

## Magnetic Interactions in $\text{CoM}_x^{3+}\text{Ga}_{2-x}\text{O}_4$ Spinel Solid Solutions: II. $\text{CoAl}_x\text{Ga}_{2-x}\text{O}_4$

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Magnetic measurements have been performed in the range 4.2 to 300°K on the spinel solid solutions  $\text{CoAl}_x\text{Ga}_{2-x}\text{O}_4$  with  $0.0 \leq x \leq 2.0$ . The magnetic properties vary with cobalt ion distribution among  $T_d$  and  $O_h$  sites; the influence of trivalent diamagnetic ions in determining the relative strengths of the various exchange interactions is discussed.

### Introduction

In our previous paper on  $\text{CoRh}_x\text{Ga}_{2-x}\text{O}_4$  (1) we correlated the observed magnetic behavior with cobalt ions distribution between *A* and *B* sites of spinel, obtaining information about the relative strength of the various exchange interactions.

In the  $\text{CoAl}_x\text{Ga}_{2-x}\text{O}_4$  solid solution, the  $\text{Co}^{2+}$  site distribution varies with composition *x* (2), exhibiting the same trend as was observed for the previous system, i.e., the  $\text{Co}^{2+}$  octahedral occupation increases with the gallium content, giving rise to concomitant *AA*, *BB*, and *AB* interactions.

The antiferromagnetic spinels  $\text{CoRh}_2\text{O}_4$  ( $T_N = 25^\circ\text{K}$ ) and  $\text{CoAl}_2\text{O}_4$  ( $T_N = 5^\circ\text{K}$ ) have been studied extensively, and the higher Néel temperature for  $\text{CoRh}_2\text{O}_4$  supported the suggestion that the trivalent ion is involved in the indirect exchange coupling between  $\text{Co}^{2+}$  ions in *A* sites (3, 4). In this work we analyze the dependence of the magnetic properties on the site distribution of the  $\text{Co}^{2+}$  ions in order to obtain evidence for the different role of  $\text{Rh}^{3+}$  compared to  $\text{Al}^{3+}$  in the exchange interactions.

### Experimental Procedures

Sample preparation and cation distribution are reported elsewhere (2). Magnetic measurements were performed for the samples prepared at 1073°K on a Faraday-type balance described previously (1). The experimental susceptibility, obtained in the range 4.2 to 300°K at  $H = 10$  kOe, was corrected for diamagnetism using the table of Selwood (5).

### Experimental results

Magnetic data and cation distribution are reported in Table I. The Curie constant *C* and the asymptotic temperature  $\theta$  were determined by fitting the linear parts of  $\chi^{-1}$  vs *T* plots with a least-squares program.

A survey of susceptibility measurements is given in Figs. 1 and 2. A careful investigation of the temperature range 4.2 to 10°K has shown the existence of a Néel point for all the samples, pointing to the presence of long-range antiferromagnetic ordering.

Below ~80°K, all the samples except  $\text{CoAl}_2\text{O}_4$  showed a large deviation from

TABLE I  
MAGNETIC DATA FOR  $\text{CoAl}_x\text{Ga}_{2-x}\text{O}_4$  SOLID SOLUTIONS<sup>a</sup>

x	Co( $O_h$ ) <sup>b</sup>	$T_N$ (°K) ± 1	T.I.P. <sup>c</sup> (emu × 10 <sup>6</sup> )	$-\theta$ (°K) ± 1		C ± 0.02		$\mu_{\text{eff}}$ (B.M.) ± 0.02	
				a	b	a	b	a	b
2.00	18	5	460	97	113	2.14	2.40	4.14	4.38
1.25	36	8	359	70	83	2.43	2.65	4.41	4.61
1.00	49	8	286	65	70	2.56	2.69	4.53	4.64
0.50	67	8	185	55	58	2.61	2.70	4.57	4.65
0.25	72	7	157	60	63	2.84	2.91	4.77	4.83
0.00	74	10	146	65	69	3.01	3.10	4.91	4.98

<sup>a</sup> a, with T.I.P. correction; b, without T.I.P.

<sup>b</sup> From Ref. (2).

<sup>c</sup> Calculated (see text). Only the value for  $x = 2.00$  is taken from experiments (see  $\delta$ ).

the Curie-Weiss law, attributed, as in  $\text{CoRh}_x\text{Ga}_{2-x}\text{O}_4$  (1), to the presence of small uncompensated clusters and to isolated paramagnetic  $\text{Co}^{2+}$  ions.

This suggestion is supported by the  $M$  vs  $H$  curves (Fig. 3) obtained at 5°K up to a maximum field of 70 kOe. Indeed, for  $\text{CoAl}_2\text{O}_4$  a linear plot was observed, but for

other specimens there was a Brillouin-type behavior, attributed to paramagnetic ions and uncompensated clusters.

#### Composition Dependence of $C$ and $\theta$

Given the lack of data in the high-temperature range it was not possible to introduce an appropriate correction for temperature-independent paramagnetism. Nevertheless, the T.I.P. term for  $\text{Co}^{2+}$  ions in

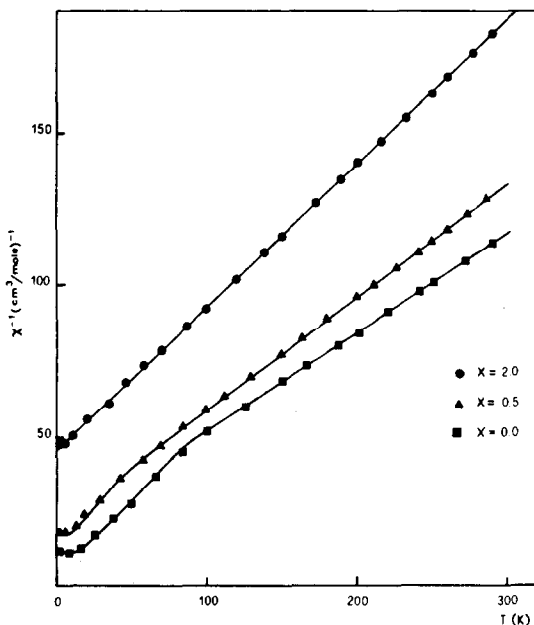


FIG. 1. Reciprocal magnetic susceptibility as a function of temperature with an applied field  $H = 10$  kOe.

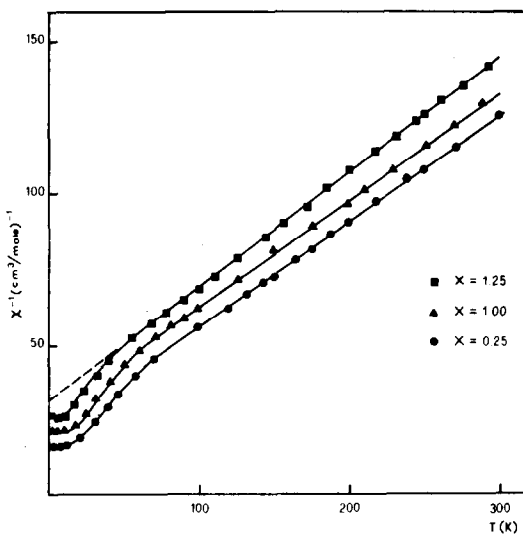


FIG. 2. Reciprocal magnetic susceptibility as a function of temperature with an applied field  $H = 10$  kOe.

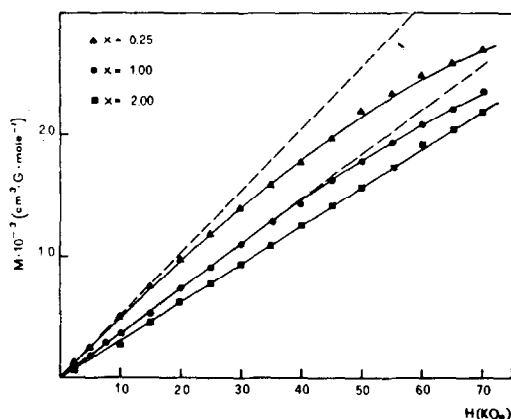


FIG. 3. Molar magnetization at 5°K as a function of applied field.

$T_d$  sites is not negligible, as found by Cossee (6) for  $\text{CoAl}_2\text{O}_4$  (T.I.P. =  $460 \times 10^6$  emu).

To estimate the influence of T.I.P. correction on the values of  $C$  and  $\theta$  we have evaluated the T.I.P. term (Table I) for each composition as a function of the tetrahedral occupation.

We used the value quoted by Cossee for  $\text{CoAl}_2\text{O}_4$ , assuming that his sample had the same cation distribution as ours (i.e., 82% of cobalt ions in  $T_d$  sites).

We remark that this is a rough estimate and that we do not expect a behavior linear with the composition of the T.I.P. value for  $\text{Co}^{2+}$  ions in  $T_d$  sites because of the gradual change in lattice site symmetry and crystal field parameters (T.I.P. =  $8N\beta^2/10 Dq$  for the  $^4A_2$  term). Indeed, the experimental T.I.P. values for the  $\text{CoRh}_x\text{Ga}_{2-x}\text{O}_4$  series (1) do not change linearly with the  $\text{Rh}^{3+}$  content and tetrahedral  $\text{Co}^{2+}$  ion occupation.

The comparison between the values of  $C$  and  $\theta$  evaluated with T.I.P. correction and without shows that the absolute values are affected by this correction. Therefore, the  $C$  and  $\theta$  values reported (Table I) should be considered only apparent, and the accuracy reported refers only to the precision limits of the instrument. However, the behavior of  $C$  and  $\theta$  (Figs. 4 and 5) remains substantially the same in both cases.

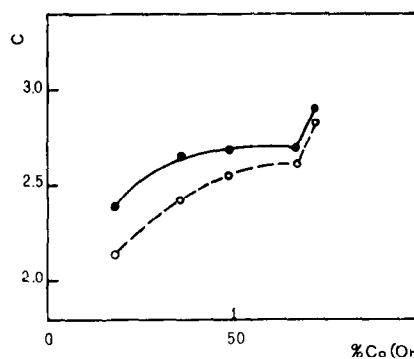


FIG. 4. Variation of the Curie constant  $C$  with percentage  $\text{Co}(O_h)$ . Full line,  $C$  values calculated without T.I.P. correction (●); dashed line, with T.I.P. correction (○).

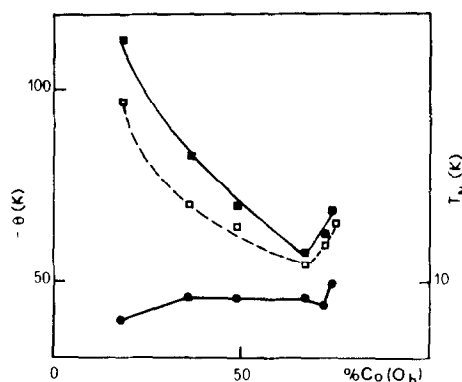


FIG. 5. Variation of  $T_N$  (●) with percentage  $\text{Co}(O_h)$ . Variation of  $\theta$  (■, □) with percentage  $\text{Co}(O_h)$ . Full line,  $\theta$  values calculated without T.I.P. correction; dashed line, with T.I.P. correction.

The nonlinear behavior of  $C$  with percentage  $\text{Co}^{2+}$  in  $O_h$  sites (Fig. 4) is due to the change of  $C_A$  and  $C_B$  within  $\text{CoAl}_x\text{Ga}_{2-x}\text{O}_4$  solid solutions, probably caused by the presence of lattice distortions. The negative value of  $\theta$  obtained from the Curie-Weiss law confirms the predominance of antiferromagnetic interactions for all the samples. There is (Fig. 5) a decrease in  $\theta$  up to 67% of  $\text{Co}^{2+}$  in  $B$  sites, and then an increase.

## Discussion

The results confirm that the distribution of  $\text{Co}^{2+}$  among the  $A$  and  $B$  sites determines the

magnetic behavior of spinel solid solutions. Comparing these results with that obtained for the  $\text{CoRh}_x\text{Ga}_{2-x}\text{O}_4$  system (1) leads to the following conclusions.

$\text{CoRh}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$  are both antiferromagnetic. While the former, which is a normal spinel, substantially follows the Néel two-sublattice theory, the latter, being partially inverse, exhibits a high  $|\theta/T_N|$  ratio ( $\approx 18$ ), revealing the presence of more than one type of interaction. Therefore, a comparison of  $T_N$  between  $\text{CoAl}_2\text{O}_4$  and  $\text{CoRh}_2\text{O}_4$  is not clearly diagnostic of the role of the trivalent ion in determining the strength of  $AA$  interactions. Indeed, as we have previously shown (1), the  $AB$  interactions tend to destroy the  $AA$  long-range ordering.

In the plot of  $T_N$  vs percentage  $\text{Co}(O_h)$  (Fig. 5) the initial increase of  $T_N$  with increase in the number of  $AB$  interactions suggests that these interactions stabilize a long-range order. This order is not simple and would take the form of an antiferromagnetic interaction between small clusters.

The higher  $T_N$  value for  $\text{CoGa}_2\text{O}_4$  than for the other samples could be due to a new kind of antiferromagnetic ordering, resulting from the new balancing between the different exchange interactions.

The behavior of  $\theta$  with  $\text{Co}^{2+}$  site distribution (Fig. 5) is quite different from that observed for the  $\text{CoRh}_x\text{Ga}_{2-x}\text{O}_4$  system. The progressive decrease in  $|\theta|$  with increase in cobalt octahedral occupation supports the presence of ferromagnetic interactions.

These interactions may be due to cobalt ions in  $B$  sites, which would be ferromagnetically coupled by the strong  $AB$  interactions, as found elsewhere (7).

The subsequent increase in  $|\theta|$  above 67% of octahedral cobalt ions reveals an increase in antiferromagnetic interactions, which may be due to the increasing importance of  $BB$  next-nearest-neighbor interactions.

## Conclusions

The magnetic properties of both spinel solid solutions  $\text{CoAl}_x\text{Ga}_{2-x}\text{O}_4$  and  $\text{CoRh}_x\text{Ga}_{2-x}\text{O}_4$  depend on the  $\text{Co}^{2+}$  distribution between  $O_h$  and  $T_d$  sites. This distribution determines the occurrence of spin uncompensated clusters and isolated ions, as revealed by low-temperature magnetic behavior.

The observed dependence of  $T_N$  and  $\theta$  on cation distribution is different for the two systems and this fact indicates that the presence of  $\text{Al}^{3+}$  instead of  $\text{Rh}^{3+}$  influences the relative strength and the balancing between the various exchange interactions  $AA$ ,  $BB$ , and  $AB$ .

Our results support the view that  $AA$  interactions are more effective when  $M^{3+} = \text{Rh}^{3+}$ , confirming the intermediate role of  $\text{Rh}^{3+}$ , as proposed by Blasse (4). Indeed, in the spinel solid solutions containing  $\text{Rh}^{3+}$  ions it appears that antiferromagnetic order is established between spins in  $A$  sites, and that  $AB$  interactions tend to destroy it. Conversely, when  $\text{Rh}^{3+}$  is replaced by  $\text{Al}^{3+}$  ion, the  $AA$  interactions become less important, and the magnetic order seems to be stabilized by the  $AB$  interactions.

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## References

1. D. FIORANI AND S. VITICOLI, *J. Solid State Chem.* **26**, 101 (1978).
2. F. PEPE, P. PORTA, AND M. SCHIAVELLO, in "Proceedings, 8th International Symposium on Reactivity of Solids," Goteborg, Sweden (1976).
3. W. L. ROTH, *J. Physique* **25**, 507 (1964).
4. G. BLASSE, *Philips Res. Repts.* **18**, 383 (1963).
5. P. W. SELWOOD, "Magnetochemistry," 2nd ed., p. 78, Interscience, New York (1956).
6. P. COSSEE AND A. E. VAN ARKEL, *J. Phys. Chem. Solids* **15**, 1 (1960).
7. K. DE STROOPER AND G. ROBBRECHT, *Physica* **86-88B**, 934 (1977).