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LETTER TO THE EDITOR

Remanent magnetization of disordered antiferromagnets at very low magnetic fields: $Mn_{1-x}Zn_xF_2$, $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ and $K_2Fe(Cl_xBr_x)_5 \cdot H_2O$

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Abstract. The magnetization of the easy-axis disordered antiferromagnets $Mn_{1-x}Zn_xF_2$, $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ and $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$ was studied at very low magnetic fields, starting from $H_{axial} \lesssim 0.01$ Oe along the easy axis. The existence of a remanent moment M_r is confirmed in the first two materials, but contrary to a recent report the sign of M_r is not random; it always agrees with that of H_{axial}. A small remanence is also found in $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$. The magnitude of M_r increases rapidly with H_{axial} when $H_{axial} \lesssim 0.1$ Oe, but approaches saturation at higher fields. The data strongly suggest that M_r would vanish if H_{axial} were exactly zero. For fields up to at least ~1 Oe, the remanent moment at all temperatures is governed by the axial field which is present as the sample cools through the Néel point.

The existence of a 'spontaneous magnetization' in the dilute (random-site) antiferromagnet $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ has been reported very recently [1]. The spontaneous moment, along the easy axis, appeared at 'zero field' below the Néel temperature T_N. No spontaneous moment was observed in random-bond antiferromagnets of the same class, e.g. $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$. Earlier, excess magnetization (or 'remanent magnetization') in the field-cooled state of $Mn_{1-x}Zn_xF_2$ was observed in magnetic fields of 50 Oe or higher [2]. The excess magnetization was also studied in other materials, but at higher fields [3,4].

The 'zero-field' data in [1] were actually taken in a superconducting magnet cooled from 77 K with its terminals open. The small residual magnetic field, due to the earth's field and local sources, was not measured, and its time stability was not ascertained. In this letter we present magnetization data on the same three systems of disordered easy-axis antiferromagnets as those studied in [1,2]. Our measurements were made in carefully controlled very low magnetic fields, starting from less than 0.01 Oe along the easy axis. Although the present results confirm some of the earlier findings, they indicate that several important conclusions reached in [1] must be modified: (1) the sign of the remanent moment M_r is not random; (2) a small remanent magnetization also exists in $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$; (3) the remanent moment probably vanishes if the sample is cooled in a true zero field. The

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dependences of the remanent moment M_r on the magnitude, sign, and history of the applied axial field H_{axial} (along the easy axis) are also discussed.

Measurements were made on three single crystals: $Mn_{1-x}Zn_xF_2$ with $x = 0.51$ (from atomic absorption), $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ with $x \simeq 0.1$, and $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$ with $x \simeq 0.25$. The first sample was from the same boule ($x = 0.5$) as that used in the neutron work of Cowley *et al* [5]. The other samples were grown at the University of São Paulo. The magnetization was measured with a SQUID magnetometer system manufactured by Quantum Design. Each of the samples was mounted with its easy axis along the vertical bore of the superconducting magnet. Most measurements were of the 'longitudinal' magnetic moment along the bore, but the 'transverse' moment was also measured occasionally. Unless otherwise stated the data are for the longitudinal moment, with the + and − signs corresponding to up and down the bore, respectively.

To minimize trapped-flux effects, the magnetic field was kept below 23 Oe, following a cool down of the magnet from room temperature. The small current through the magnet, up to 15 mA, was provided by an independent current source. The axial (longitudinal) magnetic field, H_{axial}, was calibrated repeatedly below 23 Oe by measuring the magnetization of an indium sample in the superconducting state (Meissner effect), and correcting for the demagnetization. This procedure was checked later by applying known axial fields of 50 and 100 Oe. Measurements of the magnetization of pure MnF_2 (whose susceptibility is known [6]), carried out below 1 Oe at $T \leqslant 80$ K, also confirmed the calibration of the low axial fields. Some susceptibility data were taken at 2.0 and 4.0 kOe after the low-field measurements were completed. Above T_N these data agreed with data from 0.08 to 4.0 Oe, reconfirming the calibration of the low axial fields.

The transverse fields in the magnet, of order 0.1 Oe, could not be changed. Because the alignment of the antiferromagnet's easy axis along the magnet's bore was only accurate to $\sim 1°$, the projection of the transverse field created an uncertainty of several millioersted in the field along the easy axis. Other experimental factors also produced a comparable uncertainty in H_{axial}. Thus, for data taken at $H_{axial} \lesssim 0.01$ Oe, the exact value and even the sign of H_{axial} were not known. The sign was known for $H_{axial} \geqslant 0.02$ Oe.

Magnetization data on $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ were taken in axial fields of 0.02, 0.08, 0.31, 1.15 and 4.00 Oe, and also at $H_{axial} \lesssim 0.01$ Oe. Data were first taken while cooling in a constant field (FC data). After reaching the lowest temperature more data were usually taken while heating in the same field (FH data). Typical data are shown in figure 1. The results confirmed some of the main conclusions in [1]: (1) a remanent moment M_r exists below T_N; (2) the FH data are very close to the FC data; (3) the remanent moment is parallel or nearly parallel to the easy axis. The last result is based on occasional measurements of the transverse moment.

A major difference from the results in [1] is that in the present measurements the sign of M_r always agrees with the sign of H_{axial}. This conclusion is based on many repeated measurements in both positive and negative axial fields of magnitude 0.02 Oe or larger. The random sign of the 'spontaneous moment' observed in [1] was later traced to uncontrolled fluctuations in the very small axial field; the magnitude and sign of the axial field at the sample depended on the locations of a nearby helium container and nearby steel chairs.

Figure 1 also shows that the magnitude of M_r increases with H_{axial}. This increase is rapid at low fields, $H_{axial} \lesssim 0.1$ Oe, but is much slower at higher fields. The

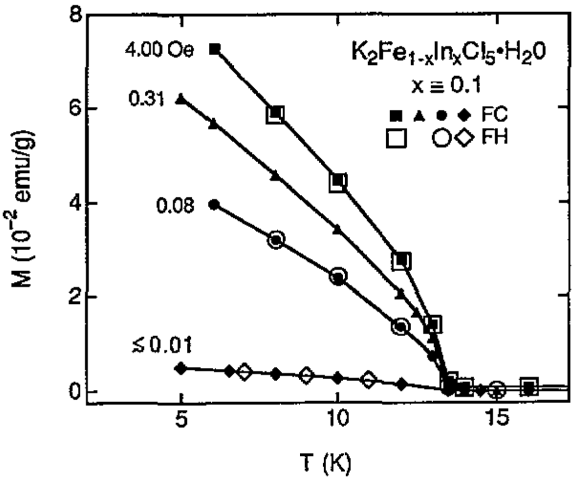

Figure 1. Magnetization M of $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ at various applied axial fields. Both field-cooling (FC) and field-heating (FH) data are shown.

data strongly suggest that had the sample been cooled in a true zero axial field, the remanent moment would have vanished. The dependence of the remanent moment on H_{axial} was not studied in [1], but recent data taken with the same setup show that by reducing the axial field in which the sample cools, M_r can be reduced below the level detectable with that system ($\sim 3 \times 10^{-4}$ emu g^{-1} for these samples).

Representative data for $Mn_{1-x}Zn_xF_2$ are shown in figure 2(*a*). The results are similar to those for $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$: a remanent magnetization, parallel or nearly parallel to the easy axis, exists below T_N. Its sign always agrees with that of H_{axial}. The magnitude of M_r increases rapidly with H_{axial} below ~0.1 Oe, but approaches saturation at higher fields. A control experiment on *pure* MnF_2, carried out at H_{axial} = 0.33 Oe, showed no remanent magnetization below T_N.

The remanent moment per gram in $Mn_{1-x}Zn_xF_2$ is an order of magnitude smaller than that in $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ at a comparable field. On the other hand, the usual 'parallel' susceptibility $\chi_\parallel$ (along the easy axis) is a factor of two larger in $Mn_{1-x}Zn_xF_2$. As a result, the susceptibility term $\chi_\parallel H_{axial}$ in $Mn_{1-x}Zn_xF_2$ makes a significant contribution to the magnetization below T_N when $H_{axial} \gtrsim 1$ Oe. To isolate the remanent magnetization M_r we express the measured magnetization M as

$$M = M_r + \chi_\parallel H_{axial}. \tag{1}$$

The susceptibility $\chi_\parallel$ for $Mn_{1-x}Zn_xF_2$ was obtained from measurements at 2 and 4 kOe, at which fields M_r is negligible compared to $\chi_\parallel H_{axial}$. Figure 2(*b*) shows M_r as a function of temperature T. These results are based on figure 2(*a*) and equation (1).

The use of equation (1) to extract M_r is supported by data for the isothermal magnetization of $Mn_{1-x}Zn_xF_2$ below T_N, measured after cooling from above T_N at constant field. The curve for M versus H_{axial} (below 23 Oe) was reversible, and it followed equation (1) with $\chi_\parallel$ agreeing with the value at 2 and 4 kOe. Thus, the intercept of the isothermal magnetization curve (straight line) with the zero-field axis was equal to M_r. This shows that M_r is the thermoremanent magnetization (TRM),

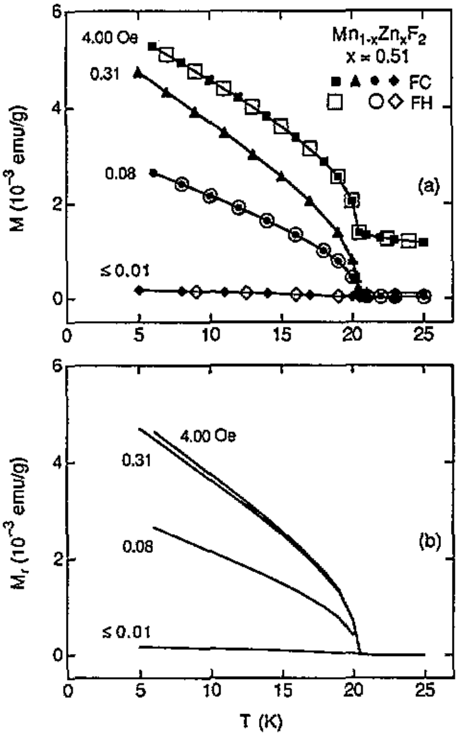

Figure 2. (*a*) Measurement magnetization of $Mn_{1-x}Zn_xF_2$ at various applied axial fields. (*b*) The thermoremanent magnetization M_r for the same fields.

i.e. the value of M obtained by cooling at a constant H_{axial} to a given temperature and then turning the field off.

Several experiments on $Mn_{1-x}Zn_xF_2$ and $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ indicate that the entire curve of M_r versus T is governed by the axial field which is present as the sample cools through T_N. Changing H_{axial}, or even reversing its sign, at a temperature below T_N has almost no effect on this curve. This result is for axial fields of at least up to ~1 Oe, and for times of at least up to ~1 h.

Results of a typical experiment leading to this conclusion are shown in figure 3. The open circles are data for cooling in a single fixed field, $H_{axial} = -0.31$ Oe. The other data were taken after cooling to 17 K at −0.31 Oe, and then changing the field to +0.28 Oe. The filled circles are FC data at +0.28 Oe, taken after the field change. The crosses are FH data at +0.28 Oe, taken after the two-step cool down (first at −0.31 Oe to 17 K, and then at +0.28 Oe). Clearly, all the data in figure 3 are very similar. The slight difference between data at −0.31 and +0.28 Oe is largely due to $\chi_{\parallel} H_{axial}$. Note that had the sample been cooled from above T_N at +0.28 Oe, it would have developed a remanent moment of the opposite sign (positive). Similar data for the same sample were also obtained by changing the field from −0.31 to +1.48 Oe at 20.0 K, which is only 0.5 K below T_N. The results for $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ in fields of up to ~1 Oe were similar, but the application of axial fields $H_{axial} \gtrsim 10$ Oe below T_N led to an irreversible magnetization and a large change in M_r.

A remanent moment was also observed below T_N in $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$, but it

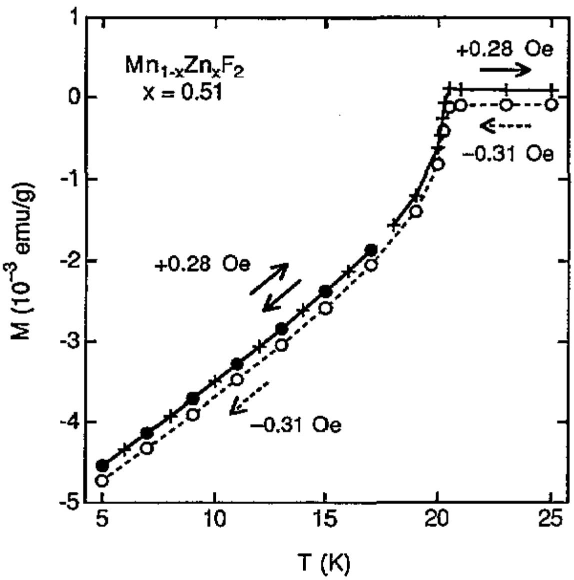

Figure 3. Magnetization of $Mn_{1-x}Zn_xF_2$ as a function of temperature. Open circles are FC data taken while cooling from above T_N to 5 K at $H_{axial} = -0.31$ Oe. The filled circles are FC data at +0.28 Oe, taken after a cool down to 17 K at −0.31 Oe and a field change at that temperature. The crosses are FH data at +0.28 Oe, taken following the two-step cool down (first at −0.31 Oe to 17 K, and then at +0.28 Oe).

was two orders of magnitude smaller than that in $K_2Fe_{1-x}In_xCl_5{\cdot}H_2O$. The remanent moment in $K_2Fe(Cl_{1-x}Br_x)_5{\cdot}H_2O$ was not detected in [1] because of the lower sensitivity of the magnetometer. The new result suggests that a remanent moment also exists in random-bond antiferromagnets. This conclusion, however, must be treated with caution. A small degree of disorder may still exist on the magnetic sites of $K_2Fe(Co_{1-x}Br_x)_5{\cdot}H_2O$, due to Fe vacancies, for example. Such a small site disorder can generate a small remanent moment.

The origin of a remanent moment in fields as low as ~0.1 Oe is unclear. Possible mechanisms for a remanent moment at much higher fields were discussed in [3, 4, 7] in connection with the random-field problem. These proposed mechanisms, however, do not seem to account for some of the salient features of the present data, e.g. the observed saturation of M_r at ~1 Oe.

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