

Phase Relationships and Some Magnetic Properties of Spinels in the Systems $M_{1-x}Ni_xCr_2S_4$ Where $M = Mn, Fe, Co$

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Phase relationships between spinel and defect NiAs structures in the systems $M_{1-x}Ni_xCr_2S_4$ (where $M = Mn, Fe, Co$) were investigated. It was found that the spinel structure is stable between $x = 0$ and $x = 0.3$ when $M = Mn$ or Fe . When $M = Co$ the spinel is formed in the region $x = 0$ to $x \sim 0.4$. The apparent stabilization of the defect NiAs phase by Ni^{2+} may be related to the strong sixfold site preference of Ni^{2+} . Curie temperatures of all three ferrimagnetic systems increases with increasing Ni^{2+} substitution. This is probably due to higher Ni-S covalency.

$FeCr_2S_4$, $CoCr_2S_4$ and $MnCr_2S_4$ form stable compounds with the cubic spinel ($Fd3m$) (1) structure. At high temperatures both $FeCr_2S_4$ and $CoCr_2S_4$ (1340 K (2) and 1400 K, respectively) undergo a spinel-defect NiAs (monoclinic $I2/m$) phase transition. $MnCr_2S_4$ exhibits the same effect under high temperature and pressure (2). Therefore (Fe, Co or Mn) Cr_2S_4 can be obtained with the defect NiAs structure as a metastable phase by thermal quenching of the samples through the transition temperature. $NiCr_2S_4$ and (Fe, Co, Mn, Ni) Cr_2Se_4 exhibit the monoclinic defect NiAs structure at room temperature (3, 4).

In the spinels $FeCr_2S_4$ and $CoCr_2S_4$, the main magnetic interactions are: (a) the $\sim 120^\circ$ antiferromagnetic A-B (Fe-S-Cr) interaction, (b) the ferromagnetic nearest-neighbor B-B (Cr-Cr) interactions, and (c) the antiferromagnetic more distant neighbor B-B interactions. Of these, the negative A-B interactions predominate as shown by the large negative Curie Weiss θ_p 's [$\theta_p = -290$ K for $FeCr_2S_4$ and -480 K for $CoCr_2S_4$ (5)]. The negative A-B and positive nearest-neighbor B-B interactions yield ferrimagnets with Curie temperatures shown in Table I. As a result, the effect of the negative more distant neighbor B-B interactions is negligible. In $MnCr_2S_4$ the negative

A-B interaction is weaker [$\theta_p = -27$ (6)] and a fourth interaction, the negative A-A (Mn-Mn) interaction, is significant at low temperature (7) causing a canting of the A sublattice. (Mn, Fe and Co) Cr_2S_4 are all semiconductors. $FeCr_2S_4$ and $CoCr_2S_4$ exhibit negative magnetoresistance effects which have been ascribed to spin-disorder scattering (8, 9).

TABLE I

UNIT CELL PARAMETERS AND T_c OF THE SPINELS IN THE SYSTEMS $M_{1-x}Ni_xCr_2S_4$ WHERE $M = Mn, Fe, Co$

Compound	a (Å)	V (Å) ³	T_c (K)
$MnCr_2S_4$	10.11 (7)	1033.4	74
$x = 0.1$	10.09 ₆	1029.1	84
$x = 0.2$	10.08 ₅	1025.7	95
$x = 0.3$	10.06 ₈	1020.5	110
$FeCr_2S_4$	9.99 ₅	998.5	185
$x = 0.1$	9.98 ₀	994.0	195
$x = 0.2$	9.96 ₅	989.5	205
$x = 0.3$	9.95 ₃	986.0	214
$CoCr_2S_4$	9.93 ₆	980.9	235
$x = 0.1$	9.92 ₈	978.6	240
$x = 0.2$	9.91 ₉	975.9	244
$x = 0.3$	9.90 ₈	972.7	250
$x = 0.4$	9.89 ₈	969.7	—

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As a result of the combination of properties exhibited by these materials, it is desirable to obtain similar compositions where $T_c \geq$ room temperature. The T_c and Curie-Weiss θ 's indicate that the strength of the A-B interactions increase in the order Mn < Fe < Co. Goodenough (10) ascribes this effect to increasing d orbital-anion overlap which, starting with Mn²⁺ (d^5), increases from left to right in the periodic table (Mn < Fe < Co < Ni). The presence of Ni²⁺ on the tetrahedral site in the spinel should result in increasing T_c .

We have therefore investigated systems of the type M_{1-x}Ni_xCr₂S₄ (M = Mn, Fe, Co) to determine the region of spinel formation and the effect of Ni substitution on the magnetic ordering temperatures.

Experimental Methods

Polycrystalline samples were prepared from the elements (freshly reduced metals) in powder (99.9% pure, 325 mesh size) form. Appropriate weights were mixed overnight in plastic bottles using rubber stoppers as mixing aides. The mixtures were pressed in pellet form and sealed in evacuated quartz tubes. The tubes were heated at 10–15°C/hr to 800°C, held at this temperature for 48 hr, and cooled to room temperature. Where necessary, the tubes were heated to 1150°C and cooled at 1–2°C/hr to obtain the most stable phase. X-ray diffractometer patterns were obtained using CuK α radiation.

In all three systems, (Mn, Fe or Co)_{1-x}Ni_xCr₂S₄, the spinel phase was obtained initially, followed by a two-phase region of spinel and defect NiAs (NiCr₂S₄), and finally a small single-phase defect-NiAs region.

In the systems Mn_{1-x}Ni_xCr₂S₄ and Fe_{1-x}Ni_xCr₂S₄ spinels are formed in the region $x = 0$ to $x = 0.3$, and in Co_{1-x}Ni_xCr₂S₄, between $x = 0$ and $x \sim 0.4$. Unit cell parameters are shown in Table I. The two-phase region (spinel + NiCr₂S₄) is very extensive and even at $x = 0.9$, X-ray diffraction patterns showed the presence of small amounts of spinel.

DTA Measurements

Both (Fe or Co)Cr₂S₄ spinels undergo high temperature spinel-to-defect NiAs phase changes (2) as mentioned in the introduction. The same transformation takes place in MnCr₂S₄ with a combination of high temperature and high pressure (2). In Fig. 1a and b we show the variation in the phase transition temperature with

increasing Ni substitution for (Fe, Co)_{1-x}Ni_xCr₂S₄ in evacuated quartz tubes. The temperature of the spinel-defect NiAs phase transition in Fe_{1-x}Ni_xCr₂S₄ varies linearly with x . In Co_{1-x}Ni_xCr₂S₄ the transition temperature is a non-linear function of x and is similar in shape to that observed in the spinel-defect NiAs system CoCr₂S_{4-x}Sc_x (11).

Magnetic Measurements

Curie temperature (T_c) measurements of (Fe or Co)_{1-x}Ni_xCr₂S₄ ($x = 0$ to $x = 0.3$) were made

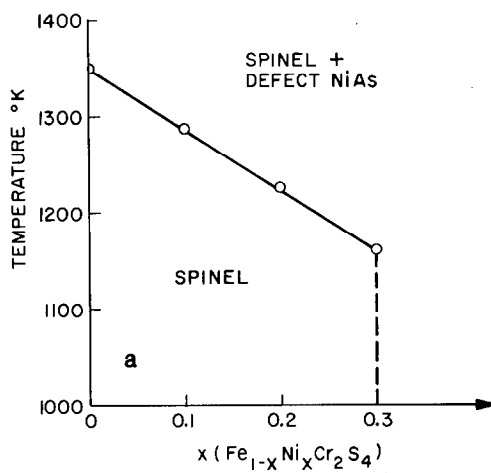


FIG. 1A.

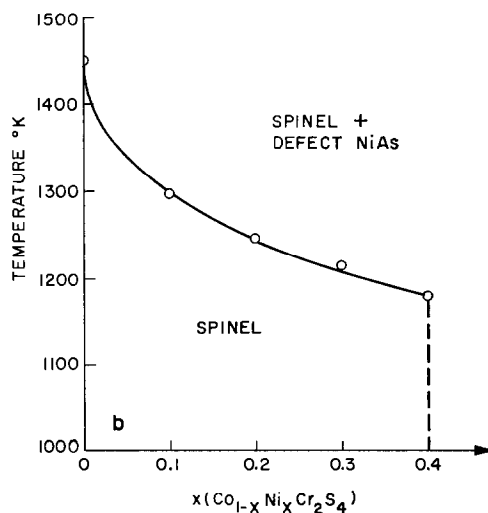


FIG. 1B.

FIG. 1. (a) Phase transition temperature vs composition in the system Fe_{1-x}Ni_xCr₂S₄ from $x = 0$ to $x = 0.3$. (b) Phase transition temperature vs composition in the system Co_{1-x}Ni_xCr₂S₄ from $x = 0$ to $x = 0.4$.

in a field of 5000 Oe by extrapolation of the steepest slope of the magnetization curve to zero moment. In the system $\text{Mn}_{1-x}\text{Ni}_x\text{Cr}_2\text{S}_4$, T_c was measured at 15,000 Oe using the point of inflection of the magnetization curve. As shown in Table I, T_c increases with increasing Ni substitution in all three systems.

Discussion and Conclusions

In a previous study (11) of the systems (Mn, Fe or Co) $\text{Cr}_2\text{S}_{4-x}\text{Se}_x$, it was concluded that the stability of the spinel phase with increasing Se substitution increased as a function of the tetrahedral site preference of the divalent ion ($\text{Mn} > \text{Fe} \sim \text{Co}$). Where Ni is substituted for Mn, Fe or Co, no such relationship is apparent since the stability of the spinel structure is similar in all three systems. The small size of the spinel region results from the strong octahedral site preference (12) of Ni^{2+} , which combined with the strong octahedral preference of Cr^{3+} would tend to stabilize the defect NiAs structure containing only octahedral cation sites.

The increase in T_c exhibited in all three Ni-substituted systems is in general agreement with the model proposed by Goodenough (10) which predicts increasing A-B interaction strength in the order $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni}$, due to increasing d orbital-anion overlap. The only departure from this model involves the magnitude of the increase. Goodenough's (13) model calls for Ni^{2+} to have significantly larger d orbital-anion overlap than Co^{2+} . This is not reflected in the observed T_c which increases very slowly in the system $\text{Co}_{1-x}\text{Ni}_x\text{Cr}_2\text{S}_4$ from 235 K at $x = 0$ to 250 K at $x = 0.3$.

It has been shown in previous work (11) as well as in Fig. 1a and b that the spinel-defect

NiAs phase transition temperature is different for substituted FeCr_2S_4 vs CoCr_2S_4 . The cause is not fully understood and would require additional investigation into the thermodynamics of this transition.

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