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 \( T_c \approx 115 \text{ K} \) 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 the composition from the exact stoichiometry \( \text{Mn}^{3+} : \text{Mn}^{4+} = \text{1} : \text{8} \). The Debye temperature \( \Theta_D = 575 \text{ K} \) and the entropy of phase transition \( \Delta S = 5.1 \text{ J/(mol K)} \) 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 tervalent 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 Mn\(^{3+} \) : 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 \( x \approx 0.15 \).

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 \( \text{Pnma} \) lattice with parameters \( a = 5.3215 \text{ Å}, b = 7.5010 \text{ Å}, \) and \( c = 5.3021 \text{ Å} ( T = 300 \text{ K}) \). With lowering temperature, \( \text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3 \) undergoes first-order phase transition into the monoclinic \( \text{P2}_1/\text{m} \) modification with parameters \( a = 5.3340 \text{ Å}, b = 7.4432 \text{ Å}, c = 5.3076 \text{ Å}, \) and \( \beta = 91.062^\circ ( T = 10 \text{ K}) \). 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 \( \text{P2}_1/\text{m} \) phase, a \( C \)-type magnetic structure appears in it at \( T \approx 125 \text{ K} \) [6].

The \( c \)-directed ferromagnetic Ising chains in this structure are coupled with each other via the antiferromagnetic interaction. In the supercooled \( \text{Pnma} \) phase, the antiferromagnetic \( G \)-type state [6] typical of \( \text{CaMnO}_3 \) is formed at \( T \approx 115 \text{ K} \).

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 \( \text{Pnma} \) clusters down to low temperatures. It is conjectured in [5] that both insulator antiferromagnetic and conducting ferromagnetic states may form in the \( \text{Pnma} \) 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 \( \text{Sm}_3\text{O}_5 \), \( \text{Mn}_2 \), and \( \text{CaCO}_3 \) 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 \( T = 300 \text{ K} \) 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-
The negative magnetoresistance of Ca$_{0.85}$Sm$_{0.15}$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 Ca$_{0.85}$Sm$_{0.15}$MnO$_3$ were measured in the zero-field-cooling (ZFC) and field-cooling (FC; $H = 0.0025$ T) regimes (Fig. 2). The χ($T$) curves show a peak at $T_c \approx 115$ 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 Ca$_{0.85}$Sm$_{0.15}$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 0.025μ$_B$ in weak fields and $M$ grows linearly with the field and reaches 0.09μ$_B$ 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 Ca$_{0.85}$Sm$_{0.15}$MnO$_3$ at low temperatures may be due to the deviation of the composition from a composition with Mn$^{3+}$ : 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 Ca$_{0.15}$Sm$_{0.85}$MnO$_3$ is presented in Fig. 4. A clearly defined $\lambda$-type anomaly confirms the presence of phase transition at $T_c \approx 115$ 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 Ca$_{0.85}$Sm$_{0.15}$MnO$_3$ either, in compliance with the smallness of the ferromagnetic component in the magnetization of this compound at low temperatures. The sum ($\beta + \delta T^n + \alpha T^5$) with parameters $\beta + \delta = (5.0 \pm 0.3) \times 10^{-5}$ J/(mol K$^4$) and $\alpha = (3.7 \pm 0.3) \times 10^{-7}$ J/(mol K$^6$) is the best fit to the experimental data in the temperature range 7–12 K. The magnon component $\delta T^3$ of the specific heat of a three-dimensional antiferromagnet and...