The spin-state crossover and low-temperature magnetic state in yttrium doped Pr$_{0.7}$Ca$_{0.3}$CoO$_3$

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The structural and magnetic properties of two mixed-valence cobaltites with formal population of 0.30 Co$^{3+}$ ions per f.u., (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ (y = 0 and 0.15), have been studied down to very low temperatures by means of the high-resolution neutron diffraction, SQUID magnetometry and heat capacity measurements. The results are interpreted within the scenario of the spin-state crossover from a room-temperature mixture of the intermediate spin Co$^{3+}$ and low spin Co$^{4+}$ (IS/LS) at the to the LS/LS mixture in the sample ground states. In contrast to the yttrium free y = 0 that retains the metallic-like character and exhibits ferromagnetic ordering below 55 K, the doped system y = 0.15 undergoes a first-order metal-insulator transition at 132 K, during which not only the crossover to low spin states but also a partial electron transfer from Pr$^{3+}$ 4f to cobalt 3d states take place simultaneously. Taking into account the non-magnetic character of LS Co$^{3+}$, such valence shift electronic transition causes a magnetic dilution, formally to 0.12 LS Co$^{3+}$ or 0.12 $t_{2g}$ hole spins per f.u., which is the reason for an insulating, highly non-uniform magnetic ground state without long-range order. Nevertheless, even in that case there exists a relatively strong molecular field distributed over all the crystal lattice. It is argued that the spontaneous FM order in y = 0 and the existence of strong FM correlations in y = 0.15 apparently contradict the single $t_{2g}$ band character of LS/LS phase. The explanation we suggest relies on a model of the defect induced, itinerant hole mediated magnetism, where the defects are identified with the magnetic high-spin Co$^{3+}$ species stabilized near oxygen vacancies.

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I. INTRODUCTION

Perovskite cobaltites display a wide variety of structural and physical properties in dependence on the composition and temperature. Two distinct behaviors can be identified. One is characteristic for the undoped LaCoO$_3$ and its rare-earth analogs. Their insulating ground state derives from Co$^{3+}$ ions in the diamagnetic low-spin (LS) states. With increasing temperature two spin-state crossovers take place. First, the paramagnetic high-spin (HS) states are induced by thermal excitation and are gradually stabilized, which results a spin-state dis-proportionated phase with strong HS/LS nearest neighbor correlations or even short-range orderings [1], that can be classified as Mott insulator. At elevated temperature the correlations melt [2], and a more uniform phase of quasi-metallic character is established. To account for this change and to explain the paramagnetic properties actually observed, the high-temperature phase of LaCoO$_3$ was tentatively described as consisting of the intermediate-spin (IS) of Co$^{3+}$ species ($S = 1, m_{eff} = 2.83 \mu_B$) [3][4]. It should be noted, however, that DMFT calculations suggest for the high-temperature phase of LaCoO$_3$ a complex global state with the main weight of LS and HS states with only short visits to IS configurations [5].

Another extreme case are the metallic ground states with bulk ferromagnetic (FM) ordering, known for hole-doped systems La$_{1-x}$Sr$_x$CoO$_3$ above a critical concentration $x_c = 0.22$ [7][8]. Recent DMFT calculations suggest also for this case a complex distribution of local cobalt valences and spin states [9], but with certain simplification, the metallic nature of these FM phases can be related to electron transfer between neighbors of the IS Co$^{3+}$/LS Co$^{4+}$ or HS Co$^{3+}$/HS Co$^{4+}$ kinds, eventually also LS Co$^{3+}$/LS Co$^{4+}$ [10][11]. At least in the compositional region close above $x_c$, the La$_{1-x}$Sr$_x$CoO$_3$ systems seem to be dominated by a dynamic mixture of IS Co$^{3+}$ and LS Co$^{4+}$ and is described for illustration as the IS/LS phase. This conclusion finds a support among others by the observed values of ordered ferromagnetic moments, making in particular 1.70 $\mu_B$ per f.u. for $x = 0.30$.

When large cations in La$_{0.7}$Sr$_{0.3}$CoO$_3$ are substituted by rare-earth or calcium ions of smaller size, the FM ordering still exists but the spontaneous moments actually observed are much suppressed. Although this effect was originally related to a phase separation into FM and non-FM, the final state at the lowest temperature is now proved, based mainly on the uniformity of molecular field acting on Nd$^{3+}$ moments in Nd$_{0.7}$Ca$_{0.3}$CoO$_3$, etc.
to be essentially of single FM phase. The observed spontaneous moments, approaching in Nd$_{0.7}$Ca$_{0.3}$CoO$_3$ and Pr$_{0.7}$Ca$_{0.3}$CoO$_3$ a limiting low value of 0.30 $\mu_B$ per f.u., can be thus ascribed to a stabilization of the LS/LS phase, i.e. to the alternative ground state of the hole-doped cobaltites, which consists of a dynamic LS Co$^{3+}$/LS Co$^{4+}$ mixture.

The present paper deals namely with Pr$_{0.7}$Ca$_{0.3}$CoO$_3$ and related compounds (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$. These systems, all with 30% doping, show a quasi-metallic conductivity at ambient conditions, but in contrast to the formation of FM state in pure Pr$_{0.7}$Ca$_{0.3}$CoO$_3$, the samples with partial substitution of Pr$^{3+}$ by isovalent Y$^{3+}$ (for $y > 0.06$) exhibit a first order transition to a weakly paramagnetic insulating state. Let us note that this distinct transition was observed for the first time in the 50% doped cobaltite Pr$_{0.5}$Ca$_{0.5}$CoO$_3$ upon a cooling below a critical point $T_M \sim 80$ K, and the change of electric properties was accompanied with important volume, magnetic and heat capacity anomalies $^{[12, 13]}$. Later on, similar transition and anomalies were found also in other praseodymium based systems in larger region of doping. A question has been raised why sharp transition is encountered solely in praseodymium containing cobaltites. As suggested by GGA calculations and some new experimental results, including analysis of the temperature change of interatomic lengths and XANES spectra in Pr$_{0.5}$Ca$_{0.5}$CoO$_3$, the reason for stabilization of the insulating low-temperature phase is a shift of the mixed valence Co$^{3+}$/Co$^{4+}$ toward pure Co$^{3+}$, enabled by valence change of some Pr$^{3+}$ ions to Pr$^{4+}$ ones. The decisive factor is, therefore, the exceptional closeness in energy of the two praseodymium states. The valence shift upon phase transition has been further confirmed and determined quantitatively by observation of the Pr$^{4+}$ related Schottky peak in heat capacity measurements $^{[14]}$ and by X-ray absorption spectroscopy at Pr L$_3$ edge $^{[15, 16]}$. In addition to the valence shift, a crossover from the IS or mixed LS/HS Co$^{4+}$ state to the LS states has been evidenced by drop of the paramagnetic susceptibility and by low values of effective moments below $T_M$, as well as by a detailed fit of the Co X-ray absorption and emission spectra $^{[17]}$.

In contrast to the prototypical compound Pr$_{0.5}$Ca$_{0.5}$CoO$_3$, which is difficult to prepare because of problems with oxygen deficiency and phase separation, the less doped systems (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ appeared more suitable for experimental studies. The presence of $M - I$ transition is demonstrated indirectly by peaks in heat capacity at $T_{MI} = 40$, 64 K, 93 K and 132 K for $y = 0.0625, 0.075, 0.10$ and 0.15, respectively (see Fig. 1). The stabilization of tetravalent praseodymium in the low-temperature phase has been indicated by appearance of the low-temperature Schottky peaks, arising due to Kramers degeneracy of Pr$^{4+}$ states and Zeeman splitting of ground doublet by action of the molecular and external magnetic fields. The quantitative analysis determines that the Pr$^{4+}$ population varies between 0.11 and to 0.18 per f.u., which means that the hole concentration is decreased upon the transition from the original 30% level to 19% doping in $y = 0.0625$ and 12% doping in $y = 0.15$ $^{[13, 18]}$. (No valence change was observed in pure Pr$_{0.7}$Ca$_{0.3}$CoO$_3$.) The motivation for present study is to elucidate the character of the Pr$^{4+}$ species formed below the $M-I$ transition and to investigate the microscopic origin of unexpectedly strong molecular field of about 17 kOe, which acts on Pr$^{4+}$ pseudospins in the low-temperature insulating phase. The study includes neutron diffraction and magnetic measurements on two selected (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ samples ($y = 0$ and 0.15) down to 0.25 K.

![Graph](image_url)

**FIG. 1**: Temperature dependence of the specific heat of (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ ($y = 0.0625 - 0.15$). The critical temperatures of $M-I$ transitions are marked.

**II. EXPERIMENTS AND CALCULATIONS**

(Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ ($y = 0$ and 0.15) samples were prepared by a solid-state reaction as described elsewhere $^{[18]}$. The powder neutron diffraction was performed on diffractometer Hb2a at Oak Ridge National Laboratory. The scans were recorded at selected temperatures between the room temperature and 0.25 K. Two crystal monochromators (Ge113 and Ge115) were used, providing neutron wavelengths $\lambda = 2.408$ Å and 1.537 Å, respectively. Data were collected between 8° and 126° of 2θ with the step of 0.08°. Structural refinements were done by Rietveld profile analysis using program FULLPROF (Version 5.30 - Mar2012-ILL JRC).

The magnetic properties were investigated in the temperature range 2 – 400 K using Quantum Design DC superconducting quantum interference device (SQUID) MPMS XL magnetometer. For the DC extraction magnetization measurements up to 140 kOe the QD PPMS AC/DC magnetometer with the ACMS Option was...
used. The experiments included the field-cooled (FC) and zero-field-cooled (ZFC) susceptibility scan in range 2 – 300 K using DC field of 20 Oe, together with the low-temperature measurements of virgin magnetization curves and complete hysteresis loops. In addition, the exchange bias experiments at 2 K were performed on field-cooled samples for bias fields from 500 Oe to 70 kOe. The thermoremanent was measured after cooling the sample in high field (typically 70 kOe) down to 2 K, switching off the field and scanning the magnetization at zero field on sample warming.

In order to determine the ground state properties of \((\text{Pr}_{1 - y} \text{Y}_y)_{0.7} \text{Ca}_{0.3} \text{CoO}_3\) cobaltites, the low-temperature magnetic contribution of the \(\text{Pr}^{3+}\) and \(\text{Pr}^{4+}\) ions was theoretically analyzed. For this sake the crystal field splitted \(4f^a\) electronic levels were calculated using ‘lanthanide’ package [14]. This program determines takes into account the free-ion (atomic) and crystal field terms, as well as interactions with the molecular and external magnetic fields. As to the spherical symmetrical free-ion Hamiltonian is concerned, it depends on many parameters, the values of which are either known experimentally or may be calculated - for details see e.g. Ref. [20]. The crystal field Hamiltonian represents more formidable problem. In the present case of \(Cs\) symmetry of rare-earth sites, the single-electron crystal field is described by fifteen parameters. The best choice for \(\text{Pr}^{3+}\) in \((\text{Pr}_{1 - y} \text{Y}_y)_{0.7} \text{Ca}_{0.3} \text{CoO}_3\) is the set of crystal field parameters determined very recently for \(\text{PrCoO}_3\) using a first principle method [21]. The output of the ‘lanthanide’ calculation shows that the \(^1\text{H}_4\) multiplet of \(\text{Pr}^{3+}\) \((4f^2)\) splits into nine non-magnetic singlets and the ground state properties are manifested by anisotropic Van Vleck susceptibility with components \(\chi_a = 0.0254\) emu mol\(^{-1}\)Oe\(^{-1}\), \(\chi_b = 0.0181\) emu mol\(^{-1}\)Oe\(^{-1}\) and \(\chi_c = 0.0123\) emu mol\(^{-1}\)Oe\(^{-1}\) along the orthorhombic axes of \(Pbnm\) structure. This yields an average value \(\chi_{ov} = 0.0181\) emu mol\(^{-1}\)Oe\(^{-1}\) for the polycrystal, which is in excellent agreement with experimental data on a related \(\text{PrCoO}_3\) system in Ref. [21], namely with its temperature nearly independent susceptibility in the range up to \(T \sim 40\) K, i.e. before the first excited level at 11 meV starts to be populated.

The calculation for \(\text{Pr}^{4+}\) (formally \(4f^{1}\) configuration but with large \(4f^2L\) admixture) is subjected to more uncertainty and, moreover, there are no orthorhovskites with \(\text{Pr}^{4+}\) majority, which would allow an experimental check. As a first estimate, the values of crystal field parameters can be taken from very detailed optical spectroscopic study of \(\text{ThAlO}_3\) [22], taking into account that this aluminate possesses the same \(Pbnm\) orthorhovskite structure and practically identical octahedral tilting as the present \((\text{Pr}_{1 - y} \text{Y}_y)_{0.7} \text{Ca}_{0.3} \text{CoO}_3\) \((y = 0.15)\) sample in the low-temperature phase. The calculation shows that the \(^2F_{5/2}\) multiplet of \(\text{Pr}^{4+}\) splits into three energy distant Kramer doublets (see Appendix of Ref. [11]). The magnetic moments associated with ground doublet \((J' = 1/2)\) are given by anisotropic \(g\)-factor with principal components \(g_x = 3.757\), \(g_y = 0.935\) and \(g_z = 0.606\). (Here, the local axes \(x\) and \(y\) are turned with respect to the main axes of the \(Pbnm\) structure, making for two inequivalent rare-earth sites a rotation to \(\pm 36^\circ\) around the orthorhombic axis \(c\)).

III. RESULTS

A. Neutron diffraction study.

The neutron diffraction pattern taken on \((\text{Pr}_{1 - y} \text{Y}_y)_{0.7} \text{Ca}_{0.3} \text{CoO}_3\) \((y = 0\) and \(0.15)\) are exemplified together with the FULLPROF fit in Fig. 2a and 2b. Although the mixed-valence cobaltites are generally subjected to an oxygen deficiency, the occupation of oxygen sites in present two samples is surely close to the ideal stoichiometry, the refined values being 2.99 ± 0.01 and 3.01 ± 0.01 per f.u., respectively. The values of other structural parameters are summarized in Tables I and II and the unit cell volume and selected interatomic distances and angles are plotted in Fig. 5a,b. There is little change with temperature for the \(y = 0\) sample, except common thermal expansion. On contrary, the \(y = 0.15\) sample shows a marked volume compression on cooling below \(T_{MI} = 132\) K, which is accompanied by an increase of orthorhombic lattice distortion. Closer inspection reveals larger deviation of the O-Co-O angles from ideal 180° and some drop of the (Pr, Y, Ca)-O binding distances, while the Co-O distances remain practically unchanged. All these signatures are manifestations of the decreased ionic size upon \(\text{Pr}^{3+} \rightarrow \text{Pr}^{4+}\) valence shift - see the similar findings for \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3\) in Ref. [23].

As the magnetic state is concerned, the \(y = 0\) sample shows below \(T_C = 55\) K a long range ferromagnetic (FM) order of cobalt spins that is readily seen in magnetic measurements (see below) but is only hardly visible in the neutron diffraction patterns as very weak increase of some lines, mainly 110+002 and 200+112+020. The value of spontaneous moment determined from the neutron data reaches 0.34 ± 0.10\(\mu_B\) at 0.25 K.

The detection of eventual FM ordering in \(y = 0.15\) is still more difficult since the cobalt subsystem is now magnetically very dilute with only 0.12 LS Co\(^{4+}\) ions per f.u. These moments alone are below the detection limit of the neutron diffraction, but some chance is offered by very low temperatures where full alignment of \(\text{Pr}^{4+}\) moments (the \(J' = 1/2\) pseudospins) due to the above-mentioned molecular field of \(H_m \sim 17\) kOe could be anticipated and might add to the cobalt FM order. Nonetheless, even at 0.25 K we failed to detect any observable diffraction intensity that could prove an existence of long range ordering in the low-temperature phase of \(y = 0.15\). Let us note that for prototypical \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3\) as well, no long-range FM order was found [24] although the molecular field in that system is as high as \(H_m \sim 75\) kOe [14]. We address this issue below and suggest an explanation.
TABLE I: Structural parameters for (Pr$_{1-y}$Y)$_0.7$Ca$_0.3$CoO$_3$ with $y = 0$ within the Pbnm space group. Refinable atom coordinates: PrCa 4c(x,y,1/4), Co 4b(1/2,0,0), O1 4c(x,y,1/4), O2 8d(x,y,z)

| T (K) | 0.25 | 2   | 40  | 298 |
|------|------|-----|-----|-----|
| a (Å) | 5.3468(2) | 5.3465(2) | 5.3463(4) | 5.3637(2) |
| b (Å) | 5.3359(2) | 5.3353(2) | 5.3352(4) | 5.3516(2) |
| c (Å) | 7.5386(3) | 7.5383(2) | 7.5388(5) | 7.5702(4) |
| x,Pr | -0.0048(9) | -0.0052(8) | -0.0047(11) | -0.0066(10) |
| y,Pr | 0.0347(7) | 0.0323(5) | 0.0350(8) | 0.0277(4) |
| x,O1 | 0.0687(7) | 0.0676(5) | 0.0704(8) | 0.0637(8) |
| y,O1 | 0.4921(8) | 0.4912(5) | 0.4923(9) | 0.4901(11) |
| x,O2 | -0.2859(7) | -0.2838(4) | -0.2880(8) | -0.2807(9) |
| y,O2 | 0.2818(9) | 0.2855(4) | 0.2820(10) | 0.2807(9) |
| z,O2 | 0.0356(3) | 0.0358(2) | 0.0356(6) | 0.0319(8) |

TABLE II: Structural parameters for (Pr$_{1-y}$Y)$_0.7$Ca$_0.3$CoO$_3$ with $y = 0.15$ within the Pbnm space group. Refinable atom coordinates: PrYCa 4c(x,y,1/4), Co 4b(1/2,0,0), O1 4c(x,y,1/4), O2 8d(x,y,z)

| T (K) | 0.25 | 2   | 10  | 132 | 170 | 298 |
|------|------|-----|-----|-----|-----|-----|
| a (Å) | 5.2827(4) | 5.2823(5) | 5.2824(5) | 5.2864(5) | 5.3041(6) | 5.3241 (4) | 5.3405(6) |
| b (Å) | 5.3283(4) | 5.3274(5) | 5.3275(5) | 5.3295(5) | 5.3349(6) | 5.3401 (4) | 5.3513(6) |
| c (Å) | 7.4853(6) | 7.4846(8) | 7.4847(8) | 7.4896(8) | 7.5051(9) | 7.5274 (6) | 7.5471(8) |
| x,Pr | -0.0075(6) | -0.0090(10) | -0.0097(9) | -0.0066(9) | -0.0061(11) | -0.0050(10) | -0.0034(11) |
| y,Pr | 0.0451(4) | 0.0431(6) | 0.0441(6) | 0.0439(5) | 0.0410(6) | 0.0377 (5) | 0.0324(2) |
| x,O1 | 0.0794(5) | 0.0791(7) | 0.0796(7) | 0.0781(7) | 0.0760(8) | 0.0722 (8) | 0.0707(10) |
| y,O1 | 0.4874(4) | 0.4861(6) | 0.4865(6) | 0.4873(5) | 0.4884(6) | 0.4902(5) | 0.4928(16) |
| x,O2 | -0.2917(3) | -0.2901(4) | -0.2902(4) | -0.2913(4) | -0.2883(5) | -0.2870(5) | -0.2848(14) |
| y,O2 | 0.2919(3) | 0.2912(4) | 0.2904(4) | 0.2917(4) | 0.2896(5) | 0.2874(4) | 0.2848(14) |
| z,O2 | 0.0399(2) | 0.0413(3) | 0.0415(3) | 0.0401(3) | 0.0382(3) | 0.0370(3) | 0.0354(10) |

FIG. 2: Neutron diffraction of $y = 0$ at low temperature.

FIG. 3: Neutron diffraction of $y = 0.15$ at low temperature.

B. Magnetic measurements.

The basic magnetic characterization of the (Pr$_{1-y}$Y)$_0.7$Ca$_0.3$CoO$_3$ system was presented in our previous paper [18]. New data on ZFC/FC susceptibilities have been taken for low DC fields. The

results are given in upper panel of Fig. 6, while the lower panel illustrates the behavior in high magnetic fields, in particular it shows the magnetization curves for the $y = 0$ and 0.15 samples, taken at 2 K in the field range 0 – 140 kOe and back.

The susceptibility data evidence a FM transition in
FIG. 4: Neutron diffraction of $y = 0.15$ around the transition.

FIG. 5: Lattice parameters and bond lengths for $y = 0.15$.

FIG. 6: Upper panel: The ZFC and FC susceptibility on $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ ($y = 0$ and 0.15) measured in DC field of 20 Oe. Note the logarithmic scale on the moment axis. Lower panel: The magnetization in fields up to 140 kOe and back, taken at 2 K.

The $y = 0$ sample at $T_C = 55$ K, determined by inflection point on the fast rise of susceptibility curves, while the $y = 0.15$ sample is characterized by a drop of susceptibility that accompanies the $M - I$ transition at $T_{MI} = 132$ K. It should be noted that preformation of FM clusters at 250 − 270 K, reported in some recent studies of similar cobaltites [25, 26], is not observed for present samples. In particular, neither ZFC/FC bifurcation nor finite remanence extending to such high temperatures can be detected.

The magnetization data for $y = 0$ in lower panel of Fig. 6 show a significant paraprocess that is superimposed on a hysteresis loop of relatively large coercivity (see Fig. 6) that reach 9 kOe at 2 K. Similar paraprocess extending to very high fields has been observed also for related manganites $Pr_{0.7}Ca_{0.3}MnO_3$ [27]. We thus ascribe this linear term to the Van Vleck susceptibility of $Pr^{3+}$ and, taking experimental data on purely LS $Co^{3+}$ system $PrCoO_3$ in polycrystalline form as a standard, $\chi_{VV} = 0.0188$ emu mol$^{-1}$ Oe$^{-1}$, or equivalently $0.0034 \mu_B/k$Oe [21], we find for valence composition $Pr_{0.7}Ca_{0.3}Co^{3+}_{0.7}Co^{4+}_{0.3}O_2$ of the $y = 0$ sample a reduction of the paraprocess by factor 0.78. This is in a reasonable agreement with the actual content of 0.70 $Pr^{3+}$.

After subtraction of the $Pr^{3+}$ related paraprocess, the magnetization of the cobalt subsystem in $y = 0$, pre-
after subtraction of the Pr field, the IS/LS phase with theoretical FM moment of 0.30 $\mu_B$. This finding is an independent confirmation of the Pr$^{3+}$ $\rightarrow$ Pr$^{4+}$ valence shift below $T_{MI}$. In fact, it is in very good quantitative agreement with the valence composition, which was deduced from Schottky peak analysis in Ref. [18] - Pr$_{0.415}$Pr$^{3+}$_{0.18}Y$_{0.105}$Ca$_{0.3}$Co$_{0.88}$Co$_{0.12}$O$_{3}^{2-}$.

The magnetization of $y = 0.15$ after the subtraction of the Pr$^{3+}$ paraprocess is presented in Fig. 3. It saturates at 140 kOe on 0.30 $\mu_B$ per f.u., of which 0.12 $\mu_B$ should be attributed to the Co$^{4+}$ contribution in the LS/LS phase and remaining 0.18 $\mu_B$ is evidently the contribution of Pr$^{4+}$ pseudospins in the $y = 0.15$ sample, supposing the value of $g_J$-factor close to 2. Let us note that such value is quite reasonable in view of our theoretical estimates for Pr$^{4+}$, $g_x = 3.757$, $g_y = 0.935$ and $g_z = 0.606$, which yield the average value $(g_{av}) = 2.07$ when a numerical integration over random orientation of the crystallites is done.

The magnetization curves observed for the $y = 0.15$ sample at low temperatures deviate largely from conventional FM behavior. At the first look, the $M$ vs $H$ dependence reminds a paramagnet close to the saturation, but compared to standard Brillouin function the increase in low fields is steeper, suggesting a presence of large spin entities with non-uniform distribution. We estimate from the observed trend that superparamagnetic domains up to 100 cobalt ions are prevailing in the $y = 0.15$ sample. On the other hand, the increase in high fields is slower as if there were strong AFM coupling between up-grown FM regions or presence of surface states with large magnetic anisotropy as known for so-called dead layer in nanoparticles. In closer inspection, one may also notice certain opening of magnetization loops at the lowest temperatures, which is characterized by coercitive field of about 200 Oe at 2 K. A finite but very weak remanent moment of 0.014 $\mu_B$/Co at 2 K quickly vanishes with increasing temperature (see Fig. 3). Similar behavior has been observed also for other (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ samples with $M - I$ transition, as well as for Pr$_{0.5}$Ca$_{0.5}$CoO$_3$ where remanent moment at 2 K is, however, an order of magnitude larger [28].

Another signature of complex magnetic state of the $y = 0.15$ sample is a presence of exchange bias, demonstrated in Fig. 4. The effect is strongly dependent on the magnitude of bias field.

IV. DISCUSSION

The cobaltites are systems with large complexity. In order to understand the physical properties of the mixed-valence cobaltites of 30% doping range, at least in an illustrative way, the IS/LS scenario for Co$^{3+}$/Co$^{4+}$ is generally applied. It is worth mentioning that this scenario implies carriers in two bands of very different characters and mobilities. The $e_g$ quasiparticles are light but
FIG. 9: The thermoremanent magnetization of \((\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) samples. The data for \(y = 0.15\) are compared with the \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3\) sample possessing at least 20× larger thermoremanence due to excessive defects.

FIG. 10: The hysteresis loops for \((\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) (\(y = 0.15\)), taken at 2 K after the cooling in exchange bias fields 1 and 20 kOe. The inset shows the exchange bias values (the abscissa shift of the loops) in broader range of fields.

FIG. 11: The heat capacity divided by temperature for \((\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) (\(y = 0.15\)), after subtraction of lattice and nuclear terms. The full lines present the theoretical fit based on the broadening due to anisotropic Zeeman splitting, supposing the axial symmetry of the g-factor. The actual values of Zeeman energy are plotted in the inset.

move in a disordered background of nearly localized \(t_{2g}\) charges and spins, and become strongly scattered, while the \(t_{2g}\) quasiparticles though heavy and short-living see a practically uniform background because of very fast fluctuations of the \(e_g\) electron subsystem. The decreased scattering in the latter case may cause that the overall conductivity is likely contributed by both the \(e_g\) and \(t_{2g}\) channels. With decreasing temperature, the system \(\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3\) of broad \(e_g\) band maintains IS/LS phase, whereas the narrow-band systems like \(\text{Pr}_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) or \(\text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) exhibit a gradual crossover towards lower spin states. In contrast to true metallic conductivity of \(\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3\), the electrical resistivity observed on \(\text{Pr}_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) or \(\text{Nd}_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) shows a steady increase with decreasing temperature but extrapolates to a finite value instead of diverging. This suggests that also in this latter case the LS/LS phase of 30% \(t_{2g}\) hole doping should be considered as intrinsically metallic.

The spin state crossover in the yttrium containing samples (\(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3\)) is much more abrupt since it is accelerated by the electron transfer from \(\text{Pr}^{3+}\) to \(\text{Co}^{4+}\) at the \(M - I\) transition. In the LS/LS ground state, the carrier concentration in the Co-O subsystem is thus reduced, in particular for the \(y = 0.15\) sample down to 12% \(t_{2g}\) hole doping. Following the observed resistivity dependence down to 6 K, the actual regime of conduction is variable range hopping. This means that the charge transport is realized via localized states close to Fermi level or, in other words, the doping level in the \(y = 0.15\) sample is below the mobility edge for the \(t_{2g}\) band of LS/LS phase.

The difference between the \(y = 0\) and \(0.15\) samples is manifested also in their magnetic state. The \(y = 0\) sample behaves at the lowest temperatures as a standard FM system with broad hysteresis loops that evidence an existence of domain structure. The long range magnetic order and spontaneous moments of about 0.30 \(\mu_B/\text{Co}\) are found by both the neutron diffraction and magnetization measurements. We may mention, however, that the transition from the paramagnetic state is unconventional. First, no heat capacity anomaly is observed at \(T_C = 55\) K. Another feature reported in some previous studies of \(\text{Pr}_{0.7}\text{Ca}_{0.3}\text{CoO}_3\) is the observation of nano-
size FM objects at temperatures as high as ~ 250 K. These have been detected by both the small angle neutron scattering and ZFC/FC bifurcation of the susceptibility. The lack of the latter anomaly in present study suggests that if such preformed FM objects are intrinsic to Pr$_{0.7}$Ca$_{0.3}$CoO$_3$, their size and number of are likely sample dependent.

The long-range FM order is absent in our $y = 0.15$ sample as well as in Pr$_{0.5}$Ca$_{0.5}$CoO$_3$, which is known as prototype of the $M - I$ transition in Pr-based cobaltites. Three magnetic contribution are effective in the insulating phase of these systems - spins of LS Co$^{4+}$, pseudospins of the Pr$^{4+}$ ground doublet and singlet states of Pr$^{3+}$ with extremely large Van Vleck susceptibility $\chi_V = 0.0188$ emu mol$^{-1}$Oe$^{-1}$, or equivalently 0.0034 $\mu_B$/kOe ($\chi_V$ for the spin and orbital singlet LS Co$^{3+}$ is two orders of magnitude smaller, 0.0002 emu mol$^{-1}$Oe$^{-1}$, and has thus negligible effect on the total magnetization).

It has been shown above that the paraprocess due to Pr$^{3+}$ contribution is simply separable, and consistent data with respect to the Pr$^{3+}$ $\rightarrow$ Pr$^{4+}$ valence shift are obtained. The resolution of the LS Co$^{4+}$ and Pr$^{4+}$ contributions appeared impossible, but their overall magnetization in Fig. 8 is suggesting for a magnetically non-uniform system. This issue has been largely discussed in relation to an opposite effect in Nd-based cobaltites.

V. CONCLUSIONS

The neutron diffraction and magnetic study have been performed on two cobaltite systems (Pr$_{1-y}$Y$_y$)$_{0.7}$Ca$_{0.3}$CoO$_3$ ($y = 0$ and 0.15) with practically ideal oxygen stoichiometry. Both samples are presumably in a dynamic mixture of IS Co$^{3+}$/LS Co$^{4+}$ states at room temperature and exhibit with decreasing temperature a spin-state crossover. In both cases, the ground state is identified, based on observed magnitudes of magnetic moments and robustness up to high fields, with a mixture of LS Co$^{3+}$/LS Co$^{4+}$ states.

The Pr$_{0.7}$Ca$_{0.3}$CoO$_3$ sample with formal concentration of 0.30 LS Co$^{4+}$ in the diamagnetic background of LS Co$^{3+}$ shows characteristics of common FM phase ($T_C = 55$ K) with prevailing long-range order. Its electronic properties evidence the intrinsic metallicity despite the granularity of ceramic sample.

The behaviour of yttrium substituted samples is much more complex because of a partial Pr$^{3+} \rightarrow$ Pr$^{4+}$ and Co$^{4+} \rightarrow$ Co$^{3+}$ valence shift, which diminishes the carrier doping in the Co-O subsystem and facilitates also the spin-state crossover to the LS/LS phase. This transition, accompanied with a drop of electrical conductivity, occurs for $y = 0.15$ at $T_{MI} = 132$ K. The transport data earlier published show that an effective conduction mechanism at the low-temperature phase is the variable range hopping, which anticipates a tunneling of $t_{2g}$ carriers between more distant Co sites close in energy. As the magnetism is concerned, the present neutron diffraction, performed down to 0.25 K, does not show any long-range ordering of Co$^{4+}$ and/or Pr$^{4+}$ moments, and also the magnetization loops display no or negligible opening and are characteristic rather for a glassy state. The main finding is the observation of uniform internal field acting on Pr$^{4+}$ pseudospins, which is surprising for the low-temperature phase of $y = 0$ with reduced concentration of cobalt spins (formally 0.12 LS Co$^{4+}$ per f.u.).
The issue deserving most attention is the origin of FM interactions that are responsible for the long-range ordering in the 30% hole doped Pr_{0.7}Ca_{0.3}CoO_3 or Nd_{0.7}Ca_{0.3}CoO_3, as well as for the strong molecular field acting on rare earth ions in the (Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3 systems with severely reduced hole dopings. Whatever the character of LS Co^{3+}/LS Co^{4+} mixture, either localized or forming a very narrow t_{2g} band, the FM interactions in a pure phase are unlike. Namely, the superexchange interactions between LS Co^{4+} (the t_{2g} configuration) should be of AFM type according to Goodenough-Kanamori rules, and also when collective t_{2g} states and single-band Hubbard model are considered, no spontaneous FM ordering can be foreseen. The double exchange interactions that are effective in the room temperature IS/LS phase are neither possible. In our opinion, a possible explanation stems from magnetic defects that arise due to minor oxygen vacancies inherently present in doped cobaltites. This results in a reduced coordination of nearby cobalt ions, likely the pyramidal one, which stabilizes local HS Co^{3+} states. Their concentration is estimated based on the near oxygen stoichiometry in our samples to be ~ 2% or less. We suggest that these very dilute defects, clearly below the percolation limit, interact ferromagnetically via itinerant t_{2g} holes. The spin polarization of the narrow t_{2g} band then mediates the nearly homogeneous molecular field over the crystal lattice.

To summarize: The sole existence of FM order in the LS/LS cobaltite phases is a general problem. Our explanation relies on a scenario of magnetic defects, which represent a non-homogeneity, but polarize t_{2g} carriers at the top of oxygen π hybridized band. Irrespective the nature of these defects and their actual location, the spin density is thus distributed over the whole sample.

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