Magnetization steps in $Mn_{0.084}Zn_{0.916}F_2$: Exchange constant and Mn distribution

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The magnetization M of $Mn_{0.084}Zn_{0.916}F_2$ was measured at 20 mK in magnetic fields H up to 115 kOe and at 0.65 K in fields up to 175 kOe. The magnetization was independent of magnetic field direction and showed no hysteresis. After a fast rise of M at low H, several magnetization steps (MS's) were observed. These MS's arose from Mn^{2+} pairs and triplets in which the spins are coupled by the dominant antiferromagnetic exchange constant, J_2 between next-nearest neighbors. The magnetic fields at the steps gave $J_2 = -1.94 \pm 0.01$ K in this diluted magnetic material. The observed magnetization curves are in very good agreement with computer simulations which assume a random Mn distribution. However, at 20 mK the widths of MS's are much larger than expected from thermal broadening alone. Possible mechanisms for nonthermal broadening are discussed. Theoretical results for cluster statistics, for J_2 clusters up to quintets, and for the fields at the MS's from the various quintet types are presented. These theoretical results also apply to nearest-neighbor (J_1) clusters in a body-centered-cubic cation lattice.

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I. INTRODUCTION

Magnetization-step (MS) spectroscopy is a relatively new method of measuring exchange constants in some classes of magnetic materials. Clusters consisting of a few antiferromagnetically coupled spins, such as pairs (dimers) or triplets (trimers), give rise to magnetization steps at low temperatures. Thus far the main application of MS's has been the determination of exchange constants J_i in diluted magnetic semiconductors (DMS's).¹⁻⁴ However, as the present work demonstrates, the MS method is not restricted to DMS's. It can be applied to any diluted magnetic material with antiferromagnetic (AF) interactions. The method is also used to study magnetic clusters in molecular crystals.⁵

In diluted magnetic materials, the MS method also gives information about the distribution of the magnetic ions in the crystal, on a length scale of several lattice constants. Such information is not readily available from other methods. Specifically, the MS method tests the common assumption that the magnetic ions are randomly distributed over the cation sites. For melt-grown II-VI DMS's containing Mn, all the data obtained so far have been consistent with a random distribution.¹ However, in some IV-VI DMS's containing Eu, a strong tendency of the Eu ions to bunch together was found.^{6,7}

Various compositions of $Mn_xZn_{1-x}F_2$ serve as experimental realizations of theoretical models. MnF_2 (x=1) is a classic example of a simple easy-axis antiferromagnet. At the other extreme, for x well below the percolation concentration ($x_p=0.24$), $Mn_xZn_{1-x}F_2$ is expected to be described by the cluster-model approach. Cluster models, which have been used for many years (see, e.g., Ref. 8), are essential for the interpretation of MS's.^{1,9,4} The cluster model used in the

present work included only the dominant exchange constant. This model gave a very good account of the data. The magnetization M in this model is the sum of the contributions from singles (isolated Mn^{2+} ions), pairs (two exchange-coupled Mn^{2+} ions), triplets, quartets, etc..

 $Mn_xZn_{1-x}F_2$ has the rutile crystal structure of MnF_2 and ZnF_2 (see Fig. 1). The cations occupy a body-centered tetragonal lattice. Because the lattice parameter *c* is significantly smaller than *a*, the nearest-neighbor (NN) cation sites are along the [001] direction. The closest cations along the equivalent $\langle 111 \rangle$ directions are the next-nearest-neighbor (NNN) cation sites. Had the cation lattice been a bodycentered-cubic lattice (*c* = *a*) the latter sites would have been the NN cation sites.

 Mn^{2+} is an S-state ion with spin S=5/2. Electron paramagnetic resonance (EPR) data for Mn^{2+} in ZnF₂ have shown that the g factor is 2.002 and that the crystal-field anisotropy parameters are small, of order 10^{-2} K.^{10,11} The exchange constants J_i in MnF₂ (x=1) have been determined



FIG. 1. The rutile structure of $Mn_xZn_{1-x}F_2$. The open circles represent the cations (Mn or Zn) and the solid circles the anions (F).

long ago.^{12–15} Using the convention in which the exchange interaction between two spins is $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$, the largest J_i is between NNN's, $J_2 = -1.76$ K. The minus sign implies an AF interaction. The second-largest exchange constant is $J_1 = +0.32$ K (ferromagnetic) for NN's. The third-neighbor exchange constant is $|J_3| < 0.05$ K. Some information about the J_i for a small concentration of Mn in ZnF₂ is available from EPR experiments:^{16,11} $J_2 \approx -2$ K and $J_1 = +0.2 \pm 0.1$ K. The present work gives a much more accurate value for J_2 , when the Mn concentration is low. It also addresses the issue of the Mn distribution in the crystal.

There are several reasons why the J_2 cluster model, which includes only J_2 , should give a good account of the data. First, $|J_2| \ge |J_1| \ge |J_3|$. Second, the number of second neighbors (8) is larger than the numbers of first or third neighbors (2 and 4, respectively). Finally, the anisotropy is much smaller than the exchange interaction,¹¹ as is also the case for MnF₂.^{12,13}

Much, but not all, of the discussion in the present paper relies on earlier works.^{1,17–19} The new theoretical results which are needed for the data analysis are summarized in the Appendix. They include (1) the magnetization and MS's due to quintets (clusters with five spins) and (2) cluster statistics for quintets and quartets. The results in the Appendix (for the J_2 model in a body-centered tetragonal cation lattice) also apply to the NN cluster model (J_1 model) in a bcc cation lattice.

II. EXPERIMENT

The Mn_{0.084}Zn_{0.916}F₂ single crystal was melt grown. After x-ray orientation, it was cut as a rectangular parallelepiped $(2.7 \times 2.7 \times 3.7 \text{ mm}^3)$ with the long edge along the *c* axis. The Mn concentration was determined from the magnetic susceptibility, measured in a magnetic field H=1 kOe between 2 and 300 K, using a superconducting quantum interference device (SQUID) magnetometer system. A small correction for the lattice diamagnetism¹⁴ was included in the analysis. Above 50 K the data obeyed the Curie-Weiss law. The Curie constant gave $x=0.084\pm0.002$ (with a Curie-Weiss temperature $\theta=-7.0\pm0.2$ K).

The magnetization was measured at 0.65 K in fields up to 175 kOe and at 20 mK in fields up to 115 kOe. Superconducting magnets were used in both cases. The 0.65 K data were taken with $\mathbf{H} \| c$ using a vibrating sample magnetometer (VSM) calibrated with a Ni sample. The experimental setup was similar to that in Ref. 20, except that the pickup coils were in the ³He bath. Traces of the magnetization of the Mn_{0.084}Zn_{0.916}F₂ sample showed no hysteresis. The overall uncertainty was about 1%. The signal to noise ratio, however, was always better than 10^{-3} . The data which are shown below are the average of field-up and field-down traces.

The data at 20 mK were taken using a force magnetometer operating in a plastic dilution refrigerator. The force was produced by a dc field gradient, 0.15 kOe/cm, superimposed on the main magnetic field, and was detected by a capacitance technique.²¹ The sample and the thermometer (a RuO₂ resistor, previously calibrated with CMN) were both inside the mixing chamber, in direct contact with the mixture. A



FIG. 2. The solid line is the measured magnetization curve at 0.65 K, for $\mathbf{H} \| c$. The dashed line is from a computer simulation based on the J_2 cluster model and a random Mn distribution. There are no adjustable parameters in the simulation.

typical sweep rate was 55 Oe/s. One experimental run was with $\mathbf{H} \| c$, in fields up to 90 kOe. Two runs were performed with $\mathbf{H} \perp c$, in fields up to 90 and 115 kOe. No hysteresis was observed in any run. The results presented below are based on the average of all the magnetization traces in each run. Absolute calibration of the magnetic moment was achieved by a comparison with the results at 0.65 K.

The experimental data presented below have all been corrected for the lattice diamagnetism.

III. RESULTS AND DISCUSSION

A. Magnetization steps

Figure 2 shows the 0.65 K magnetization curve up to 175 kOe. The fast rise of the magnetization M at low H is largely caused by the alignment of the magnetic moments of the singles.¹ There are also minor contributions from larger clusters whose ground-state magnetic moment is not zero. Examples are J_2 open triplets, and clusters with only J_1 exchange bonds (ferromagnetic).

The fast magnetization rise at low *H* is followed by MS's from J_2 pairs. All five predicted MS's from the J_2 pairs (composed of two S = 5/2 spins coupled by J_2) are seen in Fig. 2. The fourth and fifth MS's, between 100 and 150 kOe, are somewhat less distinct than the first three MS's. As discussed earlier,^{7,18} this behavior is caused by the first MS's from open triplets, which are exactly out of phase with the last MS's from pairs. It is noteworthy that even at 175 kOe, the magnetization in Fig. 2 is not saturated because clusters larger than pairs are still not saturated. The calculated saturation value for $x=0.084\pm0.002$ is $M_0=22.9\pm0.5$ emu/g.

At 20 mK the magnetization curves for $\mathbf{H} \| c$ and $\mathbf{H} \bot c$ were practically indistinguishable, consistent with the very low anisotropy of Mn^{2+} . Figure 3 shows the magnetization



FIG. 3. High-field portion of the magnetization data at 20 mK, obtained with $\mathbf{H} \perp c$ (run 2). The inset shows the fields H_n at the MS's as a function of step number *n*. These H_n , from the three experimental runs at 20 mK, are corrected for the (very minor) effects of the anisotropy. The straight line is a fit of all nine experimental points to Eq. (1).

curve obtained in one of the three runs at 20 mK. At this low temperature the MS's are much sharper than at 0.65 K.

The MS's are seen more clearly in the derivative curves, dM/dH versus *H*. Figure 4 shows the numerical derivatives of the curves in Fig. 2 (for 0.65 K) and Fig. 3 (for 20 mK). The three large peaks at 20 mK are the first three MS's from J_2 pairs. The rise of the derivative near the end of this curve is the beginning of the fourth MS from J_2 pairs. The small peak at 100 kOe is identified as the first MS from J_2 open



FIG. 4. Numerical derivative dM/dH of the experimental magnetization curves in Fig. 3 (0.02 K) and Fig. 2 (0.65 K).

triplets. At 0.65 K the derivative curve shows all five MS's from the J_2 pairs, but the MS's from the triplets are not resolved.

B. Exchange constant J_2

The exchange constant J_2 was determined from the fields H_n at the MS's from J_2 pairs. Neglecting all anisotropic interactions, the fields H_n are given by^{1,17}

$$g\mu_B H_n = 2|J_2|n + \Delta, \qquad (1)$$

where n = 1, 2, 3, 4, 5 and μ_B is the Bohr magneton. The (small) shift Δ is due to exchange constants other than J_2 . Because the MS's are much sharper at 20 mK than at 0.65 K, the 20 mK results for H_n were used. The raw values for H_n were corrected for the effects of the anisotropy. These calculated corrections were all smaller than 0.6 kOe. The corrected H_n are shown in the inset of Fig. 3. The fit of the nine data points to Eq. (1) gave $J_2 = -1.94 \pm 0.01$ K and $\Delta = 0.83$ kOe. The quoted uncertainty is the standard deviation in the fit. Analysis of the data at 0.65 K, which showed all five MS's from the pairs (albeit broader than the three MS's at 20 mK) confirmed this value. By assuming that J_2 is the only exchange constant, we get for the Curie-Weiss temperature $\theta \approx -7.6$ K. Comparing this with the value obtained from the high temperature susceptibility ($\theta = -7.0$ ± 0.2 K), we see that J_2 is really the major contribution and the other exchange constants are much smaller.

The measured value for J_2 in Mn_{0.084}Zn_{0.916}F₂is 10% higher than in MnF₂. The difference may be attributed to the several percent decrease of the lattice constants²² and to changes in the electronic structure caused by the replacement of Mn by Zn.

C. Computer simulations and the Mn distribution

Information about the Mn distribution in the crystal can be obtained by comparing the observed magnetization curves with computer simulations based on a cluster model.^{6,7} In this work the simulations were based on the J_2 model and on the crucial assumption that the Mn distribution was random. This assumption determines the populations of different types of clusters (singles, pairs, triplets, etc.).

The populations of different cluster types govern the relative proportions of various features of the magnetization curve. For example, the fast rise of M at low H is governed mainly by the number of isolated magnetic ions (singles). An observed rise at low H which is much smaller than in the simulations is a strong evidence that the magnetic ions are bunched together (which would reduce the number of singles). Conversely, a good agreement for the size of the low-H magnetization rise is evidence in favor of a random distribution. The measured size of the MS's from pairs is governed by the population of pairs, so that the actual number of pairs can be compared with the prediction from a random distribution. Similar remarks apply to larger clusters.

The computer simulations of the magnetization curves used procedures similar to those in earlier works,^{6,7,18,23} but with some exceptions. New calculations for the statistics of quartets were required because the cation lattice differs from the fcc lattice considered earlier.¹⁹ Another difference was that the largest clusters treated explicitly were the quintets, compared to quartets in earlier works.⁶ Therefore, calculations for the statistics and magnetization of quintets were required. Table I in the Appendix gives the parameters for the statistics of all the clusters.

In the J_2 model, a random distribution with x=0.084 implies that 49.6% of the Mn ions are singles, 19.7% are in pairs, 12.0% in triplets, 7.2% in quartets, and 4.4% in quintets. The remaining 7.1% are in clusters larger than quintets. To include these larger clusters in the simulation we used the approximation detailed in the Appendix. This approximation is the main source of error in the simulation, but any error in *M* is still expected to be smaller than 1%.

Figure 2 compares the experimental curve at 0.65 K with a computer simulation based on the J_2 model and a random Mn distribution. The input parameters are the experimental values of J_2 , x, the g factor, and the temperature. There are no adjustable parameters in the simulation. The overall agreement with the experimental data is very good, well within the uncertainties in the data and in the simulation. The contributions of the several types of clusters to the calculated magnetization are shown if Fig. 5. It is noticeable that, for the concentration in question, x = 0.084, all the clusters included in the model, even the quintets, have a significant contribution to the magnetization.

A minor difference between the simulation and the data is that the observed fast rise at low H is slightly slower than predicted. This is seen more clearly when the low-H portion of Fig. 2 is expanded. As will be discussed shortly, this discrepancy is much more obvious at 20 mK, but is not related to the populations of J_2 clusters.

For the calculated magnetization above described, the value for $x = 0.084 \pm 0.002$ was obtained from an independent set of susceptibility data. As a test, we have also investigated the range of *x* that would reproduce the data within a reasonable experimental uncertainty, established as $\pm 0.5\%$. Still within the framework of a random distribution, the result is a range for *x* from 0.081 to 0.085.

D. Nonthermal broadening

In the J_2 model used in the simulations, the only interactions are the exchange coupling with NNN's and the Zeeman term. The widths of the MS's and the width of the magnetization rise at low H are then fully governed by thermal broadening. In reality, weak interactions which are neglected in the J_2 model produce an additional, nonthermal, broadening. At very low temperatures, nonthermal broadening becomes dominant. The present data at 20 mK illustrate this point.

The 20 mK data in Figs. 3 and 4, for M and dM/dH, were compared with simulations. The overall agreement for M versus H is quite good. In particular, both the magnitude of the magnetization rise at low H and the size of the MS's from the J_2 pairs are consistent with a random Mn distribution. The differences between the data and the simulation are more apparent in the derivative curve dM/dH versus H. The



FIG. 5. Contributions of the several clusters to the calculated magnetization in the simulation shown in Fig. 2. The successive curves are the cumulative contributions of (1) singles, (2) pairs, (3) triplets, (4) quartets, (5) quintets, and (T) bigger clusters ("others").

observed field interval for the magnetization rise at low *H* is much wider than in a simulation which uses the actual temperature, 20 mK. As Fig. 6 indicates, even when the temperature in the simulation is increased to 0.25 K, the observed width for this initial rise remains larger. Another difference is that the observed widths of the MS's from pairs are an order of magnitude larger than the thermal width. Figure 6 shows that the widths of the first MS's observed at 20 mK corresponds to the thermal width of at least T = 0.25 K.

Several possible causes for the observed broadening were considered. Two experimental sources of broadening were the dc field gradient combined with the finite size of the sample and the demagnetizing field. Estimates showed that both were insignificant. Another possibility was that the sample's temperature was significantly higher than 20 mK. The sample and the thermometer were immersed in the 20 mK bath of the mixing chamber. If the spin system were not in thermal equilibrium with this bath, hysteresis would have resulted from magnetocaloric effects,26 but no such hysteresis was observed. Earlier data on other materials, taken in the same dilution refrigerator and with the same setup (e.g., Fig. 5 in Ref. 23), showed a MS with a width equivalent to the thermal width of 36 mK. Moreover, the width in that experiment increased with x, indicating that, in that experiment too, some nonthermal broadening existed (in the present work, no other dilute sample was available to verify the dependence of the broadening on x). Based on these considerations we are confident that the temperature of the sample is close to 20 mK and the widths observed are essentially of nonthermal nature.

Consider first the observed width of the initial magnetization rise in Fig. 6. It corresponds to a thermal width of $T \approx 0.5$ K. The single-ion anisotropy is too small to account for this discrepancy. A likely explanation is that the magnetization rise is slowed down by small AF exchange interac-



FIG. 6. Comparison between the numerical derivative of the magnetization measured at 20 mK (Fig. 4) and computer simulations based on the J_2 model. The simulation is for T=0.25 K. The magnetic field values in the simulated curves have been shifted by 0.83 kOe, corresponding to the experimental value of Δ in Eq. (1). The experimental and simulated curves cross at 3 kOe (not shown). The number of experimental points has been reduced for clarity.

tions with neighbors other than NNN's. These interactions, governed by J_3 , J_4 , etc., are ignored in the J_2 model. Support for this explanation comes from the value of the parameter Δ in Eq. (1). As discussed by Barilero *et al.*²⁴ both Δ and the slowing down of the initial rise of *M* are related to each other because both are caused by AF interactions other than the dominant one. The slowing down of the initial rise is treated conventionally by replacing the actual temperature *T* by $(T+T_0)$.²⁵ Using the relation between T_0 and Δ given by Barilero *et al.* and the experimental value $\Delta = 0.83$ kOe, the predicted nonthermal broadening of the initial magnetization rise is only a factor of 2 smaller than observed.

Turning to the widths of the MS's in Fig. 6, mechanisms which can give rise to nonthermal broadening involve interactions which are neglected in the J_2 model. They are: (1) the Dzyaloshinki-Moriya (DM) interaction (see review by Moriya²⁷), which was shown to broaden the MS's,^{28,29} (2) local strains associated with bond-length mismatch in the alloy,²⁹ (3) neglected small exchange interactions with neighbors other than NNN's,¹⁷ and (4) anisotropies. Estimates show that anisotropies may account only for a small part of the observed broadening. The other three broadening mechanisms are discussed below.

Symmetry considerations show that the DM interaction is allowed in the present material. The DM vector **D** should lie in the *c* plane, perpendicular to the line joining the two Mn ions in the J_2 pair.²⁷ The broadening of the MS's by the DM interaction, $(\delta H)_{DM}$, has certain characteristics. First, it depends on the orientation of **H**.²⁸ A considerable difference in the widths for **H** parallel and perpendicular to *c* is expected. Second, $(\delta H)_{DM}$ changes with the step number *n*, and it should increase by a factor of 3 as n changes from 1 to 3 [see Eq. (6) and Table I in Ref. 28]. Experimentally, the observed widths are independent of the field direction and are not strongly dependent on n. Therefore, the DM interaction is not a major source of the observed broadening.

Local strains generate a distribution of J_2 values for the many pairs in the sample.²⁹ There is then a spread in the fields at the MS's, which produces a broadening. Because H_n is linear in n|J|, this type of broadening should be proportional to n. The 20 mK data show some increase of the width with n, but much less than the predicted proportionality. Therefore, this mechanism alone cannot account for the observed broadening.

The broadening due to exchange interactions other than with NNN's (Refs. 17) is not amenable to a simple analysis. An attempt to include these exchange interactions was made by performing simulations using the J_1 - J_2 - J_3 model.⁹ The values $J_1 = +0.2$ K and $J_3 = -0.05$ K were used. This value for J_3 has the maximum allowed magnitude (see Sec. I). The two additional exchange constants create a structure which broadens the MS's, but this broadening is too small to explain the observed widths. Many other small exchange constants, which are yet to be determined, will have to be included in the model in order to account for the experimental data. Obviously, this is an impossible task at present. Nevertheless, we believe that the neglected small exchange interactions are major contributors to the nonthermal broadening.

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APPENDIX: CLUSTER STATISTICS AND MAGNETIZATION

Cluster statistics

Because the present calculations of cluster statistics included quintets, it was necessary to generalize the methods used earlier for smaller clusters.^{19,30} Clusters are classified both by type and by geometrical configuration. The type is determined by (1) the number *m* of spins in the cluster, which gives the cluster size, and (2) the exchange bonds which couple the various spins in the cluster. Singles have only one geometrical configuration, and the same is true for pairs. However, when m>2, each cluster type usually appears in different geometrical configurations. For example, the three spins in an open triplet may or may not be along a straight line, and there may be more than one configuration in which they are not on a straight line. A particular geometric configuration is specified by the index *g*.

The exchange Hamiltonian depends only on the exchange bonds. Therefore, it depends only on the cluster type and not on the particular configuration within this type. The enumeration of cluster types, and the configurations within each type, was accomplished with a computer program which will be described elsewhere. Table I lists the cluster types (but not the configurations) for clusters with up to five spins. These

TABLE I. Mn clusters in $Mn_xZn_{1-x}F_2$, based on the J_2 model. The first column classifies clusters by their size, i.e., by the number *m* of spins in the cluster. The second column enumerates the cluster types for each cluster size. The five types of quintets are sketched in Fig. 7. The third column gives the parameters $n_k = \Sigma n_g$ and $v_k = v_g$ for all configuration sets *k* which belong to each cluster type. These results for the J_2 clusters in the cation lattice of $Mn_xZn_{1-x}F_2$ also apply to J_1 clusters in a bcc cation lattice.

Cluster size	Type No.	(n_k, v_k)
Singles	1	(1,8)
Pairs	1	(8,14)
Triplets	1	(36,17), (36,19)
		(12,20)
Quartets	1	(48,20), (192,22)
		(96,23), (144,24)
		(96,25), (16,26)
	2	(24,20), (24,22)
	3	(96,20), (96,22)
		(32,23)
Quintets	1	(60,23)
	2	(60,23), (480,25)
		(300,26), (960,27)
		(960,28), (600,29)
		(540,30), (180,31)
		(20,32)
	3	(240,23), (600,25)
		(120,26), (120,27)
	4	(240,23), (960,25)
		(480,26), (840,27)
		(720,28), (120,29)
	5	(30,21), (160,23)
		(150,24), (10,26)

results are for the J_2 model in the body-centered-tetragonal cation lattice of $Mn_xZn_{1-x}F_2$. The three quartet types labeled as Nos. 1, 2, and 3 in Table I correspond to the "strings," "squares," and "propellers" of Ref. 19, respectively. The other three types of quartets considered in Ref. 19 do not exist in the present case. The exchange bonds for the five types of quintets are sketched in Fig. 7.

For each cluster type and the configuration g within that type, the computer program determined two parameters: (1) the number n_g of clusters of these type and configuration which can be formed, given that one of the spins is already at a pre-specified cation site, and (2) the number v_g of unoccupied NNN cation sites which surround the m spins of one such cluster. For a random distribution the probability that a given spin belongs to a particular cluster type and configuration is given by $p_g(x) = n_g x^{m-1} (1-x)^{v_g}$. The probability p(x) that a spin belongs to a particular cluster type is obtained by summing over all geometrical configurations g for this cluster type:³⁰

$$p(x) = \sum_{g} n_{g} x^{m-1} (1-x)^{v_{g}}.$$
 (A1)



FIG. 7. Schematic of the exchange bonds for the five types of J_2 quintets which are allowed in the $Mn_xZn_{1-x}F_2$ structure.

Equation (A1) can be cast in a more useful form. Consider a particular cluster type. For that type, more than one configuration g may have the same v_g . Such configurations have the same factor $x^{m-1}(1-x)^{v_g}$ in Eq. (A1). All configurations with the same v_g are therefore grouped together to form a "configuration set," labeled by an index k. One then defines $n_k = \sum n_g$, summed over all the configurations g which belong to the configuration set k. The common v_g for these configurations is labeled as v_k . Equation (A1), for the probability p(x) that a spin belongs to a particular cluster type, then reduces to

$$p(x) = \sum_{k} n_k x^{m-1} (1-x)^{v_k}.$$
 (A2)

The sum is over all configuration sets k which belong to that cluster type.

All cluster types, up to quintets, are enumerated in the first two columns of Table I. The third column gives the parameters n_k and v_k for all configuration sets k which belong to each of the cluster types. The sum over k in Eq. (A2) therefore corresponds to a sum over all pairs (n_k, v_k) in Table I for that particular cluster type. For example, the probability that a spin is in the third type of quartet is

$$p(x) = x^{3} [96(1-x)^{20} + 96(1-x)^{22} + 32(1-x)^{23}].$$

MS's from the J_2 quintets

The MS's from pairs, triplets, and quartets, in a cluster model with one AF *J*, have been discussed previously.^{18,19} Here, new results for the MS's from the quintets shown in Fig. 7 are given. The quintets are assumed to be composed of S=5/2 spins.

Table II lists the normalized fields $\alpha = g \mu_B H/|J|$ at the MS's from the five quintet types. These fields are at the energy-level crossings which lead to changes of the ground state. The energy levels were calculated using an approach similar to that discussed by Gatteschi and Pardi,³¹ except that the matrix elements were generated in a different way. The energy levels also gave the partition function, which was used to calculate the magnetization. For completeness, the

TABLE II. Ground-state total spin at H=0, $S_T(0)$ and the fields H at the MS's, for the cluster types listed in Table I. These results are for clusters composed of S=5/2 spins in a model with only one AF exchange constant J<0. The fields at the steps are given by $H=\alpha|J|/g\mu_B$.

	—))	G (0)	
Cluster Size	Type No.	$S_T(0)$	α
Pairs	1	0	2, 4,, 10
Triplets	1	5/2	7, 9,, 15
Quartets	1	0	0.95, 2.04, 3.39, 5.02,
			6.87, 8.85, 10.88,
			12.94, 15.00, 17.07
	2	0	2, 4, , 20
	3	5	12, 14,, 20
Quintets	1	5/2	7, 9,, 25
	2	5/2	4.62, 5.89, 7.18, 8.49,
			9.86, 11.29, 12.83,
			14.48, 16.24, 18.09
	3	5/2	4.95, 6.63, 8.43, 10.32,
			12.27, 14.27, 16.29,
			18.33, 20.36, 22.41
	4	5/2	2.17, 3.21, 4.63, 6.46,
			8.70, 12.00, 14.38,
			16.60, 18.74, 20.85
	5	15/2	17, 19,, 25

normalized fields at the MS's from clusters smaller than quintets are also listed in Table II.

At H=0 each quintet type has a total spin $S_T(0)$ in the ground state. The values of $S_T(0)$ are given in Table II. At very low temperatures the magnetic moment associated with $S_T(0)$ aligns readily along **H**. For the present sample the

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contribution of all the quintets to the rapid magnetization rise at low H is about 20% of the saturation magnetization of all the quintets.

Magnetization of clusters larger than quintets

In the simulations, clusters up to quintets were treated exactly, but larger clusters (defined collectively as "others") were treated only approximately. The approximation was analogous to that used in Ref. 6 to treat clusters larger than quartets. In the present sample, 7.1% of the spins were in the "others." The average magnetic moment μ of a Mn²⁺ ion in these others was approximated as

$$\mu = g \,\mu_B S[(1/7)B_{5/2}(H,T) + (6/7)(H/H_s)], \quad (A3)$$

where $B_{5/2}$ is the Brillouin function for a spin S = 5/2.

The first term on the right-hand side (RHS) of Eq. (A3) corresponds to taking the average value of $S_T(0)$ for a cluster with *m* spins in the others as (1/7) of the saturation value $S_T = mS$. The factor (1/7) used here is for clusters larger than quintets. It is smaller than the factor (1/5) used earlier for clusters larger than quartets.⁶

The second term on the RHS of Eq. (A3) describes the alignment of the remaining (6/7) of the saturation magnetic moment per Mn²⁺ ion. It represents a linear and temperature independent ramp starting at H=0 and saturating at $H = H_s$. In the simulations we used $H_s = 310$ kOe, which corresponds to $\alpha \approx 21.^{32}$ The exact value of H_s is not critical. In the present work, changing H_s by 20% will lead to a maximum change of 0.7% in the magnetization M. This maximum change will occur at the highest experimental field, H = 175 kOe.

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