

Anomalies in sound velocity and thermal expansion related to charge order and ferromagnetic transitions in $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-z}\text{Co}_z)\text{O}_3$

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Abstract

The charge order (CO), ferromagnetic (FM) and metal–insulator (M–I) transitions have been studied for $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-z}\text{Co}_z)\text{O}_3$ ($Z = 0–0.10$) by measuring the sound velocity $v_s(T)$, magnetization $M(T)$, electrical resistivity $\rho(T)$ and thermal expansion $L(T)/L_R$. The $v_s(T)$ hardening has been found to precisely monitor the CO transition, while the $L(T)/L_R$ shrink has been found to be sensitive to the onset of the FM-metallic phase. The competition of CO, FM-metallic and FM-insulating phases has been studied from the viewpoint of the enhanced electron–phonon interaction through the Jahn–Teller effect.

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The small ionic radius of Pr^{3+} enhances the distortion of MnO_6 network in perovskite $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO) and reduces the doped hole hopping between neighboring Mn ion sites. Then double exchange (DE) mechanism is suppressed, relatively enhancing the role of the competitive interaction such as the superexchange (SE) or the Jahn–Teller (J–T) coupling, etc. In pristine $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$, so-called CE-type charge/orbital order (CO) is stabilized, which is easily replaced by the ferromagnetic (FM) order by applying a magnetic field, or by a small amount of Mn substitution by other 3d transition metal elements [1–3]. In this note, we study the lattice anomalies at CO and FM transitions in $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-z}\text{Co}_z)\text{O}_3$ by measuring the sound velocity v_s and the thermal expansion $L(T)/L_R$.

PCMO polycrystals were prepared by a solid-state reaction method. The temperature dependence of $v_s(T)$ was measured by a pulse superposition method using the longitudinal waves of ~ 7 MHz between 4.2 and 300 K. $L(T)/L_R$ ($L_R =$ room temperature length) was measured by a strain gauge method. The magnetization $M(T)$ was

measured by a SQUID magnetometer and the electrical resistivity $\rho(T)$ was measured by a four-lead method. We performed detailed Rietveld analyses for the X-ray diffraction, from which the structure was determined to be a single orthorhombic phase and the doped Co spin state to be in Co^{3+} low spin (LS) configuration (t_{2g}^6 ; $S = 0$).

Fig. 1 shows $M(T)$ of PCMO(100Z%) in the field of 0.5 T. $M(T)$ of PCMO(2%) and PCMO(4%) displays an anomalous step-like increase at the FM transition, suggesting the typical first-order transition. The very sharp transition, making a marked contrast to other 3d transition metal elements, comes from the nonmagnetic nature of doped Co^{3+} (LS) [3]. The $M(T)$ of PCMO(6%) and PCMO(10%) shows a usual continuous behavior at the FM transition.

Figs. 2(a)–(d) present $v_s(T)$ and $\rho(T)$. In Fig. 2(a), $\rho(T)$ shows no anomaly at T_{CO} , where $v_s(T)$ exhibits a drastic increase accompanying a slight v_s softening above T_{CO} . In Fig. 2(b) and (c), the v_s hardening at T_{CO} is retained for PCMO(2%) and PCMO(4%), though the CO transition cannot be identified from $\rho(T)$ and $M(T)$. $\rho(T)$ of PCMO(2%) and PCMO(4%) exhibits the sharp colossal insulator–metal (I–M) transition at T_{FM} . In Fig. 2(d), v_s

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enhancement takes place at the FM (insulator) transition temperature T_{FI} . This means that the lattice hardening similar to that accompanied by CO occurs in PCMO(10%) concomitant with the transition to the insulating FM phase. The v_s behavior of PCMO(6%) is quite similar to PCMO(10%), showing the characteristic v_s hardening at T_{FI} .

Fig. 3 displays the thermal expansion $L(T)/L_R$. In pristine PCMO(0%), $L(T)/L_R$ slightly deviates upwards from the basic line around T_{CO} (volume expansion) with decreasing temperature, while $L(T)/L_R$ displays a sharp

contraction at T_{FM} in PCMO(2%) and PCMO(4%). In the metallic phase, the local Jahn–Teller distortion around the Mn^{3+} ions is released, which results in the shrink of the lattice volume. It is to be noted that the slight volume expansion similar to CO onset is noticeable also in PCMO(6%) and PCMO(10%) at T_{FI} .

In summary, by substituting low spin Co^{3+} for the Mn^{3+} site in charge ordered $Pr_{0.65}Ca_{0.35}MnO_3$, FM-metal state and FM-insulator phase successively realize with increasing doping. Spectacular changes of lattice, i.e., the

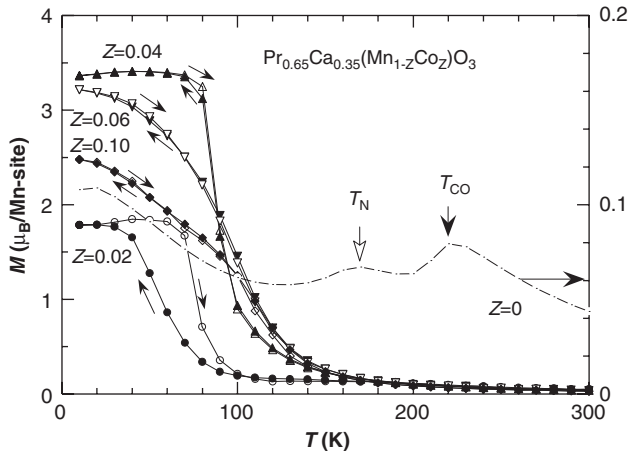


Fig. 1. Temperature dependence of magnetization $M(T)$.

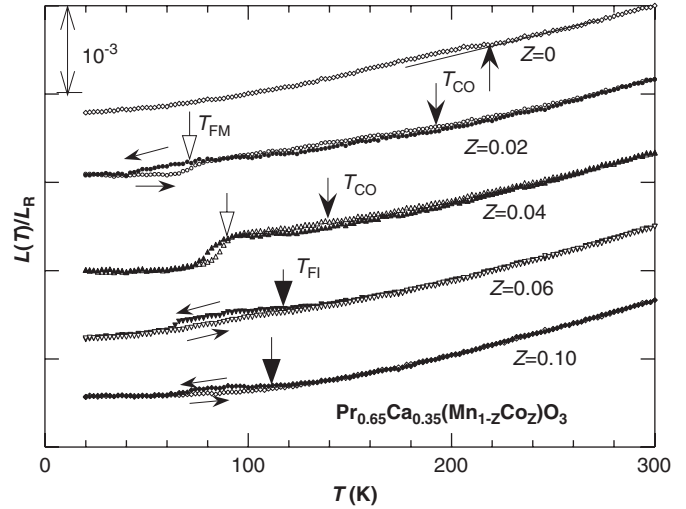


Fig. 3. Thermal expansion $L(T)/L_R$ as a function of T .

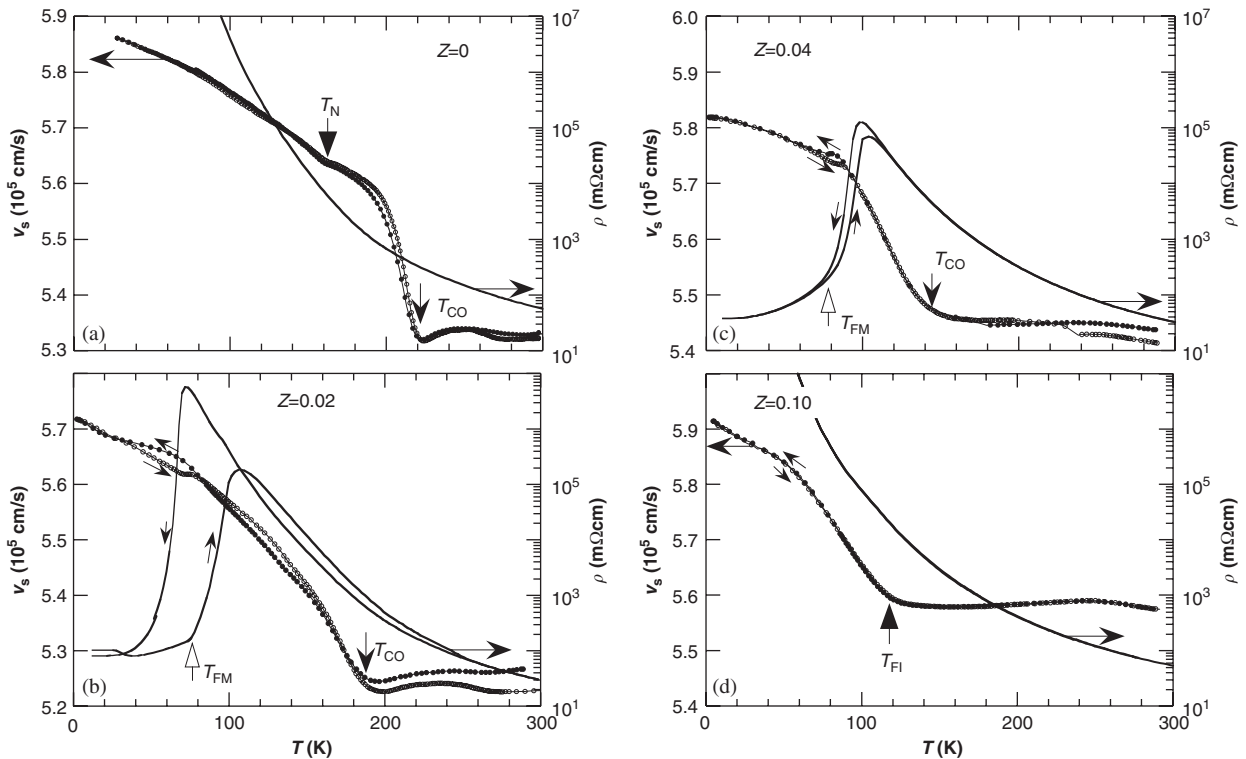


Fig. 2. Sound velocity $v_s(T)$ and resistivity $\rho(T)$ for Co^{3+} -doped PCMO.

$v_s(T)$ hardening below T_{CO} and the $L(T)/L_R$ shrink below T_{FM} , have been observed. The lattice hardening similar to that of pristine $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ at T_{CO} also takes place at the onset of the insulating FM state for PCMO(6%) and PCMO(10%). It must be emphasized that the similar lattice change occurs at T_{CO} and at T_{FI} in the Co-doped PCMO system.

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