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# Magnetic susceptibility of $Mn^{2+}$ ions in MgO and evidence of clustering

Brian L. Gordon and Mohindar S. Seehra
*Department of Physics, West Virginia University, Morgantown, West Virginia 26506*

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The temperature dependence of the dc magnetic susceptibility $\chi$, in the temperature range of 4.2–300 K, is reported for two single crystals of $Mn_pMg_{1-p}O$ (nominal $p=0.000\,84$ and 0.0048). The data are analyzed in terms of contributions from the single $Mn^{2+}$ ions (monomers) and the exchange-coupled $Mn^{2+}$-$Mn^{2+}$ pairs (dimers). It is found that the concentration of dimers determined from a theoretical fit to the data is nearly an order of magnitude larger than that expected from the random distribution of $Mn^{2+}$ ions, suggesting that $Mn^{2+}$ ions prefer to form exchange-coupled clusters in the MgO host. An exchange constant $J=22\pm4$ K is determined from the fit to the $\chi$ versus $T$ data.

## I. INTRODUCTION

The magnetic properties of the iron-group transition-metal ions in magnetically diluted systems have been the subject of a number of recent investigations.[1–17] Interesting phenomena such as spin-glass-like transitions have been observed in many systems containing $Mn^{2+}$ ions.[7,10,12,13–16] Many of these systems are characterized by "enhanced paramagnetism" at low temperatures, which has been tentatively attributed to the possibility of random cluster formation.[1,10,12–14] This enhanced paramagnetism, which appears as a downturn of the $\chi^{-1}$ versus $T$ curve below about 50 K, was at first linked to a spin-glass transition, but has since been observed whether a spin-glass transition occurs or not.[10] It has also been pointed out that, since the $\chi^{-1}$ versus $T$ curves appear to go to zero as $T\rightarrow0$ K following the Curie law, the contribution from the single-ion moments dominates at the lowest temperatures.[14]

To investigate this phenomenon, we undertook a study of two very dilute single crystals of $Mn_pMg_{1-p}O$ with nominal $p=0.000\,84$ and 0.0048. The objective was to see whether the magnetic susceptibility of such dilute systems could be theoretically understood based on the random distribution of $Mn^{2+}$ ions in the MgO host. This is an ideal system for such a study since both MnO and MgO crystallize in the NaCl structure, and $Mn^{2+}$ is an $S$-state ion. Also, the excited states lie very much above ($\sim10^4$ cm$^{-1}$) the ground state so any admixture of excited states into the ground state by spin-orbit coupling is negligible.[5] These simplifications allow the exchange coupling between $Mn^{2+}$ ions to be treated in a straightforward manner. An enhanced paramagnetism, as noted above, is also observed even in these dilute systems. Analysis of the results shows that the number of dimers ($Mn^{2+}$-$Mn^{2+}$ pairs) is nearly an order of magnitude larger than that predicted by the random distribution model, and that this clustering is responsible for the observed enhanced paramagnetism. Details of these results follow.

## II. EXPERIMENTAL DETAILS

The magnetic susceptibility measurements reported here were made with a Faraday balance in conjunction with Lewis coils for producing the gradient field, and a Cahn electrobalance (Model 2000 RG) for measuring the force. Some details of this system have been given in earlier publications from this laboratory.[3,18]

The two samples of $Mn_pMg_{1-p}O$ studied in this work were single crystals grown by W. & C. Spicer Ltd. of England, with nominal $p=0.000\,84$ and 0.0048, respectively. To correct for the diamagnetic contribution of the MgO host, magnetic susceptibility of a single crystal of MgO, also supplied by W. & C. Spicer Ltd., was measured. The observed value of $\chi_d=-2.05\times10^{-5}$ cm$^3$/mol is in agreement with some earlier estimates.[19] The magnetic susceptibilities reported below are corrected for this temperature-independent diamagnetic contribution. In all cases, these susceptibility data are given in molar susceptibility where one mole refers to Avogadro's number of $Mn_pMg_{1-p}O$ formula units.

## III. THEORETICAL CONSIDERATIONS

To derive equations for the magnetic susceptibility of monomers (isolated $Mn^{2+}$ ions) and dimers ($Mn^{2+}$-$Mn^{2+}$ exchange-coupled pairs), we start with the well-known Van Vleck expression

$$\chi=N_A\sum_i\left[\frac{(E_i^{(1)})^2}{k_BT}-2E_i^{(2)}\right]\exp(-E_i^{(0)}/k_BT)\Big/\sum_i\exp(-E_i^{(0)}/k_BT)\ . \tag{1}$$

Here $N_A$ is Avogadro's number, $k_B$ is the Boltzmann constant, and the energy of the $i$th level in a magnetic field $H$ is given by

$$E_i = E_i^{(0)} + HE_i^{(1)} + H^2E_i^{(2)} \ . \tag{2}$$

Typically only terms up to $H^2$ need to be retained, as is the case in Eq. (1).

For monomers, the only splitting of the ground state comes from the Zeeman energy. The energy shift due to the external field is $E = g\beta H m_s$, where $g$ is the $g$ value, $\beta$ is the Bohr magneton, and $m_s = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}$ for spin $S_i = \frac{5}{2}$ of the ground state of $Mn^{2+}$. Using Eqs. (1) and (2), the magnetic susceptibility of monomers, $\chi_1$, then follows

$$\chi_1 = \frac{N_A p_1 g^2 \beta^2 S_i(S_i+1)}{3k_B T} = \frac{C_1}{T} \ , \tag{3}$$

where the expression has been multiplied by $p_1$, the concentration of monomers, and $g=2$ for $Mn^{2+}$. Equation (3) is the well-known Curie law, with Curie constant, $C_1$, yielding $p_1$.

For dimers of $Mn^{2+}$-$Mn^{2+}$ coupled by exchange interaction, the additional term in the Hamiltonian is the Heisenberg exchange interaction

$$H_{ex} = J\mathbf{S}_i \cdot \mathbf{S}_j \ , \tag{4}$$

where the exchange integral $J$ is positive for antiferromagnetic interaction. For $Mn^{2+}$ in MgO, values of $J_1$ and $J_2$, the nearest-neighbor (nn) and next-nearest-neighbor (nnn) exchange constants, respectively, have been inferred to be positive and nearly equal from electron paramagnetic resonance studies ($J_1 \simeq J_2 = 28 \pm 4$ K) (Ref. 20). A similar conclusion is valid in pure MnO,

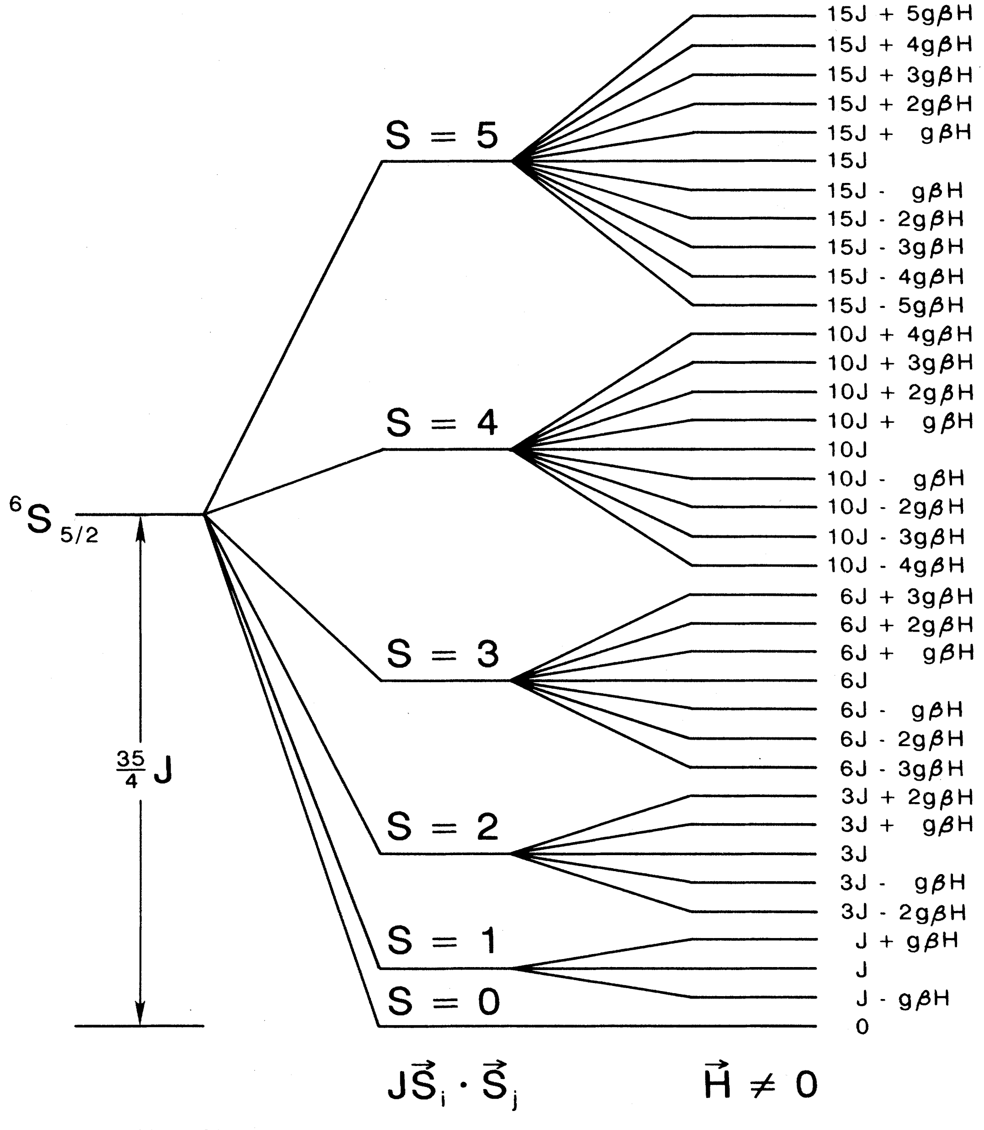

FIG. 1. Energy levels of $Mn^{2+}$-$Mn^{2+}$ pairs in an exchange field and in an applied field $H$. The zero of energy has been shifted by $-\frac{35}{4}J$ in the Zeeman levels.

where $J_1=10\pm1$ K and $J_2=11\pm1$ K have been inferred.[21] So in our calculations, we only retain a single $J$, not distinguishing between nn and nnn pairs. From Eq. (4), with $S_i=S_j=\frac{5}{2}$, it follows that the total spin $S$ of the pairs takes on the values $S=0$, 1, 2, 3, 4, and 5.[8,22] The Zeeman splitting of these spin states is shown in Fig. 1, where we have redefined the zero of energy at $-\frac{35}{4}J$ in order to simplify the calculations without affecting the results. However, the energy $-\frac{35}{4}J$, the binding energy of the pairs, has other important implications which are discussed later. Using $p_2$ as the concentration of dimers, the use of Eqs. (2) and (3) and the energy levels of Fig. 1, we obtain the following expression for $\chi_2$, the magnetic susceptibility of dimers,

$$\chi_2=\frac{2N_Ap_2g^2\beta^2}{k_BT}\left[\frac{1+5E(-2J/k_BT)+14E(-5J/k_BT)+30E(-9J/k_BT)+55E(-14J/k_BT)}{3+E(J/k_BT)+5E(-2J/k_BT)+7E(-5J/k_BT)+9E(-9J/k_BT)+11E(-14J/k_BT)}\right], \tag{5}$$

where $E\equiv\exp$. It is noted that $\chi_2\rightarrow0$ as $T\rightarrow0$. Neglecting trimers and higher order clusters whose concentrations are expected to be negligible in the very dilute samples studied here, the total susceptibility, $\chi_p$, is simply the sum of Eqs. (3) and (5),

$$\chi_p=\chi_1+\chi_2\ . \tag{6}$$

## IV. EXPERIMENTAL RESULTS, ANALYSIS, AND DISCUSSION

The temperature dependence of the paramagnetic susceptibility $\chi_p=\chi+|\chi_d|$, where $\chi$ is the measured susceptibility and $\chi_d=-2.05\times10^{-5}$ cm$^3$/mol is the diamagnetic contribution, is shown in Figs. 2 and 3 for the two samples with nominal $p=0.000\,84$ and 0.0048, respectively. The solid lines are theoretical fits using Eqs. (3)–(6) with parameters given in Table I. The procedure used to obtain the theoretical fits is now described.

As noted above, $\chi_2\rightarrow0$ as $T\rightarrow0$ K. Therefore, at the lower temperatures, $\chi_1$ dominates and a plot of $\chi_1^{-1}$ versus $T$ yields a straight line [Eq. (3)] with slope yielding $C_1$ and hence $p_1$. This also gives $\chi_1$ for all $T$, allowing the determination of $\chi_2=\chi_p-\chi_1$. These data for $\chi_2$ are then fitted to Eq. (5) with $J$ and $p_2$ as adjustable parameters.

According to Eq. (5), $\chi_2$ peaks at a temperature determined by $J$, whereas its magnitude varies linearly with $p_2$, the dimer concentration. Plots of $\chi_2$ versus temperature for a fixed $p_2$ but different $J$ values are shown in Fig. 4

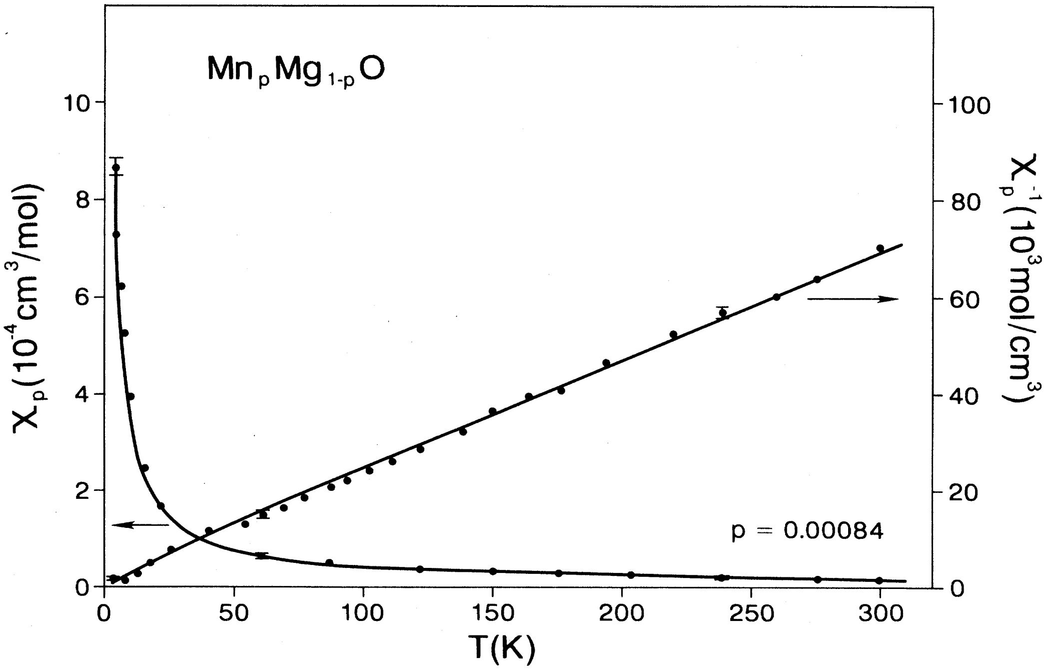

FIG. 2. Temperature dependence of the paramagnetic susceptibility, $\chi_p$, and that of $\chi_p^{-1}$ for the $Mn_pMg_{1-p}O$ sample with nominal $p=0.000\,84$. The solid lines are theoretical fits. See text for details.

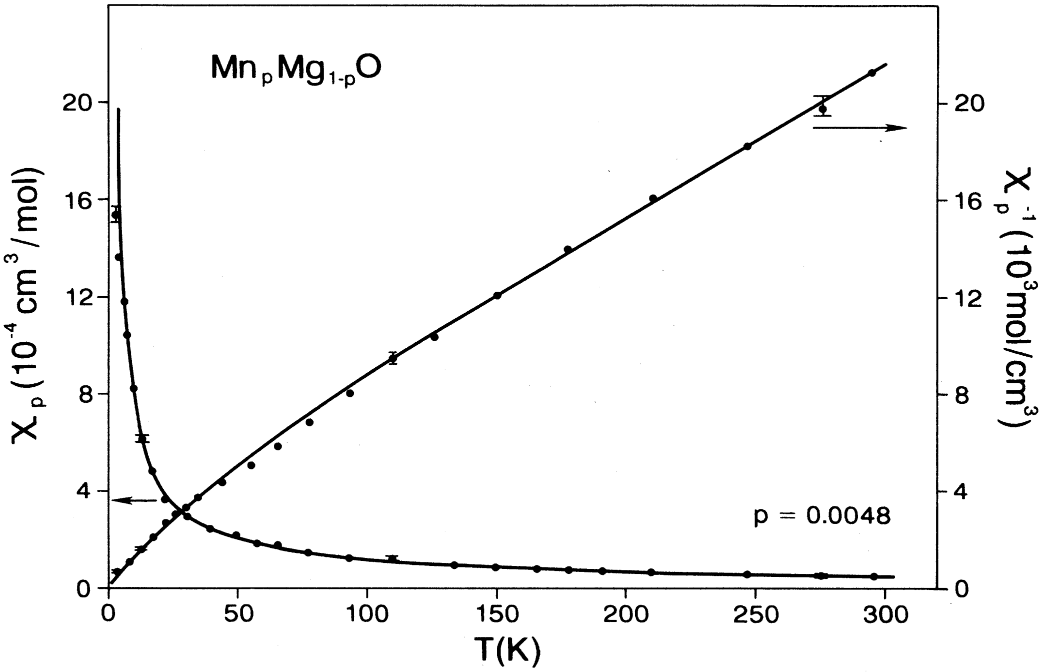

FIG. 3. Temperature dependence of the paramagnetic susceptibility, $\chi_p$, and that of $\chi_p^{-1}$ for the $Mn_pMg_{1-p}O$ sample with nominal $p=0.0048$. The solid lines are theoretical fits. See text for details.

along with the experimentally determined values of $\chi_2$. Major features of $\chi_2$ are well reproduced by the theoretical curves. It is noted that near the peak temperature of 50 K, the magnitude of $\chi_2$ is only about 10% of the total $\chi_p$, so that agreement in Fig. 4 between theory and experiment is quite reasonable. In Fig. 5, we have plotted the monomer, dimer, and total susceptibility versus temperature on a semilog plot. It is evident that on a relative scale, the contribution from the dimers is greater at higher temperatures than at lower temperatures. This, then, is the reason for the downward turn of $\chi_p^{-1}$ versus $T$ and "enhanced paramagnetism" noted in the Introduction. For both samples, a good fit between the calculated susceptibilities and experimental data is obtained in the whole temperature range (Figs. 2 and 3).

As noted earlier, Coles *et al.*,[20] using the temperature dependence of the intensity of the electron paramagnetic resonance spectra of $Mn^{2+}$-$Mn^{2+}$ pairs in MgO, determined $J=(28\pm4)$ K. The magnitude of $J$ determined in this work (Table I) is in very good agreement with this value, providing additional confidence in the analysis used in this paper. The difference in the $J$ values of $Mn^{2+}$ in MgO and those in pure MnO (Ref. 21) are presumably due to the difference in the lattice constants of MnO and MgO.

Next we consider the magnitudes of $p_1$ and $p_2$ determined in this work, and their magnitudes expected from the random distribution of $Mn^{2+}$ in the MgO lattice.[23] For the face-centered-cubic (fcc) lattice of MgO, the probabilities, $p_1$ and $p_2$, based on random distribution, are given by[23]

$$p_1=(1-p)^{12}\ , \tag{7a}$$

$$p_2=12p(1-p)^{18}\ , \tag{7b}$$

where $p$ is the concentration of $Mn^{2+}$ ions. (It is noted that the density of trimers for the concentrations used in this work are expected to be nearly two orders of magnitude lower than that for dimers,[23] and hence their contribution is expected to be negligible.) Using the nominal $p=0.00084$ yields $p_1=0.98997$, $p_2=0.00993$, and $p_2/p_1=0.01$. Similarly, for $p=0.0048$, one gets $p_1=0.9439$, $p_2=0.05282$, and $p_2/p_1=0.056$. The ratios $p_2/p_1$ obtained in this work are $p_2/p_1\simeq0.15$ for the

TABLE I. Parameters of the fits used in Figs. 2 and 3. Theoretical $p_2/p_1$ refers to the random distribution model.

| Nominal $p$ ($10^{-6}$) | $p_1$ ($10^{-6}$) | $p_2$ ($10^{-6}$) | $p_2/p_1$ (Expt.) | $p_2/p_1$ (Theor.) | $J$ (K) |
|---|---|---|---|---|---|
| 840 | 793 | 122 | 0.154 | 0.010 | 20±4 |
| 4800 | 1880 | 840 | 0.447 | 0.056 | 24±4 |

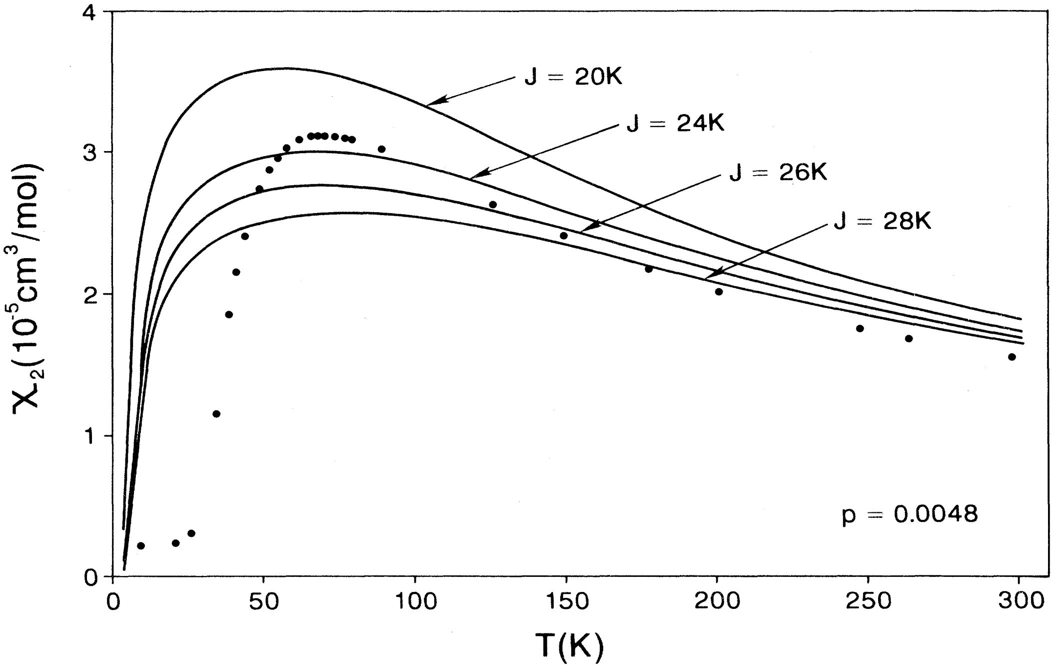

FIG. 4. Theoretical plots of the dimer susceptibility, $\chi_2$ [Eq. (5)] vs temperature for different values of $J$, and the experimentally determined values of $\chi_2$.

$p = 0.000\,84$ sample, and $p_2/p_1 = 0.447$ for the $p = 0.0048$ sample. These experimental ratios of dimers to monomers are nearly an order of magnitude larger than the values predicted by the random distribution model. Since our samples are single crystals, one should not expect such large clustering occurring simply due to sample preparation techniques. We now examine possible sources for this clustering.

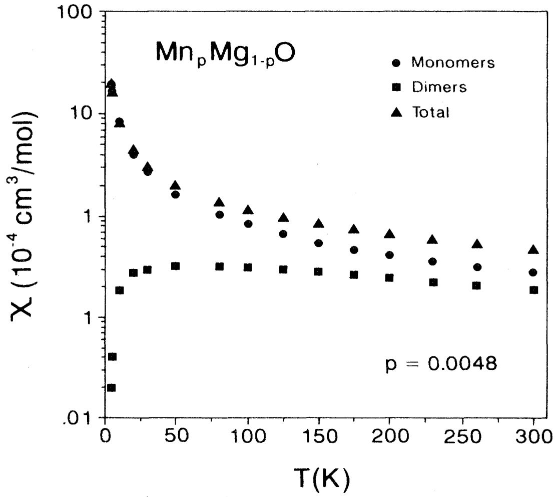

FIG. 5. Semilog plot of the susceptibiilty due to monomers ($\chi_1$) and dimers ($\chi_2$), and $\chi_p = \chi_1 + \chi_2$ vs temperature for the higher concentration sample with $p = 0.0048$ in $Mn_pMg_{1-p}O$.

For $Mn^{2+}$-$Mn^{2+}$ pairs in MgO, at least two mechanisms can affect the energy. First, the exchange coupling which we have shown in this work to equal $\frac{35}{4}J \simeq 200$ K, is quite significant and it favors clustering of $Mn^{2+}$ ions during sample preparation. Nagata *et al.*[12] reached a similar conclusion in the $Hg_{1-p}Mn_pTe$ system, although their system was more heavily doped. The second source of clustering could be the change in the lattice energy with $Mn^{2+}$ doping since the $Mn^{2+}$ ion (radius $\simeq 0.97$ Å) is slightly larger than the $Mg^{2+}$ ion (radius $\simeq 0.86$ Å), leading to lattice constants of 4.44 Å and 4.22 Å for MnO and MgO, respectively. However, we do not know whether the lattice energy is actually lowered by the substitution of $Mn^{2+}$ in the MgO lattice. This is an interesting problem which we hope will attract the attention of theorists.

## V. CONCLUDING REMARKS

The results and analysis presented in this paper have established that in the $Mn_pMg_{1-p}O$ system, $Mn^{2+}$ ions tend to cluster due to exchange coupling. This exchange clustering explains the enhanced paramagnetism observed at low temperatures in this system, and may be the explanation for similar observations in other magnetically diluted systems.

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[1] J. R. Anderson, M. Górska, L. J. Azevedo, and E. L. Venturini, Phys. Rev. B **33**, 4706 (1986).

[2] C. E. Deshpande, P. P. Bakare, M. N. S. Murthy, N. Y. Vasanthacharya, and P. Ganguly, Proc. Indian Acad. Sci. (Chem. Sci.) **91**, 261 (1982).

[3] R. Kannan and M. S. Seehra, Phys. Rev. B **35**, 6847 (1987).

[4] J. C. Gómez Sal, F. Rodríquez, M. Moreno, and J. L. Tholence, Phys. Rev. B **37**, 454 (1988).

[5] Kuang Xiao-Yu, Phys. Rev. B **37**, 9719 (1988).

[6] Yu Wan-Lun and Zhao Min-Guang, Phys. Rev. B **37**, 9254 (1988).

[7] M. Escorne and A. Mauger, Phys. Rev. B **25**, 4674 (1982).

[8] T. M. Giebultowicz, J. J. Rhyne, and J. K. Furdyna, J. Appl. Phys. **61**, 3537 (1987).

[9] M. S. Seehra, J. C. Dean, and R. Kannan, Phys. Rev. B **37**, 5864 (1988).

[10] S. P. McAlister, J. K. Furdyna, and W. Giriat, Phys. Rev. B **29**, 1310 (1984).

[11] C. M. McDonagh and B. Henderson, J. Phys. C **18**, 6419 (1985).

[12] S. Nagata, R. R. Galazka, D. P. Mullin, H. Akbaryadeh, G. D. Khattak, J. K. Furdyna, and P. H. Keesom, Phys. Rev. B **22**, 3331 (1980).

[13] H. Savage, J. J. Rhyne, R. Holm, J. R. Cullen, C. E. Carroll, and E. P. Wohlfarth, Phys. Status Solidi **58**, 685 (1973).

[14] U. Sondermann and E. Vogt, Physica **86B**, 419 (1977).

[15] J. Spalek, A. Lewicki, Z. Tarnawski, J. K. Furdyna, R. R. Galazka, and Z. Obusyko, Phys. Rev. B **33**, 3407 (1986).

[16] Ven-Chung Lee, Phys. Rev. B **34**, 5430 (1986).

[17] H. Lettenmayr, W. Jantsch, and L. Palmetshofer, Solid State Commun. **64**, 1253 (1987).

[18] M. S. Seehra and M. S. Jagadeesh, Phys. Rev. B **20**, 2897 (1979).

[19] M. S. Seehra, in *Basic Properties of Binary Oxides,* edited by A. Dominquez-Rodriquez, J. Casting, and R. R. Marquez (University of Seville Press, Seville, Spain, 1983), p. 179.

[20] B. A. Coles, J. W. Orton, and J. Owen, Phys. Rev. Lett. **4**, 116 (1960).

[21] M. E. Lines and E. D. Jones, Phys. Rev. **139**, A1313 (1965).

[22] E. C. Svensson, M. Harvey, W. J. L. Buyers, and T. M. Holden, J. Appl. Phys. **49**, 2150 (1978).

[23] R. Behringer, J. Chem. Phys. **29**, 537 (1958).