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## Magnetic susceptibilities of Co- and Ni-doped MgO

M M Ibrahim, Z Feng, J C Dean and Mohindar S Seehra†

Physics Department, West Virginia University, Morgantown, WV 26506, USA

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**Abstract.** The temperature dependence (1.7–300 K) of the DC magnetic susceptibilities  $\chi$  for the systems  $M_pMg_{1-p}O$  ( $M=Co, Ni$ ) with  $p < p_c$  (where  $p_c \simeq 0.14$  is the percolation threshold) are reported. Two sets of samples were studied for both dopants: two lightly doped samples with  $p < 0.01$  and two more heavily doped samples with  $p = 0.06$  to  $0.12$ . For the lightly doped samples, results are analysed in terms of contributions from single magnetic ions, exchange-coupled pairs and any contributions from the spin-orbit coupling. For  $Co^{2+}$  in MgO, a contribution from spin-orbit coupling leads to a temperature-dependent magnetic moment ( $\mu_T = 3.84 \mu_B$  at 5 K to  $5.15 \mu_B$  at 300 K) and an apparent Curie-Weiss variation, whereas for  $Ni^{2+}$  in MgO, the paramagnetic  $\chi_P$  follows the Curie-law variation. From this analysis, concentrations of the dopants are determined. Further, the temperature independence of  $\chi_P^B/\chi_P^A$  for two doping levels A and B at low concentrations is used to show that any contributions from exchange-coupled pairs are negligible. The more heavily doped samples show non-linear variations of  $\chi_P^{-1}$  against  $T$ , presumably due to contributions from magnetic clusters of different sizes.

### 1. Introduction

In recent years, there has been a great deal of interest in magnetic systems that have been site-diluted with non-magnetic ions since such systems simulate percolation phenomena and exhibit a variety of interesting magnetic properties when dilution is varied [1–7]. The diamagnet MgO has the same NaCl structure as the magnetic oxides MnO, FeO, CoO and NiO. In recent years we have reported on the magnetic properties of  $Co_pMg_{1-p}O$  [8–10] and  $Ni_pMg_{1-p}O$  [11, 12] systems where  $p$  is varied from 1 to 0.1. Some of the important results of these investigations include: (i) the non-linear variation of the Néel temperature  $T_N$  with  $p$ ; (ii) the percolation threshold  $p_c \simeq 0.14$ ; (iii) a transition from the large- $p$  long-range order region to the small- $p$  short-range order region occurs at  $p = 0.47$  for  $Co_pMg_{1-p}O$  and for  $p \simeq 0.30$  for  $Ni_pMg_{1-p}O$ ; (iv) the dominant role of the next-nearest-neighbour (NNN) exchange constant  $J_2$  in determining the variation of  $T_N$  with  $p$  for  $p > 0.31$  and a Curie-Weiss temperature  $\Theta(p) = \Theta(1)p$  for  $p_c \leq p \leq 1$ . The importance of  $\Theta(p)$  is that it measures the sum of all magnetic interactions and hence, in a randomly diluted system, it should vary linearly with  $p$  if there is no chemical clustering [8].

For  $p < p_c$ , a randomly diluted magnetic system is expected to consist of disconnected finite clusters of magnetic ions, and for  $p < 10^{-2}$ , primarily isolated magnetic ions should exist leading to  $\Theta(p) \rightarrow 0$ . On the other hand, if there is clustering of

† Author to whom correspondence should be addressed.

magnetic ions beyond the prediction of the random distribution [13], then a careful analysis of the magnetic susceptibility should be able to detect such clustering as has been reported recently for  $\text{Mn}^{2+}$ -doped  $\text{MgO}$  [14].

In this paper, we report experimental results and analysis of the temperature dependence of the magnetic susceptibilities of the systems  $\text{M}_p\text{Mg}_{1-p}\text{O}$  ( $\text{M}=\text{Co}$  and  $\text{Ni}$ ) and for  $p < p_c \sim 0.14$ . This work was partly motivated by the observation of Cimino *et al* [15] that in  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  systems  $\Theta(p)$  does not go to zero as  $p \rightarrow 0$  but that  $\Theta(p)$  assumes a constant magnitude of about 50 K for  $p < 0.1$ . This observation as well as the observation of clustering of  $\text{Mn}^{2+}$  ions in  $\text{MgO}$  [14] led us to examine the behaviour of the magnetic susceptibilities of Co and Ni ions weakly doped in the  $\text{MgO}$  lattice. Details of these studies are described below.

## 2. Experimental section

The single crystals of  $\text{MgO}$  doped with Co and Ni ions were obtained from W & C Spicer Ltd of England. These samples have  $p < 0.01$  and we have investigated at least two concentrations for each magnetic ion (310 and 9900 ppm for Co; 130 and 1400 ppm for Ni). Powdered samples of  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  and  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$  for  $p > 0.01$  were prepared starting from nitrates using the procedure described earlier [8] and we report data for  $p = 0.07$  and  $0.10$  for Co and  $p = 0.06$  and  $0.12$  for Ni-doped  $\text{MgO}$ . Since for  $p < 0.01$  there is no simple way to determine the concentration of magnetic ions more accurately, we determine these concentrations from the analysis of the magnetic data and compare them with the nominal compositions mentioned above. The magnetic susceptibilities were measured with a SQUID magnetometer (Quantum Design Model MPMS), although in some of the studies of  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  for  $p > 0.01$  the data reported here were taken earlier with a Faraday balance [16]. Most of the data were taken in the temperature range of 1.7–300 K, using magnetic fields  $\leq 2$  kOe.

## 3. Theoretical considerations

For concentrations of  $p \simeq 10^{-2}$  or less, most of the magnetic ions should occur either as isolated ions (monomers) or as pairs (dimers) on nearest-neighbour (NN) and next-nearest-neighbour (NNN) sites. Therefore the paramagnetic susceptibility  $\chi_P$  is expected to consist of two terms:

$$\chi_P = \chi_1 + \chi_2 = \frac{p_1 C}{T} + \frac{p_2 C}{T} f(\beta J) = \frac{p_1 C}{T} \left[ 1 + \frac{p_2}{p_1} f(\beta J) \right] \quad (1)$$

where the first term is the Curie contribution from monomers of concentration  $p_1$  ( $C$  is the molar Curie constant) and the second term is from dimers of concentration  $p_2$ . Here  $\beta = 1/k_B T$  and  $J$  is the exchange interaction between dimers. Our analysis of the susceptibility of dimers of  $\text{Mn}^{2+}$  in  $\text{MgO}$  [14] showed that  $f(\beta J)$  can be a quite complicated function of  $\beta J$  even when the NN and NNN exchange interactions are equal as in  $\text{MnO}$ . If we compare two samples, A and B, doped with different levels of the same magnetic ion, then

$$\frac{\chi_P^B}{\chi_P^A} = \frac{p_1^B}{p_1^A} \left\{ \frac{1 + [f(\beta J)p_2^B/p_1^B]}{1 + [f(\beta J)p_2^A/p_1^A]} \right\}. \quad (2)$$

In the limit  $T \rightarrow 0$ ,  $f(\beta J) \rightarrow 0$  for antiferromagnetic exchange coupling [14], leading to

$$(\chi_P^B/\chi_P^A)|_{T=0} = p_1^B/p_1^A. \quad (3)$$

Further if  $p_2 \ll p_1$  for both concentrations, then,

$$\chi_P^B/\chi_P^A \simeq p_1^B/p_1^A \quad (4)$$

at all temperatures. This suggests that if the number of dimers in the sample is insignificant, then the ratio  $\chi_P^B/\chi_P^A$  will be essentially independent of temperature. This is independent of the detailed analysis of the magnetic susceptibility of monomers which itself can be quite complicated as we see below. For example, consider the case of  $\text{Co}^{2+}$  [16, 17]. In a cubic field, the  ${}^4F$  state of  $\text{Co}^{2+}$  splits into  $\Gamma_4$  (triplet),  $\Gamma_5$  (triplet) and  $\Gamma_2$  (singlet) states. The effect of the spin-orbit interaction  $\lambda L \cdot S$  on the ground state  $\Gamma_4$  is to yield states with  $J = 1/2, 3/2$  and  $5/2$  ( $J = \text{total angular momentum}$ ). For the weak-field case, the magnetic moment  $\mu_T$  for the high-spin state can then be shown to be given by

$$\mu_T^2 = \frac{(\frac{169}{12}x + \frac{490}{9}) + (\frac{64}{15}x - \frac{2156}{225})2e^{-3x/4} + (\frac{63}{20}x - \frac{294}{25})3e^{-2x}}{x(1 + 2e^{-3x/4} + 3e^{-2x})}. \quad (5)$$

The paramagnetic susceptibility  $\chi_P$  is then given by

$$\chi_P = N_A p_1 \mu_B^2 \mu_T^2 / 3k_B T \quad (6)$$

where  $N_A \equiv$  Avogadro's number,  $\mu_B \equiv$  the Bohr magneton,  $k_B \equiv$  Boltzmann's constant and  $x = \zeta/k_B T$  with  $\lambda = -\zeta/2S$ . It is noted that equation (5) yields  $\mu_T = 5.1 \mu_B$  at 300 K with  $\zeta/k_B = 400$  K. This value of  $\mu_T$  is in excellent agreement with the experimental value for the  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  system [8]. Equation (5) can be derived from the parameters given by Griffith [16, 17] for the weak-field (high-spin) limit. The expression for  $\mu_T^2$  given by Griffith [17] for the strong-field case instead yields  $\mu_T = 4.6 \mu_B$  at 300 K.

Since  $\mu_T$  (equation (5)) is independent of concentration, then for two levels of concentrations of  $\text{Co}^{2+}$ , equations (3) and (4) are unaffected. Hence the temperature independence of the ratio of the magnetic susceptibilities at two concentration levels of the same magnetic ions shows the absence of any significant number of dimers. On the other hand, if  $\chi_P^B/\chi_P^A$  is temperature dependent, especially at lower temperatures, then it could suggest a dimer contribution to susceptibility. In [14], we have outlined a procedure for estimating the concentration of dimers and the exchange interaction in the dimers. By comparing the ratio  $p_2^B/p_1^B$  with the estimate from the random distribution model, one can then determine whether clustering of magnetic ions is present in a given system.

## 4. Experimental results and discussion

### 4.1. Diamagnetic susceptibilities

For the weakly doped materials, a significant contribution to the measured  $\chi$  comes from the diamagnetic contribution  $\chi_D$  leading to

$$\chi = \chi_P + \chi_D. \quad (7)$$

Since  $\chi_P$  decreases as  $T$  increases (equation (6)) and  $\chi_D$  is usually independent of temperature, we have estimated  $\chi_D$  by plotting  $\chi$  against  $1/T$  and taking the limit  $1/T \rightarrow 0$ .  $\chi_D$  so obtained may contain other temperature-independent contributions such as the van Vleck susceptibility which will be different for different samples. The value of  $\chi_D$  so obtained varied between  $-13$  to  $-21$  (in units of  $10^{-6}$  emu mol $^{-1}$ ) for different samples. These values are in good agreement with  $\chi_D = -20 \times 10^{-6}$  emu mol $^{-1}$  for single-crystal MgO [14], considering some of the uncertainties noted above. In any case, most of our analysis in this paper deals with the temperature dependence of the paramagnetic contribution  $\chi_P$ .

#### 4.2. Magnetic susceptibilities of $Co_pMg_{1-p}O$ ( $p < p_c$ )

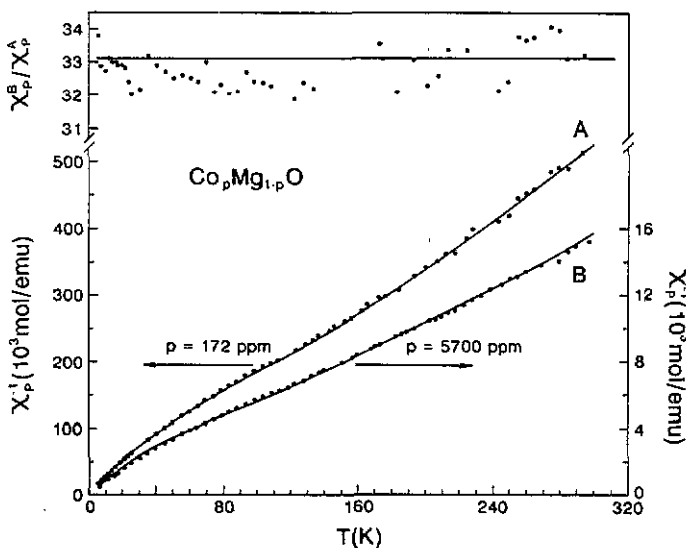
In figure 1, we show the plots of  $1/\chi_P$  against  $T$  for the two weakly doped samples, sample A with nominal doping of 310 ppm and sample B with nominal doping of 9900 ppm of Co. Also shown is the ratio  $\chi_P^B/\chi_P^A$  for those temperatures where the data for two samples were available for nearly the same temperatures. The ratio  $\chi_P^B/\chi_P^A$  is nearly temperature independent with a magnitude =  $33 \pm 1$  and it equals the ratio ( $9900/310 = 32$ ) of the nominal concentrations. According to equations (3) and (4), this suggests that contributions of dimers to the susceptibility for these samples is quite insignificant. Using the model of random distribution of magnetic ions in MgO for the FCC lattice [13], the probabilities for monomers and dimers,  $S$  and  $D$  respectively, are

$$S = (1 - p)^{12} \quad D = 12p(1 - p)^{18}. \quad (8)$$

Later, from the analysis of  $\chi_P$  against  $T$ , we determine  $p = 172$  ppm for sample A and  $p = 5700$  ppm for sample B, yielding the ratio  $5700/172 \approx 33$  (close to that obtained from nominal concentrations). Using equation (8), we obtain:  $S = 0.998$ ,  $D = 0.002$  for  $p = 172$  ppm; and  $S = 0.934$  and  $D = 0.062$  for  $p = 5700$  ppm. Thus the contributions for monomers dominate in agreement with the results of figure 1. It also follows that there is no noticeable clustering of  $Co^{2+}$  ions in MgO, as e.g. found in the case of  $Mn^{2+}$  in MgO [14].

According to equation (6),  $\chi_P = 0.1251 p_1 \mu_T^2 / T$ , where  $\mu_T$  for  $Co^{2+}$  is expected to be temperature dependent, according to equation (5). The data in figure 1 verify this, because plots of  $\chi_P^{-1}$  against  $T$  are not linear. Also, from these plots, only  $p_1 \mu_T^2$  can be determined strictly. According to equation (5),  $\mu_T$  depends on  $\zeta$ , the spin-orbit coupling parameter. Whereas  $p_1$  affects the magnitudes of  $\chi_P$ , the slope of the  $\chi_P^{-1}$  against  $T$  curve is determined by the choice of  $\zeta$ . Using these as adjustable parameters, we find that the best fit is obtained by the choice  $\zeta/k_B = 400$  K and  $p_1 = 172$  ppm for sample A and  $p_1 = 5700$  ppm for sample B. The solid lines in figure 1 are calculated curves with the above parameters. The choice of  $\zeta = 400$  K yields  $\mu_T = 3.84 \mu_B$  at 5 K increasing to  $5.15 \mu_B$  at 300 K. Thus the temperature dependence of  $\mu_T$  is the source of the deviation from the Curie law for the temperature dependence of  $\chi_P$  for  $Co^{2+}$  in MgO.

The apparent  $\Theta(p)$  in figure 1 is certainly due to the temperature dependence of  $\mu_T$  and explains the observations of Cimino *et al* [15] that  $\Theta(p)$  does not go to zero as  $p \rightarrow 0$ . From figure 1,  $\Theta(p) \approx 25$  K is estimated from the usual plot of  $\chi_P^{-1}$  against  $T$  for sample B, whereas for sample A with  $p = 172$  ppm the plot of  $\chi_P^{-1}$  against  $T$  is highly non-linear and hence  $\Theta(p)$  is not estimated. As explained above and shown in figure 1, these observations are due to the effect of spin-orbit



**Figure 1.** Plots of  $\chi_p^{-1}$  against  $T$  for two samples of  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  with nominal  $p = 310$  ppm for sample A and nominal  $p = 9900$  ppm for sample B. The listed values of  $p = 172$  ppm (sample A) and  $p = 5700$  ppm (sample B) are determined from the fit of the data (points) to equations (5) and (6) (solid line). At the top, a plot of  $\chi_p^B/\chi_p^A$  against  $T$  is shown for temperatures for which data for the two samples were available at the same temperature, with the solid line representing the ratio  $5700/172 = 33.1$ .

interaction. The magnitude of  $\zeta/k_B = 400$  K used in the fit in figure 1 is about half the free ion value for  $\text{Co}^{2+}$  in MgO. Also, the concentration  $p = 172$  ppm for sample A and  $p = 5700$  ppm for sample B are 57% of the nominal concentrations, although the ratios are unaffected, perhaps fortuitously.

In figure 2, we plot  $\chi_p^{-1}$  against  $T$  for the heavier doped samples viz.  $p = 0.07$  and  $p = 0.10$ . The solid lines represent the linear fits to the higher temperature data. From the slopes we find that  $C$  scales with  $p$ , but from the intercepts we find that the apparent  $\Theta(p)$  does not. In figure 3 we show  $\Theta(p)$  against  $p$  for  $p$  up to 0.30 (some data taken from [8]) and we note that only above  $p_c = 0.14$  does the measured  $\Theta(p)$  scale with  $p$ . Thus we infer that for  $p < p_c$  in  $\text{Co}_p\text{Mg}_{1-p}\text{O}$ ,  $\Theta(p)$  really has no meaning since it is strongly affected by the spin-orbit interaction. Above  $p_c = 0.14$ , where the system orders magnetically,  $\Theta(p)$  assumes its normal role of representing the sum of all magnetic interactions in the system.

#### 4.3. Magnetic susceptibilities of $\text{Ni}_p\text{Mg}_{1-p}\text{O}$ ( $p < p_c$ )

In figure 4, we plot  $\chi_p^{-1}$  against  $T$  for two weakly doped samples of  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$  with nominal compositions of 130 ppm for sample A and 1400 ppm for sample B. Unlike the  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  case, the variations in figure 4 are now linear suggesting Curie-law variation and temperature-independent  $\mu_T$ . Again, from equation (6), we can only determine the product  $\mu_T p_1$  from the slope of figure 4. Using  $\mu_T = 3.15 \mu_B$  for  $\text{Ni}^{2+}$  in MgO [18], the best fit to the data yields  $p_1 \simeq p = 176$  ppm for sample A and  $p_1 \simeq p = 855$  ppm for sample B, yielding the ratio  $p_1^B/p_1^A \simeq \chi_p^B/\chi_p^A = (855/176) = 4.86$ . Since this ratio is independent of temperature (figure 3), it follows that there is no significant contribution to  $\chi_p$  from dimers. This is not

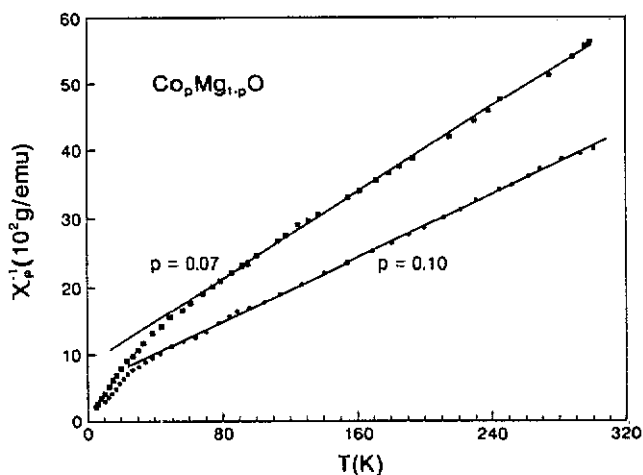


Figure 2. Plots of  $\chi_p^{-1}$  against  $T$  for  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  with  $p = 0.07$  and  $p = 0.10$ . The solid lines are linear fits to the high-temperature data, indicating apparently Curie-Weiss-type behaviour at higher temperatures.

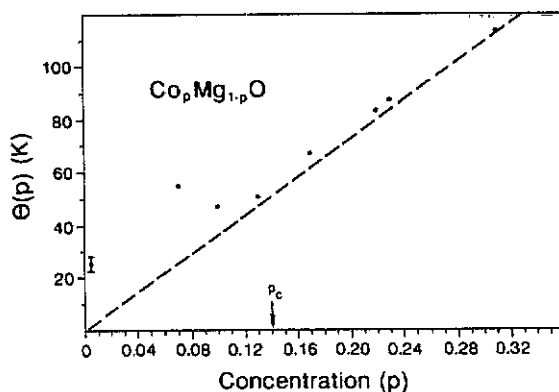


Figure 3. Plots of the apparent  $\Theta(p)$  against concentration  $p$  for  $\text{Co}_p\text{Mg}_{1-p}\text{O}$ . The dotted line is the predicted behaviour [8] neglecting spin-orbit interaction. Note that the percolation threshold  $p_c \simeq 0.14$  for this system.

unexpected since these materials are not as heavily doped as the Co-doped MgO single crystals discussed in section 4.2 above.

For two powder samples of  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$  with  $p = 0.06$  and  $p = 0.12$  respectively, plots of  $\chi_p^{-1}$  against  $T$  are shown in figure 5. Recall that  $p_c \simeq 0.14$  in these materials [8, 11] so we are still in a regime where no magnetic ordering is expected. However, significantly larger exchange-coupled clusters are expected to be present as we approach  $p_c$  from below and consequently  $\chi_p^{-1}$  against  $T$  is not expected to be linear. This is borne out by the data in figure 5, where increasing non-linearity is evident as  $p$  increases, particularly at lower temperatures. Note that the scales for the ordinates for the two compositions are scaled by a factor of two, the same as the ratio of the concentrations, so the differences between the shapes of the two curves must in some way reflect the increasing contribution of the clusters as  $p$  increases.

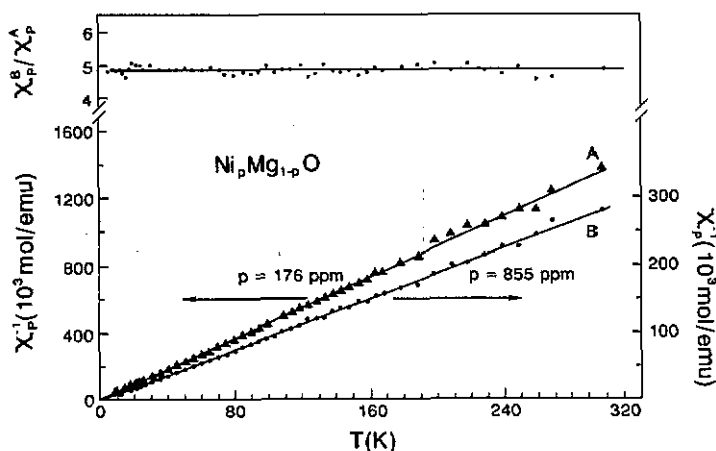


Figure 4. Plots of  $\chi_p^{-1}$  against  $T$  for two samples of  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$  (similar to figure 1 for  $\text{Co}_p\text{Mg}_{1-p}\text{O}$ ) with  $p = 176$  ppm for sample A and  $p = 855$  ppm for sample B as determined by fits of the data (points) to equations (5) and (6) (solid lines). At the top the ratio  $\chi_p^B/\chi_p^A$  is plotted against temperature with the solid line representing the ratio  $855/176 = 4.86$ .

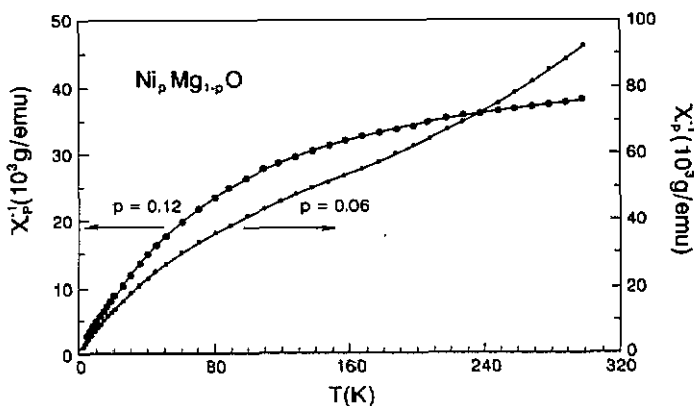


Figure 5. Plots of  $\chi_p^{-1}$  against  $T$  for  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$  with  $p = 0.06$  and  $p = 0.12$ .

The calculations of magnetic susceptibilities for cluster models including contributions from monomers, dimers and trimers has been carried out by Nagata *et al* [19] for the  $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$  system where only a single exchange constant was dominant. However, since the magnetic susceptibility measures the total magnetic response of the system, the separation of the experimental data into contributions from monomers, dimers and trimers is not easy even in simple cases. For  $\text{Mn}^{2+}$  in  $\text{MgO}$ , where the NN and NNN exchange interactions are almost equal and the effect of the spin-orbit interaction is absent, it was possible to calculate the contribution from the dimers and separate it from the contributions from monomers [14]. However, for  $\text{CoO}$  and  $\text{NiO}$ , the NN and NNN exchange interactions are quite different [20] and the effect of the spin-orbit interaction, at least for  $\text{Co}^{2+}$  in  $\text{MgO}$ , cannot be ignored. Hence it is difficult to calculate the magnetic susceptibilities for these systems for dopings as large as  $p = 0.06$  to  $0.12$ . Therefore such calculations have not been attempted.



## 5. Conclusions

Experimental results and theoretical analysis of the temperature dependence of the magnetic susceptibilities of  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  and  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$  systems for  $p < p_c \approx 0.14$  have been presented. For lightly doped samples where contributions from single ions of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  are expected to be dominant, results in  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  show that magnetic moment  $\mu$  is temperature dependent due to the effect of the spin-orbit interaction resulting in an apparent Curie-Weiss behaviour whereas in  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$ ,  $\mu$  is temperature independent with Curie-law variation. In both systems, there is no evidence of clustering of magnetic ions, as e.g. reported in the Mn-doped MgO system [14]. (This difference is probably due to large mismatch of the size of the  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  ions whereas sizes of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions are nearly equal to that of  $\text{Mg}^{2+}$ .) For larger dopings of  $p \sim 0.1$  (but still less than  $p_c$ ), the behaviour of susceptibility follows a Curie-Weiss-type behaviour in  $\text{Co}_p\text{Mg}_{1-p}\text{O}$  over an extended temperature range but not in  $\text{Ni}_p\text{Mg}_{1-p}\text{O}$ . However, because of the complexity of the problem (contributions from dimers, trimers and large clusters become increasingly significant with increasing  $p$ ), the results for the heavily doped samples are difficult to analyse rigorously.

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