Metal-insulator transition and the Pr\textsuperscript{3+}/Pr\textsuperscript{4+} valence shift in (Pr\textsubscript{1−y}Y\textsubscript{y})\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3}

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Abstract

The magnetic, electric and thermal properties of the (Ln\textsubscript{1−y}Y\textsubscript{y})\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} perovskites (Ln = Pr, Nd) were investigated down to very low temperatures. The main attention was given to a peculiar metal-insulator transition, which is observed in the praseodymium based samples with \( y = 0.075 \) and 0.15 at \( T_{M-I} = 64 \) and 132 K, respectively. The study suggests that the transition, reported originally in Pr\textsubscript{0.5}Ca\textsubscript{0.5}CoO\textsubscript{3}, is not due to a mere change of cobalt ions from the intermediate- to the low-spin states, but is associated also with a significant electron transfer between Pr\textsuperscript{3+} and Co\textsuperscript{3+}/Co\textsuperscript{4+} sites, so that the praseodymium ions occur below \( T_{M-I} \) in a mixed Pr\textsuperscript{3+}/Pr\textsuperscript{4+} valence. The presence of Pr\textsuperscript{4+} ions in the insulating phase of the yttrium doped samples (Pr\textsubscript{1−y}Y\textsubscript{y})\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} is evidenced by Schottky peak originating in Zeeman splitting of the ground state Kramers doublet. The peak is absent in pure Pr\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} in which metallic phase, based solely on non-Kramers Pr\textsuperscript{3+} ions, is retained down to the lowest temperature.

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I. INTRODUCTION

Thermally induced transitions in $LnCoO_3$ ($Ln = La, Y, \text{rare earths}$) have been studied for decades. Recent interpretation associates them with a local excitation of the octahedrally coordinated $Co^{3+}$ ions from LS (low spin, $t^6_{2g}$) to HS (high spin, $t^4_{2g}e^2_{g}$) state, followed at higher temperature by a formation of a metallic phase of IS character (intermediate spin, $t^5_{2g}\sigma^*$) - see e.g. [1] and citations therein. An attention is attracted also to the mixed-valence cobaltites like $La_{1-x}Sr_xCoO_3$ or $La_{1-x}Ca_xCoO_3$ where a similar transition from insulating LS $Co^{3+}$ ground state towards the metallic $t^5_{2g}\sigma^*$ one is obtained in the course of doping ($0 < x < 0.2$). As concerns the metallic region beyond $x = 0.2$, some heavily doped Pr-based cobaltites, in particular Pr$_{0.5}Ca_{0.5}CoO_3$ behave anomalously. At ambient temperature, they appear in the metallic $t^5_{2g}\sigma^*$ phase as expected, but on cooling they undergo a sharp M-I (metal-insulator) transition at $T_{M-I} = 90$ K, documented for the first time by S. Tsubouchi et al. [2, 3]. The same transition was observed also on the less-doped samples Pr$_{1-x}Ca_xCoO_3$ ($x = 0.3$) under high pressures or upon a partial substitution of praseodymium by smaller rare earth cations or yttrium [4–6]. The effect was tentatively ascribed to a change of the cobalt states from itinerant ones $t^5_{2g}\sigma^*$ to a mixture of localized LS $Co^{3+}$ ($t^6_{2g}$, $S = 0$) and LS $Co^{4+}$ ($t^5_{2g}$, $S = 1/2$) states. Very recently, an alternative explanation has been proposed based on electronic structure calculations and some indirect experimental data, namely the significant lattice contraction and shortening of Pr-O bond lengths that accompany the M-I transition [7, 8]. It is suggested that the formal cobalt valency in Pr$_{0.5}Ca_{0.5}CoO_3$ is changed at $T_{M-I}$ from the mixed-valence $Co^{3.5+}$ towards pure $Co^{3+}$ with strong preference for LS state, and the praseodymium valence is simultaneously increased from Pr$_{3+}$ towards Pr$_{4+}$. The spin state transition and formation of an insulating state in Pr$_{0.5}Ca_{0.5}CoO_3$ is thus an analogy of the compositional transition from ferromagnetic metal La$_{0.5}Sr_{0.5}CoO_3$ to diamagnetic insulator LaCoO$_3$ [9, 10].

The present work concerns the system $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ ($y = 0 - 0.15$), which is advantageous with respect to an easier preparation of oxygen stoichiometric samples as compared with the Pr$_{0.5}Ca_{0.5}CoO_3$ system. The M-I transition observed for $y \geq 0.075$ ($T_{M-I} = 60 - 130$ K) is manifested by pronounced anomalies in the temperature course of transport, magnetic and thermal properties. Fundamental information on the nature of the insulating phase is obtained at very low temperatures. This refers especially to the
occurrence of a Schottky peak in the specific heat, centered at $1 - 2 \text{ K}$. A comparison
with the specific heat data in $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ where similar Schottky peak is currently also
observed, allows us to conclude that the peak arises due to an exchange field splitting of the
doublet ground state of Kramers rare-earth ions, in particular $\text{Nd}^{3+}$. Its occurrence in the
yttrium doped $(\text{Pr}_{1-y}\text{Y})_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ provides a direct and quantitative evidence for the
fact that in the insulating phase, in addition to common $\text{Pr}^{3+}$ (non-Kramers ion), there is a
significant significant population of $\text{Pr}^{4+}$ (Kramers ion).

II. EXPERIMENTAL

Polycrystalline samples of $(\text{Ln}_{1-y}\text{Y})_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ ($\text{Ln} = \text{Pr}, \text{Nd}$) were prepared by a
solid-state reaction. Raw powders of $\text{Pr}_6\text{O}_{11}$, $\text{Nd}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{Co}_3\text{O}_4$, and $\text{CaCO}_3$ were
weighted with proper molar ratios and ground using an agate mortar and pestle for 1 h.
Mixed powders were calcined at $1000^\circ\text{C}$ for 24 h in air. Then they were pulverized, ground
and pressed into pellets of 20 mm diameter and 4 mm thickness. Pellets were sintered at
$1200^\circ\text{C}$ for 24 h in 0.1 MPa flowing oxygen gas. The measured densities of each sample
were greater than 90 % of the ideal density. Powder X-ray diffraction patterns were taken
for each sample using $\text{CuK}_\alpha$ radiation; the samples were confirmed to have a single phase
orthoperovskite ($\text{Pbnm}$) structure.

The magnetic measurements were performed in the temperature range from 2 to 400 K
using a SQUID magnetometer (MPMS-XL). The hysteresis loops at $T = 2$ and $4.5 \text{ K}$ were
recorded between the field -7 and 7 T. The susceptibility was measured under an applied field
of 0.1 T, employing the zero field- (ZFC) and field-cooled (FCC) regimes during warming
and cooling the sample, respectively.

Thermal conductivity, thermoelectric power and electrical resistivity were measured using
a four-probe method with a parallelepiped sample cut from the sintered pellet. The electrical
current density varied depending on the sample resistivity between $10^{-1} \text{ A/cm}^2$ (metallic
state) and $10^{-7} \text{ A/cm}^2$ (insulating state). The measurements were done on sample cooling
and warming using a close-cycle cryostat working down to $2 - 3 \text{ K}$. The detailed description
of the cell including calibration is described elsewhere [11].

The specific heat was measured by PPMS device (Quantum Design) using the two-$\tau$
model. The data were collected generally on sample cooling. The experiments at very low
temperatures (down to 0.4 K) were done using the He\textsuperscript{3} option.

III. RESULTS

A. Physical characterization

The electric transport measurements on the (Pr\textsubscript{1-\textit{y}}Y\textsubscript{\textit{y}})\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} samples for \textit{y} = 0, 0.075 and 0.15 and on Nd\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} are presented in Figs. 1 and 2. It is seen that the \textit{y} = 0 and analogous neodymium sample are metallic over the whole temperature range, tending to a finite resistivity of about 1 m\Omega cm at zero K. The yttrium doped samples, apparently in the same metallic state at room temperature, exhibit a sudden increase of the electrical resistivity and thermopower (Seebeck coefficient) at \(T_{\text{M-I}} = 64\) K and 132 K for \textit{y} = 0.075 and \textit{y} = 0.15, respectively. Concurrently, the thermal conductivity exhibits a kink, followed with a recovery at lower temperatures (Fig. 3). The magnetic susceptibility drops markedly (Fig. 4), which is a strong signature that cobalt ions transform to LS states at \(T_{\text{M-I}}\). The M-I transition in (Pr\textsubscript{1-\textit{y}}Y\textsubscript{\textit{y}})\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} is further manifested by a pronounced peak in the specific heat data (Fig. 5). The peak is very narrow \(\sim 1 - 2\) K for \textit{y} = 0.075 with lower \(T_{\text{M-I}}\), suggesting a first order character of the transition, while it is much broader \(\sim 15\) K for \textit{y} = 0.15 with higher \(T_{\text{M-I}}\). It is seen also that the values of specific heat below the M-I transition are small compared to Pr\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} retaining the metallic phase, which is indicative of a significant change of lattice dynamics in the low-temperature phase of yttrium doped samples.

The anomalies in the transport, magnetic and thermal data, similar to those in Figs. 1, 5 were observed earlier for the prototypical compound Pr\textsubscript{0.5}Ca\textsubscript{0.5}CoO\textsubscript{3} and also for the Pr\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3}-derived systems with analogous M-I transition. In important distinction to these previous reports, the transition in present samples (Pr\textsubscript{1-\textit{y}}Y\textsubscript{\textit{y}})\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} exhibits very small thermal hysteresis, which is about 0.2 K for both \textit{y} = 0.075 and 0.15. Another property deserving attention is practical absence of residual metallic phase in the insulating ground state, especially for \textit{y} = 0.15. As seen in the plot of inverse susceptibility in lower panel of Fig. 4, the metallic sample Pr\textsubscript{0.7}Ca\textsubscript{0.3}CoO\textsubscript{3} undergoes FM-like transition at \(T_C \sim 55\) K and, consistently, the magnetization data taken at low temperatures show nearly rectangular hysteresis loops with large coercivity (Fig. 6). On the other hand, the sample \textit{y} = 0.15
exhibits essentially paramagnetic behavior of inverse susceptibility and magnetization curves are of Brillouin type, though some very weak coercivity and remanence appear at 2 K.

The very low susceptibility below $T_{M-I}$ makes sample $y = 0.15$ suitable for a more quantitative analysis. The observed values are obviously smaller than the calculated contribution of praseodymium ions in trivalent state (see data of Ref. [12] in lower panel of Fig. 4), disregarding that there should also be contribution of the LS $\text{Co}^{4+}$ spins. A plausible interpretation provides the new model of M-I transition stating that some praseodymium ions are changed to tetravalent states with lower magnetic moments, and corresponding number of LS $\text{Co}^{4+}$ ions are transformed to diamagnetic LS $\text{Co}^{3+}$. The actual valence shift can be inferred from the thermopower data in Fig. 21. Namely, the thermopower in mixed-valence cobaltites is primarily determined by number of carriers, i.e. by the formal cobalt valence, and, in a less extent, by the average ionic size of large cations in perovskite A-sites. Having this in mind, we refer to the fact that Seebeck coefficient in the metallic phase of yttrium doped sample $y = 0.15$ ($T \sim 150 - 300 \text{ K}$) matches well to $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ with comparable A-site size. This means that cobalt valence in these two samples is practically the same and, consequently, praseodymium ions are essentially in trivalent state, similarly to neodymium ones. (We estimate $\text{Pr}^{3.03+}$ as upper possible limit.) Below $T_{M-I} = 132 \text{ K}$, Seebeck coefficient is enhanced and, on further cooling, it becomes comparable to samples with much lower number of carriers, in particular to $\text{Pr}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ [13]. In a rough estimate, this may mean that the formal cobalt valence in $y = 0.15$ is changed upon the M-I transition from original $\text{Co}^{3.3+}$ to about $\text{Co}^{3.1+}$.

**B. The low-temperature specific heat**

At the lowest temperatures, the insulating $y = 0.075$ and 0.15 samples exhibit a steep increase of specific heat (see the $c_p/T$ vs. $T^2$ plot in Fig. 7). Though a similar effect was reported originally for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$ the present experiments, performed down to 0.4 K, document for the first time that the increase is due to Schottky peak, centered at $T = 1-2 \text{ K}$, that adds to common lattice, electronic and nuclear contributions of low-temperature specific heat (Fig. 8). With increasing external field the peak position shifts rapidly to higher temperatures. The Schottky peak is absent in metallic $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ but is found with even larger intensity in $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ with analogous metallic ground state (see Figs. 7.
The occurrence of Schottky peak in Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ can be understood considering the Kramers character of the rare earth ions. In the orthoperovskite structure, the $^4$I$_{9/2}$ multiplet of Nd$^{3+}$ is split by crystal field effects into five relatively distant doublets [14]. The double degeneracy is lifted by an exchange field arising due to FM ordering of cobalt spins. Hence, the Schottky peak under discussion is related to thermal excitations within the ground state doublet, the location of the maximum defines the energy splitting due to exchange field ($\Delta = 0.42 \ k_B T_{max}$) and its shift with applied field bears information on the effective gyromagnetic $g_J'$ value that governs the Zeeman splitting ($\Delta = g_J' \mu_B (B + B_m)$, where $J'=\pm 1/2$ denotes two pseudospin levels of the Kramers doublet and $B_m$ is molecular field acting on the rare-earth moment). The shape of observed Schottky peak is nearly ideal with only a little extra broadening, and the integration of $c_{Schottky}/T$ over $T$ gives the total change of entropy of 3.95 JK$^{-1}$mol$^{-1}$, in good agreement with the theoretical value $0.7N k_B \ln 2 = 4.04$ JK$^{-1}$mol$^{-1}$ for Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ composition.

In the case of Pr$_{0.7}$Ca$_{0.3}$CoO$_3$ the $^3$H$_4$ multiplet of Pr$^{3+}$ is split into nine singlets [15]. In accordance with the non-magnetic (singlet) ground state, there is no Schottky peak at very low temperatures but another Schottky-like contribution emerges at $T > 10$ K, as can be seen by increased specific heat of Pr$_{0.7}$Ca$_{0.3}$CoO$_3$ in Figs. 7 and 8. It originates in an excitation to the next singlet state at an energy difference of 5 meV.

Analogously to Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ the Schottky peak in the yttrium doped samples (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ can be related to the presence of Kramers ions, which are Pr$^{4+}$ states formed presumably below $T_{M-I}$. A splitting of the $^2$F$_{5/2}$ multiplet to three doublets with large spacing is anticipated. The total entropy change is determined from data in Fig. 8 to 0.98 JK$^{-1}$mol$^{-1}$ for $y = 0.15$. This quantitative analysis enables to estimate the number of Pr$^{4+}$ states to about 0.18 per formula. For $y = 0.075$, the entropy change makes 0.61 JK$^{-1}$mol$^{-1}$ and corresponding number of Pr$^{4+}$ states is 0.12 per formula.

The change of Zeeman splitting of the ground state doublets with external field is presented in Fig. 10. There is a little shift of $T_{max}(Schottky)$ for Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ between zero field and 3 T, before it starts to rise nearly linearly. This shows that the external field does not simply add to the molecular field, in other words, there must be antiparallel or perpendicular orientation of the Nd$^{3+}$ moments with respect to the FM polarized Co spins in the ground state. On the other hand, the shift with external field in the $y = 0.15$ sam-
ple \((Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3\) is monotonous from the very beginning, which is indicative of a parallel orientation of the Pr\(^{4+}\) and Co moments.

**IV. DISCUSSION**

As established in earlier works, the M-I transition in heavily doped cobaltites, like \(Pr_{0.5}Ca_{0.5}CoO_3\) or \((Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3\) is conditioned by presence of praseodymium ions, combined with a suitable structural distortion which depends on an average ionic radius and size mismatch of the perovskite A-site ions (see \[6\] and references therein). Important finding of the recent \(GGA+U\) electronic structure calculations for \(Pr_{0.5}Ca_{0.5}CoO_3\) is the location of the occupied Pr\(^{3+}\)- 4f states closely below \(E_F\) at ambient temperature, and their splitting and partial transfer above \(E_F\) due to lattice contraction experimentally observed at \(T_{MI} = 90\) K. In ionic picture, this means that praseodymium valence in the metallic phase is Pr\(^{3+}\), and Pr\(^{4+}\) valence states are formed in the low-temperature insulating phase, compensated by a valence shift of cobalt ions towards pure Co\(^{3+}\). Such scenario is currently supported using different experiments on \((Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3\) namely the low-temperature specific heat, thermopower and magnetic susceptibility. In addition, some new information on physical properties over a broad temperature range is obtained and deserves more discussion.

The first issue is the character of electronic transport. The data in Fig. 1 suggest that the resistivity in pure \(Pr_{0.7}Ca_{0.3}CoO_3\) tends to a finite value. The metallicity is thus evident despite of the granular character of the ceramic sample. On the other hand, the \(y = 0.15\) sample of \((Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3\) shows a clear localization that is best fitted by Mott’s formula for variable range hopping (VRH), \(\rho = \rho_o \cdot \exp(T_o/T)^{1/4}\), valid for \(T < 40K\) (see Fig. 1b). The characteristic parameters are \(\rho_o \sim 4 \times 10^{-5}\) mΩcm and \(T_o \sim 8 \times 10^6\) K. The VRH mechanism is associated with a phonon-assisted tunneling of electrons from initial sites located near \(E_F\) to target sites close in energy, for which the Miller-Abrahams transfer rate applies (see e.g. recent review of N. Tessler \textit{et al.} \[16\]). This type of conduction is generally manifested with a specific \(T^{-1/2}\) dependence of thermopower, which is, however, not obeyed for present samples. Instead, the Seebeck coefficient increases steeply from zero value at the lowest temperatures in a linear metallic-like manner and then tends to a saturation, which is not reached completely because of ingoing transition. Such behavior is suggesting that
firstly, the present system possesses a quasi-continuous, very narrow band of electronic levels at \( E_F \), and secondly, the Seebeck coefficient is related to the presence of carriers rather than to their motion, \( i.e. \) the dominant contribution is the change of the net entropy of a solid upon the addition of a charge carrier, while the energy transported by carriers, divided by the absolute temperature, seems to be marginal - see \( e.g. \) Ref. [17].

Major experimental data refer, however, to specific heat in the \( y = 0.075 \) and \( 0.15 \) samples with occurrence of the M-I transition, compared to samples \( \text{Pr}_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) and \( \text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) with metallic ground state (Figs. 5 and 7). The dominant contribution to the specific heat above the liquid helium temperature is the phononic term that follows in the metallic samples a standard Debye-type dependence, though there is also extra contribution due to thermally activated population of the crystal field split levels of the rare earths (see \( e.g. \) [18]). At room temperature the \( c_p \) value reaches \( 118 \, \text{JK}^{-1}\text{mol}^{-1} \) for all the studied samples. This makes about 93\% of the saturated lattice heat taking into account the Dulong-Petit high temperature limit \( c_V = 15Nk_B \approx 125 \, \text{JK}^{-1}\text{mol}^{-1} \) in ABO\(_3\) perovskites and a minor correction for thermal expansion \( c_p-c_V \approx 1.2 \, \text{JK}^{-1}\text{mol}^{-1} \) at 300 K [18].

The phononic term in the low-temperature phase of the yttrium doped \( (\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) samples is clearly lower than that of the undoped samples. This is a strong indication that M-I transition is accompanied by a significant change of orthoperovskite structure, presumably by the lattice contraction and Pr-O bond length shortening, similar to those in \( \text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3 \).

As concerns the specific heat anomaly at \( T_{M-I} \), the associated entropy change is determined, by integration of an excess of \( c_p/T \), to 2.17 and 4.78 \( \text{JK}^{-1}\text{mol}^{-1} \) for \( (\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) with \( y = 0.075 \) and \( 0.15 \), respectively. It is of interest that the total entropy change at the gradual spin-state transitions in \( \text{LnCoO}_3 \) is about 20 \( \text{JK}^{-1}\text{mol}^{-1} \) and is distributed evenly between the first step from the LS Co\(^{3+}\) groundstate to a LS/HS mixture and the subsequent formation of the metallic phase of IS Co\(^{3+}\) character [18, 19].

At low-enough temperatures, there are two standard contributions of the specific heat, that can be easily distinguished in the \( c_p/T \) vs. \( T^2 \) plot in Fig. 7. One is the vanishing phononic term, approximated by the cubic term \( \beta T^3 \) where \( \beta \) is directly related to Debye temperature \( \Theta_D \). The parameters \( \beta \approx 0.00020 \) and \( 0.00024 \, \text{JK}^{-4}\text{mol}^{-1} \) for the \( y = 0.15 \) sample and \( \text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) shown in the fit in Figs. 8 and 9 give an estimate \( \Theta_D = 460 \) and 430 K for the insulating and metallic phase, respectively. The latter value should be
compared with $\Theta_D \sim 400$ K determined for metallic La$_{0.7}$Sr$_{0.3}$CoO$_3$ [20]. The second contribution is the linear term $\gamma T$. The $\gamma$ value $\sim 30$ mJK$^{-2}$mol$^{-1}$ for metallic Pr$_{0.7}$Ca$_{0.3}$CoO$_3$ and Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ is comparable to $\sim 40$ mJK$^{-2}$mol$^{-1}$ for La$_{0.7}$Sr$_{0.3}$CoO$_3$ [20]. The $\gamma$ parameter is, however, still larger in the insulating phase of the yttrium doped samples (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$, which corroborate the idea of charge carriers squeezed in a very narrow band. As concerns the baseline in Fig. 8 and 9, the remaining term is the nuclear contribution, manifested as the $\alpha T^{-2}$ upturn at the lowest temperature. The value $\alpha \sim 0.032$ mJK$^{-3}$mol$^{-1}$, observed on the $y = 0.15$ sample (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ is exceptionally large and apparently field independent. It is worth mentioning that recent specific heat study on La$_{1-x}$Sr$_x$CoO$_3$ report much smaller nuclear specific heat despite the bulk ferromagnetic state [20]. In these compounds, the nuclear heat originates in the Zeeman splitting of the spin $I = 7/2$ multiplet of $^{59}$Co nuclei in the hyperfine field induced by FM ordering of electronic spins. Its intensity thus probes the amount of FM phase in the sample. The very large $\alpha T^{-2}$ term in the $y = 0.15$ sample should be thus ascribed primarily to contribution of $^{141}$Pr nuclei with spin $I = 5/2$ in the hyperfine field induced by dressed Pr$^{4+}$ electronic pseudospins. On the other hand, the specific heat data for pure Pr$_{0.7}$Ca$_{0.3}$CoO$_3$ also included in Fig. 8 do not show observable nuclear contribution at zero field, but a comparable $\alpha T^{-2}$ term is induced in field of 9 T.

The Schottky peaks observed in Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ (Fig. 8) and yttrium doped (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ (Fig. 9) serve as local probe of the Kramers ions Nd$^{3+}$ and Pr$^{4+}$. Their position in the zero-field specific heat and shift with applied field allow to estimate that Nd$^{3+}$ pseudospins in Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ are characterized by effective $g_J = 1.85$ and experience a molecular field of $B_m = 2.5$ T, while for Pr$^{4+}$ pseudospins in the $y = 0.15$ sample (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ the respective values are $g_J = 3.30$ and $B_m = 1.6$ T (see Fig. 11). The origin of molecular field in metallic Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ is in ferromagnetic ordering of cobalt ions in IS states at $T_C \sim 25$ K ($M_s \sim 0.16 \mu_B$ per f.u.) and their interaction via $3d - 4f$ exchange mechanisms with spin component of the Nd$^{3+}$ moments. The situation in the low-temperature phase of (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ which exhibits essentially paramagnetic characteristics (see Figs. 4 and 6) is not clear and will require further experimental and theoretical investigation. If Pr$^{4+}$ pseudospins were ordered spontaneously, significantly sharper and higher peak (so called lambda peak) would be observed as is e.g. in the case of antiferromagnetic ordering of Nd$^{3+}$ moments in NdCoO$_3$ at $T_N = 1.2$ K [21]. The ob-
ervation of standard Schottky peak thus suggests that also in the yttrium doped samples the rare earths experience a stable molecular field formed in the cobalt subsystem. We note that the cobalt subsystem in the \(y = 0.15\) sample contains 12\% of LS Co\(^{4+}\) ions that represent spins 1/2 in a diamagnetic matrix of LS Co\(^{3+}\). Anticipating their itinerancy they may lead to certain ferromagnetic polarization of the narrow \(t_{2g}\) cobalt bands, low compared to Nd\(_{0.7}\)Ca\(_{0.3}\)CoO\(_3\) but sufficient to mediate relatively strong magnetic interactions among the Pr\(^{4+}\) pseudospins (RKKY model known for 3\(d - 4f\) intermetallics can be envisaged [22]). Such interpretation seems to be supported by two findings - the parallel orientation of praseodymium moments with cobalt spins, manifested in the field-induced shift of Schottky peak in Fig. 10, and the unusually large term \(\alpha T^{-2}\) contributed by the \(^{141}\)Pr nuclear spins, seen for the \(y = 0.15\) sample \((\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) in Fig. 8.

V. CONCLUSION

A comparative study of perovskite cobaltites \((Ln_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) perovskites (\(Ln = \text{Pr}, \text{Nd}\)) was undertaken with an aim to elucidate the character of a peculiar first-order M-I transition in some Pr-based cobaltites. Though the transition is typical for Pr\(_{0.5}\)Ca\(_{0.5}\)CoO\(_3\), the present yttrium doped systems \((\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) with \(T_{M-I} = 64\) and 132 K for \(y = 0.075\) and 0.15, respectively, appear preferable because of easier stabilization of the stoichiometric phase and complete transformation from the metallic to insulating state. The study shows that the M-I transition is manifested by a huge peak in the specific heat data and marked changes in the electrical resistivity, thermopower and thermal conductivity. A sudden drop of magnetic susceptibility indicates a change of cobalt states from the metallic \(t_{2g}^{5}\sigma^{*}\) to the mixture of LS Co\(^{3+}\) (\(t_{6g}^{5}\)) and LS Co\(^{4+}\) (\(t_{2g}^{5}\)).

An important novelty is an observation of Schottky peak in specific heat data at very low temperatures, 0.4 – 10 K. This peak is absent in pure Pr\(_{0.7}\)Ca\(_{0.3}\)CoO\(_3\) in which metallic phase is retained down to the lowest temperature, but appears with large intensity in Nd\(_{0.7}\)Ca\(_{0.3}\)CoO\(_3\) with similar metallic phase. Its occurrence follows from the Kramers character of Nd\(^{3+}\) and Pr\(^{4+}\) whose \(^{4}\)I\(_{9/2}\) and \(^{2}\)F\(_{5/2}\) multiplets are split by crystal field associated with the distorted dodecahedral coordination of the rare earths in the \(Pbnm\) perovskites. The Schottky peak thus probes the Zeeman splitting of the ground state doublet. The total entropy change associated with the Schottky peak is \(k_B ln 2\) per ion, which allows to determine
the concentration of Kramers ions in the samples experimentally, by integration of $c_{Schottky}/T$ over $T$. The analysis for the $y = 0.075$ and $0.15$ samples $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ provides values $0.12$ and $0.18 \text{Pr}^{4+}$ per formula unit, respectively. Considering that praseodymium ions are essentially in trivalent state in the high-temperature phase, the observation of $\text{Pr}^{4+}$ in the low-temperature phase is in accordance with idea that the simultaneous M-I and spin-state transition in Pr-based cobaltites is accompanied by an electronic transfer between the praseodymium and cobalt ions. In particular for $y = 0.15$, the present results are indicative of a significant change from common valence distribution in the metallic state, $(\text{Pr}_{0.85}\text{Y}_{0.15})_{0.7}\text{Ca}_{0.3}\text{Co}_{0.7}\text{Co}_{0.3}\text{Co}_{0.7}\text{O}_2^-$, to $(\text{Pr}_{0.59}\text{Pr}_{0.26}\text{Y}_{0.15})_{0.7}\text{Ca}_{0.3}\text{Co}_{0.88}\text{Co}_{0.12}\text{O}_2^-$ in the insulating state.

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FIG. 1: (Color online) The temperature dependence of electrical resistivity in $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ ($y = 0$, 0.075 and 0.15) and $\text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$. The data measured on cooling and warming are overlapping. The lower panel shows the dependence on $T^{-1/4}$. 
FIG. 2: (Color online) The enhanced Seebeck coefficient in $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ $(y = 0.075$ and $0.15)$ below the M-I transition. The data for metallic $Pr_{0.7}Ca_{0.3}CoO_3$ and $Nd_{0.7}Ca_{0.3}CoO_3$ are also shown. The solid line gives data for $Pr_{0.9}Ca_{0.1}CoO_3$ taken of Ref. [13] (see the text).
FIG. 3: (Color online) Thermal conductivity of (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ for $y = 0, 0.075$ and 0.15.
FIG. 4: (Color online) Magnetic susceptibility of $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ for $y = 0$, 0.075 and 0.15 (in log scale). The lower panel shows the temperature dependence of inverse susceptibility. The solid lines mark the theoretical contribution for $Pr^{3+}$ and $Pr^{4+}$ ions, calculated for the praseodymium amount in $y = 0.15$ using the data in Ref. [12] (see the text). The data for $(Nd_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ for $y = 0$ and 0.075 without M-I transition are added for comparison.
FIG. 5: (Color online) Specific heat of $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ for $y = 0, 0.075$ and $0.15$. The data for Nd$_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ are added for comparison.
FIG. 6: (Color online) Magnetization loops measured at 2 K (open symbols) and 4.5 K (solid symbols) on \((\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) \((y = 0\) and \(0.15\)).
FIG. 7: (Color online) The low-temperature specific heat of (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ and Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ shown in the $c_p/T$ vs. $T^2$ plot. Beside common cubic lattice term $\beta T^3$ and linear $\gamma T$ term, one may notice an additional contribution for $y = 0$, associated with excitations within the crystal field split multiplet of Pr$^{3+}$, and an important Schottky anomaly for $y = 0.075, 0.15$ and Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ that shifts with external field.
FIG. 8: (Color online) Specific heat of \((\text{Pr}_{0.85} \text{Y}_{0.15})_{0.7} \text{Ca}_{0.3} \text{CoO}_3\) down to 0.4 K, measured in fields 0 – 9 Tesla. The heat capacity for metallic \(\text{Pr}_{0.7} \text{Ca}_{0.3} \text{CoO}_3\) \((y = 0)\) added for comparison is displaced to -0.3.
FIG. 9: (Color online) Specific heat of \( \text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) down to 0.4 K, measured in fields 0 - 9 Tesla.
FIG. 10: (Color online) The shift of the Schottky peak maximum ($T_{\text{max}}$ in the $c_{\text{Schottky}}$ vs. $T$ dependence) with applied field. The lines define the effective $g$-factors of the Kramers ground state doublets of Pr$^{4+}$ and Nd$^{3+}$. The molecular field experienced by rare-earth moments at $B = 0$ is determined to $\approx 1.6$ Tesla in (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ ($y = 0.15$) and $\approx 2.5$ Tesla in Nd$_{0.7}$Ca$_{0.3}$CoO$_3$. 