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THE MAGNETIC STATE OF DIAMAGNETICALLY DILUTED ANTIFERROMAGNETIC COBALT MONOXIDE

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Magnetic neutron diffraction measurements have been performed on $(Co_{1-x}Mg_x)O$ solid solutions with $x = 0.1, 0.2, 0.3, 0.43, 0.53, 0.63$ and 0.7 at $T = 4.2$–300 K. It is shown that the concentration dependence of the average magnetic moment per atom does not obey the condition of simple dilution. The diamagnetic atom results in a local canting of the moments and an additional reduction of the average magnetic moment. One can consider this atom as a source of random magnetic field due to the appearance of a new superexchange interaction between magnetic atoms through the diamagnetic impurity. The sign of this interaction is opposite to the sign of the direct exchange interaction in the magnetic sublattice. Copyright © 1996 Elsevier Science Ltd

A. magnetically ordered materials, D. exchange and superexchange.

1. INTRODUCTION

MONOXIDES of transition metals MnO, FeO, CoO and NiO (NaCl type structure) are collinear antiferromagnets. Their magnetic structure is characterised by a ferromagnetic spin configuration in (1 1 1) planes and mutually opposite spin direction in adjacent planes [1, 2]. A new interest to these monoxides has evolved by the problem of their magnetic state under diamagnetic dilution [3, 5]. When transition metal ions are substituted by diamagnetic atoms the following situation can be postulated: (i) the diamagnetic ions act as "magnetic holes" due to the absence of spin and orbital moment; (ii) diamagnetic ions interact with some internal magnetic field and according to the Lentz law an induced magnetic moment occurs the direction of which is opposite to the sublattice magnetisation; (iii) diamagnetic ions cause a new super exchange interaction between atoms on the distance of the third co-ordination sphere. The sign of this interaction is opposite to the sign of the exchange interaction in the sublattice and then a diamagnetic ion causes frustrated bonds and can be considered as the source of a random magnetic field.

The occurrence of a magnetic moment on the diamagnetic sites was proposed by Menshikov *et al.* who consider an induced magnetic moment $M_{ef} = 0.35\,\mu_B$ on the Mg^{2+} ions in $(Ni_{1-x}Mg_x)O$ solid solutions. However the nature of this magnetic moment is not clear. Moreover, the conclusions which were obtained for the diluted nickel monoxide demand confirmation on other similar systems. In the present work we have chosen the $(Co_{1-x}Mg_x)O$ solid solutions as such an object. The lattice parameters in this system, like in $(Ni_{1-x}Mg_x)O$ solid solutions, has a very small variation throughout the whole concentration range. At the same time the Neel temperature in CoO ($T_N = 300$ K) is essentially less than in NiO ($T_N = 520$ K) and the magnetic moment on Co^{2+} ion ($\mu_{Co} = 3.8\,\mu_B$) is, on the contrary, two times larger than on the Ni^{2+} ion.

2. EXPERIMENT AND RESULTS

The $(Co_{1-x}Mg_x)O$ solid solutions with $x = 0.1, 0.2, 0.3, 0.43, 0.53, 0.63$ and 0.7 were prepared by sintering the constituent oxides. According to the X-ray diffraction the samples have a linear concentration dependence of the lattice parameter from $a = 4.262$ Å for CoO to $a = 4.215$ Å for MgO. Neutron diffraction experiments were carried out over the temperature range 4.2–300 K on the diffractometer ($\lambda = 1.81$ Å) installed on the horizontal channel of the IVV-2M reactor (Ekaterinburg). Second order contamination was removed by using a double germanium monochromator and a beryllium filter.

At $T = 4.2$ K the typical neutron diffraction pattern for ordered antiferromagnetic transition metal monoxide is obtained for all the investigated samples up to $x = 0.7$. The intensity of the magnetic reflections decreases with increasing x. It was also found that the width of coherent magnetic reflections does not change up to $x \approx 0.5$ and gradually increases for $x > 0.5$. These results are in good agreement with the neutron diffraction measurements of Giebultowicz *et al.* [3] who studied some $(\mathrm{Co}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ solid solutions near the critical concentration for magnetic long range ordering.

We have measured the temperature dependence of the intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection to determine the Neel temperature. Figure 1 shows the concentration dependence of T_N for the $(\mathrm{Co}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ and $(\mathrm{Ni}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ solid solutions. The ordering temperature decreases linearly for both systems, the extrapolation of this dependence yields $T_N = 0$ at $x = 1$.

A different behaviour was observed for the average magnetic moment per atom $\bar{\mu}$ which was calculated from the experimental intensities at $T = 4.2$ K in the framework of the magnetic structure of wave vector $\mathbf{k} = 2\pi/a\ (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Figure 2 shows the concentration dependence of $\bar{\mu}$ for the $(\mathrm{Co}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ as well as for $(\mathrm{Ni}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ solid solutions investigated earlier [4, 5]. It is seen that in both cases a linear dependence is observed but the extrapolation at large x yields $\bar{\mu} = 0$ at $x_c = 0.85$ rather than $x = 1$ according to a simple mixing law.

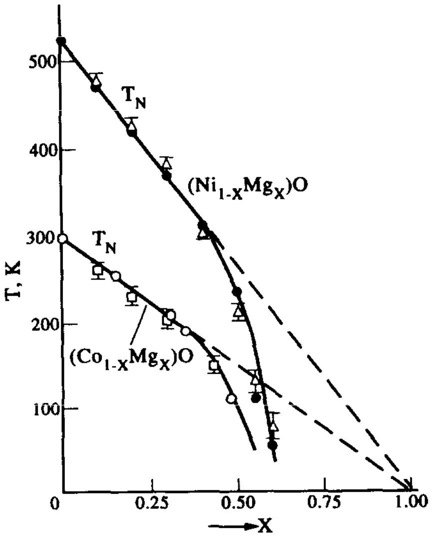

Fig. 1. The concentration dependence of the Neel temperatures for the $(\mathrm{Co}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ and $(\mathrm{Ni}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ solid solutions: ○, ● are taken from the magnetic susceptibility measurements [6]; □, △ are our diffraction measurements.

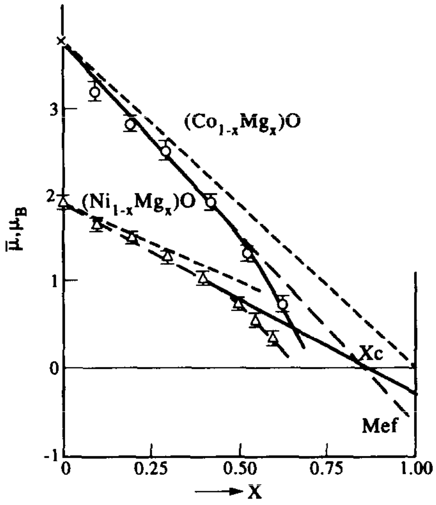

Fig. 2. The concentration dependence of the average magnetic moments per atom in the $(\mathrm{Co}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ and $(\mathrm{Ni}_{1-x}\mathrm{Mg}_x)\mathrm{O}$ solid solutions from our neutron diffraction measurements (solid lines). The dotted lines denote the proposed mixing law lines.

3. DISCUSSION

3.1. *The Neel temperature*

It is possible to consider that the Co^{2+} and Ni^{2+} magnetic moments for diamagnetically diluted monoxides are localised on the sites n and m with spin $S_{n,m}$. The Hamiltonian of exchange interactions between localised magnetic moments is of the form:

$$H_{ex} = -\tfrac{1}{2}J\sum_{n,\Delta}(1-p_n)(1-p_{n+\Delta})\mathbf{S}_n\mathbf{S}_{n+\Delta} - \tfrac{1}{2}J\sum_{m,\Delta}(1-p_m)(1-p_{m+\Delta})\mathbf{S}_m\mathbf{S}_{m+\Delta}. \quad (1)$$

Here n and m belong to different sublattices and the sum over Δ goes over Z_{NNN} next nearest neighbours. The projection operators $p_{n,m}$ are equal to 0 and 1 for an occupation of the site by a Mg^{2+} and a Co^{2+} or Ni^{2+} ion respectively, $J = |J_{NNN}| < 0$ is the superexchange integral between next nearest neighbours via intermediate oxygen atoms. We neglect the crystal field effects since, in these compounds, the single ion anisotropy is rather weak as compared to the exchange energy.

In the molecular field approximation we can transform the Hamiltonian (1) into [7]

$$H_{ex} = -g\mu_B \sum_{n=1}^{N/2} (1 - p_n) S_n^z H_{mf}^z(n) - g\mu_B \sum_{m=1}^{N/2} (1 - p_m) S_m^z H_{mf}^z(m), \qquad (2)$$

where, for example,

$$H_{mf}^z(n) = \frac{J}{g\mu_B} \sum_{\Delta=1}^{Z_{NNN}} (1 - p_{n+\Delta}) \langle S_{n+\Delta}^Z \rangle \qquad (3)$$

and $\langle \ldots \rangle$ is the thermodynamical average.

In the temperature range $T < T_N$ we obtain

$$\langle S_n^z \rangle = SB_s \left(\frac{g\mu_B H_{mf}^z(n)}{kT} \right) \approx \frac{S(S+1)}{3} \frac{g\mu_B H_{mf}^z(n)}{kT} \qquad (4)$$

and

$$kT_N \langle S_n^Z \rangle = \frac{S(S+1)}{3} J \sum_{\Delta} (1 - p_{n+\Delta}) \langle S_{n+\Delta}^z \rangle \qquad (5)$$

after concentration averaging of equation (5) over disorder ($\langle \overline{S_n^z} \rangle = \sigma$ $\langle \overline{S_{n+\Delta}^z} \rangle = -\sigma$, $\bar{p}_{n+\Delta} = x$) we find

$$T_N = \frac{S(S+1)|J_{NNN}| z_{NNN}}{3k} (1 - x). \qquad (6)$$

The principal feature of equation (6) is the linear dependence of the Neel temperature upon the concentration x of diamagnetic atoms which describe well the experimental results of Fig. 1 in the concentration range $0 < x < 0.4$.

3.2. *The average magnetic moment*

According to Fig. 2 the linear concentration dependence of the average magnetic moment per atom $\bar{\mu}(x)$ differs from the above stated concentration dependence of T_N. The value of $\bar{\mu}(x)$ equals 0 for $x = 0.85$ and the experimental dependence of $\bar{\mu}(x)$ can be described by the law

$$\bar{\mu}(x) = \mu_n(1 - x) + m_{ef}x, \qquad (7)$$

where $m_{ef} = -0.35\,\mu_B$ for the $(Ni_{1-x}Mg_x)O$ and $-0.7\,\mu_B$ for the $(Co_{1-x}Mg_x)O$ solid solutions.

To consider the nature of m_{ef} one may propose that this effective moment was induced on the Mg^{2+} site due to the existence of some internal magnetic field H_{int}, i.e.

$$m_{ef} = \chi_d H_{int}, \qquad (8)$$

where χ_d is the diamagnetic susceptibility of Mg ions. The value of m_{ef} can be approximated with $\chi_d(MgO) = -0.25 \times 10^{-6}\,cm^3\,g^{-1}$ and some H_{int} the nature of which we have to discuss now.

Firstly we can assume that this internal field has a dipole nature. The calculations show that in this case the induced magnetic moment $m_{ind}^{dip} \approx 10^{-5}\,\mu_B$ is extremely small and cannot explain the experimentally observed m_{ef}. Secondly we can propose that H_{int} has an exchange nature. We can use equation (3) for its evaluation, i.e.

$$H_{int}^{mol} = \frac{|J_{NNN}| z_{NNN}}{g\mu_B} S_n \qquad (9)$$

Then the substitution of equation (9) into equation (8) leads to the value of the induced moment $m_{ind}^{ex} \cong -(1 - 1.5) \times 10^{-2}\,\mu_B$. This value is again too small to explain the experimental values of m_{ef}.

Consequently, as there is no way to obtain a sufficiently large induced moment on the Mg atom we have to consider that the behaviour of the average magnetic moment resulted from a deviation from a collinear ordering into a canted local one inside the first co-ordination sphere around the Mg atoms. Such a non collinear arrangement will lead to a reduction of the average ordered moment. Indeed in pure CoO and NiO only the exchange interaction between next nearest neighbours contributes to the free energy because in the first and third co-ordination sphere around a magnetic ion there is an equal number of parallel and antiparallel moments. When Ni or Co ions are substituted by Mg a small induced moment of dipolar origin is induced on the Mg ions and as a result a superexchange interaction between atoms on

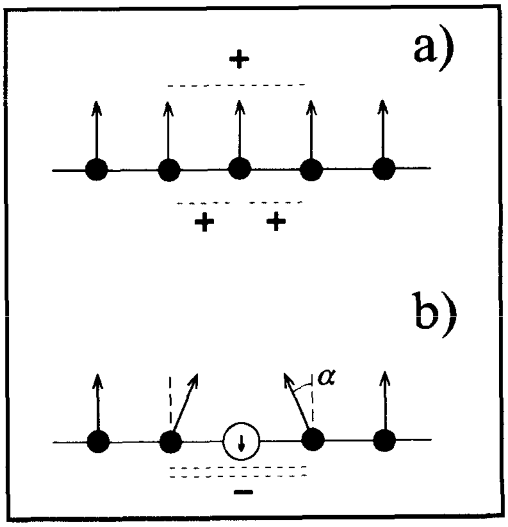

Fig. 3. The schematic pictures of a magnetic ordering in (1 1 1) plane for CoO and NiO (a) and for the $(Co_{1-x}Mg_x)O$ and $(Ni_{1-x}Mg_x)O$ solid solutions (b). Single dotted lines denote a direct exchange interaction between atoms; double dotted lines a new super exchange interaction through a diamagnetic atom.

the distance of the third nearest neighbours occurs. Then all the spins around a diamagnetic atom are deviated from the direction of the sublattice magnetisation by some angle α (Fig. 3). In this model the average magnetic moment can be written as

$$\bar{\mu} = \mu_n(1 - x) - \mu_n z_{nn} x(1 - \cos\alpha), \qquad (10)$$

where z_{nn} is the number of first neighbours. Therefore $-\mu_n z_{nn} x(1 - \cos\alpha)$ can be identified with m_{ef} and we can find the value of $\alpha \approx 10$–$11°$ for both systems.

It is interesting to notice that the linear dependence of T_N takes place up to some limiting concentration x_1 of diamagnetic atoms. We shall assume that this concentration is due to an overlapping of magnetic inhomogeneities and estimate x_1 as $x_1 = V_1/V_2$ where V_1 and V_2 are the volume of the first ($r = \sqrt{2}/2a$) and second ($r = a$) co-ordination spheres respectively. The calculated value $x_1 = 0.35$ is in good agreement with the experimental limit for the linear dependence for T_N and $\bar{\mu}(x)$ (Figs 1 and 2). Therefore when the overlapping between local canted regions is absent the Neel temperature is insensitive to this canting. At concentrations $x > x_1$ the overlapping occurs and the contribution to the free energy of antiferromagnetically ordered pairs of atoms decreases. Moreover the topologically infinite antiferromagnetic cluster breaks down into clusters of finite size. This decrease of the ordered volume leads to a decrease of the coherently scattered intensity, and T_N as well as $\bar{\mu}(x)$ depart strongly from the linear dependence (Figs 1 and 2).

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