J|A|C|S
COMMUNICATIONS

Published on Web 02/13/2004

Crossover from Positive to Negative Magnetoresistance in a Spinel

Dinah R. Parker,[†] Mark A. Green,*[,†] Steven T. Bramwell,[†] Andrew. S. Wills,[†] Jason S. Gardner,[‡,§] and Dan A. Neumann[§]

The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, U.K., Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ U.K., Brookhaven National Laboratory, Upton, New York 11973, and NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562

Received June 29, 2003; Revised Manuscript Received January 13, 2004; E-mail: mark@ri.ac.uk

A correlation between the magnetic and electrical response of a material is an essential property in a diverse range of technological applications, including magnetic sensors such as read head devices in computer hard disks. Recent advances in the science of modern materials have identified systems such as the manganate perovskites and pyrochlores that show potentially useful magnetoresistance (MR) effects.[1,2] Here we report highly unusual magnetotransport behavior with MR > 80% in the spin glass-like material $Zn_{0.95}Cu_{0.05}Cr_2Se_4$, which undergoes a field-induced transition to a long-range ordered ferromagnet. The magnetoresistance changes sign with temperature, demonstrating a new mechanism for colossal magnetoresistance (CMR) that is particularly sensitive to low magnetic fields.

Two series of materials have been shown to possess attractive magnetoresistance properties. First are the manganate perovskites of general formula $Ln_{1-x}A_xMnO_3$ (Ln = lanthanide, A = alkaline earth metal) containing a mixture of Mn^{3+} and Mn^{4+} ions whose partially filled e_g orbitals create ferromagnetic coupling mediated by electrons hopping, the so-called "double exchange" mechanism.[3] Second are the pyrochlore manganates, which contains only Mn^{4+} ions therefore precluding double exchange.[2,4,5] The CMR characteristics in this case are thought to derive from field-induced changes to the indirect scattering of conduction electrons by the distinct localized Mn^{4+} t_{2g} levels. Large magnetoresistance effects are also known in related systems, including the spinel chalcogenide semiconductors such as $HgCr_{1.9}In_{0.1}Se_4$ (60% MR in 1.2 T field),[6] $Fe_xCu_{1-x}Cr_2S_4$ (20% MR in 6 T field),[7] and $CuCr_2Se_4$ (up to 4% MR).[8] The series of selenide spinels $Zn_{1-x}Cu_xCr_2Se_4$, though of a similar crystal structure, are a completely different class of material as regards electronic properties. The pioneering work of the Katowice groups,[9−15] and that of other groups,[16−21] has, over many years, revealed a rich and complex behavior in this series. This includes modulated magnetism and semiconducting properties at low values of x that transform, via a spin glass and ferromagnetic spiral structures, to a ferromagnetic metal at higher Cu content.[9,10] The observation of Cu in its 1+ oxidation state[13,22] means that substitution of Zn^{2+} with Cu^{+} oxidizes the Cr from an average oxidation state of Cr^{3+} to $Cr^{3.5+}$. The ferromagnetism at high Cu doping levels has been reported to originate from the double-exchange interaction,[10,22,23] which is so crucial to the CMR effect in the manganate perovskites, though the structure is more analogous to the pyrochlore, particularly with the presence of the acute Cr−Se−Cr bond angles.

Magnetic magnetization measurements show dramatic transformations across the $Zn_{1-x}Cu_xCr_2Se_4$ series. For compounds in the composition range $0 \le x < 0.07$, shown in Figure 1, the field-cooled magnetization shows a maximum around 25 K, which is known to be the temperature of a transition to a spiral magnetic structure in $ZnCr_2Se_4$. In this composition range, the doping with Cu causes a consistent increase in the magnitude of the magnetization commencing at temperatures significantly above the maximum at around 100 K. The divergence between the zero-field-cooled and field-cooled magnetization in $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ (shown as an inset in Figure 1) is suggestive of a spin glass-like state below 25 K, though one that is heavily affected by cooling the sample in a magnetic field, revealing potentially interesting field induced transitions.

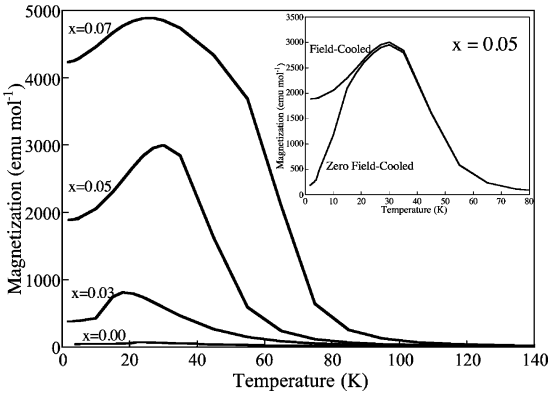

Figure 1. Magnetization measurements of $Zn_{1-x}Cu_xCr_2Se_4$ ($0 < x < 0.07$) cooled in an applied field of 100 G, showing an increase in magnetization at around 100 K, while retaining the maximum at around 25 K. The inset shows the difference between the zero-field and field-cooled magnetization of $Zn_{0.95}Cu_{0.05}Cr_2Se_4$, suggesting the ferromagnetic component transforms to a spin glass-like state when cooled in zero field.

To further probe the magnetic ground state of $Zn_{0.95}Cu_{0.05}Cr_2Se_4$, a series of powder neutron diffraction experiments were performed on the GEM instrument at ISIS, UK, with and without an applied magnetic field. Figure 2 shows a section of the diffraction pattern around the (111) reflection at 2 K. The bottom spectrum for $ZnCr_2Se_4$ shows two satellite reflections associated with the small nuclear contribution at 6.1 Å, originating from its spiral antiferromagnetic structure. The pattern for $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ in zero field shows no magnetic Bragg scattering at 2 K, confirming the lack of magnetic order, consistent with a spin glass-like state. This is understandable: the undoped material already reveals, by its incommensurate nature, competing ferro- and antiferromagnetic interactions. Doping adds additional (ferromagnetic) double-exchange interactions as well as the chemical disorder required for spin glass behavior. The application of a magnetic field drives the material into a ferromagnetic state, with magnetic scattering on the nuclear (111) reflection. A similar transition is known in some perovskite manganates.[24]

[†] Royal Institution and University College London.
[‡] Brookhaven.
[§] NIST.

10.1021/ja036965a CCC: $27.50

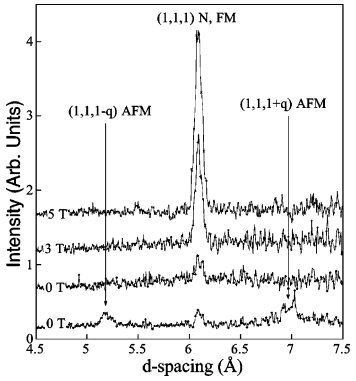

Figure 2. Neutron scattering of $ZnCr_2Se_4$ (bottom) showing the magnetic satellite reflections of the (111) associated with its modulated magnetic structure and $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ in 0, 3, and 5 T which shows no spontaneous order, but where the application of a magnetic field induces a transition to a ferromagnetic state.

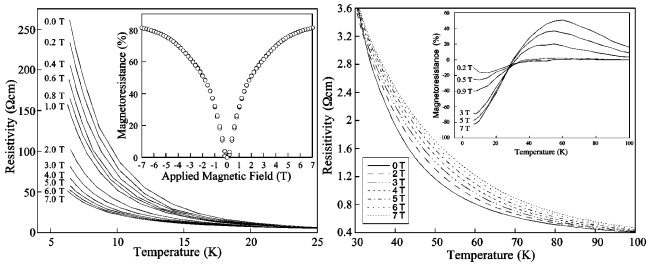

Figure 3. (Left) Magnetoresistance of $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ below 25 K, showing a negative colossal magnetoresistance effect. The inset shows the magnetoresistance effect during field cycling (−7 to 7 T) at 3.2 K. (right) Resistivity of $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ between 25 and 100 K with an increase in resistance on application of different applied magnetic fields. The inset shows the magnetoresistance both above and below the antiferromagnetic ordering temperature as a function of different applied magnetic fields.

Figure 3 (left) shows that the transport measurements of $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ below 25 K in different applied magnetic fields. The rapid increase in resistivity on decreasing temperature in zero field is indicative of thermally activated conduction. The resistivity decreases in increasing magnetic field but shows broadly similar temperature dependence. The MR was calculated from the resistivity (ρ) with and without a magnetic field and defined as, $MR = [\rho(0) - \rho(H)]/\rho(0)$. Notably, there is substantial magnetoresistance even in low magnetic field. This is particularly evident from the inset to Figure 3, which shows the magnetoresistance at $T = 3.2$ K as the magnetic field is swept from $\mu_0 H = 0$ T to 7 T, to −7 T and back to 0 T. About 40% magnetoresistance is achieved in fields of around 1.5 T, before reaching the maximum value of over 80% in the highest fields.

At temperatures above 25 K, where there is a large increase in the magnetization and deviation from the Curie−Weiss law, an extremely unusual magnetoresistance is observed. Figure 3 (right) shows the resistivity of $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ between 25 and 100 K in strong magnetic fields, with the inset showing the overall magnetoresistance from 3 to 100 K. There is now a significant *increase* in resistivity on application of the magnetic field as opposed to the reduction seen below 25 K. This positive magnetoresistance shows very different field-dependent magnitudes compared with the effect below 25 K; much larger magnetic fields now required to induce CMR, which reaches a maximum of 50% around 60 K in 7 T. There is further evidence that the change of sign of magnetoresistance is accompanied by a change in conduction mechanism. In the low-temperature regime, the temperature dependence of the resistance, $\rho(T)$, is much better described by Mott's expression for variable-range hopping conduction than it is by the expression for excitation of carriers across a fixed band gap.[25] Hence it seems likely that the low-temperature negative magnetoresistance is consistent with the variable range hopping of carriers between double-exchange clusters, which are enhanced in extent by an applied field. This interpretation is fully consistent with the reported magnetic behavior of this weakly Cu-doped sample[9,15] and with the competition of antiferromagnetism and double-exchange ferromagnetism envisaged by de Gennes.[23] In contrast, in the high-temperature regime of positive magnetoresistance, the semiconducting mechanism now provides a much better description of $\rho(T)$ than does Mott's variable range hopping scheme. This suggests that the dominant mechanism of conduction is the thermal activation of carriers across a band gap which swamps any residual double-exchange conduction. These compounds are unusual in this temperature regime in showing an enhanced ferromagnetic response to an applied field (evidenced by a positive Curie−Weiss temperature).[26] It is interesting to note potential similarities between the mechanism for magnetoresistance in $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ and the magnetic polaron explanation in, for example, EuSe.[27]

Acknowledgment. EPSRC for financial support and Professor P. Radaelli for assistance with neutron experiments.

Supporting Information Available: Fitting of the resistivity in the negative and positive magnetoresistance regimes. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Rao, C. N. R.; Cheetham, A. K. *Chem. Mater.* **1996**, *8*, 2421−2432.
(2) Shimakawa, Y.; Kubo, Y.; Manako, T. *Nature* **1996**, *379*, 53.
(3) Zener, C. *Phys. Rev.* **1951**, *82*, 403−405.
(4) Subramanian, M. A.; Toby, B. H.; Ramirez, A. P.; Marshall, W. J.; Sleight, A. W.; Kwei, G. H. *Science* **1996**, *273*, 81−84.
(5) Hwang, H. Y.; Cheong, S.-W. *Nature* **1997**, *389*, 942−944.
(6) Koguchi, N.; Masumoto, K. *J. Phys. Chem. Solids* **1980**, *41*, 1279.
(7) Ramirez, A. P.; Cava, R. J.; Krajewski, J. *Nature* **1997**, *386*, 156−159.
(8) Tsurkan, V. V.; Radautsan, S. I. *Jpn. J. Appl. Phys.* **1993**, *32*, 313.
(9) Grön, T.; Duda, H.; Warczewski, J. *J. Phys.* **1988**, *49*, 869.
(10) Krok, J.; Spalek, J.; Juszczyk, S.; Warczewski, J. *Phys. Rev. B* **1983**, *28*, 6499−6509.
(11) Juszczyk, S. *J. Magn. Magn. Mater.* **1988**, *72*, 67−70.
(12) Juszczyk, S.; Johansson, C.; Hanson, M.; Gogolowicz, M. *Phys. Lett. A* **1994**, *192*, 429−434.
(13) Juszczyk, S.; Gogolowicz, M. *J. Magn. Magn. Mater.* **1991**, *92*, 388−396.
(14) Okonska-Kozlowska, I.; Jedrzejewska, I.; Wokulska, K. *J. Alloys Compd.* **1995**, *219*, 100−102.
(15) Grön, T.; Duda, H.; Warczewski, J. *Phys. Rev. B* **1990**, *14*, 12424.
(16) Akimitsu, J.; Siratori, K.; Shirane, G.; Iizumi, M.; Watanabe, T. *J. Phys. Soc. Jpn.* **1978**, *44*, 172−180.
(17) Baltzer, P. K.; Wojtowicz, P. J.; Robbons, M.; Lopatin, E. *Phys. Rev.* **1966**, *151*, 367−377.
(18) Colominas, C. *Phys. Rev.* **1967**, *153*, 558−560.
(19) Hamedoun, M.; Hourmtallah, A.; Sayouri, S.; Chatwiti, A. *J. Phys.: Condensed Matter* **1995**, *7*, 5359−5363.
(20) Hidaka, M.; Yoshimura, M.; Takahashi, S.; Watanabe, S.; Akimitsu, J. *Phys. Status Solidi B−Basic Res.* **2003**, *236*, 209−218.
(21) Hidaka, M.; Tokiwa, N.; Wai, T. T.; Fujii, H.; Ohoyama, K.; Mizusima, S.; Sakaurai, J.; Ichikawa, F.; Itoh, K. *Phase Transit.* **2002**, *75*, 273−287.
(22) Lotgering, F. K.; van Stapele, R. P. *J. Appl. Phys.* **1968**, *39*, 417−423.
(23) De Gennes, P.-G. *Phys. Rev.* **1960**, *118*, 141−154.
(24) Sundaresan, A.; Maignan, A.; Raveau, B. *Phys. Rev. B* **1997**, *55*, 5596.
(25) Mott, N. F. *Metal−Insulator Transitions*; Taylor & Francis: London, 1990.
(26) Plumier, R.; Lecomte, M.; Miedan-Gros, A.; Sougi, M. *Phys. Lett.* **1975**, *55A*, 239−241.
(27) Shapira, Y.; Foner, S.; Oliveira, N. F.; Reed, T. B. *Phys. Rev. B* **1974**, *10*, 4765.

JA036965A