Magnetic transitions in the perovskites Pr\(_{1-x}\)Sr\(_x\)CoO\(_3\)

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Abstract. The magnetic and electrical properties of Pr\(_{1-x}\)Sr\(_x\)CoO\(_3\) cobaltites with 0.3 ≤ x ≤ 0.5 were studied in the temperature range 5 K ≤ T ≤ 1000 K and field, up to 7 T. These cobaltites exhibit two phase transitions: a paramagnetic-ferromagnetic phase transition below about 240 K and a second one below 110 K. The temperature dependences of the magnetizations of Sr doped samples show differences in the FC and ZFC data. The samples were also investigated by μSR experiments in zero field (ZF) and weak transverse field (wTF). The μSR data clearly indicate the existence of the two transitions. The samples show small negative magnetoresistances that are controlled by grain-boundary effects. The results suggest a change in the nature of magnetic coupling between Co ions at low temperature magnetic transition.

1. Introduction
The discovery of the “colossal” magnetoresistance (CMR) in the manganites with perovskite type structure has stimulated the research of the compounds exhibiting large magnetoresistance. The cobaltites with perovskite-type structure have attracted a considerable interest because of their specific properties, which make them promising materials for use in solid oxide fuel cell, chemical reactors, gas separation membranes and many other applications [1].

The perovskite cobaltites Ln\(_{1-x}\)A\(_x\)CoO\(_3\) (Ln-lantanide, A-alkaline-earth element) show a strong correlation between lattice, charge, spin and orbital degrees of freedom. In these oxides, cobalt is susceptible to accommodate various oxidation states (Co\(^{3+}\), and Co\(^{4+}\)). There are, also, various spin states for trivalent (low-spin LS: \(t^2_2\)e\(^{0}\)_g; intermediate-spin IS: \(t^5_2\)e\(^{1}\)_g; high-spin HS: \(t^4_2\)e\(^{2}\)_g) and tetravalent cobalt ions (LS: \(t^3_2\)e\(^{0}\)_g; IS: \(t^4_2\)e\(^{1}\)_g; HS: \(t^3_2\)e\(^{2}\)_g) [1]. LaCoO\(_3\) is a diamagnetic insulator at low temperatures with a low spin state (LS) of Co\(^{3+}\) (S = 0). With increasing temperature some of Co ions are progressively converted to IS or to HS state due to the small difference between Hund and crystal field energies that allows the thermal excitation of \(t^2_2\) electrons on \(e_g\) levels [1,2]. The competition between these energies leads to peculiar phase transitions in cobalt perovskites. Although, like manganites, they exhibit doping-induced ferromagnetic and metallic characters, the nature of their ferromagnetic state continues to be a matter of much discussion due to the peculiar aspects of ferromagnetism in these compounds, where the trivalent and tetravalent Co ions remain mixtures of LS or IS states [1-3]. The ferromagnetic state in cobaltites is not homogeneous. The widely studied La\(_{1-x}\)Sr\(_x\)CoO\(_3\) series shows spin glass-like (0.05 ≤ x ≤ 0.2) and cluster glass (0.3 ≤ x ≤ 0.5) behavior and SrCoO\(_3\) is a long range ferromagnet [2]. Among Ln\(_{1-x}\)Sr\(_x\)CoO\(_3\) series, Pr\(_{1-x}\)Sr\(_x\)CoO\(_3\) (0 ≤ x ≤ 0.8) stands out for unusual magnetic properties [3]. Magnetic investigations on Pr\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\) showed two phase transitions: a low temperature phase transition at \(T_A\) ≈ 110 K and a high...
temperature phase transition at $T_C \approx 220$ K [4-11]. The high temperature transition at $T_C$ is typical for cobaltites. The low temperature phase transition at $T_A$ is still controversial. Mahendiran and Schiffer [4] found a maximum in coercivity around $T_A$. Uchida et al. [8] showed that the magnetic domain structure changes below about 90 K. Very recently, Leighton et al. [10] suggested that this anomaly is “due to a novel form of coupled structural/magnetocrystalline anisotropy transition driven, in this case, by Pr-O hybridization”.

The present work is an extension of the previous studies [5-9, 11] on the magnetic behavior of $\text{Pr}_x\text{Sr}_{1-x}\text{CoO}_3$ of the system $\text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3$ to include the compounds with $x = 0.3$, and $x = 0.4$. Beside electrical and magnetic measurements we used $\mu$SR (muon spin rotation/relaxation/resonance) experiments to prove the double magnetic transition in these compounds.

2. Experimental

High-quality $\text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3$ polycrystalline samples with $x = 0.3$, 0.4 and 0.5 were prepared by standard ceramic reaction. The compounds were sintered in air at 1200 °C for 24 h with intermediate grindings. Room temperature x-ray powder diffraction patterns were taken in a Brucker Advance D8 AXS Diffractometer using Cu Kα radiation. Rietveld refinements of the diffraction patterns were carried out using the FULLPROF program. The magnetization and ac susceptibility measurements were performed in the temperature range 5 – 400 K and in magnetic fields up to 9 T using a multipurpose Oxford Instruments MagLab System 2000. The electrical resistivity was measured in a cryogen free magnet cryostat CFM - 7 T (Cryogenic Ltd.) by the four-probe technique in the temperature range from 5 to 300 K and in magnetic fields up to 7 T. The $\mu$SR (muon spin rotation/relaxation/resonance) experiments were performed at the GPD spectrometer in Paul Scherrer Institute Villigen, Switzerland. In a typical $\mu$SR experiment [13], polarized muons (elementary particles with spin 1/2, and lifetime $\tau_{\mu} \approx 2.2$ μs) are implanted into the sample (start signal), where their spin precesses around the local magnetic field at the stopping site. The muons decay emitting a positron preferentially along the direction of the muon spin (stop signal). The events are stored in histograms containing the raw $\mu$SR spectrum. The time evolution of the muon polarization, $P(t)$ can be deduced by fitting the raw spectra to the following formula:

$$N_e(t) = B + \frac{N_0}{\tau_{\mu}} \exp(-t/\tau_{\mu})[1 + A \cdot P(t)]$$

where $B$ is a time independent background and $N_0$ is a normalization constant. $A$, called average asymmetry, is a dimensionless parameter. $A \cdot P(t)$ contains all the physics of the investigated sample: local field at the muon site, field distribution, $\mu^+$ relaxation rate. The value of $A$ can be easily obtained from a calibration measurement.

3. Results and discussions

The X-ray diffraction patterns indicated that the samples were single perovskite phase, of orthorhombic ($Pbnm$) symmetry for $x = 0.3$ and of monoclinic ($P2_1/m$) symmetry for $x = 0.4, 0.5$ with the unit cell parameters in close agreement with the values reported in earlier works [7-10].

The magnetization of the samples (measured in 0.1 T magnetic field), has history dependence with a bifurcation between zero field cooling (ZFC) and field cooling (FC) at a characteristic temperature. Both FC and ZFC magnetization sharply increase below 240 K, at the Curie temperatures $T_C$’s and they show a feature below $T_A$’s, about 110 K, as shown in the inset of the Figure 1. The coercive fields ($H_C$), estimated from the hysteresis loops is rather large, it has it maximum value (0.1 T) for the sample with $x = 0.5$ at 5 K. The signatures of the two magnetic transition were also seen in the ac susceptibility measurements. In Figure 1, are described the thermal variations of the real part $\chi'(T)$ of the ac susceptibility. $\chi'(T)$ has a high and narrow peak corresponding to $T_C$ and then it decreases with decreasing temperature and it has a small maximum in the region of $T_A$. The Curie temperature $T_C$ was
also marked by a sharp dip in the nonlinear ac susceptibility, \( \chi_3'(T) \), but no feature was seen at \( T_A \) for all the investigated samples.

![Graph showing temperature dependencies of \( \chi'(T) \) and magnetizations for \( x = 0.3 \) sample.]

Figure 1. The temperature dependencies of the real part, \( \chi'(T) \), of the complex susceptibility for \( \text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3 \) with \( x = 0.3, 0.4 \) and 0.5. In the inset, the ZFC and FC magnetizations for the sample with \( x = 0.3 \) are shown.

While the \( \text{PrCoO}_3 \) is a paramagnetic insulator, the Sr-doped samples, with \( x = 0.3, 0.4 \) and 0.5, have a very different behavior. They show a metallic behavior in the high temperatures range and an intriguing upturn at low temperatures, below 100 K. In spite of the fact that this upturn is rather close to \( T_A \), it seems to be not of intrinsic origin but probably arise from the carrier scattering processes at the grain boundaries from the polycrystalline samples, as seen in polycrystalline manganites and other transition metal oxides [13]. The temperature dependence of resistivity \( \rho(T) \) has a small change of slope at \( T_C \). This behavior is typical for Sr-doped cobaltites [1]. We found no sign of magnetic changes in the \( \rho(T) \) curves, at \( T_A \). Probably, these changes are masked by disorder and grain boundary effects. The magnetoresistance seen in these compounds is rather small. A maximum value of of about 5% was obtained for the sample with \( x = 0.5 \) in a magnetic field of 7 T, in the \( T_C \) region.

We have performed \( \mu \)SR experiments on \( \text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3 \) samples (\( x = 0.3, 0.4 \) and 0.5). Only the \( x = 0.3 \) results are presented here in Figure 2, since the behaviors of the \( x = 0.4 \) and 0.5 samples are rather similar. The samples were investigated in wTF, for calibration purposes and in order to check for eventually phase separation, and ZF, to investigate the magnetic ordering. No oscillations were observed in the \( \mu \)SR spectra below the transition temperature, indicating either that the local field at the muon site is zero or that the field distribution around the local field is large.

However, valuable information could be obtained from the fit of the \( \mu \)SR spectra to:

\[
A P(t) = A_b e^{-\lambda t} + A_p e^{-\sigma t^2} + A_m \left( \frac{2}{3} e^{-\mu t} + \frac{1}{3} e^{-\nu t} \right)
\]

with \( A = A_b + A_p + A_m \), where \( b \) means the background, \( p \) = paramagnetic and \( m \) = magnetic contributions. \( A_b \) and \( A \) were obtained from calibration runs in weak transverse field (wTF) at low and respectively high temperatures. \( A_p(t) \), not shown here, decreases sharply below about 230 K in contradiction with the large magnetic transition observed in similar substituted compounds \( \text{Pr}_{1-x}\text{Ca}_x\text{CoO}_3 \) [14]. As shown in, Figure 3, \( \lambda(T) \) clearly indicates a double magnetic transition. It follows the temperature dependence of the order parameter. In general, muon spin relaxation rate \( \lambda \) gives a measure of the fluctuating local magnetic field acting at the muon site due to the neighboring magnetic ions through dipolar coupling, and is given by \( \lambda = \frac{\gamma_{\mu}^2}{\mu} \langle B_{\text{loc}}^2(0) \rangle \tau_e \), where \( \gamma_{\mu} \) is the giromagnetic ratio of the free muon, \( B_{\text{loc}}(0) \) is the amplitude of the fluctuating local field felt by the
muons at their stopping sites, and $\tau_c$ is the correlation time [12]. From these data we can only infer that since the high temperature ferromagnetic transition at $T_C$ is induced by doping, the low temperature transition at $T_A$ results from a change in the nature of magnetic coupling between Co ions.

Figure 2. $\mu$SR spectra recorded at temperatures around the magnetic phase transition rate for the sample Pr$_{0.7}$Sr$_{0.3}$CoO$_3$.

Figure 3. Temperature dependence of relaxation rate for the sample Pr$_{0.7}$Sr$_{0.3}$CoO$_3$.

4. Conclusions
A double magnetic transition was found in Pr$_{1-x}$Sr$_x$CoO$_3$ ($x = 0.3, 0.4$ and $0.5$) by using magnetic and $\mu$SR measurements. The high-temperature transition is typical for Sr-doped cobaltites, while the other transition occurs as a result of the change in the nature of the magnetic interactions between the Co ions. The electrical measurements indicate low magnetoresistance, metallic behavior at high temperatures and grain boundary scattering effect in the low temperatures region.

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References
[1] M. A. Señarís-Rodríguez and J. B. Goodenough, J. Solid State Chem. 118, (1995) 323.
[2] J.-Q. Yan, J.-S. Zhou, J.B. Goodenough, Phys. Rev. B 69, (2004) 134409.
[3] J. Wu and C. Leighton, Phys. Rev. B 67, (2003) 174408.
[4] H. W. Brinks, H. Fjellvag, A. Kjekshus, and B. C. Hauback, J. Solid State Chem. 147, (1999) 464.
[5] R. Mahendiran, P. Schiffer, Phys. Rev. B 68 (2003) 024427.
[6] I.O. Troyanchuk, D.V. Karpinski, A.N. Chobot, D.G. Votsekhovich, V.M. Dobryanski, JETP Letters, 84, (2006)151.
[7] S. Hirahara, Y. Nakai, K. Miyoshi, K. Fujiwara, J. Takeuchi, J. Magn. Magn. Mat. 310 (2007) 1866.
[8] M. Uchida, R. Mahendiran, Y. Tomioka, Y. Matsui, K. Ishizuka, Y.Tokura, Appl. Phys. Lett. 86 (2005) 131913.
[9] K. Yoshii, A. Nakamura, Physica B, 281 &282 (2000) 514.
[10] C. Leighton, D.D. Stauffer, Q. Huang, Y. Ren, S. El-Khatib, M.A. Torija, J. Wu, J.W. Lynn, L. Wang, N.A. Frey, H. Srikanth, J.E. Davies, Kai Liu, J.F. Mitchell. Phys. Rev. B (2009) in press.
[11] I.G. Deac, R.Tetean, I. Balasz, E.Burzo, J. Magn. Magn. Mater. (2009) submitted.
[12] A. Schenck, Muon Spin Rotation Spectroscopy: Principles and Applications to Solid State Physics, Hilger, Bristol, 1985.
[13] M. Ziese, Rep. Prog. Phys. 65 (2002) 143.
[14] I.G. Deac, R.Tetean, D. Andreica, E.Burzo, IEEE Trans. Magn. 44, (2008) 2922.