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Temperature-induced magnetization reversal in $FeCr_{2-x}Al_xS_4$

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Abstract

In this paper, temperature-induced magnetization reversal in $FeCr_{2-x}Al_xS_4$ ($x = 0.8, 1.0$) is reported. Low-field magnetization measurements indicate that this system displays substantial irreversibility between zero-field-cooling (ZFC) and field-cooling (FC) sequences. Upon warming, the ZFC magnetization is found to change sign twice; however, the FC magnetization changes sign only once. Magnetic hysteresis loop measurements reveal that this system displays a large coercivity at lower temperatures; with increasing temperature, the coercivity decreases abruptly. By accounting for magnetic domain freezing induced by large magnetic anisotropy and domain wall pinning of non-magnetic ions, the multiple sign changes of the magnetization are explained qualitatively.

Manganese oxides exhibiting the colossal magnetoresistance (CMR) effect have attracted much interest in the past few years because of their special electronic and magnetic properties, as well as in the context of many potential applications [1–3]. An extensive magnetic study of doped manganese oxides revealed that there are abnormal patterns of magnetic behaviour in the ferromagnetic state [4–6]. For example, the magnetization measured in low field displays irreversibility between the zero-field-cooling (ZFC) and field-cooling (FC) sequences. In our previous work, this effect has been studied on another CMR material—the spinel $FeCr_{2-x}Al_xS_4$ ($0 \leqslant x \leqslant 0.7$); our results indicate that magnetic anisotropy is a main factor in inducing such irreversible magnetic behaviour [7]. Following on from the former investigation, the magnetic properties of $FeCr_{2-x}Al_xS_4$ ($0.7 < x \leqslant 1.0$) were studied further. In this paper, temperature-induced magnetization reversal in $FeCr_{2-x}Al_xS_4$ ($x = 0.8, 1.0$) is reported. Although such magnetic moment reversals have been observed in other materials such as Co_2VO_4 with a ferrimagnetic order and YVO_3 with a structural phase transition, this phenomenon is rare [8–10]. By performing magnetic hysteresis loop measurements, it is found that $FeCr_{2-x}Al_xS_4$

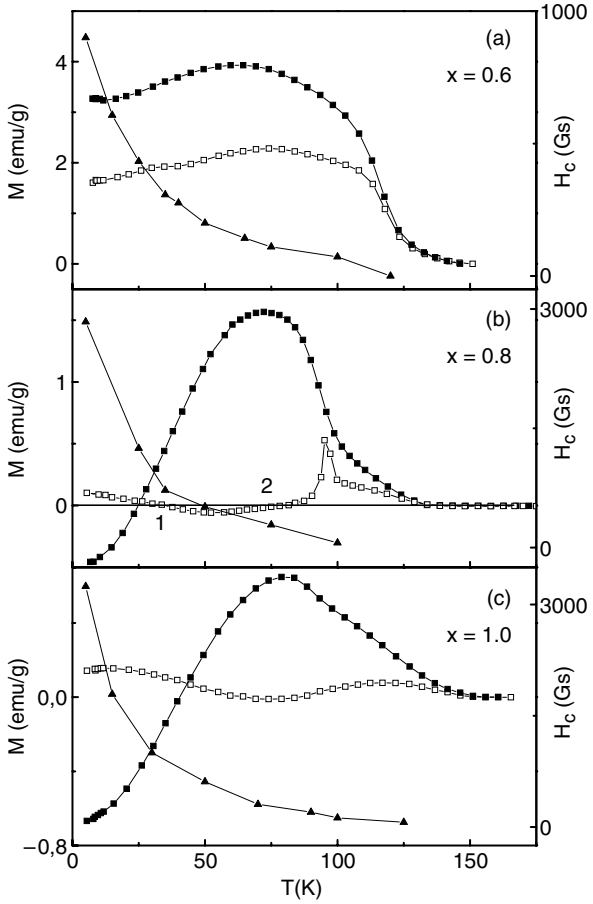

Figure 1. Zero-field-cooling (open squares, □) and field-cooling (solid squares, ■) magnetization versus temperature curves for $FeCr_{2-x}Al_xS_4$ ($0.6 \leqslant x \leqslant 1.0$), measured at $H = 0.005$ T. The solid triangles, ▲, denote the coercivity at different temperatures for all samples.

($x = 0.8, 1.0$) exhibits a large coercivity at lower temperatures. Accordingly, the temperature-induced magnetization reversal displayed in this system is explained qualitatively by taking account of magnetic domain freezing induced by the large magnetic anisotropy, as well as domain wall pinning of non-magnetic ions.

The polycrystalline $FeCr_{2-x}Al_xS_4$ ($x = 0.6$, 0.8, and 1.0) samples were prepared by a standard solid-state synthesis method [11]. Structure and phase purity were examined by x-ray power diffraction measurements, which indicate that all samples are single phase with spinel structure.

The magnetic measurements were performed using an M-9300 vibrating sample magnetometer. In figure 1, we display the magnetization as a function of temperature obtained in ZFC and FC processes with an applied field, $H = 0.005$ T. 'ZFC' means that the sample was first cooled to 5 K in zero field, then measured under the applied field of 0.005 T. In contrast, in the FC sequence, before starting the measurements, the sample was cooled to 5 K in 0.005 T. The irreversibility between the ZFC and FC magnetizations for all samples is clearly seen in figure 1. For $x = 0.8$, with increasing temperature, the ZFC magnetization first decreases and crosses zero (marked as 1 in figure 1(b)), going to a minimum at a negative value,

then increases and changes sign again (marked as 2). After reaching a positive maximum, the magnetization decreases abruptly. Clearly, the ZFC magnetization changes sign twice upon warming and shows a cusp at about 95 K. However, as seen from figure 1(b), the FC curve is completely different. The FC magnetization displays a negative magnetic moment at 5 K. With increasing temperature, the FC magnetization first rises and crosses zero at the compensation temperature (T_{comp}), then increases to reach a maximum. Upon further warming, the magnetization decreases. For $x = 1.0$, the ZFC and FC curves are just similar to those for $x = 0.8$ except that no cusp is observed in the ZFC curve. However, for $x = 0.6$, in contrast to the cases for $x = 0.8$ and 1.0, no negative magnetization is observed; both FC and ZFC curves display typical ferrimagnetic character.

Note that the compensation effect is also a characteristic of ferrimagnets, as was first predicted by Néel [12]. According to Néel's two-sublattice model, for $FeCr_2S_4$, both the Fe sublattice and the Cr sublattice are ferromagnetic, while the magnetic moment of the Fe sublattice is anti-parallel to that of the Cr sublattice due to the magnetic coupling between these two sublattices. Accordingly, the net magnetization M_s can be written as [12]

$$M_s = M_{Cr} - M_{Fe} \tag{1}$$

where M_{Cr} and M_{Fe} are the spontaneous magnetization for the Cr sublattice and the Fe sublattice, respectively. For $FeCr_{2-x}Al_xS_4$, M_{Cr} and M_{Fe} can be written as

$$M_{Cr} = (2-x)Ng_{Cr}J_{Cr}\mu_B B_{J_{Cr}}(y_{Cr})$$
$$M_{Fe} = Ng_{Fe}J_{Fe}\mu_B B_{J_{Fe}}(y_{Fe})$$
$$y_{Cr} = g_{Cr}J_{Cr}\mu_B H_{Cr}/kT$$
$$y_{Fe} = g_{Fe}J_{Fe}\mu_B H_{Fe}/kT$$

where H_{Cr} and H_{Fe} are the total molecular fields acting on Fe and Cr ions, respectively:

$$H_{Cr} = H_0 + \gamma_{FeCr}(-M_{Fe} + \beta M_{Cr}) \tag{1a}$$
$$H_{Fe} = H_0 + \gamma_{FeCr}(\alpha M_{Fe} - M_{Cr}) \tag{1b}$$

where α, β, and γ_{FeCr} are the molecular-field coefficients.

For $FeCr_2S_4$, the system displays a net positive magnetization at temperatures below T_C because M_{Cr} is larger than M_{Fe}. On replacement of Cr by Al ions, M_{Cr} will be decreased because the Al ion is non-magnetic. For $x \leqslant 0.6$, as seen from figure 1(a), M_{Cr} is still larger than M_{Fe}; thus no negative magnetization is observed for $x = 0.6$. Obviously, with further increasing x, M_{Cr} may become comparable with M_{Fe}. Using Néel's two-sublattice model, the M_s–T curves are derived, and these are illustrated in figure 2, where the parameters are chosen as follows: $\alpha = -0.5$, $\beta = 0.37$, $\gamma_{FeCr} = 239$, $H_0 = 0$, $g_{Cr} = 2$, $g_{Fe} = 2$, $J_{Cr} = 2.9$, $J_{Fe} = 4.2$ [13]. For $x = 0.8$, curve a is the theoretical M_s–T curve used to describe the experimental results. Because M_{Cr} and M_{Fe} have different temperature dependences, just like the illustrative M_{Cr} ($x = 0.8$) and M_{Fe} curves in figure 2, a compensation effect occurs. In other words, both M_{Cr} and M_{Fe} will increase with decreasing temperature; however, M_{Cr} is larger than M_{Fe} only in a certain temperature range and less than M_{Fe} in another temperature range. Because the magnetic moment of the Fe sublattice dominates at temperatures below T_{comp}, the net magnetization M_s in this temperature range is negative. Moreover, with further increasing Al content, accompanying the continuous decrease of M_{Cr}, one can expect the compensation effect to become more pronounced. As seen from the schematic representation in figure 2, with the Al content increasing to $x = 1.0$, T_{comp} moves to higher temperature, and the absolute value of the negative magnetization increases (curve b in figure 2). Clearly, Néel's model is qualitatively consistent with the FC magnetization in figures 1(b) and (c), but it cannot explain the multiple sign changes in the ZFC magnetization.

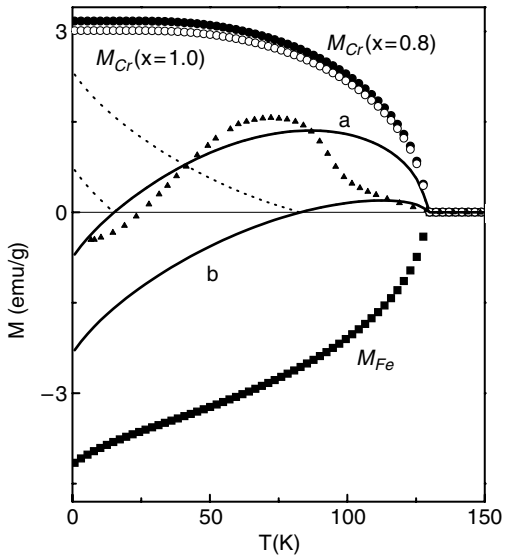

Figure 2. An illustration of Néel's two-sublattice model when x changes from 0.8 to 1.0; the values of M_{Cr} ($x = 0.8$) (solid circles, ●), M_{Cr} ($x = 1.0$) (open circles, ○), and M_{Fe} (solid squares, ■) are multiplied by 0.5. Solid triangles, ▲, show the experimental FC magnetization result for $x = 0.8$; curves a and b are illustrative M_{s}–T curves for $x = 0.8$ and 1.0, respectively; the two dashed curves denote the temperature dependences of $|M_{\mathrm{s}}|$ for $x = 0.8$ and 1.0, respectively.

In the above picture, keep in mind that the motion of the magnetic domain is not involved. However, as is known, in a magnetic field, the total energy of a magnet is at its lowest when the magnetic moment is aligned parallel to the magnetic field. Clearly, if the magnetic domain could be set in motion freely, the compensation effect would manifest itself as shown by the dashed curves in figure 2, because a magnet with a net magnetic moment opposing the applied field is energetically unfavourable.

However, in our previous work, study of the magnetic hysteresis loop in $FeCr_{2-x}Al_xS_4$ ($0 \leqslant x \leqslant 0.7$) revealed that the magnetic domain in these samples could not move easily, especially at lower temperatures. To examine whether the case is the same for $FeCr_{2-x}Al_xS_4$ ($x = 0.8$ and 1.0), we further performed hysteresis loop measurements. The hysteresis loops for $FeCr_{2-x}Al_xS_4$ ($x = 0.8$) at different temperatures are shown in figure 3. Clearly, the hysteresis loop at 5 K displays a large coercivity. With increasing temperature, the coercivity decreases quickly. The temperature dependence of the coercivity, H_{c}, for the $x = 0.8$ sample is shown in figure 1(b). For comparison, the temperature dependences of the coercivity, H_{c}, for $x = 0.6$ and 1.0 are also shown in figures 1(a) and (c), respectively.

It is noteworthy that the magnetic domain in a sample with a large coercivity cannot be set in motion easily. In the ZFC sequence, for the $x = 0.8$ sample, since no magnetic field is applied while cooling the sample through the ordering temperature, the magnetic domains are locked in random directions. When a small field of 0.005 T is applied at 5 K, which is not sufficient to rotate the magnetic domain, the resultant magnetization is positive and small because the energy of the system tends to be lowest in this case. In the two-sublattice model, as seen from figure 2, at temperatures below the compensation temperature, $|M_{\mathrm{s}}|$ decreases with increasing temperature; thus the ZFC magnetization decreases upon warming. With increasing temperature, on crossing the compensation temperature, the net magnetic moment will change sign from positive to negative because of the pinning of the magnetic domain,

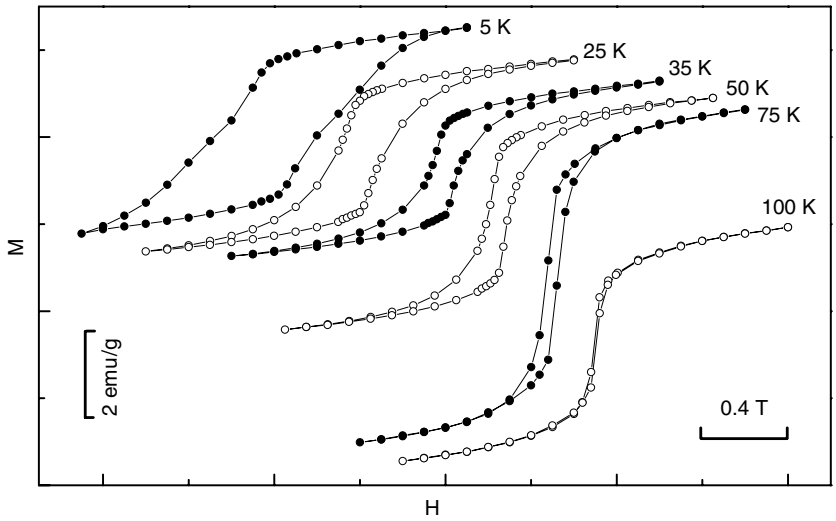

Figure 3. Hysteresis loops at different temperatures (5, 25, 35, 50, 75, and 100 K) for $x = 0.8$ with the maximum field of 1.0 T.

where the magnetic domains are still locked in the original directions. With further increasing temperature, accompanying the quick reduction of the coercivity, the magnetic domain can be set in motion more easily. Thus at a certain temperature, the thermal fluctuation may overcome the magnetic frustration; as a result, the magnetic moment tends to be parallel with the applied field, and the magnetization increases and changes sign again. As seen from figure 1(b), the ZFC curve displays a cusp at a temperature near 95 K. Note that in this temperature range, a paramagnetic–ferrimagnetic (PM–FM) phase transition takes place; the Curie temperature T_C, defined as the peak temperature of the differential curves of the FC M–T curve, is 92.8 K. Moreover, the magnetic domain can be set in motion easily because the coercivity tends to zero at this temperature. Accordingly, the magnetization measured in this temperature range is modulated by at least two factors: one is the rotation of the magnetic domain, and the other is the variation of M_s with temperature. As seen from figure 1, the amplitude of the PM–FM transition for $x = 0.8$ is larger than that for $x = 1.0$. For $x = 0.8$, the coercivity tends to zero at temperatures where the PM–FM transition changes abruptly; however, for $x = 1.0$, the coercivity tends to zero at temperatures where the PM–FM transition just takes place. Consequently, the $x = 0.8$ sample has a cusp in its ZFC curve; however, the $x = 1.0$ curve just displays a bump.

During the FC process, the sample is cooled through its Curie temperature, T_C, in the presence of a magnetic field. Therefore the magnetic domains will be locked in a particular direction, depending on the strength of the applied field, as soon as the system is cooled below its ordering temperature. With temperature decreasing to 5 K, accompanying an increase of the coercivity, the magnetic domain state at higher temperatures is frozen. Because the rotation of magnetic domains is not involved, the magnetization in the FC sequence only changes sign once, in agreement with Néel's two-sublattice model just discussed above.

Clearly, by taking account of the magnetic domain freezing, both ZFC and FC magnetizations can be explained qualitatively. To overcome the freezing, a magnetic field greater than the coercive field is needed. Thus, in order to examine the reversal of the magnetic moment by a magnetic field, we further performed magnetization measurements in a field of 0.5 T (greater than the coercive field at 5 K for $x = 0.8$ and 1.0).

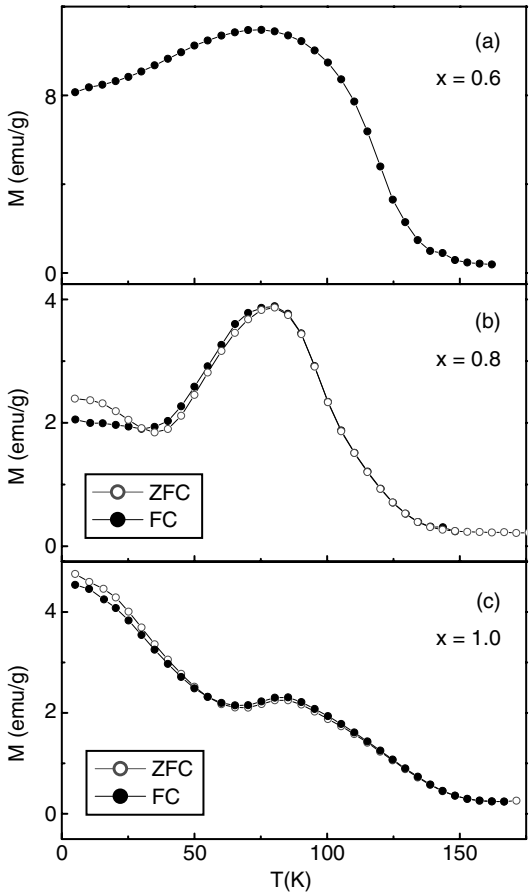

Figure 4. Zero-field-cooling (open symbols) and field-cooling (solid symbols) magnetization versus temperature curves for $FeCr_{2-x}Al_xS_4$ ($0.6 \leqslant x \leqslant 1.0$), measured at $H = 0.5$ T.

The temperature dependence of the high-field magnetization for all samples is shown in figure 4. As seen from figure 4, just as expected, no negative value is observed for any sample. Because the magnetic moment can be reversed by a field of 0.5 T, once they align anti-parallel with each other, the magnetization just displays a minimum at a temperature near T_{comp} and no negative value is observed, in qualitative accord with the dashed curves in figure 2.

As discussed in our previous work, the magnetic domain freezing in $FeCr_{2-x}Al_xS_4$ ($0 \leqslant x \leqslant 0.7$) can be attributed to two factors: one is the large magnetic anisotropy at lower temperatures; the other is the pinning of magnetic domain walls [7]. For $x = 0.8$ and 1.0 samples, both factors should also take effect and influence the movement of magnetic domains. For $x = 0.8$, because of the increase in the Al content with respect to that of the $x = 0.6$ sample, the contribution of domain wall pinning made by non-magnetic ions may increase. As a consequence, this sample has a larger coercivity at 5 K. The field of 0.5 T may be inadequate to overcome the magnetic frustration completely. Evidently, as seen from figure 4, $x = 0.8$ and 1.0 samples exhibit slight irreversibility between ZFC and FC magnetizations at lower temperature; however, this phenomenon is not observed for the $x = 0.6$ sample.

To conclude: the magnetic properties of $FeCr_{2-x}Al_xS_4$ ($0.6 \leqslant x \leqslant 1.0$) have been studied. The experimental results indicate that this system displays a large coercivity H_c at

low temperatures, which is a reflection of the magnetic domain freezing. With increasing temperature, accompanying an abrupt decrease of H_c, the magnetic domain motion is facilitated. By further taking account of the respective temperature dependences of M_{Cr} and M_{Fe}, the temperature-induced magnetization reversal in $FeCr_{2-x}Al_xS_4$ ($0.8 \leqslant x \leqslant 1.0$) has been explained qualitatively.

Acknowledgments

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