



## Valence Shift of Pr Ion from 3+ to 4+ in $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ Estimated by X-Ray Absorption Spectroscopy

Hiroyuki FUJISHIRO\*, Tomoyuki NAITO, Satoru OGAWA, Naoki YOSHIDA,  
Kiyofumi NITTA<sup>1</sup>, Jiri HEJTMÁNEK<sup>2</sup>, Karel KNÍŽEK<sup>2</sup>, and Zdenek JIRÁK<sup>2</sup>

*Faculty of Engineering, Iwate University, Morioka 020-8551, Japan*

<sup>1</sup>*Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679-5198, Japan*

<sup>2</sup>*Institute of Physics, ASCR, Cukrovarnická 10, 162 00 Prague 6, Czech Republic*

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The temperature dependence of the X-ray absorption near-edge structure (XANES) spectra at the Pr  $L_3$  edge was measured for the  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  samples ( $y = 0.075$  and  $0.15$ ), in which a peculiar metal–insulator (MI) transition and a spin-state (SS) transition took place simultaneously at a critical temperature  $T_{\text{MI}}$ . The valence states of praseodymium ion were determined using the analyses of XANES spectra. The results suggest that the average valence of the praseodymium ion increases below room temperature from the common value  $3.0+$ , undergoes a steepest change at  $T_{\text{MI}}$ , and reaches finally  $3.15+$  and  $3.27+$  at 8 K for the  $y = 0.075$  and  $0.15$  samples, respectively. The final valences are consistent with those estimated by the entropy change using the Schottky peak due to the  $\text{Pr}^{4+}$  Kramers doublet in the low-temperature specific heat shown in our previous paper [Phys. Rev. B **82** (2010) 165107].

KEYWORDS: Pr–Ca–Co–O, XANES, Pr valence shift, metal–insulator transition

### 1. Introduction

The undoped perovskite cobaltites  $\text{RECoO}_3$  (RE: rare-earth element and Y) show a temperature-induced spin-state (SS) transition of  $\text{Co}^{3+}$  ions from a low spin state (LS;  $t_{2g}^6 e_g^0$ ) to a high spin state (HS;  $t_{2g}^4 e_g^2$ ), followed by the formation of the metallic state of the intermediate spin state (IS;  $t_{2g}^5 \sigma^*$ ) at higher temperatures.<sup>1)</sup> The transition indicates a small difference in the electronic energy  $\delta E$  between the crystal-field splitting and Hund's coupling energy.<sup>2,3)</sup> The doped systems with a mixed  $\text{Co}^{3+}/\text{Co}^{4+}$  valence generally show a stable metallic state, but a first-order metal–insulator (MI) transition was observed on cooling some Pr-based cobaltites, reported for the first time in  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$  at  $T_{\text{MI}} = 90$  K under ambient pressure by Tsubouchi and coworkers.<sup>4,5)</sup> The electronic structure of this system was investigated by photoemission spectroscopy soon after the first report, revealing that the electronic structure changes at  $T_{\text{MI}}$ .<sup>6)</sup> The mechanism of the transition was tentatively ascribed to a spin-state crossover from itinerant cobalt states  $t_{2g}^5 \sigma^*$  to an ordered mixture of localized LS  $\text{Co}^{3+}$  ( $t_{2g}^6 e_g^0$ ,  $S = 0$ ) and LS  $\text{Co}^{4+}$  ( $t_{2g}^5 e_g^1$ ,  $S = 1/2$ ) states. Shortly thereafter, the existence of  $\text{Co}^{3+}/\text{Co}^{4+}$  ordering was questioned since the same transition was evidenced in the less doped samples  $\text{Pr}_{1-x}\text{Ca}_x\text{CoO}_3$  ( $x = 0.3$ ) under high pressures,<sup>7)</sup> or in  $(\text{Pr}_{1-y}\text{RE}_y)_{1-x}\text{Ca}_x\text{CoO}_3$  ( $0.2 \leq x \leq 0.5$ ) with a partial substitution of Pr by smaller RE cations or Y under ambient pressure.<sup>8,9)</sup> It has been found that MI transition accompanied by SS transition is conditioned not only by the presence of praseodymium ions, but also by a suitable structural distortion that depends on the average ionic radius and size mismatch of perovskite  $A$ -site ions.<sup>9)</sup> Furthermore, the critical temperature  $T_{\text{MI}}$  changes depending on the applied magnetic field, so that  $T_{\text{MI}}$  decreases with increasing magnetic field and the metallic state is finally stabilized.<sup>10,11)</sup> The applied field effect is thus opposite to the pressure dependence of  $T_{\text{MI}}$ , where  $T_{\text{MI}}$  increases with increasing applied pressure.<sup>7)</sup>

An alternative explanation has been proposed by Knížek *et al.* on the basis of electronic-structure calculations and some experimental data for  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$  such as the significant lattice contraction and decrease in Pr–O bond lengths that accompany MI transition.<sup>12)</sup> It is suggested, in their paper, that the formal cobalt valence changes below  $T_{\text{MI}}$  from mixed-valence  $\text{Co}^{3.5+}$  toward pure  $\text{Co}^{3+}$  with strong preference for the LS state, and that the praseodymium valence increases simultaneously from  $\text{Pr}^{3+}$  toward  $\text{Pr}^{4+}$ . The SS transition and formation of an insulating state are thus an analogy of the compositional transition from the ferromagnetic metal  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  to the diamagnetic insulator  $\text{LaCoO}_3$ .<sup>13,14)</sup>

The idea of praseodymium valence shift was experimentally confirmed in a study of the transport, magnetic, and thermal properties of  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  ( $y = 0–0.15$ ) by Hejtmánek *et al.*<sup>15)</sup> The crucial finding is the occurrence of a Schottky peak at a low-temperature specific heat, which results from a significant population of Kramers  $\text{Pr}^{4+}$  ions. Very recently, the valence transition of Pr has been probed in  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$  using Pr  $L_3$  and  $M_{4,5}$  edge X-ray absorption spectroscopy (XAS) by García-Munoz *et al.*<sup>16)</sup> They estimated that the valence of Pr ion shifted from  $3.0+$  to  $3.15+$  at 10 K. This seems to be a rather modest change in view of the above-mentioned theoretical predictions and specific-heat measurements in related  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ .

In this work, we applied a similar XAS spectroscopy to the analysis of  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  ( $y = 0.075$  and  $0.15$ ), the same samples as those used previously in the study of a low-temperature specific heat.<sup>15)</sup> A detailed temperature dependence of the XANES spectra around the Pr  $L_3$  edge was measured using the bulk sensitive transmission method, and population of the  $\text{Pr}^{4+}$  state was derived from the spectra. In the calculation of average Pr valences, the detected  $\text{Pr}^{4+}$  ions are taken as formally tetravalent, although their electronic state is in fact a combination of the ionic  $4f^1$  and oxygen-hole  $4f^2\bar{L}$  configurations, making the number of  $4f$  electrons a non-integer. The  $\text{Pr}^{3+}$  ions are essentially in an ionic  $4f^2$  electron configuration.

\*E-mail: fujishiro@iwate-u.ac.jp

## 2. Experimental Procedure

Polycrystalline  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  ( $y = 0, 0.075, \text{ and } 0.15$ ) samples were prepared by a solid-state reaction. The detailed sample preparation procedures were described elsewhere.<sup>15)</sup> For the XANES measurements, some of the samples were pulverized, mixed with 3N boron nitride (BN) powder with proper molar ratios in order to optimize absorption, and pelletized to be 6 mm in diameter and 0.5 mm in thickness.

The Pr  $L_3$ -edge XANES spectra of the samples were measured at BL01B1 of SPring-8 in Japan. The beam was monochromatized using a Si(111) double-crystal monochromator. The spectra were recorded in the transmission mode with the detectors of the ionization chambers and obtained at various temperatures from 8 to 300 K using a cryocooler. The valence of all the Pr ions was supposed to be 3.0+ for the samples at 300 K. This is a justified assumption for  $T \gg T_{\text{MI}}$ , also supported by the oxygen stoichiometry of the present samples fabricated under the ambient pressure, in contrast to common problem of oxygen deficiency in the prototypical  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$  system.<sup>8)</sup> To determine the mixed  $\text{Pr}^{3+}/\text{Pr}^{4+}$  content at low temperatures, a comparative measurement of  $\text{Pr}_6\text{O}_{11}$  was carried out.

The recorded XANES spectra were modeled by the sum of three Lorentzian functions and one arctangent function representing the step like edge of continuum excitations. One Lorentzian function (peak A: 5966 eV) shows an excitation from  $2p_{3/2}$  to  $4f^25d^*$ , which represents  $\text{Pr}^{3+}$  ions. The other Lorentzian functions (peak B2: 5969 eV and peak B1: 5979 eV) show the excitations from  $2p_{3/2}$  to  $4f^2\bar{L}5d^*$  and  $4f^15d^*$ ,  $\bar{L}$  being a ligand hole in the O  $2p$  orbital, both of which represent  $\text{Pr}^{4+}$  ions.<sup>17,18)</sup> The energy differences between peaks A, B2, and B1 were fixed according to results of Hu *et al.*<sup>19)</sup> The curve fittings were performed in the energy range from 5944 to 5985 eV using Athena software.<sup>20)</sup>

## 3. Results and Discussion

### 3.1 Physical properties

The electrical resistivities and specific heats of the  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  samples for  $y = 0.075$  and  $0.15$  are presented in Figs. 1 and 2. (More detailed physical properties of the samples are reported in ref. 15.) The  $y = 0$  sample, which is metallic over the entire temperature range, is also shown for comparison. For the Y-substituted samples, the resistivity exhibits a sharp jump below the transition temperatures of  $T_{\text{MI}} = 64$  and  $132$  K for  $y = 0.075$  and  $0.15$ , respectively, and increases further with decreasing temperature, pointing to a localized character of the low-temperature phase. Note that magnetic susceptibility drops markedly at the same temperature, which is a strong sign that cobalt ions transform to LS states below  $T_{\text{MI}}$ .<sup>15)</sup> MI transition was further manifested by a pronounced peak in the specific heat, as shown in Fig. 2(a). The transitions in the resistivity and specific heat of the  $y = 0.075$  sample are very sharp, suggesting a first-order character, while those for the  $y = 0.15$  sample are much broader.

The low-temperature specific heat of the samples is shown in the  $C_p/T$  vs  $T$  plot in Fig. 2(b), in which the lattice and linear electronic terms of  $C_p$  as well as the nuclear heat

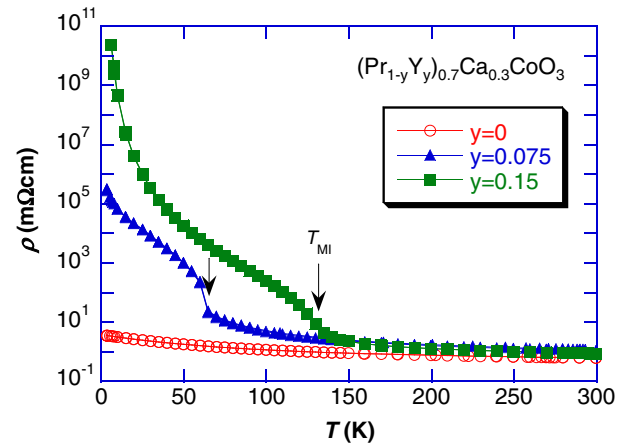


Fig. 1. (Color online) Temperature dependence of the electrical resistivity of  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  ( $y = 0, 0.075$  and  $0.15$ ).<sup>15)</sup>

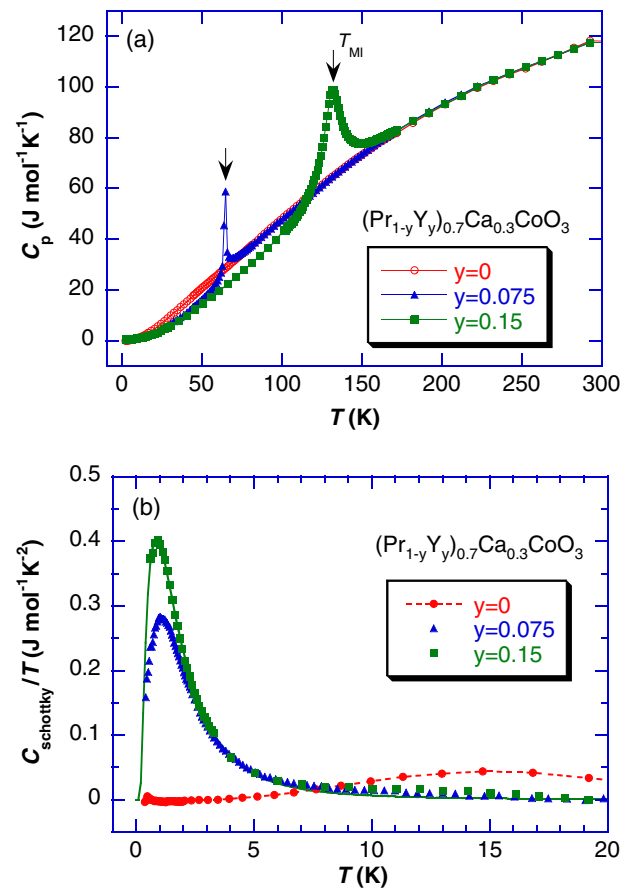


Fig. 2. (Color online) (a) Temperature dependence of the specific heat of  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  ( $y = 0, 0.075$  and  $0.15$ ).<sup>15)</sup> (b) Low-temperature specific heat shown in the  $C_{\text{Schottky}}/T$  vs  $T$  plot. The lattice and linear electronic terms for  $C_p$ , as well as the nuclear heat anomaly at low temperatures, were subtracted. (The full line shows the fit of the Schottky peak for  $y = 0.15$ .)

anomaly at low temperatures were subtracted. The anomalous peak observed for the  $y = 0.075$  and  $0.15$  samples is understood as a Schottky peak associated with the ground doublet of Kramers ion  $\text{Pr}^{4+}$ , split by the internal magnetic field existing in the samples. On the other hand, for the  $y = 0$  sample, there is no Schottky peak in the range of 1–2 K,

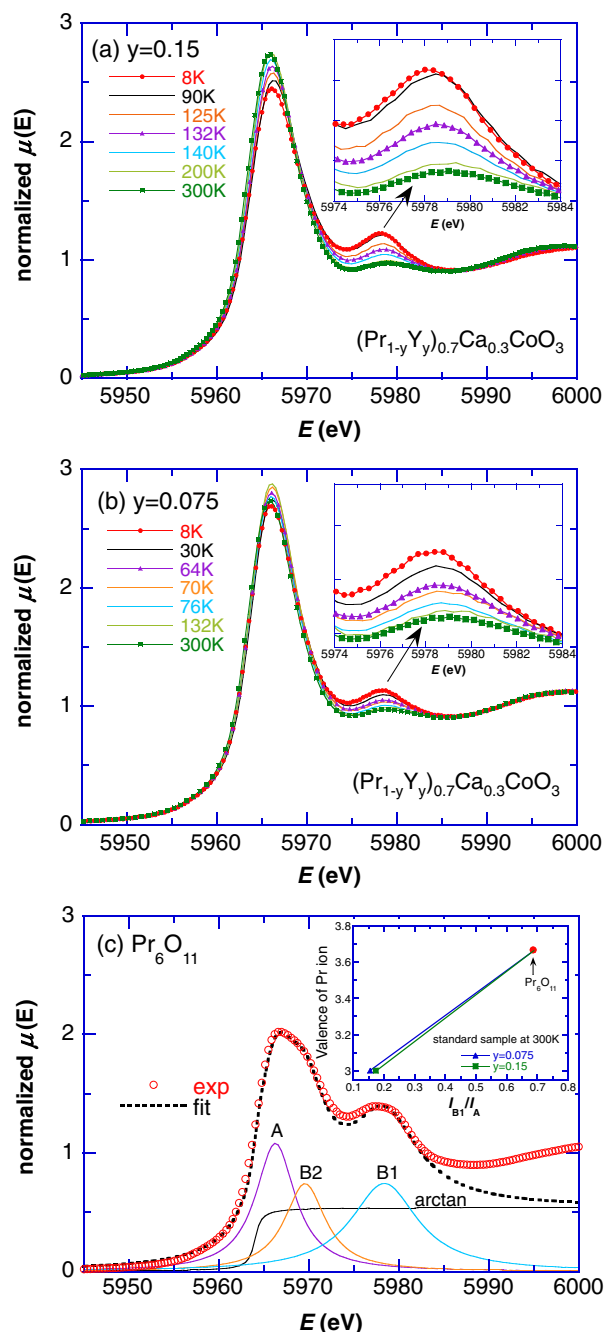
because all praseodymium ions remained in the  $\text{Pr}^{3+}$  valence with a nonmagnetic singlet ground state.<sup>21)</sup> Instead, one may notice a broad maximum in Fig. 2(b) with a center at about 17 K, which is a sign of a closely-lying excited singlet state at an energy of about 4 meV. The total entropy change, which was obtained by the integration of  $C_{\text{Schottky}}/T$  over  $T$ , was determined to be 0.61 and  $0.98 \text{ J K}^{-1} \text{ mol}^{-1}$  for the  $y = 0.075$  and  $0.15$  samples, respectively. Considering the theoretical  $R \ln 2 = 5.77 \text{ J K}^{-1} \text{ mol}^{-1}$ , the number of Kramers ions amounts to 0.12 and 0.17  $\text{Pr}^{4+}$  per f.u., which corresponds to average valences of praseodymium, i.e., 3.17+ and 3.29+ for the  $y = 0.075$  and  $0.15$  samples, respectively.

It should be noted that the original interpretation of the low-temperature Schottky peak in the  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  samples presumed a purely ionic state of  $\text{Pr}^{4+}$ , particularly the free-ion multiplet  ${}^2F_{5/2}$  split by a crystal field to Kramers doublets. The character of these states may change significantly in the covalent case, but the number of  $\text{Pr}^{4+}$  species determined in ref. 15 remains valid, since both the ionic  $4f^1$  and oxygen-hole  $4f^2\bar{L}$  states involve odd number of electrons and display Kramers degeneracy.

### 3.2 XAS measurements

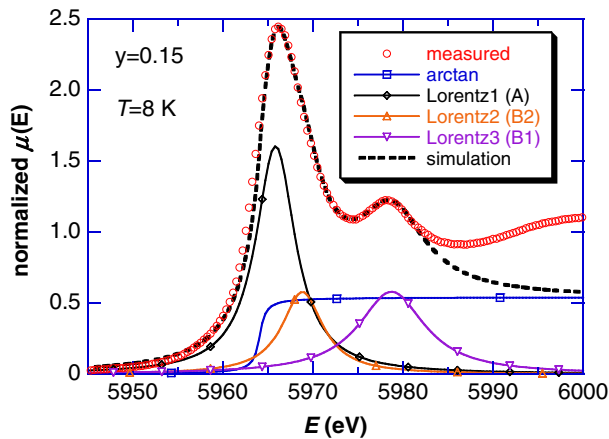
Figure 3(a) shows the temperature dependence of the XANES spectra at the Pr  $L_3$ -edge for the  $y = 0.15$  sample. The two main peaks situated at 5966 and 5979 eV (named peaks A and B1) originate from the Pr  $2p \rightarrow 5d$  transitions. At 300 K,  $\text{Pr}^{3+}(4f^2)$  sites essentially contribute to the peak A, with a little component at peak B1 caused presumably by multiple scattering, which is commonly introduced in the theoretical calculation of XANES.<sup>16)</sup> When the temperature crosses the transition temperature  $T_{\text{MI}} = 132 \text{ K}$ , the shape of the XANES spectra changes markedly. The intensity of peak B1 increases and, at the same time, the intensity of peak A decreases and a new component (peak B2 at 5969 eV) can be resolved on its high-energy slope. The B1 and B2 peaks are manifestations of  $\text{Pr}^{4+}$  states, namely, of the configurations  $4f^1$  and  $4f^2\bar{L}$ , respectively.<sup>17–19)</sup> Similar behaviors are also observed for the  $y = 0.075$  sample below  $T_{\text{MI}} = 64 \text{ K}$ , as shown in Fig. 3(b). These results suggest that the valence of the Pr ions increases from 3+ toward 4+ below  $T_{\text{MI}}$ , consistently with what was reported for the  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$  sample by García-Munoz *et al.*<sup>16)</sup> The temperature dependence of the XANES spectra at the Pr  $L_3$ -edge was also measured for the  $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  sample (not shown), which was metallic over the entire temperature range. There was no spectral change down to 8 K, which suggested that the valence of the Pr ion remained at 3.0+, as shown in the results of the metallic  $\text{Pr}_{0.55}\text{Ca}_{0.45}\text{CoO}_3$  sample.<sup>16)</sup>

In order to determine the valence shift quantitatively, the XANES spectra were fitted to a sum of three Lorentzian functions (peak A for  $\text{Pr}^{3+}$  and peaks B1 and B2 for  $\text{Pr}^{4+}$ ) and one arctangent function representing the continuum excitations, as indicated in §2. The  $\text{Pr}_6\text{O}_{11}$  spectrum shown in Fig. 3(c), in which no relevant spectroscopic changes were detected at low temperatures, was regarded as a standard for  $\text{Pr}^{3.667+}$ . The spectra at 300 K for each of the  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  samples served as standards of  $\text{Pr}^{3.0+}$ . In the fitting of the temperature-dependent spectra,



**Fig. 3.** (Color online) Temperature dependence of the XANES spectra at the Pr  $L_3$ -edge for the (a)  $y = 0.15$  and (b)  $0.075$  samples. The inset of each figure shows the magnification of the spectra related to  $\text{Pr}^{4+}$  ions. (c) XANES spectra for  $\text{Pr}_6\text{O}_{11}$  at 300 K, for which the fitting were performed (see text). The inset shows the calibration line for the determination of the valence of the Pr ion used in the study.

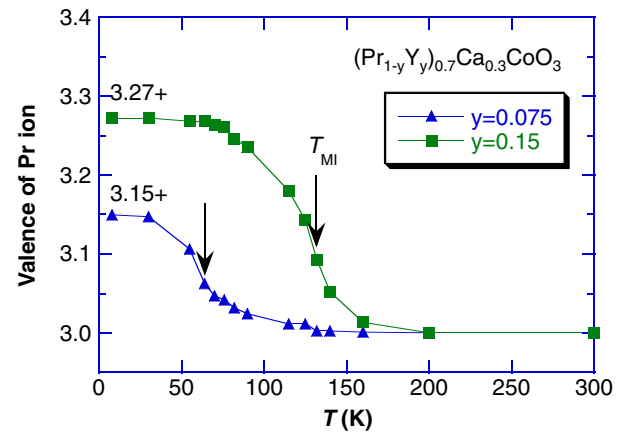
the intensity ratio of B1 to B2 was fixed to be unity. The valence of Pr ions for the samples in the course of temperature was simply deduced from the intensity ratio  $I_{\text{B1}}/I_{\text{A}}$  of the B1 spectral peak to the A spectral peak<sup>22)</sup> using the calibration line in the inset of Fig. 3(c). The validity of this procedure is based on the fact that the  $\text{Pr}^{3+}$  and  $\text{Pr}^{4+}$  valence states in  $\text{Pr}_6\text{O}_{11}$  are manifested in XANES spectra by single and double peaks, respectively (see also ref. 23), which points to the same ionic  $4f^2$  and covalent  $4f^1/4f^2\bar{L}$  configurations as those of the praseodymium ions in the present cobaltites.



**Fig. 4.** (Color online) Example of the fitting of the XANES spectrum for the  $y = 0.15$  sample at 8 K. For the fitting, one arctangent function and three Lorentzian functions are used (see text).

Figure 4 shows an example of the fitting curve of the XANES spectrum for the  $y = 0.15$  sample at 8 K, where the valence change achieves a maximum. It is seen that the XANES spectrum can be well fitted within the energy range including the related peaks of  $\text{Pr}^{3+}$  and  $\text{Pr}^{4+}$ . The B2 component is also resolved and appears notable so that the resemblance with the  $\text{Pr}^{3+}/\text{Pr}^{4+}$  mixture in  $\text{Pr}_6\text{O}_{11}$  is obvious. The temperature course is shown in Fig. 5. The average valence changes gradually on cooling from 300 K, with the steepest increase at  $T_{\text{MI}}$ , and reaches final values of 3.15+ and 3.27+ at 8 K for the  $y = 0.075$  and 0.15 samples, respectively. The ambiguity of the estimated valence values is  $\pm 0.03$ , which results from the arbitrariness of the parameters in the arctangent and Lorentzian functions used. We also deduced the average valence of Pr ions from the intensity ratio  $(I_{\text{B1}} + I_{\text{B2}})/(I_{\text{A}} + I_{\text{B1}} + I_{\text{B2}})$  of the B1, B2, and A spectral peaks using another calibration line, in which all the contributions of  $4f^1$ ,  $4f^2$ , and  $4f^2\bar{L}$  were considered to be the same as those adopted by Yamaoka *et al.*<sup>17)</sup> Under this condition, the average valences of Pr ions were 3.15+ and 3.31+ for the  $y = 0.075$  and 0.15 samples, which are nearly the same as that decided from the intensity ratio  $I_{\text{B1}}/I_{\text{A}}$ . Note that the estimated valences of the Pr ions are in very good agreement with that determined from the low-temperature specific-heat experiments, i.e., 3.17+ and 3.29+ for the  $y = 0.075$  and 0.15 samples, respectively.<sup>15)</sup> The gradual increase in the average valence of the Pr ions at  $T > T_{\text{MI}}$  on cooling from 300 K also suggests that the valence of the Co ion must evolve from 3.3+ to a lower value in order to maintain the charge neutrality. This means that, with decreasing temperature, part of the  $\text{LS-Co}^{4+}$  changes to  $\text{IS-Co}^{3+}$  still within the metallic phase, and then the  $\text{IS-Co}^{3+}$  states transform to  $\text{LS-Co}^{3+}$  below  $T_{\text{MI}}$ . The gradual charge transfer between the praseodymium and cobalt subsystem is in striking contrast to the abrupt (first-order) character of the physical properties such as resistivity and susceptibility, especially at  $y = 0.075$ .

The valences of the Pr ions of 3.15+ and 3.27+ for the  $y = 0.075$  and 0.15 samples, respectively, estimated from the intensity ratio  $I_{\text{B1}}/I_{\text{A}}$  in XANES spectra, correspond to 0.097 and 0.161  $\text{Pr}^{4+}$  per f.u. and is indicative of a significant change in doping level in the cobalt subsystem



**Fig. 5.** (Color online) Temperature dependence of the valence of Pr ions in the samples estimated using the XANES spectra and curve fitting.

( $\text{Co}^{4+}$  content) in the low-temperature insulating state. For  $y = 0.075$ , the common valence distribution in the metallic state ( $T \gg T_{\text{MI}}$ ), i.e.,  $(\text{Pr}_{0.925}^{3+}\text{Y}_{0.075}^{3+})_{0.7}\text{Ca}_{0.3}^{2+}\text{Co}_{0.7}^{3+}\text{Co}_{0.3}^{4+}\text{O}_3^{2-}$ , changes to  $(\text{Pr}_{0.786}^{3+}\text{Pr}_{0.139}^{4+}\text{Y}_{0.075}^{3+})_{0.7}\text{Ca}_{0.3}^{2+}\text{Co}_{0.797}^{3+}\text{Co}_{0.203}^{4+}\text{O}_3^{2-}$  ( $T \ll T_{\text{MI}}$ ). For  $y = 0.15$ , the  $(\text{Pr}_{0.85}^{3+}\text{Y}_{0.15}^{3+})_{0.7}\text{Ca}_{0.3}^{2+}\text{Co}_{0.7}^{3+}\text{Co}_{0.3}^{4+}\text{O}_3^{2-}$  in the metallic state changes to  $(\text{Pr}_{0.620}^{3+}\text{Pr}_{0.230}^{4+}\text{Y}_{0.15}^{3+})_{0.7}\text{Ca}_{0.3}^{2+}\text{Co}_{0.861}^{3+}\text{Co}_{0.139}^{4+}\text{O}_3^{2-}$  in the low-temperature insulating state. The electron transfer between the praseodymium and cobalt subsystems thus acts as the driving force for the stabilization of the  $\text{LS-Co}^{3+}$  states in the low-temperature insulating state. Discussions of the relation between the valence shift and the transition temperature  $T_{\text{MI}}$ , and of the effect of the Ca ions on the transition are in progress.

#### 4. Conclusion

The temperature dependence of the X-ray absorption near edge spectra (XANES) at the Pr  $L_3$ -edge was measured for two  $(\text{Pr}_{1-y}\text{Y}_y)_{0.7}\text{Ca}_{0.3}\text{CoO}_3$  samples ( $y = 0.075$  and 0.15), in which a peculiar metal-insulator (MI) transition and a spin-state (SS) transition took place simultaneously at critical temperatures  $T_{\text{MI}} = 64$  and 132 K, respectively. The existence of two distinct praseodymium species was evidenced: the  $\text{Pr}^{3+}$  valence state of the ionic  $4f^2$  configuration and the formal  $\text{Pr}^{4+}$  valence state of highly covalent character with admixed  $4f^1$  and oxygen-hole  $4f^2\bar{L}$  configurations. The average valences of the praseodymium ion were estimated by analyzing the XANES spectra. The important experimental results and conclusions are summarized as follows.

(1) The room-temperature XANES experiment spectra show a dominant single-peaked feature A (5966 eV), characteristic of the presence of the pure  $\text{Pr}^{3+}$  valence state. On cooling across the transition temperature  $T_{\text{MI}}$ , an increasing population of  $\text{Pr}^{4+}$  states becomes evident from the fast increase in the intensity of peak B1 (5979 eV) in the spectrum. At the same time, the intensity of peak A due to  $\text{Pr}^{3+}$  decreases.

(2) The results obtained are indicative of a rather gradual charge transfer between the praseodymium and cobalt sites in the perovskite structure, which precedes the spin-state



transition of cobalt ions that occurs abruptly at a well-defined  $T_{MI}$ .

(3) Below  $T_{MI}$ , the population of  $Pr^{4+}$  ions continues to increase, reaching saturation at low temperatures. Using the quantitative analysis of the XANES spectra, the average valence of Pr ions at 8 K is determined to be 3.15+ and 3.27+ for the  $y = 0.075$  and 0.15 samples, respectively. These valences are in good agreement with those obtained from the entropy change using the Schottky peak due to the  $Pr^{4+}$  Kramers doublet in the low-temperature specific heat, i.e., 3.17+ and 3.29+.

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