Anomalous magnetic behavior in single-crystal $La_{0.9}Sr_{0.1}MnO_3$

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We report detailed magnetization studies of single-crystal samples of $La_{0.9}Sr_{0.1}MnO_3$. This perovskite compound undergoes a paramagnetic-insulator to ferromagnetic-insulator transition around 150 K and then a transition to a canted antiferromagnetic insulating state at 110 K [H. Kawano *et al.*, Phys. Rev. B **53**, R14 709 (1996)]. Magnetization data show a strong anomaly in the temperature range from 105 to 118 K. There is a sharp increase in magnetization around 110 K and the temperature of this transition increases with an increase in magnetic field. The field dependence of the magnetization suggests a field-induced magnetic transition in the temperature range of 105–118 K with a large magnetic entropy change. [S0163-1829(98)08437-9]

I. INTRODUCTION

During the past year we have concentrated on studying the magnetic transition, the field-dependent microwave loss [electron paramagnetic (PM) resonance[1] for $T>T_C$, ferromagnetic (FM) resonance (FMR) (Ref. 2), and ferromagnetic antiresonance (FMAR) (Ref. 3) for $T<T_C$] and dc magnetization[4] in single crystals of $La_{1-x}Sr_xMnO_3$ with, nominally, $x=0.3$, 0.2, and 0.1. The (La, Sr)MnO_3 system is prototypical of the wide variety of manganites which are under intense scrutiny because (i) they exhibit colossal magnetoresistance,[5,6] which makes them attractive for applications and (ii) they present interesting challenges to our fundamental understanding of strongly correlated electron systems. Their complexity has led various investigators to invoke double exchange (DE),[7,8] Jahn-Teller distortions,[9] magnetic polarons,[10] superexchange, and combinations thereof[11] to account for specific observations. The properties are rather sensitive to homogeneity. Single-crystal specimens are essential and even then one has to be extremely careful. In our experiments, attempts were made to measure all the properties on the same sample. For the $x=0.3$ system, which is probably the best candidate for DE, careful study of the PM-FM transition ($T_C\approx 360$ K), using several techniques shows that it is continuous and second order, the critical exponent for the magnetization, β being 0.4.[3] Apart from an early mean field estimate,[12] there is no theoretical guidance regarding the value of β expected for a DE system. From the FMR studies it is clear that the magnetocrystalline anisotropy is very small, $H_{an}\approx 100$ Oe. The g value is close to 2 indicating weak spin orbit coupling. The intrinsic linewidth is $\leqslant 50$ Oe at 10 GHz.

In the $x=0.2$ material, again, a thorough study of the PM-FM transition yields a sharp second order transition at $T_C=302$ K with $\beta\approx 0.40$. The most interesting result in this case is that the peak temperature in the resistivity (ρ) vs temperature (T) curve lies nearly 20 K above T_C showing unequivocally that long-range spin alignment is not essential to the observed drop in ρ, and the concomitant quasimetallic T dependence, for $T<T_p$.[13] This observation presents an interesting challenge to models which tie the so called metal-insulator transition to T_C and the onset of ferromagnetism. FMR data are consistent with $g\approx 2$ and a weak crystalline anisotropy but the lines are not particularly narrow.

The $x=0.1$ single-crystal material is the subject of the present investigation. This material has been studied previously and exhibits the following properties of interest: (a) Urushibara *et al.*[14] found that it is orthorhombic and undergoes a paramagnetic to ferromagnetic transition at 145 K. They proposed that for $T<T_C$, it is a ferromagnetic insulator. (b) Kawano *et al.*,[15] using neutron scattering also obtained $T_C\approx 150$ K but interpreted their low-T data to suggest that for $T\leqslant 110$ K the material was a canted antiferromagnet, perhaps of the kind originally proposed by De Gennes[11] who invoked the competition between double exchange and superexchange to get two transitions in the dilute mixed manganite. (c) Anane *et al.*[16] made magnetization measurements which indicate that the material has sizable magnetocrystalline anisotropy and a somewhat anomalous temperature dependence for M for $T\approx(T_C=40$ K). (d) Apart from a slight hesitation around 120 K, the resistivity exhibits activated behavior down to low temperature, with an activation energy of ≈ 140 meV, well in accord[17] with activation energies found in the other manganites for $T>T_C$. Our studies of the dc magnetization in a single crystal plate (0.3 mm thick and roughly 1 mm×2 mm in area) of the $x=0.1$ compound were initiated to further understand the magnetic state of this system for $T<T_C$. The results are truly unexpected. One finds that the field dependent dc magnetization exhibits strong anomalies in the temperature range 105–118 K. The magnetization anomalies may be related to subtle structural changes induced by the magnetic field. Magnetically field induced structural changes have been observed by Kawano

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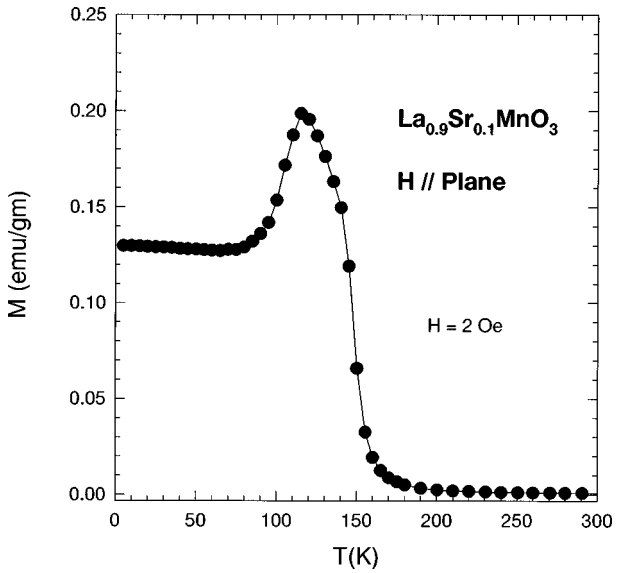

FIG. 1. Temperature dependence of the magnetization (M) of $La_{0.9}Sr_{0.1}MnO_3$ for applied field $H=2$ Oe.

et al.[15] in $La_{0.875}Sr_{0.125}MnO_3$ and Asamitsu *et al.*[18] in $La_{0.825}Sr_{0.175}MnO_3$.

II. EXPERIMENT

The $La_{0.9}Sr_{0.1}MnO_3$ crystal was grown by the floating zone technique at the Moscow State Steel and Alloys Institute. A detailed description of the sample preparation is given in Ref. 19. Both electron dispersive x-ray analysis and x-ray diffraction data showed the crystal to be homogeneous. A plate was cut from the single crystal boule so that the c axis is nearly normal to it. dc magnetization data were obtained by using a superconducting quantum interference device (Quantum Design Inc., model MPMS) magnetometer. Measurements were done with the magnetic field applied both parallel and perpendicular to the plane of the crystal. The temperature was stabilized to within 0.1 K in the range $5\ \mathrm{K}<T<300$ K. Field-dependent data were taken 30 min after stabilizing the temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the in-plane ($H\|$ to ab plane) magnetization for an applied field of 2 Oe. The data show that a ferromagnetic transition takes place around 150 K. This agrees with previous studies.[14] This transition has also been confirmed by our ac susceptibility measurements.[20] In addition, the low-field magnetization exhibits a peak around 120 K which would imply either that there is spin canting below 120 K or that the coercive field exceeds the applied field and rises rapidly with decreasing T. As shown in Ref. 20, the anisotropy field increases rapidly as T drops below 150 K, thus a rise in coercivity is highly likely. The low temperature anomalies become more marked with increasing field, as we shall see below.

Figures 2(a) and 2(b) show the magnetic isotherms at 140 K for in-plane and out-of-plane orientations, respectively. It is expected that for the latter case ''saturation'' should occur at $H=4\pi M$ ($\approx$2000 Oe in this case). In the former geometry for an isotropic material it is expected to saturate with the application of very small magnetic field. However, in this case, it takes close to 1.6 kOe to obtain technical saturation. This clearly indicates that there is a large magnetocrystalline anisotropy in this material and the ab plane is the ''hard'' plane. The same sample was studied by FMR techniques where it was shown that the in-plane demagnetization field is quite small. These measurements, which are reported in detail elsewhere,[20] confirm that the magnetocrystalline anisotropy is large ($\approx$kOe) with the c axis being the easy axis.

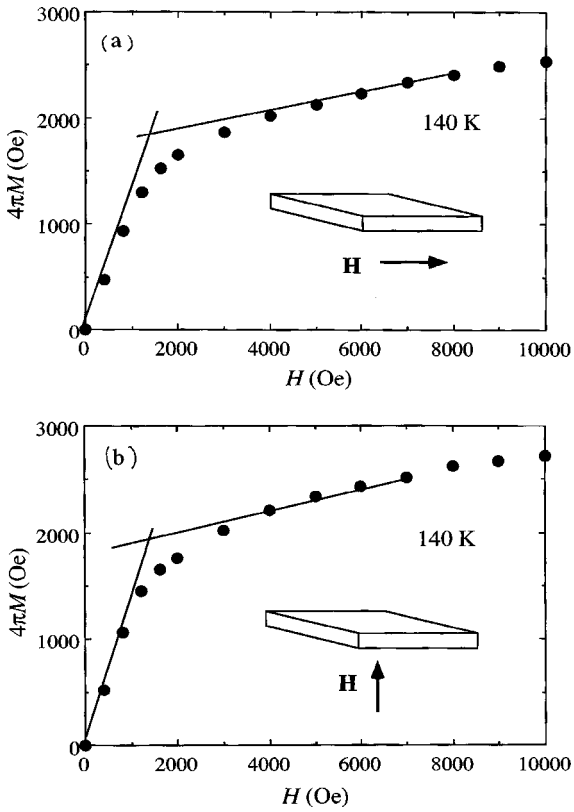

FIG. 2. M vs H at 140 K for (a) in plane magnetization, (b) out of plane magnetization.

Figure 3(a) shows the in-plane magnetic isotherms at several temperatures. At temperatures well below and well above the so-called canting transition temperature ($T_{CA}=110$ K), the behavior appears to be that of a normal ferromagnet. However, in the vicinity of T_{CA} the isotherms exhibit dramatically different behavior. To elucidate this further, Fig. 3(b) shows the isotherms for $100\leqslant T\leqslant 125$ K. In this regime the high-field magnetization exhibits a ''stepped'' response. That is, at 118 K, M begins to rise rapidly (see arrow) when H exceeds 35 kOe. At 116 K, there are two steps located at about 30 and 40 kOe and finally at 112 K one observes three steps at $\approx$15, 28, and 40 kOe. To our knowledge, this is the first observation of multiple magnetic anomalies in the (H,T) plane of a dilute manganite.

Another instructive method for displaying these M vs H anomalies is to look at the isochamps (const H,M vs T curves) shown in Fig. 4. Starting around $T_C(=150\ \mathrm{K})$ the magnetization increases roughly as expected for a ferromagnet when T is lowered. However, for T around 110–120 K, depending on the applied field, there is a sharp increase in M before the M vs T curve essentially flattens at lower tem-

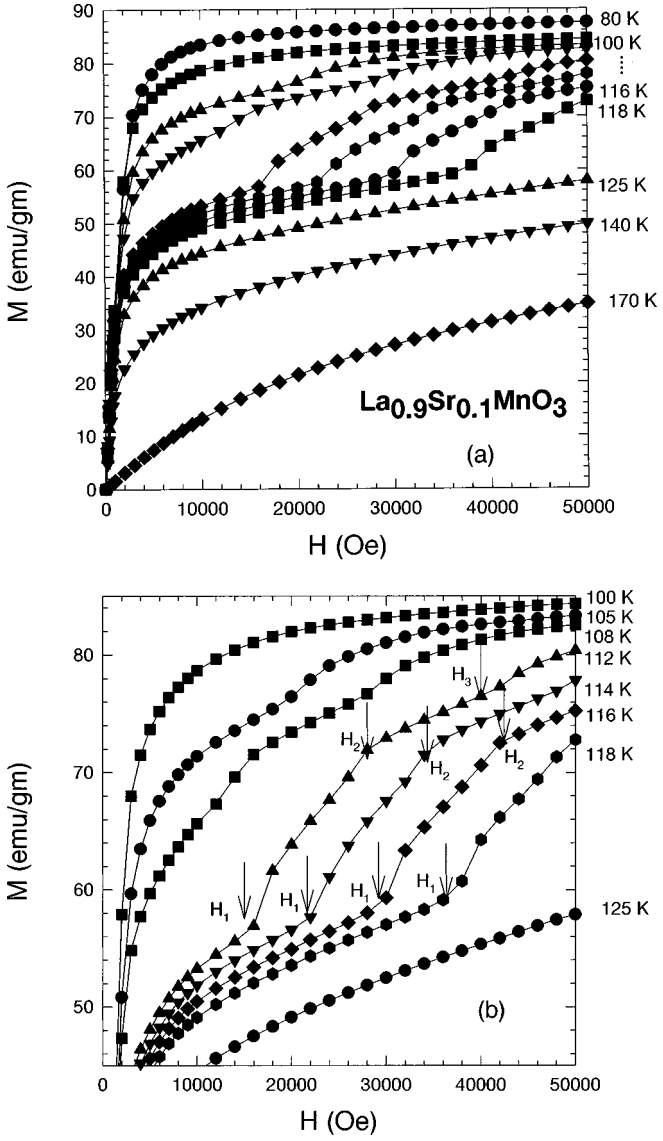

FIG. 3. (a) M vs H at different temperatures. Anomalous behavior between 105–118 K is discussed in the text. (b) Same plot as (a) with expanded scale in the temperature range between 100–125 K.

peratures. This field-induced transition temperature $T_1(H)$ clearly rises with increasing H.

A sharp change in $(dM/dT)_H$ has immediate thermodynamics implications. The magnetic entropy must exhibit a jump. Using a Maxwell relation the change in the magnetic entropy $\Delta S_M(T,H)$ is given by

$$\Delta S_M(T,H)=S_M(T,H)-S_M(T,0)=\int_0^H (dM/dT)_H dH \tag{1}$$

and the results derived from the data of Figs. 3(a) and 3(b) are summarized in Fig. 5 for $H=16$ kOe. Near T_C, ΔS_M varies rather smoothly. However, around T_1, ΔS_M exhibits a large peak. In particular, $\Delta S_M(50\text{ kOe},110\text{ K})\approx 6.5$ J/kg K. This remarkable large value is comparable to that reported for Gd (Ref. 21) as well as polycrystalline samples of

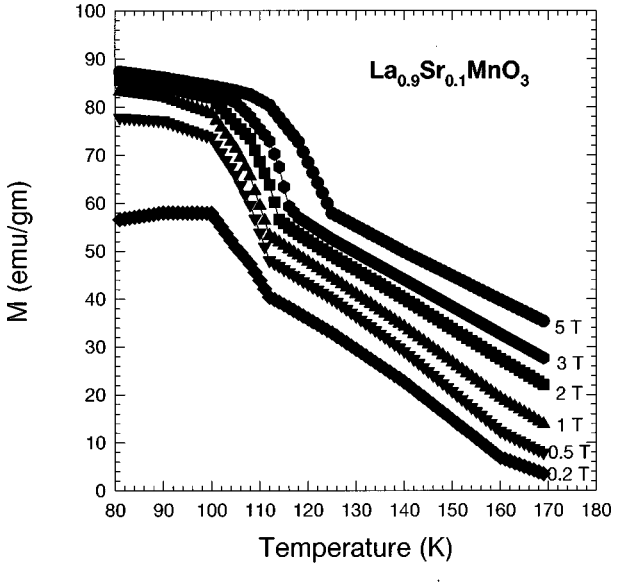

FIG. 4. M vs T at different applied magnetic fields. The sharp increase in M for T between 110–120 K increases in temperature with increase in the applied magnetic field.

$La_{0.8}Ca_{0.2}MnO_3$ (Ref. 22) and suggests[22] that the perovskite manganese oxides should be suitable candidates as magnetic refrigerants.

The magnetic anomalies noted above are not fully understood in so far as one cannot write explicit expressions to reproduce the data. However, it is clear that the transition around 110 K is not a simple change from ferromagnetic alignment to a spin canted state as was proposed in Ref. 15, especially in the presence of a magnetic field. The steps provide unequivocal evidence that the transitions are toward more fully aligned spin configurations. Some clues as to the possible origin of these unexpected phenomena is to recall that in other dilute $La_{1-x}Sr_xMnO_3$ materials there are subtle

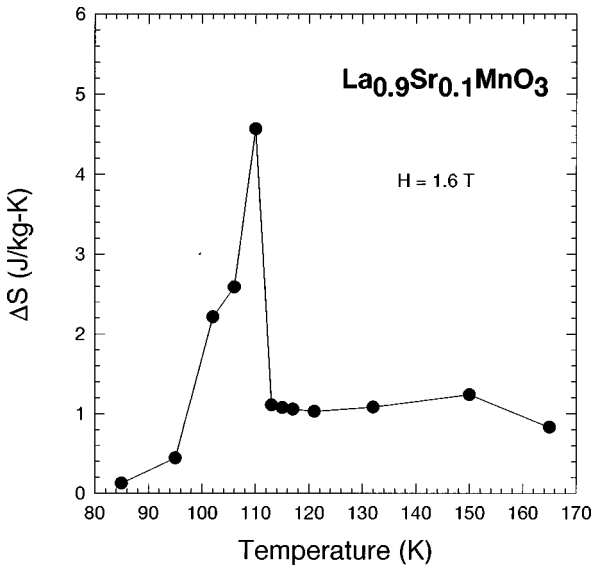

FIG. 5. Change in magnetic entropy (ΔS_M) vs temperature at a magnetic field $H=1.6$ kOe. The temperature of the maximum magnetic entropy change is at 110 K, close to the canted AF transition temperature.

structural transitions within the ferromagnetic phase.[15] Also, in $La_{0.825}Sr_{0.125}MnO_3$, a large structural transition, from a rhombohedral to an orthorhombic phase, is induced by a magnetic field.[18] It is also generally held that in the manganites the onset of spin alignment is accompanied by a release of Jahn-Teller distortion (which in turn promotes greater overlap). All of these taken together lead us to propose that in the present material the steps in the magnetization are caused by field-induced structural changes. The structural effects may be quite small and probably will require very careful diffractometry to determine unequivocally.

IV. CONCLUSIONS

In summary, we have made detailed magnetization studies below T_C and close to the canting transition temperature (T_{CA}) in single crystal $La_{0.9}Sr_{0.1}MnO_3$. The magnetization data show large anomalies around 110 K and the temperature at which this occurs increases with magnetic field. They do not support the idea[15] that the 110 K transition leads to a spin canted state. A remarkably large magnetic entropy change is associated with this phenomenon. These anomalies are most likely due to subtle changes in the crystal structure induced by a magnetic field.

[1] S. E. Lofland *et al.*, Phys. Lett. A **233**, 476 (1997).

[2] S. E. Lofland *et al.*, J. Appl. Phys. **81**, 5737 (1997).

[3] S. E. Lofland, V. Ray, P. H. Kim, S. M. Bhagat, A. Manheimer, and S. D. Tyagi, Phys. Rev. B **55**, 2749 (1997).

[4] V. N. Smolyaninova, J. J. Hamilton, R. L. Greene, Y. Mukovskii, S. G. Karabashev, and A. M. Balbashov, Phys. Rev. B **55**, 5640 (1997).

[5] R. von Helmolt *et al.*, Phys. Rev. Lett. **71**, 2331 (1993); K. Chahara *et al.*, Appl. Phys. Lett. **63**, 1990 (1993); S. Jin *et al.*, Science **264**, 413 (1994).

[6] H. L. Ju, C. Kwon, Qi Li, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **65**, 2108 (1994).

[7] C. Zener, Phys. Rev. **82**, 403 (1951).

[8] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[9] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); A. Shengelaya *et al.*, *ibid.* **77**, 5296 (1997); Guo-meng Zhao *et al.*, Nature (London) **381**, 676 (1996).

[10] J. M. De Teressa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. del Moral, and Z. Arnold, Nature (London) **386**, 256 (1997).

[11] P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

[12] K. Kubo and N. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972).

[13] S. E. Lofland, S. M. Bhagat, K. Ghosh, R. L. Greene, S. G. Karabashev, D. A. Shulyatev, A. A. Arsenov, and Y. Mukovskii, Phys. Rev. B **56**, 13 705 (1997).

[14] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Takura, Phys. Rev. B **51**, 14 103 (1995).

[15] H. Kawano, R. Kajimoto, M. Kubota, and H. Yoshizawa, Phys. Rev. B **53**, R14 709 (1996).

[16] A. Anane *et al.*, J. Phys.: Condens. Matter **7**, 7015 (1995).

[17] G. C. Xiang *et al.*, Solid State Commun. **97**, 599 (1996).

[18] A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Ariama, and Y. Tokura, Nature (London) **373**, 407 (1995).

[19] A. M. Balbashov, S. G. Karabashev, Y. M. Mukovskii, and S. A. Zverkov, J. Cryst. Growth **167**, 265 (1996).

[20] S. E. Lofland, V. Ray, P. H. Kim, S. M. Bhagat, K. Ghosh, R. L. Greene, S. G. Karabashev, D. A. Shulyatev, A. A. Arsenov, and Y. Mukovskii, J. Phys.: Condens. Matter **9**, L633 (1997).

[21] T. Hashimoto, T. Numasawa, M. Shino, and T. Okada, Cryogenics **21**, 647 (1981).

[22] Z. B. Guo, Y. W. Du, J. S. Zhu, H. Huang, W. P. Ding, and D. Feng, Phys. Rev. Lett. **78**, 1146 (1997).