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Magnetic Interactions in $CoM_x^{3+}Ga_{2-x}O_4$ Spinel Solid Solutions: I: $CoRh_xGa_{2-x}O_4$

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The magnetic susceptibility of polycrystalline solid solutions $CoRh_xGa_{2-x}O_4$ with a spinel structure have been measured between 4.2 and 1000°K. The magnetic properties have been found to vary with the composition x as a consequence of the variation in the distribution of Co^{2+} ions among tetrahedral and octahedral sites. The low-temperature magnetic behavior reveals an antiferromagnetic order and the concomitant presence of finite clusters of exchange coupled Co^{2+} ions and of isolated paramagnetic ions.

Introduction

The nature of the magnetic exchange interactions in compounds having a spinel structure has been a subject of continuing interest. Previous work (*1–4*) has shown that the magnetic properties of spinels cannot be interpreted only in terms of nearest-neighbor interactions, but it is also necessary to take into account distant-neighbor superexchange interactions.

The *A–A* (tetrahedral–tetrahedral) and the *B–B* (octahedral–octahedral) interactions have been investigated in spinels with the magnetic ions on, respectively, *A* sites (*3*, *5*) or *B* sites (*2*, *6*). Some different exchange paths have been proposed in these types of magnetic lattices (*3*, *4*, 6).

We now describe an investigation of the magnetic properties of the spinel solid solutions $CoRh_xGa_{2-x}O_4$, with the magnetic on Co^{2+} distributed (as a function of the composition x) among both tetrahedral and octahedral sites, giving rise to concomitant *AA*, *BB*, and *AB* interactions. The work was carried out with the aim of correlating the magnetic properties with the cation distribution and thus obtaining information on the relative strengths of the various exchange interactions in the magnetic ordering.

Experimental

The sample preparation, lattice parameters, and cation distribution are reported elsewhere (*7*). Magnetic measurements (*8*) were performed on $CoRh_xGa_{2-x}O_4$ polycrystalline solid solutions, prepared at 1273°K, using two Faraday-type balances.

Low-Temperature Measurements: 4.2–300°K

In the range 4.2 to 300°K the magnetic measurements were carried out on a Faraday balance system (Oxford Instruments Cryogenic System) similar in principle to that described by Gardner and Smith (*9*).

The magnetic field H_z and the field gradient dH/dz were generated by two different superconducting NbTi coils, allowing both H_z and dH/dz to be set independently of each other.

The main coil and gradient coils could be energized to a maximum of 70 kOe and 1 kOe/cm, respectively. The changes in weight were measured on an electronically controlled

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vacuum microbalance (Sartorius) with a resolution of 1 μg.

The temperature was measured with a gold (+0.03%) Fe versus chromel P thermocouple. The main field was calibrated, dH/dz remaining constant at maximum value, using $HgCo(SCN)_4$.

The accuracy of our measurements is limited primarily by the accuracy with which the magnetic susceptibility of $HgCo(SCN)_4$ is known (*10*), i.e., 5 parts in 10^3.

High-Temperature Measurements

In the range 300 to 1000°K the magnetic susceptibility measurements were performed using a magnetic balance described in detail in (*11*).

The experimental susceptibility was correlated for diamagnetism using the table of Selwood (*12*) and for temperature-independent paramagnetism (T.I.P.) using our own results, obtained from high-temperature measurements by plotting χ vs $1/(T-\theta)$.

Experimental Results

The cation distribution in the solid solutions $CoRh_xGa_{2-x}O_4$ has been found by X-ray diffraction to be a function of temperature and composition x (*7*).

Magnetic measurements were performed on the series prepared at 1273°K (*8*), within which the Co^{2+} distribution among the tetrahedral and octahedral sites varies with composition x. This leads to a variation of the magnetic behavior (Table I). $CoRh_2O_4$ is a normal spinel, as reported by Blasse (*3*).

Differently from Rh^{3+} ion, which always occupies octahedral sites in all solid solutions, the Ga^{3+} has been found to occupy both T_d and O_h sites. Consequently, $CoGa_2O_4$ is a partially inverse spinel ($Co_{0.29}Ga_{0.71}[Co_{0.71}Ga_{1.29}]O_4$).

Substitution of Rh^{3+} by Ga^{3+} has been found to produce a progressive displacement of Co^{2+} ions from T_d toward O_h sites.

The Co^{2+} site occupation and the magnetic data determined by susceptibility measurements in the range 4.2 to 1000°K are reported in Table I at various compositions.

All samples are antiferromagnetic, as deduced from the occurrence of a Néel point and from the negative value of the asymptotic Curie temperature θ.

The values of C and θ were evaluated by fitting with a least-squares program the χ^{-1} vs T plots in the range 300 to 1000°K, where any contributions from short-range order are absent.

Low-Temperature Data

(*a*) *Temperature-dependent susceptibility measurements.* A survey of susceptibility measurements at fields of 10 kOe is given in Figs. 1 and 2, which show the χ^{-1} vs T plots. $CoRh_2O_4$ and $CoRh_{1.5}Ga_{0.5}O_4$, with higher Co^{2+} T_d occupation compared to that in the other samples of the series, exhibit a regular

TABLE I

MAGNETIC DATA FOR $CoRh_xGa_{2-x}O_4$ SOLID SOLUTIONS

x	$Co(O_h)^a$ (%)	T.I.P. (emu × 10^6)	T_N(°K) ± 1	$-\theta$ (°K) ± 1	$C \pm 0.02$	μ_{eff} (B.M.) ±0.02
2.00	0	582	25	29	2.15	4.15
1.50	28	502	15	31	2.20	4.20
1.00	44	418	7	54	2.36	4.35
0.50	50	94	6	72	2.46	4.44
0.00	71	18	10	55	3.07	4.90

[a] From Ref. (*7*).

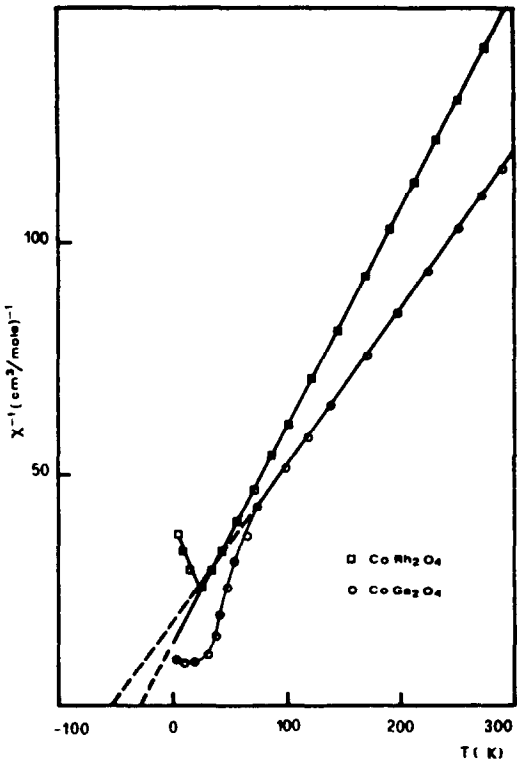

FIG. 1. Reciprocal magnetic susceptibility as a function of temperature with an applied field, $H = 10$ kOe.

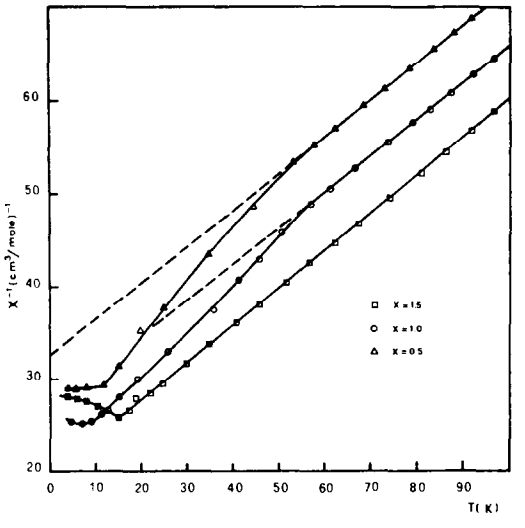

FIG. 2. Reciprocal magnetic susceptibility as a function of temperature with an applied field, $H = 10$ kOe.

antiferromagnetic behavior and a Curie–Weiss law that holds at temperatures down to T_N.

The remaining samples ($x = 1.0$, $x = 0.5$, $x = 0.0$), with lower tetrahedral Co^{2+} occupation, are still antiferromagnetic, but the χ^{-1} vs T plots exhibit the following differences at lower temperatures:

χ^{-1} decreases rapidly with decreasing temperature.

The Néel point appears flattened.

χ^{-1} deviates considerably from a Curie–Weiss law at temperatures up to $\simeq 10T_N$.

(*b*) *Field-dependent magnetization measurements.* A survey of the magnetization measurements at fields up to 70 kOe at 5°K is given in Fig. 3 as M vs H plots. For $CoRh_2O_4$ the magnetization is linear with field, while for the remaining samples a field-dependent susceptibility is observed and the plot shows a curve concave toward the H axis at high fields.

High-Temperature Data

A survey of the temperature-dependent susceptibility measurements from 300 to 1000°K at fields of about 9 kOe is given in Fig. 4 as χ^{-1} vs T plots. $CoRh_2O_4$ exhibits a curve concave toward the T axis due to temperature-independent paramagnetism. In the plots of the other solid solution this concavity decreases as the composition

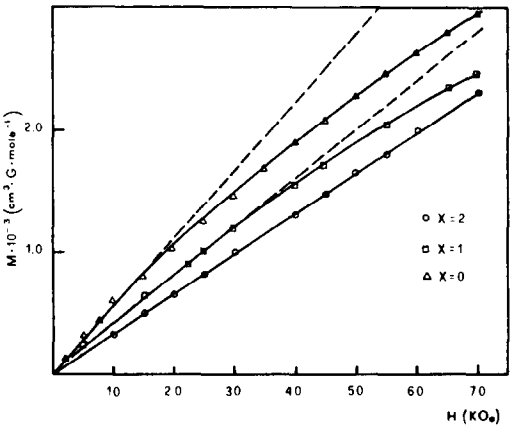

FIG. 3. Molar magnetization at 5°K as a function of applied field.

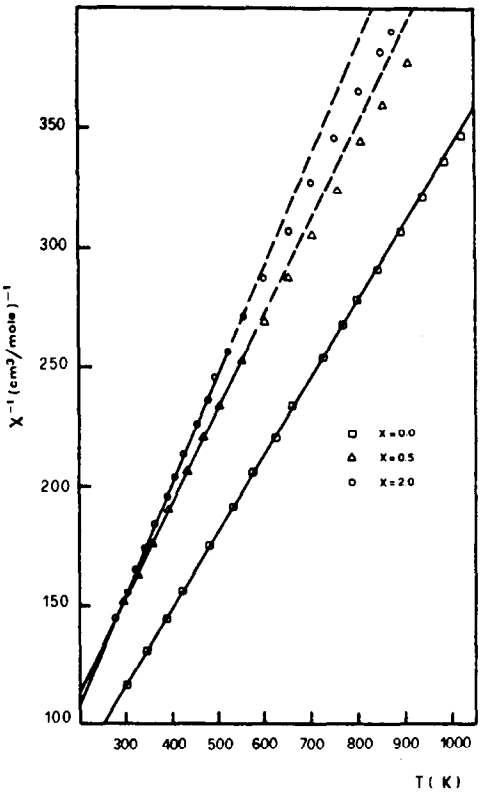

FIG. 4. High-temperature magnetic susceptibility measurements.

approaches $x = 0$, until it disappears for $CoGa_2O_4$, which shows a linear behavior (*13*).

Discussion

In the series of $CoRh_xGa_{2-x}O_4$ solid solutions, the Co^{2+} site distribution determines the overall magnetic interaction strength, as revealed by the dependence of θ on the composition (Fig. 5) due to the relative force and to the number of the various types of exchange interaction, i.e., *AA*, *BB*, and *AB*.

The composition dependence of the T_N (Fig. 5) results from the variation of the balancing out of the various types of exchange interactions, which would produce a change in the kind of antiferromagnetic ordering present.

The dependence of C on the composition is the result of changes in the distribution of

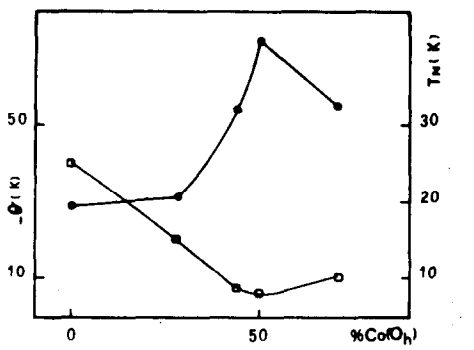

FIG. 5. Variaton of T_N (□) and θ (●) with percentage $Co(O_h)$.

Co^{2+} ions over O_h and T_d sites and changes of the Curie constant for each of these sites. (Fig. 6).

Low-Temperature Magnetic Behavior

The $CoRh_2O_4$ spinel shows (Fig. 1) an antiferromagnetic behavior with a Curie–Weiss Law holding at temperatures almost down to T_N. This fact demonstrates that short-range ordering is practically absent above the Néel point.

The observed ratio $|\theta/T_N| = 29/25 = 1.16$ is very close to unity, as predicted from the simple two sublattice model, where the nearest-neighbor *AA* interactions dominate. The larger value for θ may mean that there are contributions from next-nearest neighbors, as proposed by Blasse (*3*).

The χ^{-1} vs T plot for the solid solution with $x = 1.5$ (Fig. 2) still shows a regular antiferromagnetic behavior, but a larger difference between T_N (15°K) and θ (−31°K) is observed. This indicates that more than one type of interaction is present, as a consequence of Co^{2+} distribution among T_d (72%) and O_h (28%) sites. For the remaining samples ($x = 1.0$; $x = 0.5$; $x = 0.0$), the rapid decrease of χ^{-1} at lower temperatures is attributed to the presence of small, uncompensated, isolated clusters of exchange-coupled Co^{2+} ions and to a fraction of paramagnetic Co^{2+} ions.

In the very low temperature range, the susceptibility is almost completely determined by these particles, bearing a net moment and

having a susceptibility that increases rapidly with decreasing temperature. For this reason that T_N is almost obscured, appearing as a broad minimum in χ^{-1} vs T plots.

The presence of isolated clusters of exchanged Co^{2+} ions is confirmed by the M vs H curves at 5°K. Indeed, while $CoRh_2O_4$ shows a magnetization linear with the field, for the other compounds the M vs H curve shows a Brillouin-type behavior, as expected in systems where uncompensated clusters and paramagnetic Co^{2+} ions are present.

High-Temperature Magnetic Behavior

The χ^{-1} vs T plot (Fig. 4) for $CoRh_2O_4$ in the high-temperature range 300 to 1000°K shows the same behavior as found for Co^{2+} ions in the tetrahedral interstices of an oxide lattice (*14*). The concavity toward the T axis is due to T.I.P., arising from T_d Co^{2+} ions by "mixing" in the magnetic field of the ground state $^4A_2$ with the upper state $^4T_2$ and from O_h Rh^{3+} ions, by mixing of the ground state $^1A_{1g}$ (t_{2g}^6) with the excited state $^1T_{1g}(t_{2g}^5 e_g)$. Therefore the experimental values of T.I.P. (Table I) were found to decrease on approaching the composition $x = 0$, i.e., as the T_d Co^{2+} occupation and the Rh^{3+} content decrease.

Composition Dependence of C, θ, and T_N

The Curie constant C increases as octahedral Co^{2+} occupation increases (Fig. 6). The nonlinear behavior of C vs percentage Co^{2+} (O_h) demonstrates that C_A (Curie constant for A sites) and C_B (Curie constant for B sites) do not remain constant throughout the series of $CoRh_xGa_{2-x}O_4$ solid solutions. The reason could be a gradual change in lattice site symmetry and crystal field parameters with composition.

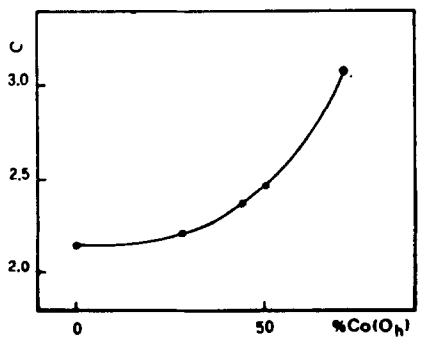

FIG. 6. Variation of the Curie constant C with percentage $Co(O_h)$.

There is an increase in the asymptotic temperature $|\theta|$ (Fig. 5) as the O_h Co^{2+} occupation increases, reaching a maximum at 50% O_h. This behavior could be due to the increasing number of AB antiferromagnetic interactions, which are stronger than the antiferromagnetic AA interactions. Indeed $|\theta|$ reaches the maximum value for the composition $x = 0.5$ (50% O_h; 50% T_d), in correspondence with the maximum number of AB interactions.

The following decrease in $|\theta|$ may be due to the decreasing number of antiferromagnetic AB interactions and/or to the increasing number of B–B ferromagnetic exchange interactions.

The AB superexchange interactions seem to be the strongest, in line with Goodenough's predictions (*15*), since the B-site Co^{2+} ions have half-filled e_g orbitals and the A-site Co^{2+} ions have half-filled t_{2g} orbitals, intervening in the superexchange mechanism.

Note that in our case the experimental θ value does not allow absolute estimation of the interaction strength, because it does not depend only on exchange interactions. Indeed, because of contributions of spin–orbit coupling and low-symmetry crystal fields, even in the absence of exchange, the susceptibility of a system of isolated "octahedral" Co^{2+} ions with a $^4T_1$ ground term apparently obeys a Curie–Weiss law with non-negligible asymptotic temperature θ.

At low temperature the magnetic susceptibility increases even more rapidly than given by Curie–Weiss behavior (i.e., $1/\chi$ tends toward zero at 0°K) (*16*, *17*). This means that the composition dependence of the Curie constant of octahedral Co^{2+}, as determined from the slope of $1/\chi$ vs T, is also influenced

by these parasitic single-ion contributions. In spite of this effect, however, the experimental θ value can be used to obtain an estimate of the dependence of the interaction strength on the composition. The dependence of T_N on the octahedral site occupation (Fig. 5) decreases until it reaches a minimum at 50% Co^{2+} in B sites. In normal spinel $CoRh_2O_4$ there is an antiferromagnetic long-range ordering of Co^{2+} spins on T_d sites. The decrease in T_N with increase in octahedral occupation may be due to the dilution effect and to the intervening AB interactions.

Thus, the AB interactions tend to destroy the AA antiparallel order and would impart some noncollinear character to the spins. The increase in T_N for $CoGA_2O_4$ would arise as a result of the changed equilibrium between the various competitive interactions, which probably produces a complicated kind of antiferromagnetic ordering.

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