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Magnetization and magnetoresistive response of $LiMn_2O_4$ near the charge ordering transition

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We report magnetization and magnetoresistance studies of the geometrically frustrated spinel compound $LiMn_2O_4$ near its charge ordering temperature. The effect of a 7 T magnetic field is to very slightly shift the transition in the resistivity to lower temperatures resulting in large negative magnetoresistance with significant hysteresis. This hysteresis is not reflected in the magnetization. These observations are compared with what is found in the colossal magnetoresistance and charge ordering perovskite manganese oxides. The manner in which geometric frustration influences the coupling of charge and spin degrees of freedom is examined.

Introduction

There are a number of good reasons to study the spinel compounds LiM_2O_4 where M is an early transition metal. $LiTi_2O_4$ was the first oxide superconductor with a transition temperature exceeding 10 K.[1] LiV_2O_4 shows all the characteristics of a heavy Fermion system with an effective mass enhancement of the order of 100, the first d electron system to do so.[2] $LiMn_2O_4$, a very important positive electrode material for commercial Li-ion batteries[3] has been shown to display unequivocal crystallographic evidence for the real-space ordering of holes and electrons below a first order phase transition near the room temperature.[4] Such evidence has in fact been hard to come by in the recently much-examined colossal magnetoresistance (CMR) perovskite manganese oxides,[5] and the precise nature of ordering in Fe_3O_4, the first material in which the Verweij transition was realized,[6] remains unclear. Added to this is geometric frustration of nearest-neighbor antiferromagnetism inherent in the spinel structure type,[7] shown by Wills *et al.*[8] to manifest in $LiMn_2O_4$. The study of frustrated magnetic systems yields insights into ubiquitous and fundamental phenomena associated with complex potential energy landscapes.

Here we report aspects of $LiMn_2O_4$ including magnetization near the charge ordering transition, the effect on the charge ordering transition of relatively high magnetic fields and evidence thereof for the robustness of the charge ordered state, and finally, the demonstration of rather large negative magnetoresistance effects near the charge ordering transition. The negative magnetoresistance arises due to reasons that are very different from the effects seen in perovskite manganese oxides. The possibility of enhancing such MR effects are examined. Hysteresis is observed in the isothermal *R*–*H* traces on ramping the magnetic field at temperatures close to the phase transition. The origin of this hysteresis in the absence of any sort of spin ordering is delved into.

Experimental

The spinel samples were prepared as reported earlier[10] from Li_2CO_3 and manganese oxalate [$Mn(\textsc{ii})C_2O_4\cdot 2H_2O$] taken in suitable stoichiometric amounts. Well-ground powders were pre-fired in air at 1023 K for 24 h. This was followed by regrinding, pelletizing and firing in air for 12 h at 1073 K. Powder X-ray diffraction in the reflection ($\theta-2\theta$) geometry was recorded with $CuK\alpha$ radiation on a Siemens D5005 diffractometer and treated with Rietveld analysis as implemented in the XND computer code.[9] Mn oxidation states were determined through chemical titrations involving the Fe(II)/Fe(III) couple with the end-points being determined potentiometrically. The cubic spinel cell parameter at room temperature was $a = 8.244(7)$ Å and the oxygen x parameter was refined to 0.2623(5).

These values correspond closely with those reported in the literature.[11,12] Both the X-ray analysis and titrations suggest stoichiometric oxygen. The phase transition was followed by differential scanning calorimetry on a Perkin-Elmer DSC2C instrument employing heating and cooling rates of 20 K min^{-1}. Magnetic measurements were made on small pellets held in gelatine capsules in a Quantum Design MPMS SQUID magnetometer. Transport properties in zero and finite magnetic fields were measured by the four-probe technique on a Quantum Design PPMS system in fields up to 7 T.

Results

$LiMn_2O_4$ displays a strongly first order phase transition [Fig. 1(a)][12,13] near room temperature, observed by scanning calorimetry (DSC) to be centered around 280 K on cooling at 20 K min^{-1}. On heating, the same transition is centered around 295 K. The total width of both transitions is about 10 K. This transition manifests in the SQUID magnetic susceptibility as a slight enhancement [Fig. 1(b)]. The data were acquired on ramping the temperature under a 0.1 T field after cooling in zero field so the transition temperature is seen to correspond with the heating transition in the calorimetric trace. Inverse susceptibility suggests a nearly Curie–Weiss regime above the

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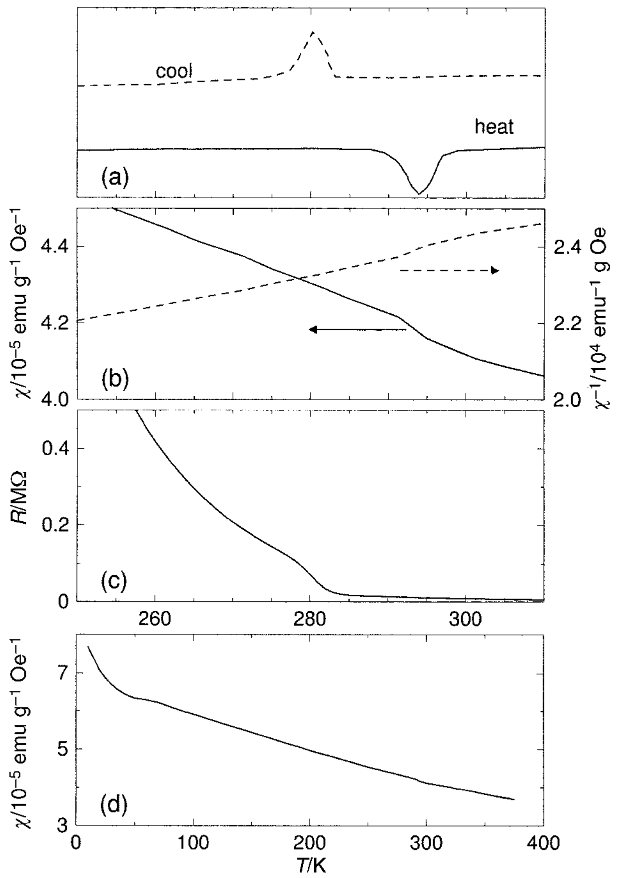

Fig. 1 (a) Scanning calorimetric traces of the charge ordering transition in $LiMn_2O_4$. (b) Magnetic susceptibility and its inverse acquired under a 0.1 T field on heating after cooling under zero field. (c) Four-probe electrical resistance near the charge ordering transition. (d) Magnetic susceptibility over a larger temperature range showing the onset of antiferromagnetic order around 60 K.

transition and between 320 K and 380 K, the data are fitted to the Curie–Weiss expression $1/\chi = T/C + \theta_{CW}/C$ with the values $\theta_{CW} = 299(1)$ K and $C = 4.50(5)$ emu K mol^{-1}. While θ_{CW} corresponds closely to the value reported by Wills *et al.*[8] and by Shimakawa *et al.*,[14] the C value which is indicative of the number of unpaired electrons differs from the quoted value (expected for spin-only $Mn^{3.5+}$) by about 7%. This discrepancy perhaps arises from the insufficiently small temperature range used here for the Curie–Weiss fit.

Fig. 1(c) displays the electrical resistance of $LiMn_2O_4$ in the region of the transition. The data were acquired on cooling the sample and the transition temperature therefore corresponds to the cooling transition observed in the DSC trace. At the transition, the resistivity suddenly jumps. Plots of ln(R) *vs.* $1/T$ confirm that both above and below the transition, the transport is activated. Across the transition, there is only a small change in the activation energy ($\approx$3900 K above the transition and $\approx$4400 K below). The situation is different in perovskite manganese oxides such as $Nd_{0.5}Sr_{0.5}MnO_3$[15] where charge ordering is associated with a large change in the activation energy since the transition is from a metallic high-temperature phase, to an insulating low-temperature phase.

Fig. 1(d) shows the temperature dependence of the magnetic susceptibility of $LiMn_2O_4$ in the temperature range 10–375 K on warming under a 1 T field after cooling in zero field. It is seen that apart from the small change corresponding to the charge ordering transition near 290 K, there is a small hump in the susceptibility corresponding to the onset of antiferromagnetic order near 60 K. The ratio ($\approx$5) of the Weiss intercept ($\theta_{CW} = 300$ K) to the Néel temperature (60 K) is indicative of magnetic frustration[7] as has been pointed out by Wills *et al.*[8]

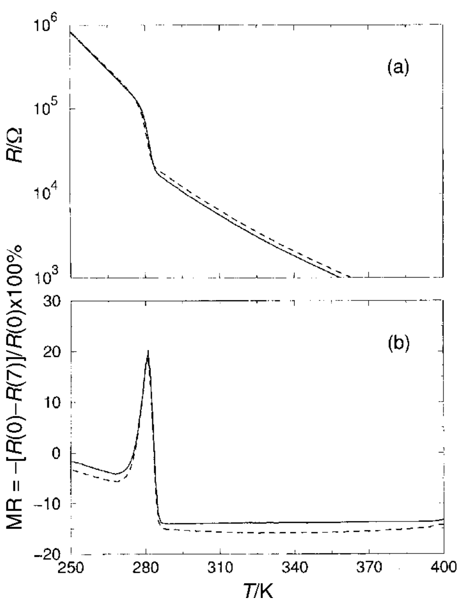

Fig. 2 (a) Electrical resistance of $LiMn_2O_4$ under zero field (solid line) and under a 7 T field (dashed line). (b) Magnetoresistance under a 7 T field of two separate samples of $LiMn_2O_4$.

Resistance measurements made in the absence and in the presence of a magnetic field [Fig. 2(a)] suggest that even a 7 T field has very little effect on the charge ordering transition. This suggests that charge ordering is rather robust in this system, in keeping with the strongly first-order nature of the transition. This robustness perhaps derives from significant structural distortions that take place at the transition associated with cooperative Jahn–Teller ordering of Mn(III) in the low-temperature phase.[4] Examining the transition closely (plotting the logarithm of the resistance as a function of temperature) we see that the effect of the 7 T field is to very slightly shift the transition to lower temperatures. Since at the transition, the change in the resistance is rather steep, the difference in the resistances and in the absence of a field translates into a rather large negative magnetoresistance [defined as $-[R(0) - R(7\ \mathrm{T})]/R(0) \times 100\%$] of about 20% at the transition temperature of 280 K. This is displayed in Fig. 2(b). The data were acquired on ramping the temperature in the presence of a magnetic field after cooling under zero field. Above and below the transition, the magnetoresistance is *positive* arising from transverse scattering of charge carriers by the magnetic field. Two traces are shown in this panel corresponding to independent measurements on samples from different preparative batches.

In order to better understand the magnetoresistance behavior, we have studied the isothermal resistance as a function of a ramped magnetic field at different temperatures. This is shown in Fig. 3. Once again, the data were acquired in steps of increasing temperature after cooling under zero field. At 250 K, which is below the transition, there is a small positive component in the magnetoresistance. At 270 K, large negative magnetoresistance is observed. This corresponds to the region of the negative magnetoresistance peak in Fig. 2(a). The behaviour at 270 K confirms that the magnetoresistance is intrinsic to the sample and is not a measurement artifact arising from some shift in the temperature scale between experiments. There is significant hysteresis in the magnetoresistance. In the absence of any corresponding hysteresis in the magnization (shown in Fig. 4), we must conclude that it arises from the magnetic field switching off the charge ordered state in the case of the 270 K magnetoresistance data. At higher temperatures, the magnetoresistance is positive. This arises from the manner in which the temperature-dependence of the resistivity is affected by the applied magnetic field as shown in Fig. 2(a). The data displays hysteresis, with the state at high magnetic field being frozen in

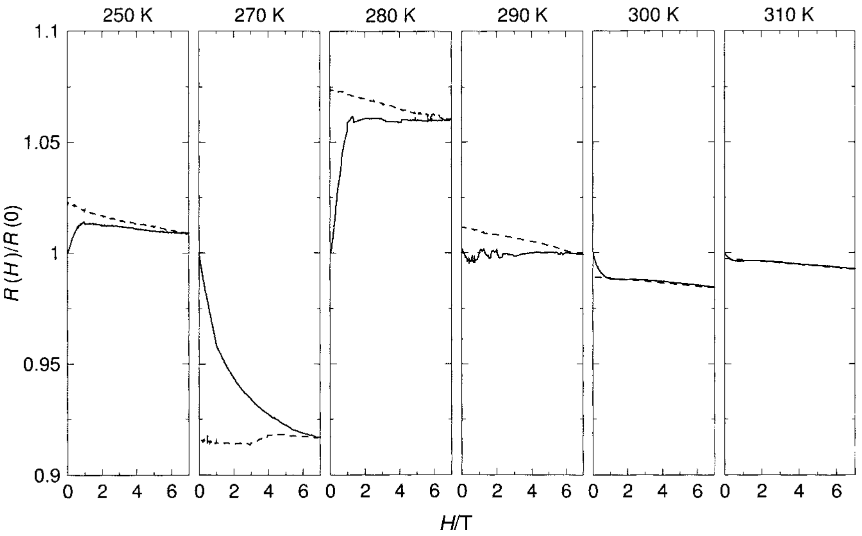

Fig. 3 Isothermal resistance of $LiMn_2O_4$ scaled to the zero-field value as a function of a ramped magnetic field. The different temperatures at which the data were acquired are indicated. The solid line is on ramping up the field while the dashed line corresponds to the field being ramped down.

after a certain critical field so that on ramping down the field, the resistance is nearly unchanged from the high field value. At temperatures higher than the transition, the effects of a magnetic field are small and there is little or no hysteresis.

In Fig. 4, magnetization traces corresponding to the temperatures at which the isothermal magnetoresistance traces were acquired are displayed. It is seen that the samples are paramagnetic in this region with little or no hysteresis, and no evidence for any sort of magnetic ordering, through a metamagnetic transition for example.

Discussion

The application of a 7 T field results in very little change in the charge ordering behavior of $LiMn_2O_4$ except to lower the transition temperature very slightly. This slight lowering of the transition temperature is sufficient to yield 20% negative magnetoresistance. Isothermal magnetoresistance studies near the transition indicate that it is highly hysteretic. This hysteresis arises because the field is able to switch the system from the charge ordered state to the normal state. This takes place at a region in the *R*–*H* trace that has a large slope, so the ensuing effects are significant. Since there is only a very small change in the magnetization (or the magnetic susceptibility) near the charge ordering transition temperature, the switching of the charge ordered state does not translate into large hysteresis effects in the field dependence of the magnetization.

It is instructive to compare the present system with the charge ordering perovskite manganese oxides.[5] These typically have the formula $RE_{0.5}A_{0.5}MnO_3$ where RE is a trivalent rare-earth cation and A is a divalent alkaline earth cation. The average radius of A and RE can be tuned either through selecting different combinations of rare-earth and alkaline-earth cations or by tuning x in a system such as $RE^1_{0.5-x}RE^2_xA_{0.5}MnO_3$ where RE^1 and RE^2 are trivalent rare-earth cations of differing sizes. The average size of these cations modulates the Mn–O–Mn bond angle and thereby, the width of the conduction band derived from Mn e_g states and O p states. Decreasing this bandwidth tunes the nature of the transition (coming from high to low temperatures) as follows. (i) Paramagnetic insulator to ferromagnetic metal when the bandwidth (and the average size of the cations) is large. There is no charge ordering in such systems. (ii) Ferromagnetic metal to antiferromagnetic insulator associated with charge ordering when the average 9-coordinate Shannon[16] radius is of the order of 1.25 Å. (iii) Charge-ordered paramagnetic insulator to antiferromagnetic insulator when the average size and therefore the bandwidth are small, of the order of 1.15 Å. In case

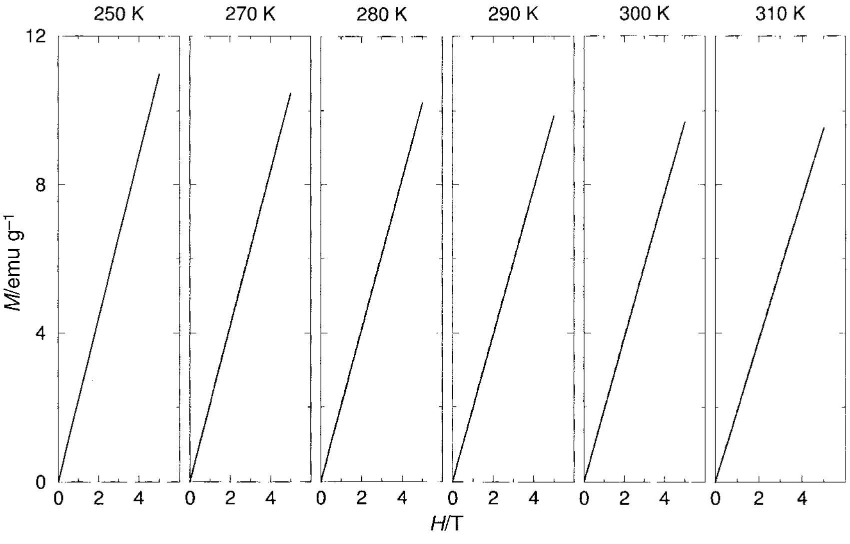

Fig. 4 Isothermal magnetization of $LiMn_2O_4$ as a function of a ramped magnetic field. The different temperatures at which the data were acquired are indicated. The solid line is on ramping up the field while the dashed line corresponds to the field being ramped down.

(iii), charge and spin degrees of freedom are somewhat decoupled, and even large magnetic fields cannot destroy charge ordering, unlike for case (ii) which corresponds to systems such as $Nd_{0.5}Sr_{0.5}MnO_3$.[15,17] With edge-shared MnO_6 octahedra, the bandwidth in $LiMn_2O_4$ is intrinsically small and the behavior corresponds to case (iii). Geometric frustration of nearest-neighbor antiferromagnetic interactions[7] additionally helps decouple charge and spin degrees of freedom so that even though charge ordering takes place near 300 K, which is θ_{CW}, the observed Néel temperature is only 60 K.

The present study establishes negative magnetoresistance in $LiMn_2O_4$ with magnitudes of about 20% near the charge ordering transition temperature of 280 K under a 7 T magnetic field. The magnetoresistance arises through a slight lowering of the temperature at which charge ordering takes place on the application of a strong magnetic field. The nature of the charge ordering in terms of its robustness, the semiconducting behavior both above and below the transition and the decoupling of charge and spin degrees of freedom in terms of distinct resistive and magnetic ordering transitions suggest a resemblance between the present system and those perovskite manganese oxides with small tolerance factors and therefore small conduction bandwidths. The widening of the bandwidth in the present system through suitable chemical substitution and likewise, the introduction of ferromagnetic (or ferrimagnetic) coupling could result in enhanced magnetoresistance effects. Effects to this end are in progress.

Acknowledgements

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