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Thermal Properties of Some RE$_{1-x}$EA$_x$MnO$_3$ Compounds


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Abstract: The Seebeck-effect and the thermal diffusivity $\kappa$ of epitaxial layers of La$_{0.67}$Ca$_{0.33}$MnO$_{3-\delta}$ and bulk samples of Nd$_{0.67}$Sr$_{0.33}$MnO$_{3-\delta}$ were investigated in the temperature range $35K < T < 300K$ using the time resolved thermoelectric power (flash) method. In the temperature regime of the high magnetoresistance (GMR) which is close to the maximum resistivity $\rho_{\text{max}}$ of the La-Ca compound, we find a sign change of $S(T)$ and a step in heat conductivity which we attribute to a temperature-induced metal-insulator transition at about 80K. For Nd$_{0.67}$Sr$_{0.33}$MnO$_{3-\delta}$ such a transition is also observed, but around 160K; here $S(T)$ is always positive except for a gradual sign change at 370K and the changes in $\kappa$ are also more gradual. For temperatures above $\rho_{\text{max}}$ we find evidence of a spin glass like state in both cases.

1. TEMPERATURE INDUCED ORDER–ORDER TRANSITION

Magnetization measurements have shown that while stoichiometric La$_{0.67}$Ca$_{0.33}$MnO$_{3-\delta}$ is a double exchange ferromagnet, oxygen deficient samples, e.g. La$_{0.67}$Ca$_{0.33}$MnO$_{3-\delta}$, 0 $\leq$ $\delta$ $\leq$ 0.3 exhibit a sequence of different magnetically ordered phases with decreasing temperature, i.e. spin glass like (sg), antiferromagnetic (afm) and canted [1]. While thermally activated, i.e. semiconducting behaviour of the resistivity is found in the spin-compensated phases, though with different temperature dependences, for the magnetic phases with a ferromagnetic component the conductivity is higher and metallic, which produces the resistivity maximum. The heat conductivity (fig. 1, La-Ca compound) also discriminates between the magnetically ordered and disordered phases: note the jump in $\kappa$ at the canted-afm transition at $T_1 = 80K$ and the more continuous drop in $\kappa$ for the afm-sg like transition, $T_\beta$; when paramagnetism is finally installed at $T_f$, $\kappa$ increases again. All this suggests that the large GMR found close to the maximum resistivity is connected with a field-induced change of the afm state into the canted state, accompanied by a change in conductivity type from insulating to metallic [1, 2]. For the pressure dependence of the order-order transition temperature in Nd-Sr, $T_1$, which is usually equivalent to a field dependent change, we find $\alpha_{\rho}$ $\approx$ 2.4 $K$. The thermoelectric power practically only differentiates between the magnetically ordered metallic and the semiconducting states, through a sign change for the La-Ca compound [2] and through a different sign of slope $\frac{dS}{dT}$ in the case of the Nd-Sr compound; there is, however, a sign change of S(T) close to $T_f$ for Nd-Sr. For the La-Ca compound in the thermally activated region S becomes a constant suggesting polaron transport [2].

2. SPIN GLASS LIKE STATE

Specific heat capacity measurements on the La-Ca epitaxial layer were not available; however, a small dip in the thermal diffusivity is observed at 120 K [2], suggesting a heat capacity peak as $C_p(T)$ of Nd-Sr reveals a peak around 240 K which we have to interpret as an afm-sg transition; also there is a change of slope of $\rho(T)$ at this temperature. At 160 K there is no anomaly in $C_p(T)$, as we expect for a magnetic order-order transition; also, the magnetic moment is near zero for all temperatures between 160 K and 450 K, consistent with compensated magnetic
states in this temperature range. Further evidence for the sg-like state comes from resistivity measurements $\rho(T)$: we observe a second resistivity peak around 415 K which probably signals the sg-pm transition [3]. While the sequence of long range ordered magnetic phases have been predicted to occur in double exchange systems by de Gennes, the spin random phase at higher temperatures has been tentatively connected with thermally activated random atom displacements [4].

![Diagram](image-url)

**Figure 1** Heat conductivity $\kappa$ of La-Ca compound divided by density $\rho_0$ versus temperature $T$

- $T_f$ freezing temperature, $T_a$ spin glass–antiferromagnetic transition, $T_1$ afm-canted order–order transition

**References**


