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LETTER TO THE EDITOR

Spontaneous magnetization in the diluted low-anisotropy antiferromagnets $K_2FeCl_5 \cdot H_2O$:In

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Abstract. Spontaneous magnetization and monodomain behaviour were observed, at zero applied field, in single crystals of the diluted low-anisotropy antiferromagnets $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$. The spontaneous magnetization M appears at the Néel temperature, and is directed along the easy axis (either up or down). The magnitude of M depends on x. For $x = 0.15$ and 4.2 K, M corresponds to 0.2% of the calculated saturation magnetization. The spontaneous moment appears only when substitution is made at the Fe site; replacing K by Rb, or Cl by Br, does not lead to a spontaneous moment. This is the first observation of a spontaneous moment in any diluted low-anisotropy antiferromagnet.

Compounds of the general formula $A_2MX_5 \cdot H_2O$ where A = K or Rb, M = Fe or In and X = Cl or Br, are isomorphous [1, 2]. The crystal structure is orthorhombic, and all these compounds are good insulators. The Fe systems are low-anisotropy antiferromagnets. Since solid solutions of $A_2MX_5 \cdot H_2O$ can be readily grown, they are well suited for studies of the effects of disorder at the A, M and X sites on the magnetic properties and of the phase diagram of the ordered antiferromagnets at non-zero magnetic field. Substitution on the A and X sites leads to a 'random-bond' system [3], whereas substitution at the M site leads to a 'random-site' system [4].

Previous studies in these systems focused on the spin-flip transition of Cl substituted for with Br in $K_2FeCl_5 \cdot H_2O$ [5,6] and on zero-field AC susceptibility measurements in Fe substituted for with In in $Rb_2FeCl_5 \cdot H_2O$ [7].

In this work we concentrate on the zero-field and low-field behaviour of $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$. We found that the replacement of Fe by In results in a net spontaneous magnetic moment, at zero field, and in a monodomain-like behaviour. This is the first observation of net spontaneous moment in diluted antiferromagnets.

Magnetization measurements were made with a vibrating sample magnetometer. Magnetic moments as low as 5×10^{-5} emu could be detected. The single crystals of $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ were grown from aqueous solution. Samples with $x = 0$, 0.03, 0.09, 0.15, 0.20 and 0.27 were mounted with their easy axis (a axis) parallel to the axis of the pick-up coils. Typical dimensions of the crystals were $5 \times 4 \times 2$ mm, with the longer length along the easy axis. Most measurements were made at zero applied field (except for the local Earth magnetic field). Hysteresis loops, at finite fields

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directed along the easy axis, were obtained in a superconducting magnet. To avoid trapped flux, all the zero-field measurements were made after the superconducting magnet was cooled from 77 K with its terminals open. The concentration x was obtained from fits of the susceptibility at high temperatures to a Curie–Weiss law, with x as a fitting parameter. The high-temperature susceptibility was measured with an AC modulation technique.

Pure $K_2FeCl_5 \cdot H_2O$ has a Néel temperature $T_N = 14.0$ K. Increasing x decreases T_N. When the magnetization M of the pure system was measured in a zero external applied field we found, as expected for an antiferromagnet, that $M = 0$ at all temperatures. On the other hand, in samples with the concentrations x other than zero a net spontaneous magnetization appears on cooling through the Néel temperature $T_N(x)$. This spontaneous magnetization M can be either up or down along the easy axis, apparently in a random way. At zero field, once the magnetization is up (down) it will remain up (down) until the sample is warmed above T_N. A subsequent cooling of the sample to temperatures below $T_N(x)$ may or may not reverse the direction of M. As long as the sample remains below $T_N(x)$ the curve of spontaneous magnetization versus temperature is reversible. The appearance of the spontaneous magnetization in the crystal and the antiferromagnetic order occur at the same temperature $T_N(x)$.

Figure 1 shows the results of a run obtained at zero field for a sample with $x = 0.15$. Results for other concentrations are similar. In this run the sample was cooled from above $T_N(x)$ starting at point 1, down through $T_N(x)$ towards point 2. At $T_N(x)$ a spontaneous magnetization in the positive direction appeared in this case. Subsequently the sample was warmed up to a temperature above $T_N(x)$ (point 1). During this warm-up, the curve of M versus T was the same as in the initial cool-down. Following the warm-up to point 1, the sample was cooled to point 3. As it happened, a negative spontaneous moment appeared in this case. The magnitude of the negative spontaneous moment was the same as that of the positive moment in the initial cool-down at the same temperature.

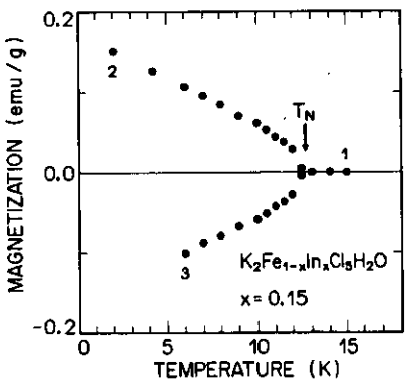

Figure 1. Spontaneous magnetization of diluted $K_2Fe_{1-x}In_xCl_5 \cdot H_2O$ at zero applied field. Either the upper or the lower branch of the curve may result as the sample is cooled through the ordering temperature T_N (see text).

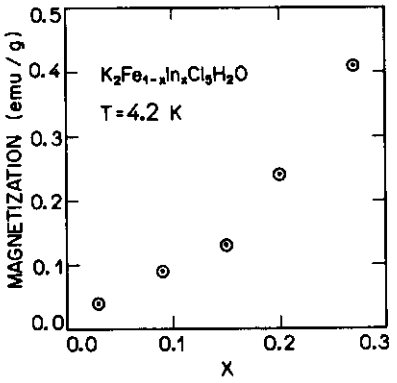

Figure 2. The measured spontaneous moment at 4.2 K is plotted as a function of In concentration x. The saturation moment of the pure antiferromagnetic $K_2FeCl_5 \cdot H_2O$ is 84.8 emu g^{-1}.

The appearance of the spontaneous magnetization is highly unexpected. Even for

a ferromagnet, in a macroscopic sample a domain structure with a total (net) moment $M = 0$ appears as a rule. It should be emphasized that the spontaneous moment appears only when In substitution is made at the Fe site. Similar measurements performed in samples where K was partially replaced by Rb or Cl partially replaced by Br did not show a spontaneous magnetic moment. Thus a spontaneous magnetic moment appears only in the random-site case but not in the random-bond cases.

The spontaneous magnetization at a given temperature increased with the In concentration x. The initial increase at low x was almost linear, but the increase was faster at larger x. Figure 2 shows the measured spontaneous moment at 4.2 K for five different concentrations. At this temperature the spontaneous moment for $x = 0.15$ is 0.2% of the calculated saturation magnetization for this sample.

We also measured samples with the same concentration and shape but with different volumes. We found that the total magnetic moment of the crystal is proportional to its volume, i.e. the spontaneous magnetization M (moment per unit volume) is volume independent.

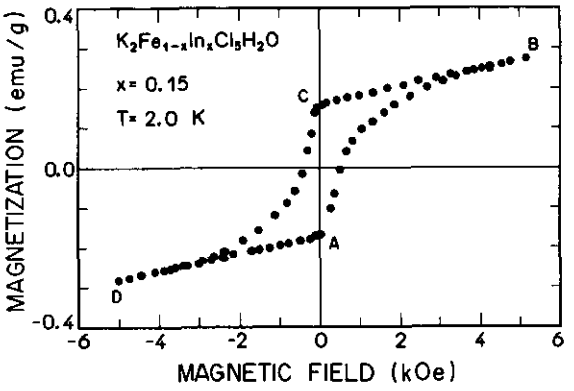

Figure 3. Hysteresis loop obtained at 2.0 K for $K_2Fe_{1-x}In_xCl_5{\cdot}H_2O$, $x = 0.15$. A linear reversible behaviour is observed in the B–C and A–D segments of the hysteresis cycle. The slope dM/dH in these segments agrees with the expected value for the susceptibility of the antiferromagnetic phase. This indicates that the sample behaves as a monodomain.

Figure 3 shows a typical hysteresis loop obtained for these samples below $T_N(x)$. The curve is for a sample with $x = 0.15$ at $T = 2.0$ K. At $H = 0$, the loop can only be started either at points A or C. The value of M at these points corresponds to the spontaneous (up or down) magnetization that appears after a zero-field cooling to that temperature. If the cycle is started at A (i.e. with a downward magnetization), then an increase in H leads initially to a non-linear increase of M with H, followed by a linear increase at fields above a few kOe (from A to B). The slope dM/dH of the linear region corresponds to the expected susceptibility for the antiferromagnetic phase. Decreasing the field (from B to C) the same linear dependence extends down to $H = 0$. Continuing from point C in the direction of negative fields (from C to D) M decreases until it attains again a linear behaviour. The loop is symmetric and segment D–A is similar to segment B–C with M and H reversed. In these linear regions the magnetization curve is reversible, i.e. if the field increases from point C (decreases from point A) the same curve results. The loop never goes through the origin. The presence of segments B–C and D–A of linear reversible behaviour indicates that the sample behaves as a monodomain.

The occurrence of a weak ferromagnetic moment due to the Dzyaloshinsky–Moriya interaction is excluded, because canting between the sublattices will generate a moment perpendicular to the easy axis. In fact we measured the moment in

directions perpendicular to that axis. A very small moment was observed but its value can be fully explained by the accuracy within which we were able to orient the sample inside the pick-up coils ($\simeq 3°$). We also considered the presence of uncompensated spins, as the origin of the spontaneous net moments. Domains, each with net magnetic moment, are expected to occur in a random-site antiferromagnet. If a domain contains N spins then the net moment is expected to be of the order of $(N)^{1/2}$; however, the magnetization of a macroscopic sample containing many domains is expected to vanish. Only the occurrence of 'correlated' domains containing typically 10^6 spins can be consistent with the observed volume effect and a spontaneous magnetization of the order of 0.1% of the saturation magnetization. The origin of such a 'correlation' mechanism in this diluted antiferromagnet is unclear.

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