of the normal spinel until half

TABLE IX

LATTICE CONSTANTS

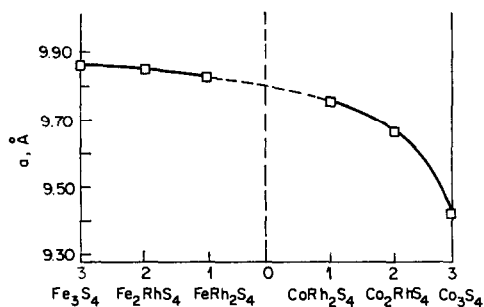| $Fe_xRh_{3-x}S_4$	$a_{exp}(\pm 0.003$ Å)	$Co_xRh_{3-x}S_4$	$a_{exp}(\pm 0.003$ Å)
$FeRh_2S_4$	9.830	$CoRh_2S_4$	9.753
Fe_2RhS_4	9.848	Co_2RhS_4	9.670
Fe_3S_4	9.874(47)	Co_3S_4	9.420
	9.870(48)		9.416(49)

FIG. 3. Dependence of the lattice constant of $Me_x Rh_{3-x} S_4$ (Me = Co, Fe) on the composition of the compounds. Abscissa, composition $Me_x Rh_{3-x} S_4$ (Me = Co, Fe); ordinate, the value of a in angstroms.

FIG. 4. Dependence on composition of values of ΔH°_{f298} for the $Me_x Rh_{3-x} S_4$ compounds. Abscissa, composition $Me_x Rh_{3-x} S_4$ (Me = Co, Fe); ordinate, the value of $-\Delta H^\circ_{f298}$ (kcal/mole).

the octahedral sites are filled by Rh^{3+} ions. Further replacement leads to a migration of the Co^{2+} ions from the tetrahedral to the octahedral sites and an inversion of the spinel. An analogous phenomenon was observed by Poix in the case of oxospinel solid solutions (37).

The reason for the difference in the dependence of lattice constant on composition for the iron- and cobalt-containing spinels has to be sought in the electronic structure. Co^{3+} and Rh^{3+} ions have $3d^6$ and $4d^6$ configurations, respectively. It may be suggested that each of these ions has three filled d shells and is in a low-spin state. Hence, in an octahedral field, when Rh is substituted for Co, orbital symmetry changes insignificantly, although the character of the bond is fixed primarily by the Rh–S interaction. Therefore, even when half the Rh has been substituted, the normal structure remains stable. In the case of iron-containing spinels, the Fe^{2+} and Rh^{3+} ions are isoelectronic; therefore, an inversion of the spinel accompanies replacement of the Rh for the Fe. In solid solutions of $Fe_3 S_4$–$FeCr_2 S_4$, similar inversion sites of the spinel and a low spin state of the Fe^{2+} on the octahedral sites are substantiated by experimental data (10, 50).

Figure 4 shows the dependence on composition of the enthalpy of formation for $Me_x Rh_{3-x} S_4$ from the simple components. As is seen, a change in the formation enthalpy as a function of composition of the thiorhodites in $Fe_3 S_4$–$FeRh_2 S_4$ occurs regularly
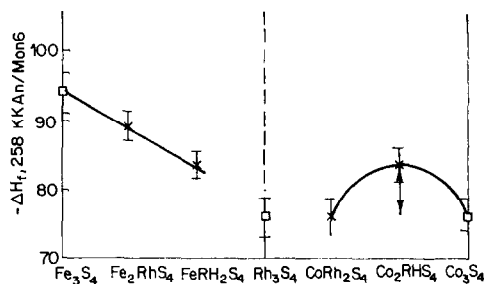
with changes in lattice constant. In the $Co_3 S_4$–$CoRh_2 S_4$ system, a positive deviation is observed, as is true also for the dependence of the lattice constant.

It may be suggested that the excess enthalpy of formation of the solid solution by the reaction $\frac{1}{2} CoRh_2 S_4 + \frac{1}{2} Co_3 S_4 = Co_2 RhS_4$, which is equal to $\Delta H_{f975} = -7.3 \pm 3.3$ kcal/mole, is connected with the ordering of the cobalt ions only. Then, by use of the relation between enthalpies and the degree of ordering (without taking into account the error in the magnitude ΔH_{f975}), the suggestion of Navrotsky and Kleppa (51) that $-\Delta H/RT = \ln[x^2/(1-x)(2-x)]$ may show that $Co_2 RhS_4$ has the structure of a practically normal spinel, which confirms the crystallochemical model of this compound. A calculation of the lattice parameter according to the invariability method for a normal spinel gives the value $a_{calc} = 9.670$ Å, which coincides with the experimental value of $a_{exp} = 9.670$ Å.

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