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Magnetic properties: Mössbauer, x-ray absorption spectroscopy, and specific-heat studies of $Pr_{1.5}Ce_{0.5}MSr_2Cu_2O_z$ (M=Ta, In, Nb, Nb+Ga) compounds

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We have investigated $Pr_{1.5}Ce_{0.5}MSr_2Cu_2O_z$ (z=9 or 10) materials (M=Ta, In, and Nb+Ga) by complementary experimental techniques. All materials studied are not superconducting. Magnetic susceptibility studies for M=Ta reveal one magnetic anomaly at 23 K and irreversibility phenomena at higher temperatures. The presence of 0.5% ^{57}Fe dramatically affects the positions of the anomalies, and Mössbauer spectroscopy studies (MS) reveal that the Cu(2) sites are magnetically ordered below T_N(Cu)=130 K. This low T_N(Cu) obtained is discussed. No specific heat anomaly was observed at 23 K, suggesting that the Pr sublattice does not order magnetically, and the anomalies in the susceptibility originate from the Cu moments. No anomalies in the susceptibility curves are found for M=In and Nb+Ga compounds. However, MS indicate that for the mixed compound, the Cu sites are magnetically ordered at low temperatures. The magnetic behavior of M=Ta is compared to similar systems with two anomalies for M=Nb at 11 and 52 K, and three anomalies for M=Ga at 12, 52, and 94 K. X-ray absorption spectroscopy (XAS) indicates that in all materials studied, the Pr has a mixed valence close to 3. The Pr valence does not change with temperature. [S0163-1829(96)06746-X]

INTRODUCTION

Much attention has been focused on a phase resembling the superconducting (SC) $YBa_2Cu_3O_7$ (YBCO) materials having the composition $R_{1.5}Ce_{0.5}MSr_2Cu_2O_z$ (R=rare earth, M=Nb, Ga, or Ta, and z=9–10).[1–5] The $R_{1.5}Ce_{0.5}MSr_2Cu_2O_z$ (RCeMSCO) structure evolves from the YBCO structure by inserting fluorite type $R_{1.5}Ce_{0.5}O_2$ layers (instead of the R layer in YBCO), thus shifting alternate perovskite blocks by $(a+b/2)$. It is assumed that the M ions reside in the Cu(1) site and only one distinct Cu site [corresponding to Cu(2)] exists with fivefold pyramidal coordination. The CuO_2 layers are separated on one side by MO_6 (or GaO_4), which replaces the Cu-O chains, and on the other side by fluorite-structure $R_{1.5}Ce_{0.5}O_2$ layers. Two different crystal symmetries have been reported for the homologous RCeMSCO compounds. For M=Nb or Ta the compounds crystallize in a tetragonal structure with the space group $I4/mmm$,[4,5] whereas for M=Ga, an orthorhombic unit cell was proposed with the possible space group $Fmmm$.[6]

The $R_{1.5}Ce_{0.5}NbSr_2Cu_2O_{10}$ compounds (R=Nd, Sm, Eu, and Gd) are SC with $T_c\sim28$ K, independent of R. On the other hand, $Pr_{1.5}Ce_{0.5}NbSr_2Cu_2O_{10}$ (PrCeNSCO) is not SC, and magnetic studies at low fields reveal two magnetic anomalies in the susceptibility curves, at 11 and 54 K.[3–5] Both peaks always appear together and are sensitive to oxygen concentration. They are presumed to arise from an interlayer spin reorientation of the Cu moments. The presence of Fe as a dopant in the CuO_2 layers drastically affects the peak at 54 K. This peak shifts to higher temperatures with increasing nominal Fe content, and the largest shift (117 K) was observed for 5 at. % of Fe.[7] No superconductivity has been found in the orthorhombic $R_{1.5}Ce_{0.5}GaSr_2Cu_2O_9$ family. In $Pr_{1.5}Ce_{0.5}GaSr_2Cu_2O_9$ (PrCeGSCO) three anomalies were observed in the susceptibility curves at 12, 54, and 94 K. The position and the relative intensity of each anomaly is extremely sensitive to oxygen concentration.[6] While the anomalies in both PrCeNSCO and PrCeGSCO compounds are clearly identified by magnetic measurements, no specific heat (C_p) anomaly was observed at any temperature. The interpretation of the peaks at 11 or 12 K, which always accompany the anomalies at high temperatures, is not conclusive. In our previous papers we assumed that they are *not* associated with magnetic ordering of the Pr sublattice.[4,6] At low temperature, the Cu-Cu and/or Pr-Cu interactions begin to dominate, leading to reorientation of the Cu moments, and the anomaly in the susceptibility is observed. This reorientation leads to a negligibly small latent heat, which cannot be observed in the C_p curve. On the other hand, the peak at 12 K for PrCeNSCO has been assigned to an ordering of the Pr sublattice[3,5] based on an analogy with $PrBa_2Cu_3O_7$ ($PrBCO_7$) (Ref. 8) and $PrBa_2NbCu_2O_8$ (Ref. 9) materials which are antiferromagnetically ordered at T_N=17 and 12 K, respectively.

Recently, Bennahmias *et al.* have studied in detail the magnetic properties of the $Pr_{1.5}Ce_{0.5}TaSr_2Cu_2O_{10}$ (PrCeTaSCO),[5] which exhibits irreversible phenomena at $T_{\rm irr}$ (which is field dependent), and only one peak, at T=19 K. It

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is assumed that below T_{irr} the weak ferromagneticlike behavior is due to some local distortion which allows an anisotropic Dzyaloshinsky-Moriya (DM) exchange to occur between neighboring Cu moments, which breaks the tetragonal symmetry of the CuO_2 planes.[5] By forming the intermediate compounds from 100% Nb to 100% Ta, these authors also show that the apparent single peak at 19 K in PrCeTaSCO is a result of the overlap of the two peaks, which are well separated in PrCeNSCO.[5]

The main purpose of this study, employing several experimental techniques, is to compare the systems mentioned above, to the new tetragonal $Pr_{1.5}Ce_{0.5}MSr_2Cu_2O_z$ materials, in which a complete substitution of M is made by Ta, In, and Nb+Ga. Our magnetic studies on PrCeTaSCO also exhibit irreversible phenomena at 48 K and only one peak, at 23 K, thus confirming the results obtained in Ref. 5. No anomaly in the specific heat studies is observed at 23 K, and a high γ value of 242 mJ/mol Pr K^2 was obtained. Therefore, the peak at 23 K is attributed to reorientation of the Cu moments. Mössbauer spectroscopy studies (MS) on an Fe doped PrCeTaSCO sample indicate that the magnetic ordering of the Cu sublattice is at $T_N \sim 130$ K. For a mixture of $M = 0.8\,\mathrm{Nb} + 0.2\,\mathrm{Ga}$, no anomaly is observed in the susceptibility curves. However, Mössbauer spectroscopy on ^{57}Fe doped sample indicates that the Cu sublattice is magnetically ordered at low temperatures. X-ray absorption spectroscopy (XAS) of Pr-L_{III} shows, that in all materials studied, the Pr has a mixed valence (close to 3). This is in contrast to electron-energy-loss spectroscopy (EELS) measurements published recently, which indicate a pure trivalent state of Pr in several PrCeNbSCO based samples.[10]

EXPERIMENTAL DETAILS

Ceramic samples with a nominal composition $Pr_{1.5}Ce_{0.5}MSr_2Cu_2O_z$ ($z = 9,10$) were prepared by solid state reaction techniques. Required amounts of Pr_6O_{11}, CeO_2, $SrCO_3$, CuO, and MO_x were mixed pressed into pellets, and calcinated at 1000–1050 °C for about 1 day in the presence of flowing oxygen at atmospheric pressure. The products were cooled, reground, and sintered at 1130 °C for 72 h under slightly pressurized oxygen (about 1.1 atm), and the samples were then cooled to ambient temperature. The 0.5 at. % ^{57}Fe doped samples (substituted for Cu) were prepared under the same conditions. Powder x-ray diffraction (XRD) measurements indicate that for all samples studied, the materials are nearly single phase (~96%) and have the tetragonal structure shown in Fig. 1 of Ref. 1. Additional peaks were observed (7–8 %) in the XRD pattern of the PrCeInSCO, and our attempts to get completely rid of them were unsuccessful. We could not replace in PrCeTaSCO the Ba for Sr, and the main phase obtained was $PrBa_2TaO_6$,[11] with CeO_2 and CuO as extra phases.

The dc magnetic measurements on solid ceramic pieces in the range of 2–300 K were performed in a commercial (Quantum Design) superconducting quantum interference device magnetometer (SQUID). The magnetization was measured by two different procedures. (a) The sample was zero field cooled (ZFC) to 5 K, a field was applied, and the magnetization was measured as a function of temperature. (b) The sample was field cooled (FC) from above 300 to 5 K, and the magnetization was measured. The MS were carried out using a conventional constant acceleration spectrometer and a 50 mCi ^{57}Co:Rh source. The ^{57}Fe isomer shifts (IS) are reported with respect to metallic Fe at 300 K. The specific heat of compact pieces (about 100 mg) cut from the pellets were carried out by using the ac calorimetry technique (at $H = 0$ T) in the temperature range 0.8–100 K.[12]

TABLE I. Crystallographic, magnetic, and chemical valence (CV) data for PrCeMSCO.

M	a (Å)	c (Å)	Peak position (K)			CV±0.05
Ta	3.881(2)	28.87(1)	23			3.12
Nb	3.895	28.78	11	54		3.22
Nb[a]	3.886	28.74	11	54		3.12
Ga	5.471 $b = 5.543$	28.43	12	54	94	3.13
In	3.876	29.21				
Nb+Ga	3.887	28.63				

[a] For $Pr_{1.0}Ce_{0.5}NbSr_2Cu_2O_z$.

XAS measurements were performed at the French synchrotron radiation facility (LURE) in Orsay, using the x-ray beam of the DCl storage ring (working at 1.85 GeV and 220 mA) on the EXAFS D21 station. A double Si 311 crystal was used as a monochromator, and the rejection of third order harmonics was achieved with two adjusted parallel mirrors to cut off energies higher than ≈9 keV. Experiments were carried out in the energy ranges of 5680–5840 and 5920–6080 eV which contain the L_{III} edge of Ce and Pr, respectively, at 10 and 300 K. The background was subtracted in a standard manner.[13]

EXPERIMENTAL RESULTS

A. Lattice parameters and oxygen content

XRD studies show that the PrCeMSCO compounds (except for $M = \mathrm{Ga}$) have a tetragonal structure, with the space group $I4/mmm$. The lattice parameters obtained are listed in Table I. The atomic positions for $M = \mathrm{Ta}$, determined by Rietveld analysis of the full XRD pattern, are in excellent agreement with data published for $M = \mathrm{Nb}$, in Ref. 3. This similarity is due to the fact that Nb^{5+} and Ta^{5+} have the same ionic radius (0.64 Å). The Cu atoms reside in the $4e$ atomic position ($0.0.z$) and for $z = 0.142$ the shortest Cu-Cu distance along the c direction is ≈6.08 Å, which is much longer than the 3.52 Å Cu(2)-Cu(2) distances which exist in YBCO. For $Pr_{1.5}Ce_{0.5}InSr_2Cu_2O_9$, the c lattice parameter is larger (the ionic radius of In^{3+} is 0.81 Å) and the least-square fit of the XRD pattern on the basis of a tetragonal structure (Table I) left a few peaks due to $(Pr\text{-}In)_2O_3$ and CeO_2 phases, and few minor reflections, unaccounted for. Single phase $Pr_xCe_{0.5}NbSr_2Cu_2O_z$ materials with $1.5 > x > 0.8$ (deficiency of Pr) have been prepared and their lattice parameters are similar to that of $x = 1.5$ (Table I). Determination of the absolute oxygen content in these materials is difficult, because CeO_2 is not completely reducible to stoichiometric oxides on heating to high temperatures.[2]

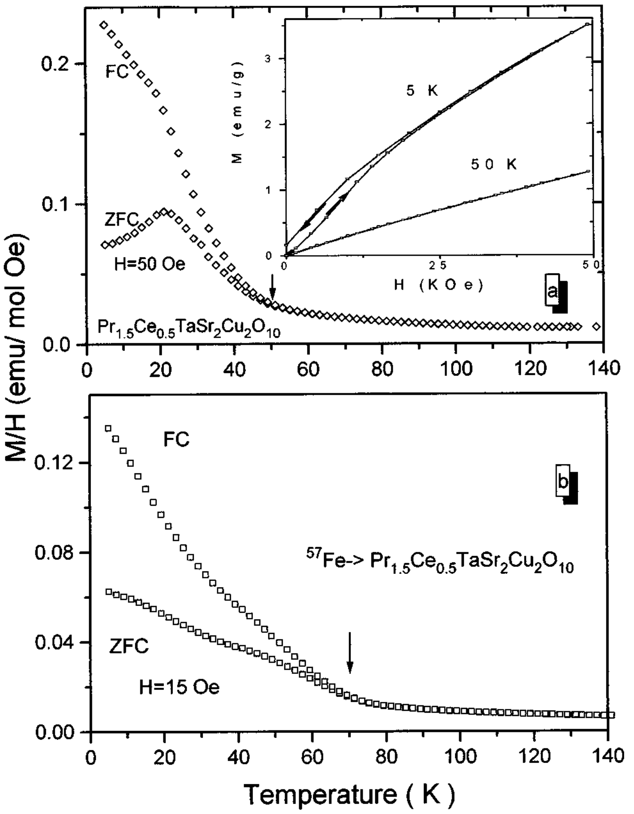

FIG. 1. (a) Temperature dependence of the ZFC and FC susceptibility for PrCeTaSCO and (b) for Fe doped PrCeTaSCO samples. The inset shows the isothermal magnetization curves at 5 and 50 K up to 50 kOe. Note that the ZFC and FC branches merge at 48 K (a) and 70 K (b).

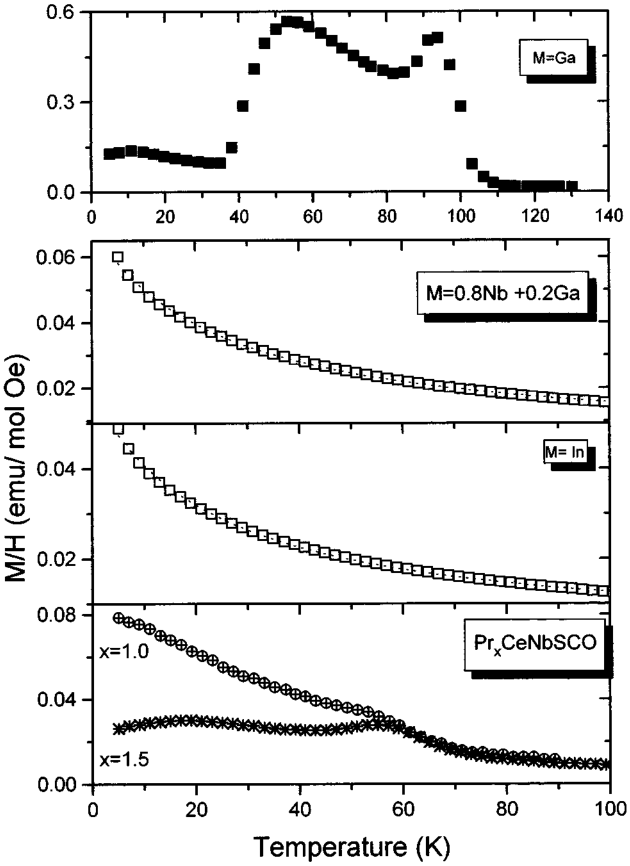

FIG. 2. Temperature dependence of the ZFC susceptibility for various PrCe*M*SCO compounds (M=Ga, Nb+Ga, and In) and for Pr_xCeNbSCO (x=1.0 and 1.5) measured at 50 Oe.

B. Magnetic measurements

Our main interest here is to compare the magnetic behavior of PrCeMSCO (M=Nb+Ga and In) materials with those of the isomorphous M=Nb and Ta based systems. We shall first refer to our magnetic studies of M=Ta, and then compare the data to that reported in Ref. 5. In the subsequent figures, unless otherwise specified, the susceptibility is in units of emu/mol Oe, and has been defined as the ratio of the magnetization M to the applied field $H(\chi = M/H)$.

1. Magnetic behavior of RCeTaSCO samples

The ZFC and FC magnetic susceptibilities, measured at 50 Oe for PrCeTaSCO are shown in Fig. 1(a). In both branches, only one distinct peak is observed at T=23 K, in full agreement with Ref. 5. T_{irr} at 48 K is defined as the merging temperature of the ZFC and FC branches, where the difference between the branches becomes less than $\Delta\chi = 1\times 10^{-4}$ emu/mol Oe. No other anomalies were observed at higher temperatures. Neither annealing in high oxygen pressure (50 atm), nor reductive treatment by annealing in nitrogen, affected the magnetic behavior of this compound. The magnetic ordering temperature T_N (Cu) of PrCeTaSCO *is not* at T_{irr}. The susceptibility curves in Fig. 1 do not lend themselves to an easy determination of T_N (Cu), because of the high susceptibility of Pr^{3+} ions, which masks this transition. For this purpose we adapted the MS technique, on PrCeTaSCO doped with 0.5% ^{57}Fe, described in detail in the next section, which indicates clearly that T_N (Cu)=130 K.

As we shall argue, the Pr sublattice does not order magnetically. Therefore, all the magnetic anomalies in Figs. 1 and 2 are related to the CuO_2 planes. The irreversibility at 48 K (below T_N), probably arises from an antiferromagnetic (AFM) alignment of the CuO_2 planes. In the FC process, a weak ferromagnetic component arises as a result of an antisymmetric exchange coupling of the DM type,[5] between neighboring Cu moments induced by a local distortion, which breaks the tetragonal symmetry of the Cu-O planes. This canting abruptly aligns a component of the moments with the direction of the field, and the FC branch is obtained. At low temperatures, the Cu-Cu and/or Pr-Cu interactions begin to dominate, leading to reorientation of the Cu moments, and the peak at 23 K is observed. This is consistent with the absence of an anomaly in the specific-heat measurements presented in the next section. The exact nature of the local structural distortions causing the DM interactions is presently not known.

The weak ferromagnetic component is clearly shown in the isothermal magnetization curves measured up to 50 kOe at several temperatures. As an example, Fig. 1 (inset) shows the nonlinear curve obtained below T_{irr} (at 5 K) and a hysteresis loop opens below ~20 kOe, as the external field is decreased, as compared to the linear dependence of the M above T_{irr} (at 50 K). The effect of the applied field on T_{irr} in

PrCeTaSCO, was studied by Bennahmias *et al.*, who applied the Almeda-Thouless relationship. Note, that 20 kOe, deduced directly from our $M(H)$ curve at 5 K, agrees perfectly with the saturation magnetic field (H_0) obtained as a free parameter (see Table I in Ref. 5). Fe as a dopant (0.5 at. %) smears the peak at 23 K, and affects drastically T_{irr} which is shifted to 70 K; see Fig. 1(b). We shall address these points in the subsequent discussion.

Above T_{irr}, the susceptibility of PrCeTaSCO adheres closely to the Curie-Weiss (CW) law: $\chi=\chi_0+C/(T-\theta)$, where χ_0 is the temperature independent part of the susceptibility, C is the molar Curie constant, and θ is the Curie-Weiss temperature. The paramagnetic values extracted strongly depend on the temperature range of the fitting. The fit in the range $50<T<140$ K yields $\chi_0=4.7\times10^{-3}$, $C=0.94(1)$ emu K/mol(Pr)Oe, and $\theta=21.6(4)$ K. Since (a) the saturation magnetic moment of Cu at $T>50$ K is extremely small (0.001–0.002 μ_B/Cu),[5] and (b) in most HTSC materials, the Cu ions bear a small paramagnetic moment of about 0.5–0.6 μ_B/Cu (Ref. 14) (which means $C\sim0.06$–0.08 emu K/mol Oe), the contribution of Cu ions to C was neglected. The derived effective magnetic moment of Pr, $P_{\mathrm{eff}}=2.74\mu_B$, and the θ value obtained, compare well with Ref. 5.

2. Paramagneticlike behavior of PrCeMSCO

Magnetic measurements performed on PrCeInSCO and $M=0.8$ Nb+0.2 Ga, show that all anomalies in $\chi(T)$ are absent, and the susceptibility exhibits paramagneticlike behavior down to 5 K (Fig. 2). The CW fit to the data in the range of $5<T<100$ K, yields $\theta=24$ and 25 K, the same $\chi_0=2\times10^{-3}$ and $C=0.87(1)$ and 1.11(1) emu K/mol(Pr)Oe, which corresponds to $P_{\mathrm{eff}}=2.64$ and 2.98 μ_B for Pr for $M=\mathrm{In}$ and Nb+Ga, respectively. These values fit perfectly the values reported for PrCeNbSCO (Ref. 4) and are entirely consistent with the estimated P_{eff} values of Pr in compounds with related structures.[2] For the sake of comparison, Fig. 2 shows also the $\chi(T)$ curves for the parent $M=\mathrm{Nb}$ and Ga compounds. For the mixed $M=\mathrm{Nb+Ga}$, the magnetic hyperfine splitting in the MS at 4.1 K, shown in Fig. 3 and discussed later, indicates clearly that the Cu sublattice *is* magnetically ordered at low temperatures, although such an ordering is not observable in the $\chi(T)$ curve. Unfortunately, we cannot derive T_N (<90 K) for this compound at the present time. Using the same arguments, we may assume that also in PrCeInSCO, the Cu sublattice is AFM ordered at low temperatures. Because of extra unidentified phases in the sample, the results extracted from our MS are not conclusive.

C. Mössbauer spectroscopy studies (MS) of PrCe*M*SCO

MS has been proven to be a powerful tool in the determination of the magnetic nature of the Fe site location. When the ions of this site (Cu) become magnetically ordered, they produce an exchange field on the Fe ions residing in this site. The Fe nuclei experience a magnetic hyperfine field leading to a sextet in the observed MS spectra. As the temperature is raised, the magnetic splitting decreases, and disappears at T_N. It is well accepted that in YBCO, the Fe atoms are found to occupy predominantly the Cu(1) site, with an increased fraction occupying the Cu(2) sites as the total amount of Fe increases. Since the crystal structures of PrCeTaSCO and YBCO are closely related, we assign the doublets obtained here according to the Fe-site assignment in YBCO.[15] Using the MS technique on Fe doped in PrCe*M*SCO ($M=\mathrm{Nb}$ and Ga), we have shown[4,6] that Fe ions occupy predominantly (70–80 %) the M site, and the rest occupy the Cu sites. Present studies show that the Fe distribution in PrCe*M*SCO ($M=\mathrm{Ta}$ and Nb+Ga) behaves in a similar way. MS spectra of 0.5 at. % ^{57}Fe doped PrCe*M*SCO measured at various temperatures are shown in Fig. 3.

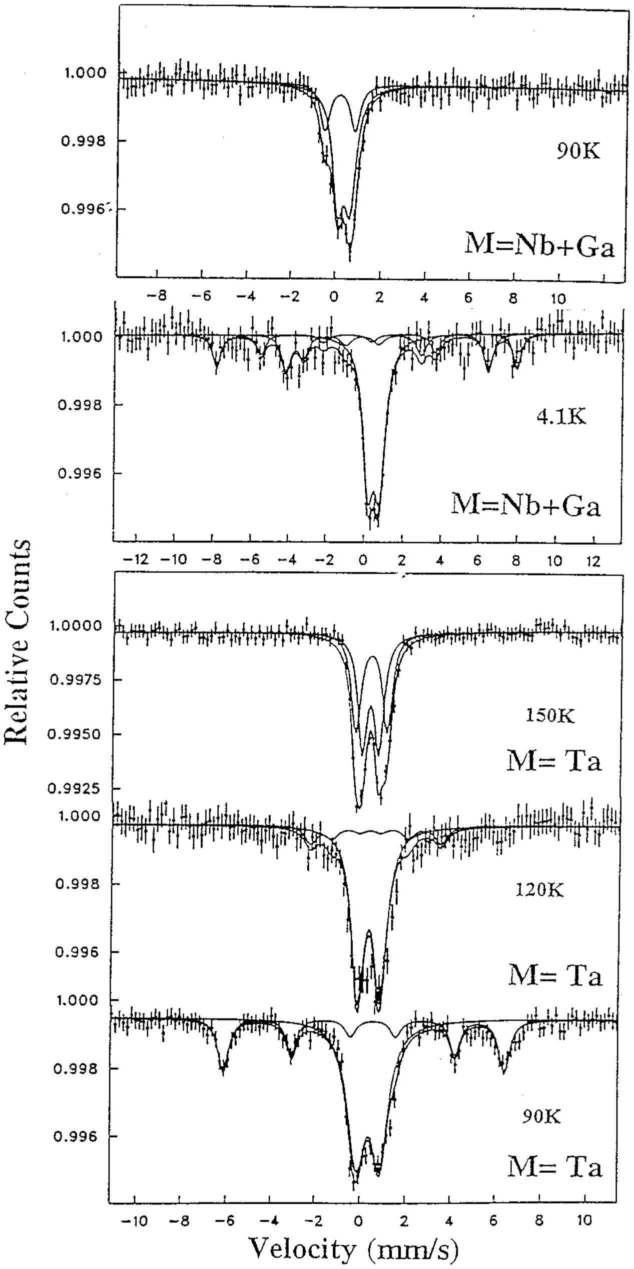

FIG. 3. Mössbauer spectra of PrCe*M*SCO for $M=\mathrm{Ta}$ and Nb+Ga in the paramagnetic and AFM states. The solid curves are theoretical least square fits in terms of subspectra corresponding to inequivalent Fe sites.

1. MS of the paramagnetic state

The main information obtained from visual and computer analysis for the spectra measured for $M=\mathrm{Ta}$ at 150 and 300

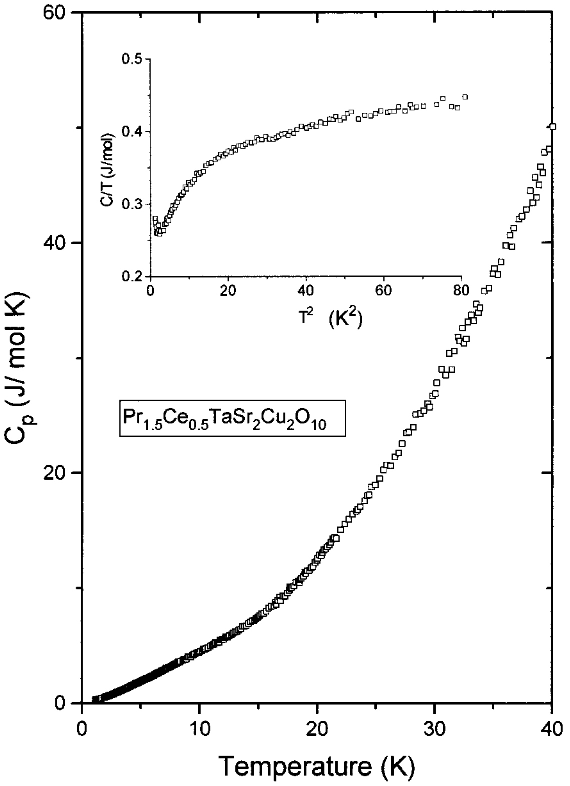

FIG. 4. Specific-heat curves at $H=0$ T for PrCeTaSCO. In the inset is the C_p/T vs T^2 behavior showing the γ high value.

K, and for M=Nb+Ga at 90 K, is the presence of two quadrupole doublets corresponding to inequivalent Fe sites, which are identified by their hyperfine parameters: the isomer shift (IS) and quadrupole splitting ($\Delta=1/2e^2Qq$) values. For M=Ta, the dominant doublet which accounts for 65% of the spectral area, with IS=0.39(1) and $\Delta=1.18(2)$ mm/s, can be assigned as Fe^{3+} in a high spin state ($S=5/2$). Similar values are obtained in other oxygen-rich YBCO materials and are always considered as the fingerprint of Fe in the Cu(1) site.[15] Therefore, this doublet is attributed to Fe ions in their original M [Cu(1)] site. The minor doublet (35%) with IS=0.36 and $\Delta=0.73$ mm/s corresponds to Fe in the fivefold pyramidal configuration of the Cu(2) sites. For both sites the linewidth is 0.35(2) mm/s. For M=Nb+Ga at 90 K, the hyperfine parameters for the major (65%) and minor (35%) doublets are IS=0.36 and 0.17 mm/s, $\Delta=0.53$ and 1.07 mm/s, respectively, with a common linewidth of 0.35(2) mm/s.

2. MS in the AFM state

At low temperatures, all spectra display magnetic hyperfine splitting, which is a clear evidence for long-range magnetic ordering. The interpretation of the spectra was constrained to be consistent with the site assignment obtained at high temperatures.

For M=Ta, the spectrum obtained at 4.1 K (not shown) exhibits the superposition of two magnetic subspectra with different magnetic ordering temperatures. The average magnetic hyperfine field obtained is $H_{\mathrm{eff}}=486$ kOe. The most informative and revealing data are obtained at elevated temperatures. We start with the spectrum measured at 90 K (Fig. 3). The well defined sextet [32(3)%] which corresponds to the minor doublet, shows that in the Cu(2) sites, the Fe ions are equivalent in terms of their oxygen environment. The fitting parameters are IS=0.35(1) and linewidth=0.46(1) mm/s, $H_{\mathrm{eff}}=390(3)$ kOe, and an effective quadrupole splitting value of $\Delta_{\mathrm{eff}}=1/2e^2Qq_{\mathrm{eff}}=-0.36(10)$ mm/s. Using the relation $\Delta_{\mathrm{eff}}=\Delta/2(3\cos^2\Theta-1)$, we obtained for the Cu sites the hyperfine field orientation $\Theta=90°$, which means that the Fe magnetic moments lie perpendicular to the tetragonal symmetry c axis. The rest of the spectral area [66(2)%] contains a doublet with hyperfine parameters: IS=0.36 and $\Delta=1.02$. Similar values for this doublet were obtained at higher temperatures. As the temperature is raised, the magnetic splitting decrease and disappear completely above $T_N=130$ K. Consistent with the sextet observed at 90 K, the magnetic H_{eff} values obtained at 105, 113, and 120 K are 352(3), 312(5), and 178(5) kOe. At 140 K, *no* magnetic splitting is observed, and the spectrum obtained is similar to that at 150 K. Therefore, we may say with high confidence that for PrCeTaSCO, $T_N(\mathrm{Cu})=130(5)$ K.

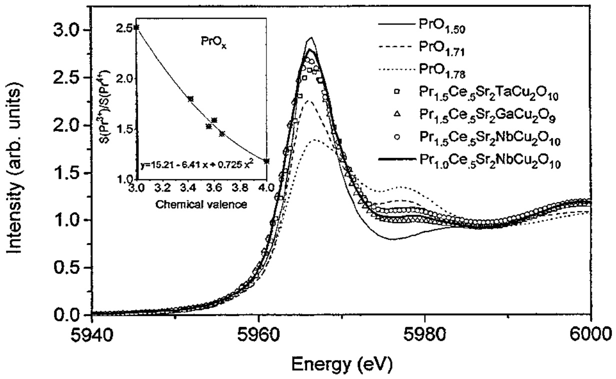

FIG. 5. Pr-L_{III} XAS spectra of RCeMSCO measured at 300 K. The inset shows the variation of the area ratio (Pr^{3+}/Pr^{4+}) with CV in PrO_x.

Figure 3 also exhibits the MS for M=Nb+Ga at 4.1 K. One observes a complicated spectrum and the major problem confronting any quantitative analysis is the Fe distribution over at least three inequivalent sites, of which one is nonmagnetic, and contributes to the doublet in the center of the spectrum, and two of them are magnetically split with different magnetic fields and quadrupole interactions. The interpretation of this spectrum was made to be consistent with the site assignment obtained at 90 K. The doublet which accounts for 64% of spectral area with IS=0.49(2) and $\Delta=0.58(2)$ mm/s can be associated with Fe in the M site. The total intensity of the magnetic subspectra (36%) agrees perfectly with the intensity of the minor doublet obtained at 90 K. Regardless of the model used to fit the spectrum, we have clear evidence for long-range magnetic ordering of the Cu sites at 4.1 K. Our fit yields $H_{\mathrm{eff}}=492(5)$ and 330(4) kOe. However, this is of little importance in our present discussion. As the temperature is raised both magnetic splittings decrease, and disappear at $T<90$ K. Unfortunately, we cannot derive $T_N(<90$ K) for this compound at the present time.

D. Specific heat measurements

The peak in the susceptibility curve at 23 K for PrCeTaSCO (Fig. 1) has been previously assigned as the ordering temperature of the Pr sublattice.[5] In order to reveal the nature of this peak, the specific heat at 0 T was measured up to $T=100$ K. Figure 4 shows, in the vicinity of 23 K, only a small change in the curvature, but *no* clear features indicative of a magnetic origin can be observed, despite the fact that a sizable magnetic entropy is normally expected for such magnetic transitions. It should be noted that in other similar Pr based systems such as $PrBCO_7$, $Pr_{0.75}Y_{0.25}Ba_2Cu_3O_7$,[16] and $PrBa_2NbCu_2O_8$,[9] in which direct magnetic studies and/or neutron diffraction measurements show that the Pr sublattice is magnetically ordered, a well defined peak is observed in the $C_p(T)$ curves at T_N.

The C_p/T versus T^2 plot [Fig. 4 (inset)] is linear in the range $20<T^2<200$; however, a downward curvature is observed below $T^2=20$ K. A fit in the range $2<T<10$ K with the sum of a linear term for the electronic contribution and a Debye approximation for the lattice contribution, $C_p=\gamma T+\beta T^3+\delta T^5$, yields $\gamma=242(3)$ mJ/mol(Pr)K^2, $\beta=0.35(1)$ mJ/mol K^4, corresponding to $\theta_D=425(5)$ K, and $\delta=3.3\times 10^{-7}$ mJ/mol K^6. A value of $\gamma=257(2)$ mJ/mol(Pr) K^2 was calculated by the usual procedure of extrapolating the linear variation of C_p/T versus T^2 from high temperatures to $T=0$. This γ compares well with $\gamma=257$ mJ/mol (Pr) K^2 obtained for PrCeNbSCO,[4] but is significantly higher than $\gamma=111$ mJ/mol (Pr) K^2 obtained for PrCeGaSCO.[6] The spin-wave contribution to C_p for an AFM material ($C_M \propto T^3$) is assumed to be small, at least at low temperatures, and cannot be extracted from our data. The absence of a clear anomaly in $C_p(T)$ at low temperatures supports our interpretation of the magnetic origin for the peak in the susceptibility as discussed above.

E. Ce-L_{III} and Pr-L_{III} near-edge absorption study

The local electronic structure of the Pr and Ce ions in PrCe*M*SCO was studied by XAS at the Pr-L_{III} and Ce- L_{III} edges, and the results obtained at room temperature are shown in Table I and Fig. 5. Our XAS measurements of the Ce-L_{III} on PrCe*M*SCO ($M=$Nb, Ta, and Ga) show that the Ce ions in all samples have the same absorption edge. It consists of two major peaks which corresponds to the $4f^0$ (Ce^{4+}) and to $4f^1L^{-1}$ (Ce^{3+}) initial state configurations. Thus the ground state of Ce is a mixture of the two initial states. Generally speaking, the spectra and interpretation of the intermediate valence of Ce in PrCe*M*SCO are identical to those observed in CeO_2 and more details are readily available in Ref. 18. On the other hand, Fig. 5 shows that for the Pr-L_{III} absorption edge, the spectra vary from one compound to another. They exhibit two peaks, at 5966.4 and 5978.6 eV, which are attributed to Pr^{3+} and Pr^{4+}, respectively. For the sake of comparison, Fig. 5 exhibits XAS performed on several samples of PrO_x ($x=1.50$–1.78).[17] The peak at 5978.6 eV is absent in the $PrO_{1.5}$ (Pr_2O_3) spectrum but appears in PrO_x, where $x=1.71$ and 1.78, and in the PrCe*M*SCO materials. Thus in all PrCe*M*SCO compounds studied, the Pr ions are in a mixed valence state close to 3+. This is in contrast to EELS measurements published recently, which indicate a pure trivalent state for Pr in several PrCeNSCO based samples.[10]

The chemical valence (CV) values listed in Table I have been obtained by straightforward method based on a calibration curve obtained from PrO_x data. Although Pr occupies several distinct sites in the intermediate oxides, their average CV is taken as equal twice their oxygen stoichiometry (CV of Pr is $2x$). In Pr oxides-PrO_x, namely, PrO_2(2.00), $Pr_{12}O_{22}$(1.83), Pr_9O_{16}(1.78), Pr_7O_{12}(1.71), and Pr_2O_3(1.50), the (Pr^{4+} for PrO_2 and Pr^{3+} for Pr_2O_3), the L_{III}-edge peak intensity varies regularly with x. The inset of Fig. 5 was obtained by plotting CV of Pr in PrO_x versus the ratio R. R is the integrated area below the peak corresponds to Pr^{3+} [$S(Pr^{3+})$] divided by the area of the peak corresponds to Pr^{4+} [$S(Pr^{4+})$]. A polynomial fitting (solid line) is then used to estimate CV of Pr in other related compounds, providing the neighboring ions of Pr are essentially oxygen. Therefore, the peak ratio in Fig. 5 yields immediately the CV for all PrCe*M*SCO as reported in Table I. XAS measurements for $M=$Nb and Ga performed at 10 K yield the same CV, indicating that the Pr valence does not change with the temperature. For the sake of comparison we also performed XAS measurements on closely related similar compound, such as $PrBa_2NbCu_2O_8$, in which the Pr sublattice orders magnetically at 12 K (Ref. 9) and the CV obtained is 3.04(6), indicating the Pr is completely trivalent.

DISCUSSION

The magnetic behavior of PrCe*M*SCO studied here can be compared to those of other isostructural systems such as PrCeNSCO (Ref. 4) and PrCeGSCO.[6] Comparison of the susceptibility results is possible despite the fact that the measurements were performed on samples containing elements of different valence, i.e., Nb^{5+}, Ta^{5+}, and Ga^{3+}, In^{3+} and therefore their oxygen content is different. We observed only one peak in PrCeTaSCO in full agreement with Ref. 5, in contrast to $Pr_{1.5}Ce_{0.5}MSr_2Cu_2O_z$ ($M=$Nb or Ga) in which two or three anomalies have been observed in the $\chi(T)$ curves (Fig. 2 and Table I). For all samples studied, irreversibility phenomena are observed, with T_{irr} always above the peak positions. No such transitions were observed in the $\chi(T)$ curves of PrCeInSCO and for a mixed $M=$Nb+Ga sample.

A previous assumption was that Pr orders magnetically in PrCeTaSCO near 23 K,[5] analogous to Pr ordering in $PrBCO_7$ at 17 K and $PrNbBa_2Cu_2O_8$ at 12 K. However, the absence of an anomaly in the C_p curves (Fig. 4) casts some doubt on this interpretation, because a sizable magnetic entropy $S=R\ \ln 3=9.2$ J/mol K is normally expected for the ordering of Pr^{3+} ions. In fact, PrCeTaSCO resembles to $Pr_{0.75}Y_{0.25}Ba_2Cu_3O_7$ in which 25% of the Pr site is occupied by Y and the Pr ions are AFM around 12 K. This magnetic transition is apparently observable in the $C_p(T)$ curves.[16] It is reasonable to assume that the absence of an anomaly in the C_p curves is a result of the presence of two layers of Pr ions in PrCeTaSCO (instead of one in $PrBCO_7$) which might lead to a different specific-heat behavior, due to a nonsimple magnetic ordering caused by some frustration. A more preferable second interpretation is that in all PrCe*M*SCO compounds, Pr is not magnetically ordered down to 2 K, and all anomalies in the $\chi(T)$ curves are due to the CuO_2 planes. The absence of this peak in the oxygen reduced PrCeNSCO (Ref. 4) as well as in the mixed $M=$Nb+Ga (Fig. 2) materials supports this assumption. Due to the high contribution of Pr^{3+} to the susceptibility, T_N (Cu) cannot be extracted directly from the $\chi(T)$ curves, but it is easily determined from the MS studies. Our MS indicate that for PrCeTaSCO, T_N(Cu)~130 K, in full agreement with 100 K predicted by Bennahmias *et al.*[5] We tend to believe that the same T_N(Cu) also exists in PrCeNSCO and PrCeGSCO, and thus our present interpretation differs slightly from the previous one.[7]

Regarding the magnetic properties of the Cu(2) sublattice, it is worth discussing the origin of anomalies in the $\chi(T)$ curves and comparing the number of peaks observed in various PrCe*M*SCO materials. For all Fe doped PrCe*M*SCO samples, as well as for other HTSC materials, our MS studies indicate that Fe ions in Cu(2) planes serve only as a dopant probe and reveal the magnetic behavior of the Cu sublattice.[19] T_N(Cu)~130 K for PrCeTaSCO (as well as for M=Nb and Ga), is lower than T_N~420 K obtained in $YBa_2Cu_3O_6$ ($YBCO_6$). In $YBCO_6$ the Cu ions in the CuO_2 planes are in a pyramidal configuration, and order magnetically in a simple AFM structure with nearest neighbor Cu(2) spins antiparallel in all three dimensions. The AFM ordering of Cu moments can be modeled well by large AFM super exchange coupling (J/k_B~1000–1500 K) between the Cu^{2+} spins ($s=1/2$) in the CuO_2 planes.[20] This strong intraplanar exchange yields large, two dimensional (2D) AFM correlations, with dynamic short-range AFM ordering at high temperatures. The three-dimensional (3D) coupling is driven by a relatively weak interplane exchange interaction $J_+ \sim 10^{-5}$ J between the CuO_2 layers, and T_N(Cu) can be evaluated according to the expression $kT_N = JS^2/\ln J/J_+$.[21] In the PrCe*M*SCO, the CuO_2 layers are separated on one side by MO_4 tetrahedra (or MO_6 octahedra), and on the other side by fluorite structured $R_{1.5}Ce_{0.5}O_2$ layers. The short Cu-Cu distance along the c direction, about 6.08 Å, is much longer than the 3.36 Å found in $YBCO_6$. This leads to a weaker J_+, and as a result to a lower T_N(Cu). It appears that it is possible to affect T_N(Cu) by inserting different separator layers between the CuO_2 planes.

Below T_N, some local structural distortions (their nature is not yet known) break the local tetragonal symmetry of the unit cell and allow for a local canting of the Cu moments via a DM interaction.[5] Above $T_{\rm irr}$ the magnetization is reversible. At $T_{\rm irr}$ the Cu moments are slightly canted in the AFM state, giving rise to the weak ferromagnetic component from each CuO_2 plane. The magnitude of the components as well as the $T_{\rm irr}$ position appears to be strongly depend on M and on whether the Cu-O planes are doped or not. Note that the M/H values for M=Ga are an order of magnitude higher than for M=Nb and Ta (Figs. 1 and 2). For the Fe doped PrCeTaSCO sample, both the peaks position and $T_{\rm irr}$ are shifted to higher temperatures. On the other hand for Pr_xCeNbSCO, a deficiency in the Pr concentration (x=1.25 or x=1.0) effects only the magnitude of the ZFC branch but not the peak positions (Fig. 2). Note, that for x=1.0 CV =3.12 is lower than CV of x=1.5 (Table I). Further, Fig. 2 shows that mixing of Nb with Ga [T_N(Cu)<90 K] and/or a full substitution of Ta by In, have the effect of depressing the weak ferromagnetism behavior of the CuO_2 planes. This indicates that the canting of the Cu moments via the antisymmetric DM interactions are very sensitive to the local structural distortion such as lattice defects, oxygen disorder, or variation in the oxygen stoichiometry.

The peaks in the ZFC $\chi(T)$ curves exhibited in Figs. 1 and 2 are probably associated with the reorientation of the Cu moments. For M=Ga the first peak which appears at 94 K shifts downward to 54 K for M=Nb (Fig. 2) (for both x=1.5 and 1) and to 23 K for M=Ta. Note that PrCeGaSCO has an orthorhombic unit cell with lower local symmetry than the tetragonal structure found for all the rest of the PrCe*M*SCO compounds studied. Presumably, the lower local symmetry encourages the antisymmetric DM type interactions. Table I shows that the c lattice parameter (Cu-Cu distance) increases in the order Ga<Nb<Ta<In. The first peak position varies also in the same manner; therefore we may assume that the absence of anomalies in the M/H curves for M=In may be due to its larger c lattice parameter. We tend to believe that at low temperatures, the Cu-Cu and/or Pr-Cu interactions begin to dominate, leading to the reorientations which are observed as anomalies in the susceptibility curves. The magnetic interactions driving this reorientation and the number of peaks observed are clearly independent of the valence of M or of oxygen concentration. These reorientations, which are independent of T_N(Cu), lead to a negligibly small latent heat which cannot be observed in the C_p curves. The absence of anomalies in the $\chi(T)$ curve for the mixed M=Nb+Ga and the fact that a tiny amount of Fe smears this peak [Fig. 1(b)] both support this interpretation.

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