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Spontaneous and field-induced magnetostructural transitions, giant magnetostriction, and specific heat in $Ca_{0.85}Sm_{0.15}MnO_3$

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We report on the magnetic, magnetoelastic, as well as the specific heat measurements of the electron-doped manganite $Ca_{0.85}Sm_{0.15}MnO_3$. The low-temperature monoclinic phase which is antiferromagnetic exhibits a first-order field-induced transition into the ferromagnetic state. This transition is accompanied by a strong decrease in volume. The latent heat calculated from the Clapeyron-Clausius equation coincides with that of the structural phase transition determined from the specific heat measurements. We thus deduce that the observed metamagnetic transition in $Ca_{0.85}Sm_{0.15}MnO_3$ is due to the field-induced structural transformation from the monoclinic phase to the orthorhombic phase.

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The hole doped manganites, $L_{1-y}D_yMnO_3$ ($L=Bi,Y,La,Pr,Nd,\ldots$; $D=Pb,Ca,Sr,Ba$) exhibiting colossal magnetoresistance (CMR) effect for $0<y\leqslant 0.5$ have been extensively investigated in the recent past.[1,2] The simultaneous presence of Mn^{4+} and Mn^{3+} ions in these compounds lead to the ''double exchange mechanism''[3] and can account for the appearance of ferromagnetism and the accompanied semiconductor to metal transition. However, several reports[4,5] have pointed out that the role played by the electron-phonon interaction mediated mainly by the Jahn-Teller distortion of Mn^{3+} ion environment should not be neglected. Other reports[6,7] have stressed the phase separation aspect in view of the fact that these manganites are not homogeneous ferromagnets at a microscopic level. There is a strong need to investigate further these compounds in order to understand in detail the mechanism behind the origin of the physical properties.

On the other hand, the rare earth (and Bi) poor manganites, known as electron doped compounds in which the Jahn-Teller distortion is expected to be minimal have not been investigated in detail. Mahendiran *et al.*[8] have reported a magnetoresistance (MR) of 82% in $Ca_{0.9}La_{0.1}MnO_3$ whereas Chiba *et al.*[9] also reported MR in $Ca_{0.85}Bi_{0.15}MnO_3$. Recently, Martin *et al.*[10] and Maignan *et al.*[11] have reported similar data in $Ca_{1-x}L_xMnO_3$ ($L=Pr,Sm,Gd$). This was followed by several reports[12–18] in quick succession.

In particular, the electron-doped $Ca_{1-x}Sm_xMnO_3$ manganite, with $x=0.15$, was found to exhibit some unique properties. The CMR effect is observed only in the vicinity of this composition which is the boundary between the cluster-glass-type state ($x<0.15$) and charge-ordered antiferromagnetic insulator state ($x>0.15$). On lowering the temperature, $Ca_{0.85}Sm_{0.15}MnO_3$ exhibits[17] a structural transformation from an orthorhombic *Pnma* phase to a monoclinic $P2_1/m$ phase. The low-temperature phase is the *C*-type antiferromagnet, which possesses, however, a weak ferromagnetic moment. Up till now, magnetic properties of high-temperature orthorhombic phase were not investigated in detail. While approaching the structural transformation temperature the magnetization sharply increases and according to neutron scattering data the ferromagnetic correlations become evident.[17] Nevertheless, it is still unclear whether the long-range ferromagnetic ordering can be reached in the orthorhombic phase.

The aim of the present work is to establish the magnetic state of the high-temperature orthorhombic phase of $Ca_{0.85}Sm_{0.15}MnO_3$ in the vicinity of structural transformation and to find the relation between the metamagnetic transition at low temperatures and structural transformation through the measurements of high field magnetization and magnetostriction, and specific heat. A preliminary account of the specific heat was published recently.[19]

We, indeed, found a field-induced ferromagnetic transition that was accompanied by a negative magnetostriction. Further, the latent heat calculations showed that the observed metamagnetic transition in $Ca_{0.85}Sm_{0.15}MnO_3$ is due to the field-induced structural transformation from the monoclinic phase to the orthorhombic phase.

Polycrystalline samples of $Ca_{0.85}Sm_{0.15}MnO_3$ were synthesized from the stoichiometric mixture of previously dried Sm_2O_3, $CaCO_3$, and MnO_2 compounds by direct solid state synthesis. The mixture was heated and ground several times by increasing successively the sintering temperature from 980 to 1300 °C. A final sintering was carried out at 1400 °C for 36 h. Powder x-ray diffraction at room temperature was carried out on a part of the sample. Rietveld pattern analysis indicated a good agreement between the experimental and the calculated spectrum by assuming the *Pnma* space group. The lattice parameters were found to be $a=5.316$ Å, $b=7.494$ Å, and $c=5.298$ Å. Further, the energy dispersive x-ray analysis of the fractured surface indicated the compo-

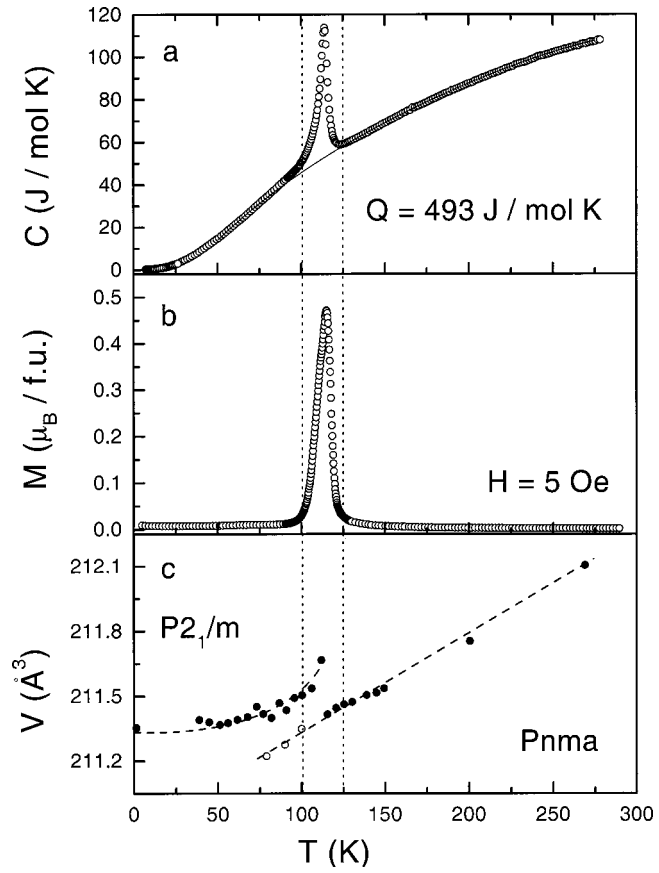

FIG. 1. Temperature dependencies of (a) the specific heat, (b) the low field magnetization, and (c) the unit cell volume (full circles—the neutron diffraction data, from Ref. 17, open circles—volume of virtual *Pnma* phase, estimated from the magnetostriction data, see text) of $Ca_{0.85}Sm_{0.15}MnO_3$.

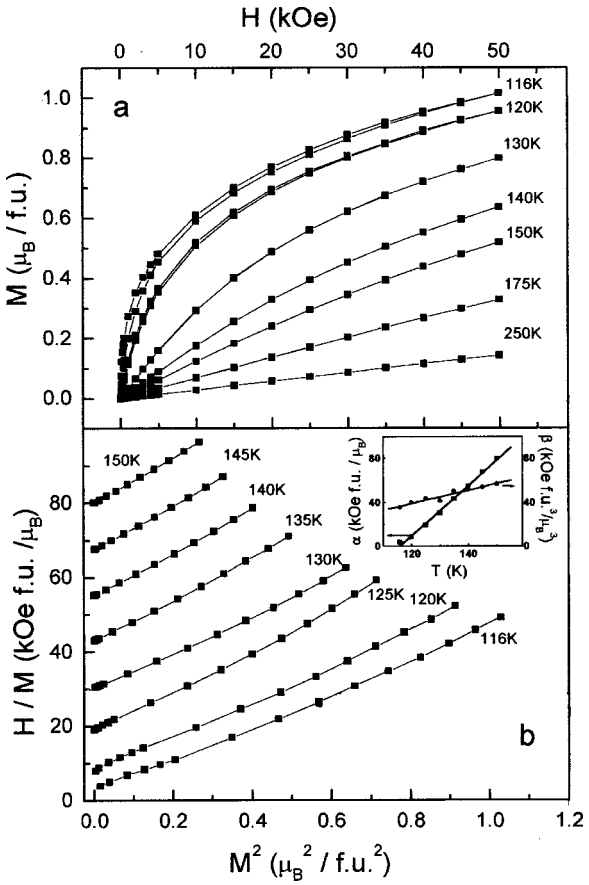

FIG. 2. The field dependencies of (a) static magnetization in *Pnma* phase and (b) the Belov-Arrott's plots (inset: temperature dependencies of Landau's theory coefficients α and β) of $Ca_{0.85}Sm_{0.15}MnO_3$.

sition to be close to that of the nominal composition. Whereas the static magnetization up to 5 T was measured by a commercial superconducting quantum interference device magnetometer, a pulsed magnetic field up to 20 T was used to measure the same by an inductive technique. Magnetostriction was measured by the piezoquartz plates glued to the sample[20] in a pulsed magnetic field up to 20 T with the magnetic field parallel (longitudinal magnetostriction $\lambda_\parallel$) and perpendicular (transverse magnetostriction $\lambda_\perp$) to the measuring direction. Specific heat in a wide temperature range was measured by a quasiadiabatic microcalorimeter.

The temperature dependence of the specific heat of $Ca_{0.85}Sm_{0.15}MnO_3$ [Fig. 1(a)] reveals one well-pronounced anomaly at $T \approx 115$ K. At the same temperature, a sharp peak of low-field magnetic susceptibility is observed [Fig. 1(b)]. Note that this temperature is close to that of the first-order structural transformation in this compound determined from the neutron diffraction data[17] [Fig. 1(c)]. It can be deduced therefore that these anomalies are due to the coupled structural and magnetic phase transitions of the first order. From the area under the anomalous part of the curve, we determined the latent heat Q of the magnetostructural transformation as 493 J/mol.

The field dependencies of static magnetization of $Ca_{0.85}Sm_{0.15}MnO_3$ in high-temperature orthorhombic phase are shown in Fig. 2. At high temperatures these dependencies are linear, but on lowering the temperature, the $M(H)$ curves deviate from linearity and absolute value of magnetization sharply increases. To define whether the transition into ferromagnetic state occurs in the orthorhombic phase, the $M(H)$ curves were treated in the framework of Landau's theory of second-order phase transition. In Belov-Arrott's formalism:

$$H/M = \alpha + \beta M^2 + \cdots .$$

Temperature dependencies of α and β are shown in the inset in Fig. 2. In Landau's theory, the transition into the ferromagnetic state occurs at $\alpha = 0$. However, down to $T = 115$ K, α is found to be positive, indicating that the long-range ferromagnetic ordering is not reached in the orthorhombic phase of $Ca_{0.85}Sm_{0.15}MnO_3$.

According to static magnetization data the paramagnetic susceptibility in the range 115–250 K follows the Curie-Weiss law with paramagnetic Curie temperature $\Theta = (115 \pm 1)$ K and effective magnetic moment $\mu_{\text{eff}} = 4.41\mu_B$/f.u., which is close to the theoretical value of $4.16\mu_B$/f.u.

It was noted earlier that the low temperature monoclinic phase is antiferromagnetic and that magnetic field induces

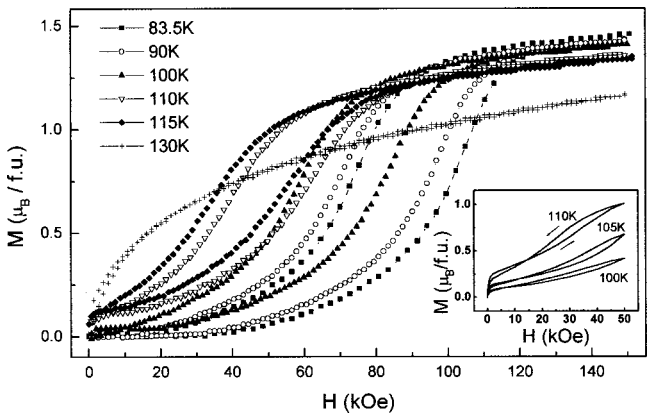

FIG. 3. The field dependencies of magnetization in pulsed magnetic field of $Ca_{0.85}Sm_{0.15}MnO_3$. Inset: the $M(H)$ curves in static magnetic field.

the transition from low to high magnetic moment state.[17,18,21] Our measurements confirm the existence of this transition. The $M(H)$ curves in $Ca_{0.85}Sm_{0.15}MnO_3$ taken in pulsed magnetic fields at low temperatures are shown in Fig. 3. The metamagnetic character of $M(H)$ curves and hysteresis observed indicate the first-order nature of the transition. The $M(H)$ dependencies taken in static magnetic field up to 50 kOe are qualitatively similar to those taken in pulsed magnetic field (see the inset to Fig. 3) but differ quantitatively. In our view, the difference in absolute values of low field magnetization measured in pulsed and static magnetic field is due to relaxation-type effects. The self-crossing of the magnetization loops evident in static magnetic field measurements was seen also in pulsed magnetic field measurements, which indicates the sensitivity of the results obtained to the magnetic prehistory of the sample.

Field dependencies of longitudinal $\lambda_\parallel$ and transverse $\lambda_\perp$ magnetostriction in $Ca_{0.85}Sm_{0.15}MnO_3$ are shown in Fig. 4. The application of a magnetic field in monoclinic phase induces giant negative practically isotropic ($\lambda_\parallel \approx \lambda_\perp$) magnetostrictive deformations reaching $\Delta l/l \sim 3\times10^{-4}$ at saturation. The change of volume at metamagnetic transition reaches $\omega = \lambda_\parallel + 2\lambda_\perp = -9\times10^{-4}$ at 80 K.

Our magnetostriction data allow us to estimate the volume of field-induced low-temperature ferromagnetic phase from the equation

$$V_{\text{ferro}} = V_{\text{antiferro}}(1-\omega).$$

The comparison of V_{ferro} with that of neutron diffraction data for orthorhombic phase extrapolated to low temperatures shows their good correspondence [see Fig. 1(c)]. This indicates that a metamagnetic transition is due to the structural transformation from the antiferromagnetic monoclinic phase $P2_1/m$ to the ferromagnetic orthorhombic phase *Pnma*. Note, that the volume magnetostriction of orthorhombic phase itself is rather low and positive and does not exceed 3×10^{-5}.

The latent heat of metamagnetic transition can be estimated from the temperature dependence of critical field H_C according to Clapeyron-Clausius formalism:

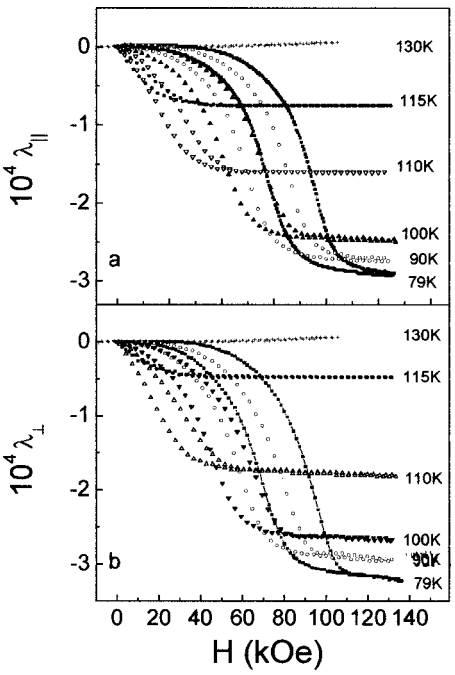

FIG. 4. The field dependencies of (a) longitudinal $\lambda_\parallel$ and (b) transverse magnetostriction $\lambda_\perp$ of $Ca_{0.85}Sm_{0.15}MnO_3$.

$$Q = \Delta M H_C T/\Delta T,$$

where ΔM is the difference between the high and the low field magnetization, $\Delta T = T_C - T$ and $T_C = 115$ K—the structural transition temperature in the absence of a magnetic field. In the temperature range studied, we found $Q = (450 \pm 100)$ J/mol, which coincides with the latent heat of the structural phase transition at T_C determined from the specific heat measurements as discussed earlier. Hence, once again we can claim that the metamagnetic transition in low temperature phase is due to the field-induced structural transformation.

It may be relevant here to comment briefly on the recently observed[22] field induced first-order transition accompanied by a negative magnetostriction in the double layered manganite $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ though a structural transition was not reported. It was proposed that the appearance of the field induced ferromagnetism is intimately related to the orbital degree of freedom, that is the occupancy of the $3d$ e_g orbitals. Now, in the present case of the electron doped manganite, the *C*-type antiferromagnetic ordering is coupled to the polarization of $3d_{z^2-r^2}$ orbitals of Mn^{3+} along the *c* axis. Since the polarization of $3d_{z^2-r^2}$ orbitals differ in monoclinic and orthorhombic phases the magnetic field induced structural phase transitions may perhaps be treated in fact as the change in $3d_{z^2-r^2}$-orbital polarization. However, measurements such as the recently reported[23] magnetic Compton-profiling technique would be necessary to substantiate this hypothesis.

In summary, by combining magnetization, magnetostriction and specific heat measurements, we have investigated the magnetic state of the electron doped manganite, $Ca_{0.85}Sm_{0.15}MnO_3$. The structural transition from the paramagnetic orthorhombic $P2_1/m$ to antiferromagnetic mono-

clinic *Pnma* phase accounts for the observed specific heat anomaly and peak of low field magnetization at 115 K. Below this temperature, a first-order field-induced transition to a ferromagnetic state is accompanied by a giant negative magnetostriction. The latent heat of spontaneous structural transformation determined from the specific heat data equals that of field induced transition determined from the magnetization data. This indicates that the appearance of the field-induced ferromagnetic phase is due to a field-induced structural transition from the monoclinic to the orthorhombic phase. While this work was nearing completion, we learned of a report[24] describing similar magnetization and magnetostriction data. Our data are in close agreement with those reported in Ref. 24.

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