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Hysteresis at the spin-flop transition in the antiferromagnets $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$

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Magnetic hysteresis is found at the first-order spin-flop transition in $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$ ($x=0.1$, 0.2, and 0.3). From measurements of the ac susceptibility χ and from a study of the dependence of χ on the modulation field h at the transition, the hysteresis field ΔH^* is determined. It is found that ΔH^* decreases with increasing temperature along the first-order line. No hysteresis was observed in pure ($x=0$) samples.

I. INTRODUCTION

In an antiferromagnet with low anisotropy, a magnetic field H applied parallel to the easy axis can induce a transition to a phase in which the magnetic moments lie in a direction perpendicular to H. This is the so-called spin-flop phase (SF). In the magnetic field versus temperature (H-T) plane, the boundary separating the antiferromagnetic phase (AF) from the SF phase is a line of first-order transitions at which the magnetization M has a discontinuity. As expected in first-order transitions, hysteresis can occur at the spin-flop line.[1-3] Upon increasing H, the AF phase remains stable up to a field H_1, where the system switches to the SF configuration. Starting from the SF phase and decreasing the field, this phase remains stable down to a field $H_2 < H_1$, where the AF phase is recovered. These two metastability fields are related to the softening of the spin-wave frequencies of the AF and SF phases, respectively. For an antiferromagnet with exchange field H_E and single-ion-anisotropy field H_A, these fields are related at $T=0$ by[2-4]

$$H_2 = \frac{2H_E - H_A}{2H_E + H_A} H_1 \ . \tag{1}$$

As the temperature increases, the difference between H_1 and H_2 decreases until it vanishes at the bicritical point.[5] It should be mentioned that, in the case of exchange anisotropy, spin-wave calculations indicate the absence of hysteresis between the antiferromagnetic and the spin-flop phase.[6] The thermodynamic transition field H_{SF} at which both phases have the same free energy occurs at a field intermediate between H_1 and H_2, i.e., $H_{SF} = (H_1 H_2)^{1/2}$.

Although the predicted hysteresis may be large for an antiferromagnet with a moderate anisotropy, experimentally the reported cases are scarce and in general no hysteresis at all is observed in antiferromagnets.[4,7-9] Keffer and Chow[4] have explained the absence of hysteresis at the spin-flop transition through the instability generated by the softening of surface magnons. This prevents the system from reaching the field H_1 (or H_2), and thus the transition should occur at the thermodynamic transition field.

In this paper we report on the first systematic observation of hysteric behavior at the spin-flop transition. The phenomenon clearly appears when ac magnetic susceptibility experiments are used to observe the first-order transition in the compounds $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$ with $x=0.1$, 0.2, and 0.3.

The series of antiferromagnets of the general formula $A_2FeX_5 \cdot H_2O$ (A=K, Rb, NH$_4$ for X=Cl, and A=Rb for X=Br) are all isomorphous at room temperature, with orthorhombic structure given by the space group *Pnma*. Although the compounds $A_2FeBr_5 \cdot H_2O$ (A=K, NH$_4$) have not been described yet, their structures are expected to be isomorphous with the other compounds of the series, since also $A_2InCl_5 \cdot H_2O$ (A=K, NH$_4$) and $(NH_4)_2MoX_5 \cdot H_2O$ (X=Cl, Br) have been found isomorphous.[10] The phase diagram of $K_2FeCl_5 \cdot H_2O$ has been studied using susceptibility data. The Néel temperature T_N is 14.0 K and the spin-flop field at $T=0$ is $H_{SF}(0) = 26.0$ kOe.[11] No such studies are available for $K_2FeBr_5 \cdot H_2O$, but usually the substitution of chlorine for bromine in a compound series tends to increase T_N and enhance the magnetic anisotropy.[12] For $Rb_2FeCl_5 \cdot H_2O$ and for all the chorine derivatives of the series, the easy axis of antiferromagnetic alignment is parallel to the *a* crystallographic axis.

II. EXPERIMENTAL RESULTS

A. Experimental configuration

The cryostat used in the experiment consisted of a small double-wall vacuum-insulated temperature-controlled chamber, mounted in the bore of a superconducting magnet and immersed in a liquid He bath. Liquid He can also be admitted inside the chamber. The magnetic susceptibility $\chi = dM/dh$ was measured with an ac mutual inductance bridge. The secondary (pick-up coils) were placed inside the chamber. A carbon glass resistance thermometer and a small heater were placed near the secondary. The primary coil was mounted in the He bath, concentric with the superconducting magnet and the secondary coils. The samples were mounted at the end of a rod that can be vertically moved from the top of the cryostat, and placed at the center of the secondary. Below 4.2 K the measurements were made with the sample immersed in liquid helium that was admitted inside the chamber.

Measurements of $\chi = dM/dh$ were made at 155 Hz with the ac modulation field h ranging from 0.1 to 160 Oe. Data were taken at fixed temperatures between 1.5 and 10 K, varying the applied dc magnetic field H at different sweep rates dH/dt. The crystal was oriented with the easy axis parallel to the applied field H within about 0.5°. Data of χ versus T at $H=0$ were also taken up to 30 K.

Single crystals of $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$ were grown from suitable solutions of $FeCl_3 \cdot 6H_2O$, KCl, and KBr; the crystals exhibit the same external morphology as the pure chlorine compound. All the crystals studied here have the same shape; consequently, the demagnetization factor is considered to be the same for each; each sample weight was approximately 50 mg.

B. Zero-field susceptibility

Figure 1 shows the parallel and perpendicular susceptibility as a function of T at zero applied dc field for the sample with $x = 0.3$. The easy axis is along the a direction as in the chloride compound, and $T_N = 15.2$ K. The rise of χ at lower temperatures is probably due to the paramagnetic contribution of free Fe ions in finite clusters. This behavior has already been observed in other mixed crystals.[13]

C. Effect of h and dH/dt on the shape of χ at the SF transition

In Fig. 2, data for χ as a function of an external field applied along the easy axis for a pure sample of $K_2FeCl_5 \cdot H_2O$ are shown. The data were measured at 4.2 K with a modulation field of 0.5 Oe and by sweeping the external field at a rate of 14 Oe/s. The peak locates the SF transition. The shape of this curve at the transition is unaffected by the strength of h up to 160 Oe, the highest value used in our study.

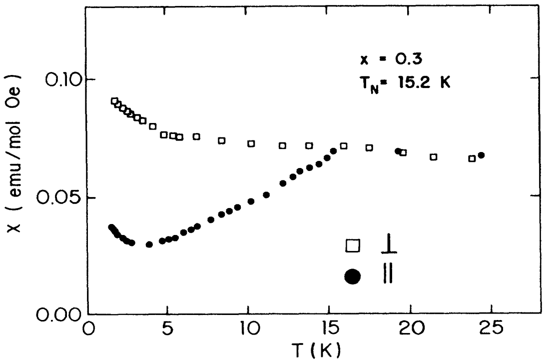

FIG. 1. Zero-field magnetic susceptibility parallel and perpendicular to the easy axis for $K_2Fe(Cl_{0.7}Br_{0.3})_5 \cdot H_2O$ as a function of the temperature.

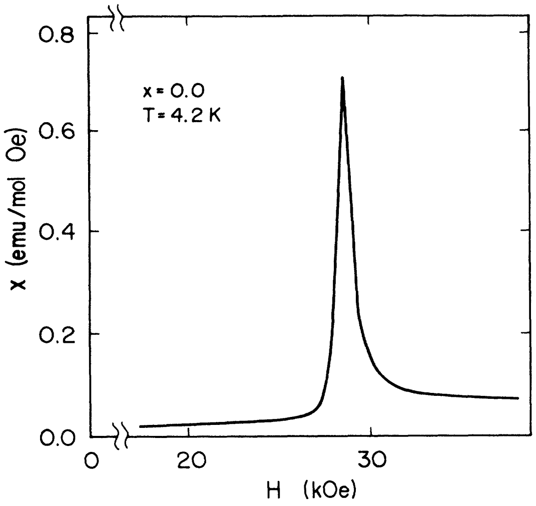

FIG. 2. Magnetic susceptibility as a function of the applied field for $K_2FeCl_5 \cdot H_2O$. The peak corresponds to the first-order AF-SF transition.

The results are very different when mixed samples are used in the experiment. The curves depicted in Fig. 3 are for the sample with $x = 0.1$. They show the field dependence of the susceptibility at 4.2 K in the region of the SF transition at distinct values of h. The modulation field increases from curve a to curve d. For $h = 55$ Oe (curve a) or below, the transition is seen as a step in the curve. As h increases, a peak develops in the transition region (curves b, c, and d) and a sharp peak is observed at the

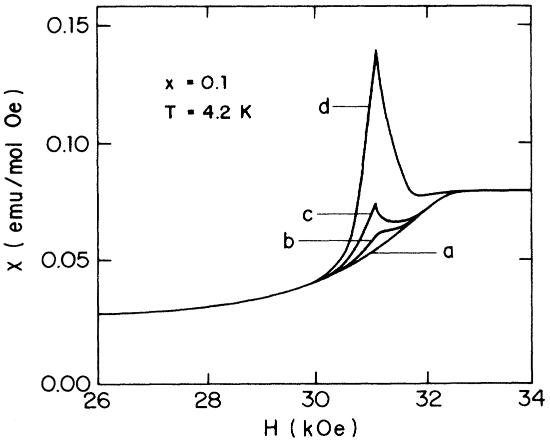

FIG. 3. Susceptibility as a function of the external applied field in the region of the AF-SF transition in $K_2Fe(Cl_{0.9}Br_{0.1})_5 \cdot H_2O$ for different peak-to-peak values of the modulation field: (a) 55 Oe, (b) 70 Oe, (c) 85 Oe, and (d) 110 Oe.

highest values of h. This behavior is in marked contrast with that found in the pure chlorine derivative (Fig. 2). The SF field at 4.2 K is 31 kOe for this sample, a value higher than that measured for the chloride compound. A similar behavior is observed in crystals with $x=0.2$ and 0.3 except that in the $x=0.3$ case there is no peak in the susceptibility curve at 4.2 K even at the highest values of h used in the experiment. Only at temperatures around 8 K and higher is the peak observed. The SF transition fields for these samples at 4.2 K are, respectively, 34 and 45 kOe.

We can define a critical modulation field h_c as the value of h below which only a single step is seen at the transition. At each temperature, h_c can be determined by extrapolating the height of the susceptibility peak, $\tilde{\chi}_p$, measured as a function of h, down to $\tilde{\chi}_p=0$. For the samples with $x=0.1$ and 0.2 these fields are $h_c=60$ Oe and $h_c=100$ Oe, respectively, at 4.2 K. Figure 4 illustrates the temperature dependence of h_c for the crystal with $x=0.1$. The decrease of h_c with increasing temperature is noteworthy.

It was also found that the behavior of the χ curves depends on the sweep rate (dH/dt) of the external applied field. For $h<h_c$ and for large dH/dt a peak can appear at the transition; the larger dH/dt, the higher the peak. For $h>h_c$, a peak always appears in χ even for $dH/dt=0$ (i.e., when the data is taken in a static applied field at fixed temperature).

D. Hysteresis at the spin-flop transition

The existence of hysteresis at the SF transition was checked by carrying out runs of χ versus H for increasing and decreasing external field H. Figure 5 shows two such runs taken at 2 K for the samples with $x=0.1$ and $x=0.3$. The measurements were made with a small dH/dt and the modulation field was kept well below h_c in order to avoid the appearance of the peak in χ. Note the difference between the curves for increasing and decreasing field, which gives hysteresis width values of $\Delta H^*=120$ Oe and $\Delta H^*=520$ Oe for the samples with $x=0.1$ and $x=0.3$, respectively. The observed hysteresis decreases with increasing temperature. If $h>h_c$, so that a peak appears at the transition, no difference in the transition critical field is detectable for increasing and decreasing H. We have already mentioned that for the pure chloride compound the peak is always observed, even for very small values of h. Consequently, no hysteresis has been detected in this case.

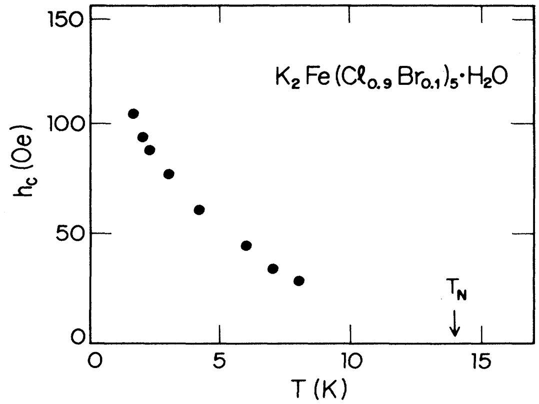

FIG. 4. Extrapolated modulation field h_c at several values of temperature; h_c is related to the hysteresis observed at the SF transition (see text).

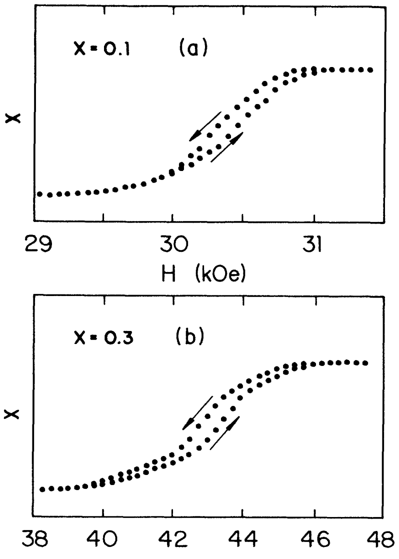

FIG. 5. Susceptibility (χ) versus applied field (H) for increasing and decreasing H. The modulation field was 1 Oe and the temperature 2.0 K. Note the different scale of the field axis. The curves were taken at very slow dH/dt.

III. DISCUSSION AND CONCLUSION

The observed dependence of the ac susceptibility at the SF transition on the modulation field h and on the sweep rate dH/dt of the applied field can be related to the hysteresis found in the experimental curves (Fig. 5) for $h<h_c$. A similar behavior was found at the first-order transitions present in the phase diagram of the modulated magnetic system MnP.[14] Our explanation, based on the arguments given in Ref. 14, goes as follows: if there is a hysteresis of width ΔH^* at the first-order transition, for slow dH/dt two possibilities exist, depending on whether the peak-to-peak value (h) of the modulation field $[h(t)=h_0\cos(\omega t)]$ is smaller or greater than ΔH^*. We refer to Fig. 6 to exemplify both situations. If $h>\Delta H^*$ the resultant of the external field $H(t)$ and the modulation field $[H_r(t)=H(t)+h(t)]$ is such that in a cycle $(2\pi/\omega)$ the hysteresis region will be crossed from the AF phase to the SF phase and vice versa [Fig. 6(a)]. Since the magnetization M has different values in each phase, $\chi=dM/dH$ will show a peak at the transition field. If $h<\Delta H^*$ and H_r is within the hysteresis width, minor hysteresis loops will occur [Fig. 6(b)]. Their slope $\Delta M/h$ tends to be smaller than the slope dM/dH in the SF

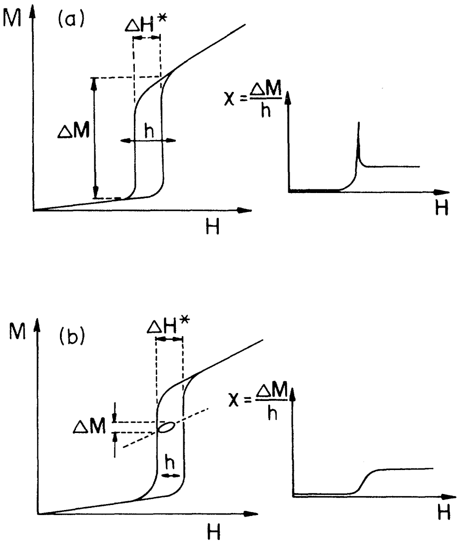

FIG. 6. Schematic representation of the magnetization M and susceptibility at the first-order AF-SF transition when hysteresis ΔH^* is present: (a) when $h > \Delta H^*$ the measured susceptibility $\Delta M/h$ shows a sharp peak at the transition. (b) when $h < \Delta H^*$ the measured $\Delta M/h$ is given by the slope of the minor hysteresis loop.

phase and higher than dM/dH at the AF phase. This leads to a gradual increase of the susceptibility across the transition region and to the suppression of the peak. This is in agreement with the behavior found in the curves shown in Fig. 3. In this way the extrapolated field h_c formerly introduced can be interpreted as a measure of the width ΔH^* of the hysteresis at the transition. The directly measured hysteresis from the data in Fig. 5(a) for the sample with $x=0.1$ at 2K ($\Delta H^*=120$ Oe) is comparable to the value of ~ 100 Oe obtained from Fig. 4 at this same temperature.

The experimentally observed dependence of dM/dH on the sweep rate dH/dt for $h < h_c$ also fits in this explanation. For fast dH/dt, such that the resulting field $H_r(t)$ is always increasing (this will happen for frequencies not too high), the transition width will be crossed once and the sudden change in M will show as a peak in dM/dH.

The experimentally obtained T_N and H_{SF} can be combined to estimate the exchange and anisotropy fields in the mixed compounds. As the anisotropy of these systems is predominantly of the single-ion type,[11] a hysteresis given by Eq. (1) is expected at the SF transition. Since these systems have low anisotropy, H_E is proportional to T_N and $H_{\mathrm{SF}}^2 \cong 2H_E H_A$. The values quoted in Ref. 11 for $K_2FeCl_5 \cdot H_2O$ ($x=0$) are $H_E=199$ kOe, $H_A=1.7$ kOe, and $T_N=14.0$ K. From our data we found $H_E=204.7$ kOe, $H_A=2.3$ kOe for $x=0.1$, and $H_E=216$ kOe, $H_A=4.3$ kOe for $x=0.3$. These results show that an increase in bromine concentration increases the anisotropy, as already observed in other mixed systems.[12] The calculated values for the hysteresis in the SF transition at $T=0$ using Eq. (1) are approximately 500 Oe for $x=0$, 700 Oe for $x=0.1$, and 1700 Oe for $x=0.3$. The observed hysteresis at 2 K for $x=0.1$ is 120 Oe [see Fig. 5(a)]. For $x=0.3$ at 2 K we obtain $\Delta H^* \sim 520$ Oe [Fig. 5(b)]. These values are well below the predicted ones. Indeed, for $x=0$ no hysteresis was observed at all. A summary of there values is listed in Table I. Theoretically ΔH^* is expected to decrease with increasing T.[5] Our observation of the dependence h_c with the temperature shown in Fig. 4 agrees with this behavior.

To our knowledge $CoBr_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ are the only previously reported cases where hysteresis was observed at the spin-flop transition. In $CoBr_2 6H_2O$, a hysteresis of ~ 50 Oe was found in the isentropic curves obtained when the magnetic field was swept up and down across the SF boundary.[15] The sweeping rate dH/dt used in these measurements is not given. In this kind of experiment, it may happen that when the spin lattice relaxation time is high, the temperature of the spins may not follow the lattice temperature, then giving rise to an apparent hysteresis in the data if dH/dt is not kept small enough. In the $CuCl_2 \cdot 2H_2O$ a very small hysteresis (2 Oe) is found at the SF transition by means of frequency-modulation antiferromagnetic resonance experiments.[1] This very small hysteresis could be hidden when the field-modulation technique was used instead. In this case the predicted hysteresis using Eq. (1) is 13 Oe. We should mention that, in this copper compound, the isentropic curves were observed to be reversible and showed no significant hysteresis at the spin-flop transition.[16]

In conclusion, we have shown the existence of hysteresis associated with the SF transition by using the ac susceptibility technique. Hysteresis is absent in the pure sample; however, the mixed ones do show hysteresis. The observation of a lack of hysteresis in pure $K_2FeCl_5 \cdot H_2O$ is in agreement with previous observations in other homogeneous magnetic systems.[4,7–9,16] Therefore, it seems that a certain degree of inhomogeneity is required for the spin-flop transition to show hysteresis. In the theoretical explanation of Keffer and Chow,[4] the nonobservation of "superheating" and "supercooling" in homogeneous systems is due to the nucleation of the phases caused by "surface spin-flop states which broaden with increasing field and which catastrophically spread inward across the three-dimensional material as the critical field is approached."

TABLE I. Summary of the fields of $K_2Fe(Cl_{1-x}Br_x)_5 \cdot H_2O$ in units of kOe. ΔH^* (cal) correspond to the hysteresis values at $T=0$ K, calculated using H_E and H_A. ΔH^*(meas) are the measured hysteresis at $T=2$ K.

x	H_E	H_A	ΔH^*(cal)	ΔH^*(meas)
0	199	1.7	0.50	0.00
0.1	204.7	2.3	0.70	0.12
0.3	216	4.3	1.70	0.52

Our measurements in mixed samples show a hysteresis that is below that predicted using Eq. (1) but that has the expected qualitative dependence on temperature.[5] One possible explanation for the appearance of hysteresis is that inhomogeneities may act as "pinning" centers for the surface spin-flop states, preventing (or delaying) their spread inside the bulk of the sample. In this way the phases may be sustained beyond the thermodynamic transition field.

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