Single-crystal neutron-diffraction study of a structural phase transition induced by a magnetic field in $La_{1-x}Sr_xMnO_3$

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(Received 7 November 1996)

The compound $La_{1-x}Sr_xMnO_3$ undergoes structural and magnetic phase transitions as a function of temperature and pressure. The temperature at which the structural phase transition from a high-temperature rhombohedral phase to a low-temperature orthorhombic phase takes place is very sensitive to the level of doping (x) and pressure, the magnetic transition temperature to a ferromagnetically ordered state less so. Recent magnetostriction and resistivity measurements have suggested that the structural transition may also be driven by the application of a magnetic field. We have performed single-crystal neutron-diffraction experiments which confirm that by carefully controlling the level of doping the structural phase transition can be induced at constant temperature by application of a magnetic field. [S0163-1829(97)50514-5]

Recently there has been considerable interest in the magnetoresistance of oxides of the type $R_{1-x}A_xMnO_3$ where R is a rare earth and A is an alkaline earth. These include $La_{1-x}Sr_xMnO_3$, which exhibits a range of structural and magnetic phase transitions as a function of temperature and pressure, with transition temperatures which depend strongly on the level of doping x.

The parent compound $LaMnO_3$ is an antiferromagnetic insulator containing Mn^{3+} ions. Replacing a fraction x of the La ions with divalent Sr changes an equivalent amount of Mn^{3+} ions to Mn^{4+} ions. This results in a ferromagnetic ground state with a Curie temperature (T_c) which increases from 238 to 283 K with a small change in doping from $x=0.150$ to 0.175. This behavior is qualitatively explained in terms of the double exchange interaction[1–3] between the Mn^{3+} and Mn^{4+} ions, which is mediated via a neighboring oxygen atom; however, double exchange alone cannot explain the magnitude of the magnetoresistance.[4]

The structural phase transition in $La_{1-x}Sr_xMnO_3$ is from a high-temperature rhombohedral phase ($R3c$) to a low-temperature orthorhombic phase ($Pbnm$). In contrast to T_c the temperature, T_s, at which this structural phase transition takes place, decreases rapidly with increasing x. For example x increases from 0.15 to 0.175, T_s falls from 380 to 190 K.

In a recent study by Asamitsu *et al.*[5] of $La_{1-x}Sr_xMnO_3$ ($x=0.17$), which included resistivity, striction, and x-ray diffraction measurements as a function of temperature and magnetic field, it was suggested that for a suitable range of doping levels, the structural phase transition observed in these materials could be induced, at a fixed temperature, by the application of a magnetic field. In order for this field-induced transition to take place, T_c and T_s have to be similiar, with T_c below T_s. It was reasoned that in the orthorhombic phase, the Mn-O-Mn bond angle is distorted (away from 180°), reducing the electron transfer interaction. Near T_c, the application of a magnetic field increases this interaction by fully aligning the spins favoring the formation of the rhombohedral phase in which the Mn-O-Mn bond angle is 180°. In this paper we describe neutron-diffraction experiments which give the first direct observation of this transition.

Single crystals of $La_{1-x}Sr_xMnO_3$ with $x=0.165$ and 0.170 were grown from polycrystalline rods of these compositions in an infrared image furnace using the floating-zone method. The precursor materials were prepared using stoichiometric quantities of La_2O_3, $SrCO_3$, and MnO_2. The powders were ground and calcined three times at 1300 °C for 12 h and then pressed into rods which were sintered at 1400 °C for 12 h. The crystal growth was carried out in air at a speed of 6–8 mm/h. Crystals measuring approximately $2\times2\times7$ mm^3 were cut from the grown boule for the neutron-diffraction experiments.

X-ray Laue photographs showed that the samples were high-quality single crystals. The single crystals were characterized by measuring the temperature dependence of the ac susceptibility, magnetization, and resistivity. Figure 1 shows the resistivity and magnetization curves as a function of temperature for the single-crystal sample of $La_{0.835}Sr_{0.165}MnO_3$ used in this work. The magnetization curve shows a T_c of 264 K. The resistivity shows an increase at about 296 K. This change is associated with the structural transition from the rhombohedral to the orthorhombic phase. The curve shows hysteresis indicating the first-order nature of the structural transition. The large decrease at 264 K coincides with the onset of ferromagnetic order.

Neutron-diffraction measurements were carried out using the reactor source at the Institut Laue-Langevin in Grenoble, France. Preliminary measurements were carried out on the D10 single-crystal diffractometer. Measurements on a sample of $x=0.170$ composition showed a T_s of 183 K and a T_c of 283 K, while Asamitsu *et al.* quote a T_c of 264 K and a T_s of 290 K (Ref. 6) for the same composition. Our measurements on the $x=0.165$ crystal, however, gave a T_c of 264 K and a T_s of 295 K, making this sample identical to the crystal composition on which Asamitsu *et al.* performed

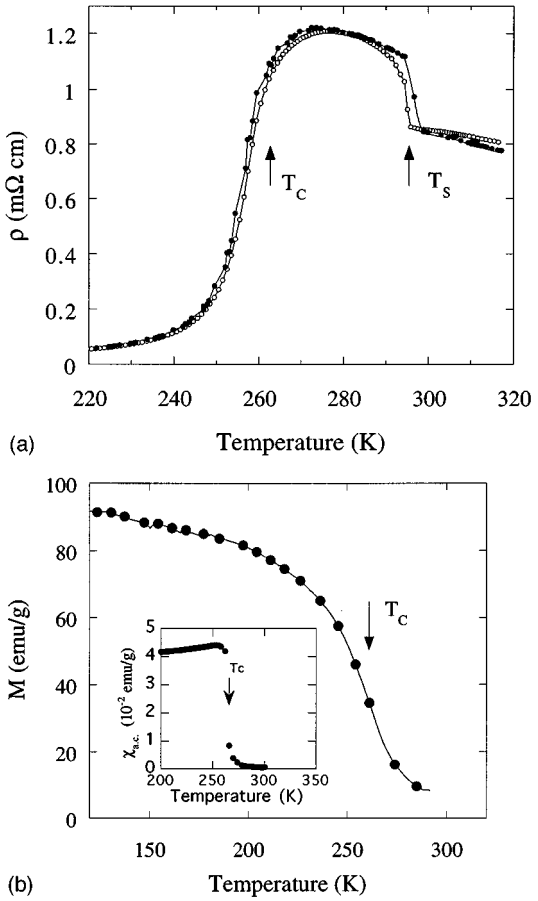

FIG. 1. (a) Resistivity, (b) magnetization, and inset, ac susceptibility of single-crystal $La_{0.835}Sr_{0.165}MnO_3$ as a function of temperature. The structural and magnetic phase transitions are marked with T_s and T_c respectively. (a) The resistivity was measured by a standard four-probe method; the open circles are for cooling and the filled circles are for warming. (b) The magnetization was measured using a vibrating-sample magnetometer in a 1-T field and the ac susceptibility using a standard magnetic inductance technique with a frequency of 403 Hz and a field of 7 Oe.

their switching experiment. To determine the temperature of the structural phase transition the intensity of the orthorhombic [4 4 5] and [2 0 0] reflections were measured as a function of temperature for a crystal of the $x=0.165$ composition. The [4 4 5] reflection is only present in the low-temperature orthorhombic phase and a measurement of its intensity can be used to determine the temperature of the structural phase transition. The T_s of 295 K for the $x=0.165$ crystal agrees well with the resistivity data and is hysteretic with a width of 5 K [see also resistivity data in Fig. 1(a)]. The [2 0 0] is a weak nuclear reflection which shows a large increase in intensity at the onset of the ferromagnetically ordered state. This measurement indicates a T_c of 264 K.[7] The crystal structure was refined in both the low-temperature and high-temperature phases and the results will be published separately. From the measured transition temperatures, it was clear that the $x=0.165$ sample satisfied the proposed criteria for observing the field-induced structural transition, i.e., that T_c and T_s are close together with T_c below T_s.

The experiments to directly observe the field-induced switching of the crystallographic structure were carried out

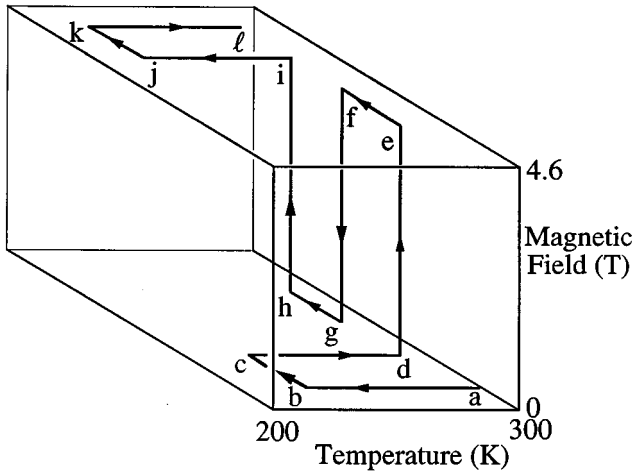

FIG. 2. Schematic representation of the chronological sequence of temperature and magnetic-field variations on the single-crystal sample of $La_{0.835}Sr_{0.165}MnO_3$ during the experiment on D3 to observe the structural phase transition induced by a magnetic field.

on the polarized-neutron normal-beam diffractometer D3 equipped with a 4.6-T cryomagnet. In these experiments the [4 4 5] and [2 0 0] reflections were followed as a function of temperature. In these experiments because of hysteresis, it is important to note the chronological order of changes in temperature and magnetic field and the sequence followed for our experiment is shown schematically in Fig. 2. In the first measurement, the structural phase transition was induced at constant temperature by application of a magnetic field. After alignment, the sample was cooled ($a \rightarrow b$ Fig. 2) and the intensity of the [4 4 5] reflection was followed in order to observe the transition from the rhombohedral to the orthorhombic phase. The data are shown in Fig. 3. The transition is clearly observed at about 295 K. The sample was cooled to 220 K, at which point the transition to the orthorhombic phase was judged to be complete as the intensity of the reflection had leveled out. The sample was then warmed to 290.5 K ($c \rightarrow d$ Fig. 2), a temperature which lies in the middle of the hysteretic region of the structural transition, but leaves the sample in the low-temperature orthorhombic phase (see also phase diagram in Ref. 5). At this temperature the magnetic field was gradually increased ($d \rightarrow e$ Fig. 2) and

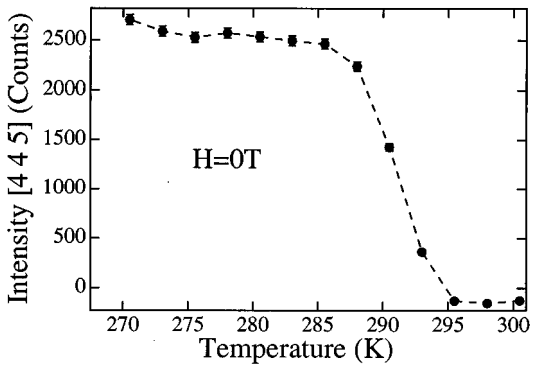

FIG. 3. Intensity of [4 4 5] reflection as a function of temperature (cooling) in zero magnetic field. The increase in intensity at 295 K shows the structural phase transition from the rhombohedral to the orthorhombic phase.

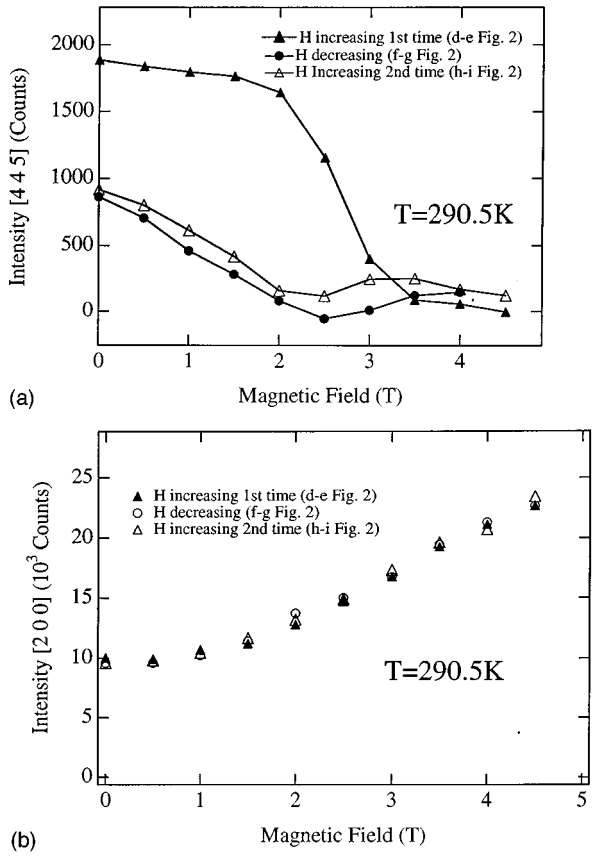

FIG. 4. Intensity of the (a) [4 4 5] and (b) [2 0 0] orthorhombic reflections as a function of magnetic field at 290.5 K. When the field is increased the first time, the intensity of the [4 4 5] reflection disappears at ~3 T showing the transition to the rhombohedral phase. On decreasing the field, the intensity of the [4 4 5] reflection increases only slightly, indicating a partial transformation to the orthorhombic phase. On increasing the field for the second time, the intensity follows the same path as the decreasing field and the sample goes fully into the rhombohedral phase at high fields. (b) The intensity of the [2 0 0] reflection increases starting from ~0.5 T, showing that there is an increased ferromagnetic alignment along the field direction when the structural phase transition is induced by the field. On decreasing and then increasing the field again, the intensity follows the same path as before.

the intensities of both the [4 4 5] and [2 0 0] reflections were monitored. The data collected are shown in Fig. 4. The intensity of the [4 4 5] reflection decreases rapidly in fields above 2 T and by 3 T the intensity has dropped to zero, indicating that the sample has reverted to the rhombohedral structure. As the field-switching experiment was carried out above T_c=264 K, the intensity of the [2 0 0] was followed to see when the magnetic contribution to the intensity appears. The intensity of the [2 0 0] reflection shows an increase in intensity starting at about 0.5 T showing that there is increased ferromagnetic alignment of the magnetic moments when the field induces the structural phase transition. This indicates that the ferromagnetic alignment of the spins encourages the structural phase transition to the rhombohedral phase in the presence of a field. As the field is initially reduced ($f \rightarrow g$ Fig. 2), there continues to be zero intensity in the [4 4 5] peak indicating the sample remains in the rhombohedral phase. However, at $H<2$ T some intensity returns,

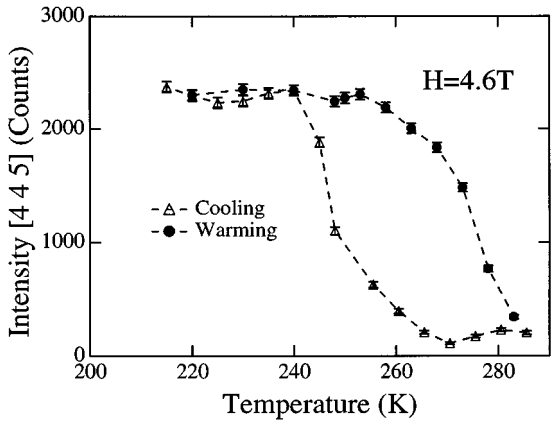

FIG. 5. Intensity of the orthorhombic [4 4 5] reflection as a function of temperature in a 4.6-T field, showing that there is large hysteresis when the structural transition takes place in a field.

indicating that the system partially transforms back into an orthorhombic structure but is unable to completely transform at this temperature. On increasing the field once more ($h \rightarrow i$ Fig. 2), the intensity follows the same path taken in the decreasing field cycle and the sample again settles fully into the rhombohedral phase at high fields. Both on decreasing the field and increasing it for the second time the intensity of the [2 0 0] reflection follows the same path with no hysteresis.

In the second measurement, we observed the structural phase transition in an applied field of 4.5 T and the results are presented in Fig. 5. The temperature was decreased while keeping the field at 4.5 T and at 270 K the crystal underwent a transition to the orthorhombic phase ($i \rightarrow j$ Fig. 2). The sample was then warmed up until it underwent the transition back to the rhombohedral phase ($k \rightarrow l$ Fig. 2). This occurred at about 285 K. There is a large hysteresis in the presence of the magnetic field.

We have performed a series of neutron-scattering experiments in which we have directly observed and confirmed the bulk nature of the magnetic-field-induced structural phase transition in a single crystal of $La_{1-x}Sr_xMnO_3$ (x=0.165). At the temperature at which the switching was performed (290.5 K), removal of the magnetic field does not produce a switch back to the low-temperature phase and the transition is permanent. In a magnetic field of 4.5 T, as in zero field, the material can be switched between the two structures by increasing or decreasing the temperature. In the presence of a magnetic field the structural transition is much more hysteretic than the same transition in zero field.

By carefully controlling the level of doping, x, the structural, magnetic, and electronic properties of the compound $La_{1-x}Sr_xMnO_3$ can be adjusted so that they are closely linked with the result that a structural phase transition can be induced by the application of a magnetic field. When the field is applied it induces an increased alignment of the magnetic moments before the structural transition takes place, indicating that a ferromagnetic alignment of the spins encourages the structural phase transition from the orthorhombic to the rhombohedral phase in the presence of a magnetic field.

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[4] The double exchange interaction competes against the antiferromagnetic superexchange interaction. Although double exchange gives a qualitative explanation for many of the properties of these materials including colossal magnetoresistance, it has been shown [A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995)] that additional physics involving electron-phonon interactions may be required to fully explain the magnitude of the observed effects.
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[6] The difference in T_c and T_s of the crystals grown by us and those of Asamitsu *et al.* for the same nominal starting composition may be due to the rapid variation of T_c and T_s with x and slight variations in oxygen stoichiometry which could also affect the transition temperatures; see J. F. Mitchel *et al.*, Phys. Rev. B **54**, 6172 (1996).
[7] Further evidence for a ferromagnetic contribution to the [2 0 0] reflection came from the observation of a flipping ratio.