

Phase Transition in Electronic Manganite $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$

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The resistivity, the magnetic susceptibility, the magnetization, and the specific heat of electronic manganite $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ were studied. The data obtained suggest that this compound undergoes phase transition into the insulator antiferromagnetic state at $T_c \sim 115$ K and displays negative magnetoresistance at $T < T_c$. A minor ferromagnetic component of $0.025\mu_B$ in the magnetization of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ may be caused by the deviation of this composition from the exact stoichiometry $\text{Mn}^{3+} : \text{Mn}^{4+} = 1 : 8$. The Debye temperature $\Theta_D = 575$ K and the entropy of phase transition $\Delta S = 5.1$ J/(mol K) were derived from the temperature dependence of specific heat. © 2001 MAIK "Nauka/Interperiodica".

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Perovskite-like manganites $\text{A}_{1-x}\text{B}_x\text{MnO}_3$, where A is trivalent lanthanide and B is bivalent alkaline-earth metal, attract interest as materials with colossal negative magnetoresistance. The ratio between A and B cations determines the $\text{Mn}^{3+} : \text{Mn}^{4+}$ ratio in the structure of these compounds. Electronic manganites ($x > 0.5$) with predominating Mn^{4+} have been studied much less thoroughly than hole manganites with predominating Mn^{3+} ($x < 0.5$). Nevertheless, they are of considerable interest because the phase diagrams of hole and electronic manganites are qualitatively different [1, 2]. For instance, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ exhibits a broad region of compositions $0.18 \leq x < 0.5$, where the system undergoes transition into the metallic ferromagnetic state upon lowering temperature. Hole manganites display colossal magnetoresistance precisely in this phase. In the electronic manganite $\text{Ca}_{1-x}\text{Sm}_x\text{MnO}_3$, the metallic ferromagnetic state occurs for none of the x values and the colossal magnetoresistance effect is observed only in a narrow range of compositions near $x \sim 0.15$.

The studies of the structure and the transport and magnetic properties of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ were initiated in [3–5]. At high temperatures, this compound has the orthorhombic $Pnma$ lattice with parameters $a = 5.3215$ Å, $b = 7.5010$ Å, and $c = 5.3021$ Å ($T = 300$ K). With lowering temperature, $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ undergoes first-order phase transition into the monoclinic $P2_1/m$ modification with parameters $a = 5.3340$ Å, $b = 7.4432$ Å, $c = 5.3076$ Å, and $\beta = 91.062^\circ$ ($T = 10$ K). During this transition, the high- and low-temperature phases of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ coexist in a certain temperature range, and in each of them its own antiferromagnetic order is established with lowering temperature. Simultaneously with the formation of the $P2_1/m$ phase, a C-type magnetic structure appears in it at $T \sim 125$ K [6].

The c -directed ferromagnetic Ising chains in this structure are coupled with each other via the antiferromagnetic interaction. In the supercooled $Pnma$ phase, the antiferromagnetic G -type state [6] typical of CaMnO_3 is formed at $T \sim 115$ K.

Magnetization measurements systematically indicate the presence of a compositionally dependent ferromagnetic moment in $\text{Ca}_{1-x}\text{Sm}_x\text{MnO}_3$ ($x \leq 0.15$) at low temperatures. In $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$, this moment is equal to approximately $0.015\mu_B$ per formula unit in weak magnetic fields [5]. There are different guesses in the literature as to the origin of the ferromagnetic component [3, 5]. According to [3], ferromagnetism is caused by the canting of antiferromagnetic G phase that remains in the $Pnma$ clusters down to low temperatures. It is conjectured in [5] that both insulator antiferromagnetic and conducting ferromagnetic states may form in the $Pnma$ clusters.

A wealth of proposed structural and magnetic states in $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ has stimulated this work, in which the measured specific heat is compared with the results of our measurements of magnetization, magnetic susceptibility, and resistivity of this compound.

$\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ ceramic was prepared by solid-phase synthesis from the nominal Sm_2O_3 , MnO_2 , and CaCO_3 composition. A powder-pressed pellet was repeatedly ground and annealed at temperatures gradually increasing in the range 980–1200°C. The final synthesis was conducted in air atmosphere at 1300°C for 36 h followed by cooling in a furnace. The homogeneity of the sample and the correspondence of its cationic composition to the nominal composition were confirmed by X-ray powder diffraction at $T = 300$ K and by local X-ray spectrum analysis. The physical properties of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ were measured over the tempera-

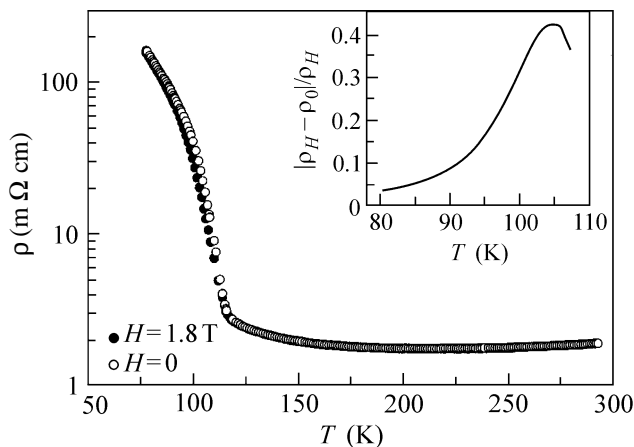


Fig. 1. Temperature dependences of the resistivity of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ in zero magnetic field and in the field $H = 1.8$ T. Temperature dependence of the negative magnetoresistance is shown in the inset.

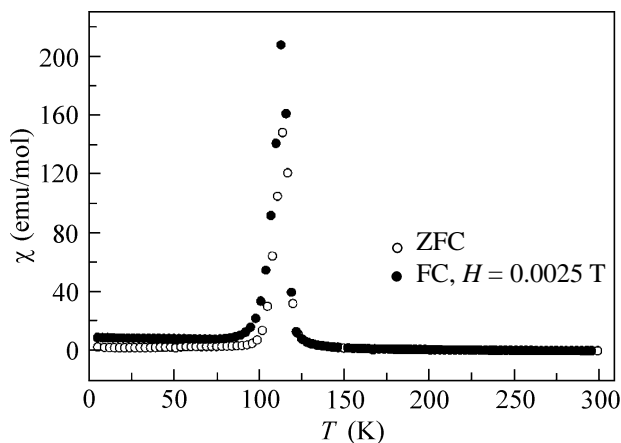


Fig. 2. Temperature dependences of the magnetic susceptibility of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$, as measured in the zero-field-cooling (ZFC) and field-cooling (FC; $H = 0.0025$ T) regimes.

ture range 5–300 K. The magnetization and magnetic susceptibility were measured by a SQUID magnetometer (Quantum Design) in fields of up to 5 T. The resistivity was measured by the standard four-probe technique. The specific heat was measured using a quasi-adiabatic microcalorimeter by the heat pulse technique.

The temperature dependences of the resistivity ρ of the ceramic sample of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ in zero field and in field $H = 1.8$ T are shown in Fig. 1. At high temperatures, the resistivity displays a weak metallic behavior and sharply rises at $T_c \sim 115$ K, indicating the transition into the insulator state. At $T < T_c$, the magnetoresistance is negative; its magnitude in the field $H = 1.8$ T at $T = 105$ K equals $|\rho_H - \rho_0|/\rho_H = 40\%$. In the range of magnetic fields studied in this work, the magnitude of negative magnetoresistance of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ is

comparatively small, although in fields ~ 7 T it reaches values typical of hole manganites [3, 6].

The temperature dependences of the magnetic susceptibility of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ were measured in the zero-field-cooling (ZFC) and field-cooling (FC; $H = 0.0025$ T) regimes (Fig. 2). The $\chi(T)$ curves show a peak at $T_c \sim 115$ K. At $T < T_c$, the FC susceptibility markedly exceeds the ZFC one. These features of magnetic susceptibility are typical of the systems undergoing transition into the spin (or cluster) glass state. However, for $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$, this state is quite specific. As seen from the field dependence of magnetization M shown in Fig. 3, there is a ferromagnetic component of about $0.025\mu_B$ in weak fields and M grows linearly with the field and reaches $0.09\mu_B$ at $H = 5$ T. The $M(H)$ curve shows a weak hysteresis in the entire range of magnetic fields studied. The appearance of a small ferromagnetic component in the magnetization of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ at low temperatures may be due to the deviation of the composition from a composition with $\text{Mn}^{3+} : \text{Mn}^{4+} = 1 : 8$. For this ratio, the Mn^{3+} and Mn^{4+} positions may be ordered to form the antiferromagnetic structure. The magnetic moments of the Mn^{3+} and Mn^{4+} ions are $\mu_{\text{Mn}^{3+}} = 4.9\mu_B$ and $\mu_{\text{Mn}^{4+}} = 3.9\mu_B$, respectively. For the composition with 2.5% excess Mn^{3+} ions, the uncompensated ferromagnetic moment is $M = 0.025(\mu_{\text{Mn}^{3+}} - \mu_{\text{Mn}^{4+}}) = 0.025\mu_B$.

The temperature dependence of the specific heat of $\text{Ca}_{0.15}\text{Sm}_{0.85}\text{MnO}_3$ is presented in Fig. 4. A clearly defined λ -type anomaly confirms the presence of phase transition at $T_c \sim 115$ K.

Generally, the specific heat of a magnet contains at $T < T_c$ the phonon C_{ph} , the electronic C_{el} , and the magnon C_{mag} components:

$$C = C_{ph} + C_{el} + C_{mag}.$$

At low temperatures, the lattice contribution is $C_{ph} = \beta T^3 + \alpha T^5$, the electronic contribution is $C_{el} = \gamma T$, and the contribution of spin excitations is $C_{mag} = \delta T^n$. The exponent n depends on the type of spin excitations; $n = 3/2$ or 3 for the magnons in a three-dimensional ferromagnet or antiferromagnet, respectively [7].

The fact that the linear electronic contribution to the specific heat was not observed indicates that the low-temperature state of the sample is dielectric. No contribution proportional to $T^{3/2}$ was revealed in the specific heat of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ either, in compliance with the smallness of the ferromagnetic component in the magnetization of this compound at low temperatures. The sum $(\beta + \delta)T^3 + \alpha T^5$ with parameters $\beta + \delta = (5.0 \pm 0.3) \times 10^{-5} \text{ J}/(\text{mol K}^4)$ and $\alpha = (3.7 \pm 0.3) \times 10^{-7} \text{ J}/(\text{mol K}^6)$ is the best fit to the experimental data in the temperature range 7–12 K. The magnon component δT^3 of the specific heat of a three-dimensional antiferromagnet and

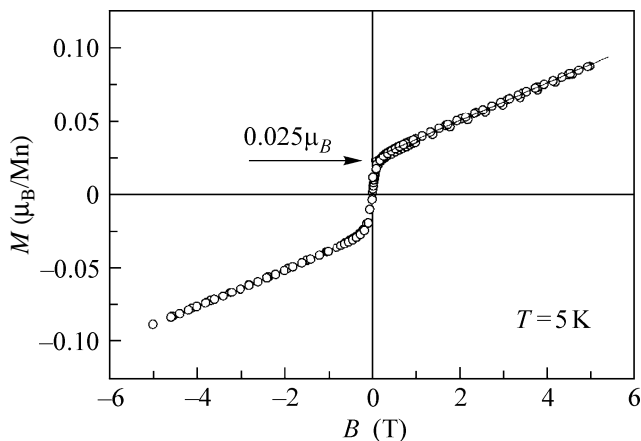


Fig. 3. Field dependence of the magnetization of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ at $T = 5 \text{ K}$.

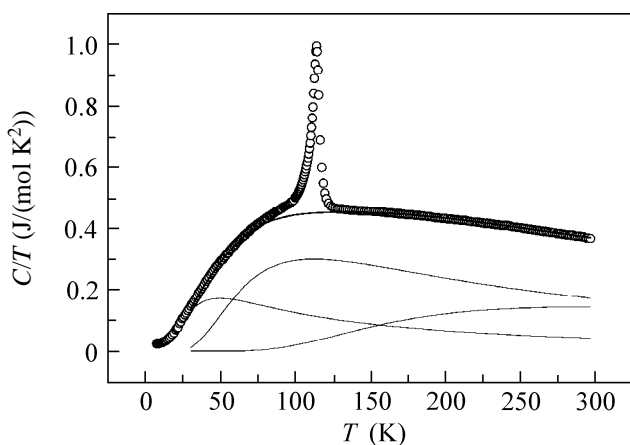


Fig. 4. Temperature dependence of the specific heat of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$. Solid line is the approximation of phonon contribution by the sum of three Einstein modes.

the phonon component βT^3 are additive. Using the formula $\beta = 12\pi^4 Rv/5\Theta_D^3$, where R is the universal gas constant and $v = 5$ is the number of atoms in formula unit [8], the lower bound to the Debye temperature was estimated at $\Theta_D \sim 575 \text{ K}$. This value agrees rather well with the results of systematic studies of the parameters of Ca-containing manganites. For instance, Θ_D in the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system increases from 368 K in $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ [9] to 500 K in $\text{La}_{0.37}\text{Ca}_{0.63}\text{MnO}_3$ [10].

Excluding the phase transition region, the specific heat of the sample studied can be approximated by three Einstein optical modes $\hbar\omega_{E1}/k_B = 130 \text{ K}$, $\hbar\omega_{E2}/k_B = 290 \text{ K}$, and $\hbar\omega_{E3}/k_B = 760 \text{ K}$ over a wide temperature range. As shown in Fig. 4, this allows the entropy of phase transition to be estimated at $\Delta S = 5.1 \text{ J}/(\text{mol K})$. The theoretical estimate of magnetic contribution to the entropy of phase transition $\Delta S_{\text{mag}} = R \ln(2S + 1) = 8.314(0.15 \ln 5 + 0.85 \ln 4) = 11.8 \text{ J}/(\text{mol K})$

markedly exceeds this value. However, it should be noted that the procedure of setting off the entropy of phase transition is highly sensitive to the interval where the Einstein approximation is used. The agreement between the experiment and theory betters if the magnetic entropy released in the pretransition fluctuation region is included in ΔS .

In our measurements of the transport, magnetic, and notably thermal properties, clear-cut anomalies are observed for $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ only at the temperature $T_c = 115 \text{ K}$. The obvious contradiction with the results of studies [2, 3, 5], where several phase transitions were observed at close temperatures, is probably caused by the fact that the experiments were conducted at different rates. Different structures and magnetic phases of $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ are energetically close to one another, so that the system undergoes transition into the phase-separated state of the cluster-glass type upon fast cooling [5]. Under quasi-adiabatic conditions, the system with a multiwell potential can transfer to the lowest energy state. Under these conditions, a nearly homogeneous antiferromagnetic state with a small fraction of ferromagnetic clusters is likely formed at low temperatures. The applied magnetic field lowers the energy of the ferromagnetic state at low temperatures, leading to an increase in the volume of ferromagnetic clusters over which electron transport is possible.

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REFERENCES

1. P. Schiffer, A. P. Ramírez, W. Bao, and S.-W. Cheong, *Phys. Rev. Lett.* **75**, 3336 (1995).
2. C. Martin, A. Maignan, M. Hervieu, and B. Raveau, *Phys. Rev. B* **60**, 12 191 (1999).
3. C. Martin, A. Maignan, M. Hervieu, *et al.*, *J. Magn. Magn. Mater.* **205**, 184 (1999).
4. C. Martin, A. Maignan, F. Damay, *et al.*, *J. Solid State Chem.* **134**, 198 (1997).
5. R. Mahendiran, A. Maignan, C. Martin, *et al.*, *Phys. Rev. B* **62**, 11 644 (2000).
6. V. M. Loktev and Yu. G. Pogorelov, *Fiz. Nizk. Temp.* **26**, 1 (2000) [*Low Temp. Phys.* **26**, 171 (2000)].
7. A. I. Akhiezer, V. G. Bar'yakhtar, and S. V. Peletminskii, *Spin Waves* (Nauka, Moscow, 1967; North-Holland, Amsterdam, 1968).
8. E. S. R. Gopal, *Specific Heat at Low Temperatures* (Plenum, New York, 1966).
9. L. Ghivelder, I. Abrego Castillo, N. McN. Alford, *et al.*, *J. Magn. Magn. Mater.* **189**, 274 (1998).
10. P. Schiffer, A. P. Ramírez, S.-W. Cheong, *et al.*, *Phys. Rev. Lett.* **76**, 3188 (1996).

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