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Transition from itinerant to polaronic conduction in $La_{1-x}Sr_xCoO_3$ perovskites

R. Caciuffo[1], J. Mira[2], J. Rivas[2], M. A. Señarís-Rodríguez[3], P. G. Radaelli[4] F. Carsughi[1,5], D. Fiorani[6] and J. B. Goodenough[7]

[1] *Istituto Nazionale per la Fisica della Materia and Università di Ancona Via Brecce Bianche, 60131 Ancona, Italy*
[2] *Departamento de Física Aplicada, Universidade de Santiago E-15706 Santiago de Compostela, Spain*
[3] *Departamento Quimica Fundamental e Industrial, Universidade da Coruña 15071 A Coruña, Spain*
[4] *Rutherford Appleton Laboratory, ISIS Facility - Chilton, UK*
[5] *Institut für Festkörperforschung des Forschungszentrum - 52425 Jülich, Germany*
[6] *Istituto di Chimica dei Materiali, CNR - 00016 Monterotondo, Roma, Italy*
[7] *Center for Materials Science and Engineering, University of Texas at Austin Texas 78712-1063, USA*

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Abstract. – Neutron diffraction and small-angle scattering on $La_{1-x}Sr_xCoO_3$ ($0 < x \leq 0.30$) show that for $x = 0.3$ the system is near a two-phase percolation threshold and undergoes a transition from itinerant to polaronic conduction at the Curie temperature T_C. The stabilization of superparamagnetic clusters on warming through T_C is revealed by an anomalous thermal expansion of the volume and a deviation of the paramagnetic susceptibility from the Curie-Weiss law. The development of a temperature-dependent small-angle-scattering signal confirms that regions of short-range ferromagnetic order are present above T_C.

The cross-over from localized to itinerant electronic behavior in mixed-valent transition-metal oxides with the perovskite or a perovskite-intergrowth structure has received extensive and intensive study since the discovery of high-temperature superconductivity in the copper oxides and of a "colossal" negative magnetoresistance (CMR) in the manganese oxides. Where there is an orbital degeneracy that may be removed by a cooperative Jahn-Teller (J-T) deformation, a transition from static to dynamic local site distortions at the localized-itinerant electronic cross-over may either stabilize a phase with a peculiar "vibronic" state having the characteristics of a bad metal or undergo a dynamic phase segregation into mobile domains rich

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in charge carriers within a matrix poor in charge carriers [1]. This phenomenon occurs because cooperative oxygen-atom displacements may create not only local J-T deformations, but also charge density waves and phase segregation. Static cooperative J-T oxygen displacements in the $La_{1-x}Ca_xMnO_3$ system could be predicted in 1955 [2] on the basis of lattice-parameter and magnetic-order determinations by neutron diffraction [3]. In the copper oxides the first identification of a dynamic phase segregation into stripe domains was obtained by XAFS [4]; stripe domains were previously observed by neutron diffraction, but in a phase where the stripes were pinned [5]. Ferromagnetic clusters above T_C have been observed by neutron scattering in $La_{0.67}Ca_{0.33}MnO_3$ [6] and $Nd_{0.7}Sr_{0.3}MnO_3$ [7]. De Teresa *et al.* described the ferromagnetic clusters in $La_{0.67}Ca_{0.33}MnO_3$ as "magnetic polarons" and used small-angle neutron scattering (SANS) to follow their growth in a magnetic field above T_C [8]. Whether these regions of ferromagnetic short-range order represent conventional magnetic polarons [9] or the segregation of a hole-rich, more conductive second phase [10] remains an open question.

The $La_{1-x}Sr_xCoO_3$ perovskite adds another dimension of complexity; cobalt spin configurations change with temperature and Sr concentration to give a rich variation of magnetic and transport properties that has attracted considerable attention over the last four decades [11-17]. Moreover, a large negative magnetoresistance ratio has been observed [18,19] for low Sr doping that appears to be analogous to the CMR found in some manganese perovskites. In the parent compound $LaCoO_3$, the Co(III) ions undergo a progressive transition from low-spin (LS) t^6e^0 to localized intermediate-spin (IS) t^5e^1 configurations with increasing temperature, but as the population of localized IS configurations exceeds 50%, the σ-bonding e orbitals become more itinerant with increasing temperature in the range $350 < T < 650$ K and stabilize an itinerant IS state $t^{5-\delta}\sigma^{*(1+\delta)}$ in which δ appears to increase with temperature [20]. The σ^* electrons of e-orbital parentage introduce ferromagnetic interactions between the localized t^5 spins, and the e^1 parentage of a σ^{*1} band is orbitally degenerate. Detection of short-range fluctuations of localized IS and LS configurations as the population of IS ions approaches 50% was not possible with a diffraction experiment [21]; the fluctuations become too fast by 77 K for even a Mössbauer measurement to distinguish between cobalt atoms [22]. However, the increasing population of antibonding σ^* electrons is manifest not only in the paramagnetic susceptibility, but also by an anomalous thermal expansion of the mean Co-O equilibrium bond length.

The substitution of Sr for La in the oxygen-stoichiometric system $La_{1-x}Sr_xCoO_3$ introduces x holes per formula unit into the CoO_3 array. Each hole stabilizes IS configurations over a cluster of cobalt atoms; and for $x < 0.2$, the holes stabilize isolated IS clusters containing σ^* electrons of e-orbital parentage in cluster molecular orbitals. The σ^* electrons introduce ferromagnetic interactions between the localized spins of the t^5 configurations within a cluster that are manifest by superparamagnetism below about 220 K; at lowest temperatures, the superparamagnetic clusters interact to form a spin glass [11,23-25]. In the range $0.2 \leq x \leq 0.3$, a percolation threshold for interactions between clusters occurs below T_C and for $0.3 \leq x \leq 0.6$ a ferromagnetic IS matrix is stabilized within which Co(III)-rich clusters may persist. At $x = 0.3$, the IS matrix has a Curie temperature $T_C \approx 230$ K.

A metallic temperature dependence of the resistivity appears below T_C for $x \approx 0.2$. Compositions $x = 0.20$ and 0.25 have exhibited a resistance maximum at $T_{MI} = T_C - \Delta T$, where ΔT decreases with increasing x extrapolating to $\Delta T = 0$ at $x \approx 0.3$. A transition temperature T_S, which was interpreted to be a maximum temperature for a dynamic ordering of high-spin (HS) and LS ions, extrapolated to $T_S \approx 300$ K at $x = 0.3$ [11]. On the other hand, the resistance retained a metallic temperature dependence through T_C in the compositional range $0.3 \leq x \leq 0.6$. The $x = 0.3$ composition is at an interesting cross-over at T_C.

In this letter, we report thermal-expansion, paramagnetic susceptibility, and SANS data for $La_{0.7}Sr_{0.3}CoO_{3-\delta}$, $\delta = 0.02 \pm 0.01$. On heating, the results indicate a transition at T_C

from itinerant σ^* electrons in a percolating IS state to a dynamic phase segregation producing the appearance of clusters of a ferromagnetic second phase with a Curie temperature $T_{\rm C}^* \approx 300\ {\rm K} > T_{\rm C}$ [11]. An anomalous increase in the thermal expansion signals the introduction of localized IS and/or HS configurations and accompanies the segregation into Co(IV)-rich clusters and a Co(IV)-poor matrix.

Specimens of $La_{1-x}Sr_xCoO_3$ ($0.10 \leq x \leq 0.30$) were prepared by the coprecipitation method described elsewhere [11]. The products were close to stoichiometric and no evidence for any impurity phase was found in either X-ray or neutron diffraction. Neutron powder diffraction experiments were carried out in Grenoble on the high-resolution neutron diffractometer D2B and the high-intensity diffractometer D20 of the Institute Laue Langevin (ILL). On both instruments, data were collected at several temperatures on warming from 2.5 to 300 K. Rietveld analysis of the diffraction patterns was performed with a modified version of the GSAS suite of crystallographic routines [26]. In general, agreement factors R between 2 and 4% were obtained.

In the range $0 \leq x \leq 0.3$, the $La_{1-x}Sr_xCoO_3$ system has a rhombohedrally distorted perovskite structure with $R\bar{3}c$ symmetry. With increasing x, the rhombohedral distortion decreases. The volume of the unit cell expands sharply with x in the range $0 \leq x \leq 0.1$; it increases linearly with x for $x > 0.1$; the room-temperature Co-O bond length jumps between $x = 0$ and $x = 0.1$, but remains constant in the range $0.1 \leq x \leq 0.3$. The intensity of the low-angle Bragg peaks increases below the Curie temperature $T_{\rm C}$, revealing the occurrence of ferromagnetic order. No magnetic satellites have been observed, which excludes antiferromagnetic order of any kind, at least down to 2 K. Analysis of the magnetic contribution to the diffraction profile indicates that the Co magnetic moments are aligned in the [100] direction of the rhombohedral cell. The saturation magnetization $M(0)$ at 4.2 K changes from 0.3 to about 1.70 $\mu_{\rm B}$ per Co atom as x increases from 0.10 to 0.30. The low value of $M(0)$ for $x = 0.10$ is consistent with a ferromagnetic intermediate-spin phase that occupies only a fraction of the volume. Whether and to what extent this ferromagnetic phase is pinned to Sr^{2+}-rich regions depend on the preparation conditions, but this question is not critical to the present discussion.

Figure 1 shows the temperature dependence of the rhombohedral cell parameter $a_{\rm R}$ for $La_{0.7}Sr_{0.3}CoO_3$. In the ferromagnetic phase below $T_{\rm c} \approx 230$ K, the lattice thermal expansion is typical for a solid and can be fitted to the formula

$$a_{\rm R}(T) = a_0 \left\{ 1 + \frac{\alpha_0 T_{\rm E}}{2} \left[\coth\left(\frac{T_{\rm E}}{2T} \right) - 1 \right] \right\} ,$$

which is obtained from the Grüneisen approximation for anharmonic phonon potentials and the Einstein model for the constant-volume specific heat; a_0 is the rhombohedral lattice parameter for $T = 0$ K, $T_{\rm E}$ is the Einstein temperature and α_0 is the linear thermal expansion coefficient for $T \gg T_{\rm E}$. The solid line in the figure is the calculation with the above formula for $a_0 = 5.3933$ Å, $T_{\rm E} = 142$ K and $\alpha_0 = 9.2 \cdot 10^{-6}\,{\rm K}^{-1}$. A departure from the Grüneisen behavior above $T_{\rm C}$ is evident, the lattice parameter becoming larger than expected. For $x < 0.3$ the thermal expansion is regular up to room temperature (the parameters of the fit to the Grüneisen law for $x \leq 0.3$ are shown in the inset of fig. 1.)

A second unusual finding, peculiar to the $x = 0.3$ composition, is shown in fig. 2; the equilibrium Co-O bond length $d_{\rm Co\text{-}O}$ remains constant on warming from 2.5 K up to $T_{\rm C}$, but it increases steadily in the paramagnetic phase. The correlation between the temperature variation of $d_{\rm Co\text{-}O}$ and the anomalous thermal expansion of the lattice is demonstrated in the inset of fig. 2 where the ratio $[d_{\rm Co\text{-}O}(T) - d_{\rm Co\text{-}O}(0)]/d_{\rm Co\text{-}O}(0)$ is compared to the relative difference between experimental and calculated values of the lattice parameter.

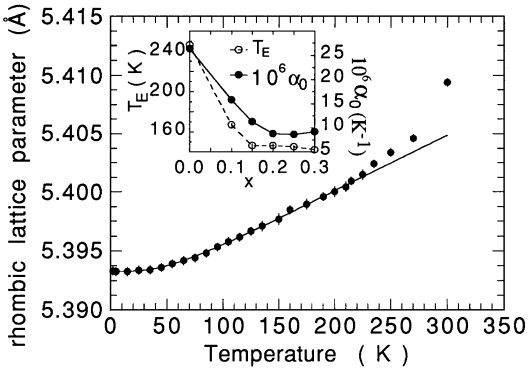

Fig. 1

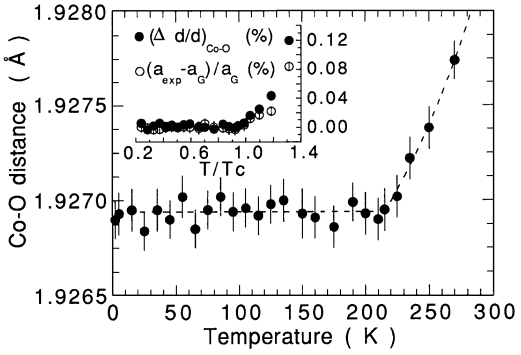

Fig. 2

Fig. 1. – Temperature dependence of the rhombohedral lattice parameter a_{R} for $La_{1-x}Sr_xCoO_3$ ($x = 0.3$). The solid line is a fit to the Grüneisen-Einstein model with the parameters quoted in the text. The x-dependence of the Einstein temperature T_{E} and the linear thermal expansion coefficient, α_0, for $T \gg T_{\mathrm{E}}$ is shown in the inset.

Fig. 2. – The equilibrium Co-O bond length d as a function of temperature for $La_{0.7}Sr_{0.3}CoO_3$. The broken line is a guide to the eye. The inset shows the comparison between the relative variation $[d(T) - d(0)]/d(0)$ and the relative departure of the lattice parameter from the value predicted by the Grüneisen-Einstein formula.

A similar anomaly in the thermal expansion has been observed for $(La, Ca)MnO_3$ and interpreted as the effect of a gradual carrier localization process with the formation of magnetic polarons [8]. This conclusion was supported by magnetic SANS, which grew in intensity on warming at the boundary between the ordered and disordered magnetic phases. To verify whether a similar phenomenology occurs in the $La_{0.7}Sr_{0.3}CoO_3$, we performed a SANS experiment at the D22 facility of the ILL. The sample was the same powder used for the diffraction measurements packed inside a flat aluminum sample holder. The amplitude Q of the scattering vector varied between 0.01 and 0.25 $\mathrm{Å}^{-1}$. Data were collected at different temperatures between 150 and 300 K, with and without a magnetic field of 0.3 T applied in the horizontal plane in the direction perpendicular to the incident beam. After corrections for transmission, background, detector efficiency and dead time, the measured SANS intensity could be fitted to the superposition of a weak Guinier signal, rapidly increasing as T_{c} is approached, and a larger temperature-independent Porod component [27],

$$I(Q,T) = I_{\mathrm{G}}(T)\exp[-Q^2R_{\mathrm{G}}^2/3] + I_{\mathrm{P}}/Q^4\,.$$

The Porod term I_{P}/Q^4 is attributed to the scattering from the surface of the sample grains (with size of the order of 700 nm), while the temperature-dependent Guinier component is due to the growth of short-range ferromagnetic correlations over regions with a size of the order of $\xi = 2R_{\mathrm{G}}$. The variation on warming through T_{C} of the magnetic SANS intensity at $Q = 0$ is shown in fig. 3; it indicates that the number of magnetic inhomogeneities suddenly increases at the Curie point, as does their size (see the inset in fig. 3). It must be noted that in a SANS experiment the energy of the scattering beam is not analyzed and what is obtained is the magnetic response integrated over a large energy window centered at zero energy transfer. This means that the observed clustering effect can be dynamic, as suggested by the strong deviation of the magnetic susceptibility from the Curie-Weiss law; this deviation persists well above T_{C} (fig. 4) and indicates that the system enters into a cluster-fluctuation regime below $T \approx 300$ K.

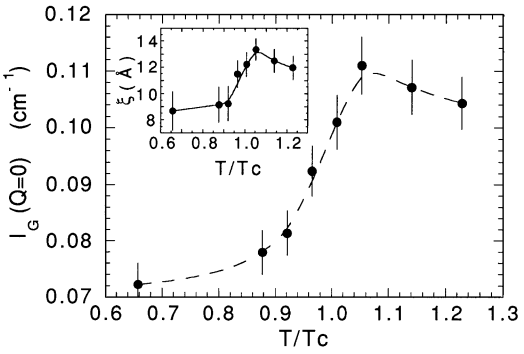

Fig. 3

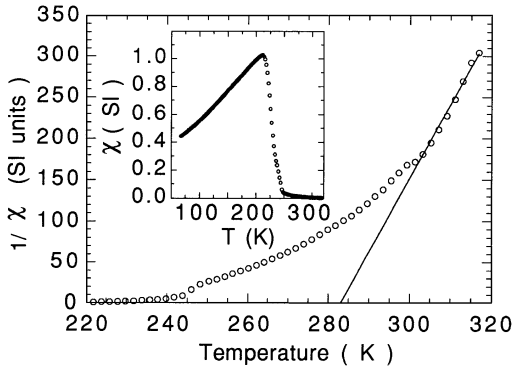

Fig. 4

Fig. 3. – Intensity at $Q = 0$ of the temperature-dependent SANS Guinier component from $La_{0.7}Sr_{0.3}CoO_3$. The Guinier term is attributed to the presence of ferromagnetic clusters with spatial extension ξ (inset). The lines are guides to the eye.

Fig. 4. – Temperature dependence of the inverse magnetic susceptibility $1/\chi$ for $La_{0.7}Sr_{0.3}CoO_3$. The solid line is a fit to the Curie-Weiss law.

With reference to the phase diagram proposed in [11], a zero-temperature ordered magnetic moment of 1.7 μ_B/Co for $La_{0.7}Sr_{0.3}CoO_3$ suggests the presence below T_C of a majority phase with Co ions in the IS configuration $t^5\sigma^{*1-x}$, and any LS Co(III)-rich minority phase occupies a relatively small volume. With localized electrons in the t states and itinerant electrons in a σ^* band of e-orbital parentage, the most straightforward interpretation of these experimental results is a segregation above T_C of a hole-rich superparamagnetic volume fraction into a hole-poor paramagnetic region. Retention of a metallic temperature dependence of the conductivity above T_C requires that the superparamagnetic clusters remain mobile like large magnetic polarons having a mobility that is not activated, but is nevertheless constrained by strong coupling to cooperative oxygen-atom vibrations. A relatively large coherence length for the superparamagnetic domains, up to 15 Å, suggests that each contains more than one mobile hole, which would mean they are not conventional magnetic polarons but are more easily understood as second-phase vibronic domains at a cross-over from localized to itinerant behavior of the σ^* electrons.

Such a phase segregation can also account for the sudden onset of an increase of $d_{\text{Co-O}}$ on heating above T_C. An AMO_3 perovskite that would retain $(180° - \phi)$ M-O-M bonding via σ^* electrons in a narrow band of width $W_\sigma \sim \cos\phi\langle\cos(\theta_{ij}/2)\rangle$, where θ_{ij} is the angle between localized spins on neighboring M atoms, has a thermal expansion that occurs preferentially in the A-O bond length, $d_{\text{A-O}}$. In $La_{0.7}Sr_{0.3}CoO_3$, thermal expansion of the A-O bonds with retention of a constant $d_{\text{Co-O}}$ increases toward unity the geometric tolerance factor $t = d_{\text{A-O}}/d_{\text{Co-O}} < 1$. Increasing t decreases ϕ and broadens W_σ in opposition to its narrowing by increased spin-disorder scattering. At T_C, the bending angle ϕ has become small, and the loss of long-range magnetic order narrows W_σ sufficiently that the system breaks up into isolated superparamagnetic clusters in a paramagnetic matrix. The superparamagnetic clusters are clearly manifest in the interval $T_C < T \leq 300$ K not only by the SANS data, but also by the deviation of the paramagnetic susceptibility from a Curie-Weiss law (fig. 4). Magnetic ordering within the superparamagnetic clusters occurs below $T_C^* \approx 300$ K, which indicates they are not conventional magnetic polarons; some new spin configuration is being

stabilized in the superparamagnetic clusters. The abrupt increase in the thermal expansion of $d_{\text{Co-O}}$ above T_{C} indicates electron localization and/or the thermal excitation of high-spin Co^{3+} configurations above T_{C}. $T_{\text{C}}^{*} \approx T_{\text{S}}$ invites the suggestion that the "magnetic polarons" are, in this case, fluctuations of ordered localized-spin e^1 or e^2 configurations and low-spin Co(IV) nearest neighbors. Such an ordering would accommodate the larger size of a localized e^1 or e^2 configuration with a minimum cost in elastic energy by cooperative displacements of the O^{2-} ions away from the localized-spin configuration toward the low-spin near neighbor. Moreover, containment of the Co(IV) within a vibronic cluster would lower the kinetic energy of the electrons to give an additional contribution to the abrupt increase in $d_{\text{Co-O}}$ on heating through T_{C} [28]. From the virial theorem of classical mechanics, which states for central force fields that $2\langle K\rangle + \langle V\rangle = 0$, an increase in the mean kinetic energy $\langle K\rangle$ of the electrons on crossing from itinerant to polaronic behavior, *i.e.* from occupancy of the crystal volume to the polaron volume, would be compensated by an increase in the magnitude of their mean negative potential energy $\mid \langle V\rangle \mid$. Where the localized electrons occupy antibonding states, an increase in $\mid \langle V\rangle \mid$ means an increase in $d_{\text{Co-O}}$. A progressive increase with $T > T_{\text{C}}$ in the volume fraction of paramagnetic localized electrons would contribute to an anomalous thermal expansion of the mean Co-O bond length.

In summary, our neutron experiments reveal that the increasing cell volume with increasing Sr doping places the σ^* band of the intermediate-spin state for $x = 0.3$ at the threshold of a transition from itinerant to localized configurations at T_{C}. The Co-O bond length shows little thermal expansion in the ferromagnetic phase in order to retain itinerant-electron behavior; above T_{C} the system transforms to a polaronic state and the mean equilibrium Co-O distance increases. The volume of the magnetic clusters increases with the correlation length of the short-range order, so it decreases with increasing temperature above T_{C}; but at a given temperature it should increase in an applied magnetic field. Where the paramagnetic matrix contains isolated ferromagnetic clusters above T_{C} at $x \leq 0.20$, a growth in volume of the Co(IV)-rich superparamagnetic clusters to a percolation threshold appears to be the origin of the observed negative magnetoresistance.

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