PHYSICAL REVIEW B **69**, 140403(R) (2004)

Pressure-induced insulating state in (La,Sr)CoO$_3$

R. Lengsdorf,[1] M. Ait-Tahar,[1] S. S. Saxena,[2] M. Ellerby,[3] D. I. Khomskii,[1,4] H. Micklitz,[1] T. Lorenz,[1] and M. M. Abd-Elmeguid[1]
[1]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, 50937 Köln, Germany*
[2]*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CD3 0HE, United Kingdom*
[3]*Department of Physics and Astronomy, University College of London, Gower Street, London WC IE6BT, United Kingdom*
[4]*Laboratory of Solid State Physics, Groningen University, Nijenborgh 4, 9722 AG Groningen, The Netherlands*

(Received 19 December 2003; published 6 April 2004)

We have investigated the effect of pressure on the electronic, magnetic, and structural properties on a single crystal of conducting, ferromagnet ($T_C = 157$ K) La$_{0.82}$Sr$_{0.18}$CoO$_3$ located near the boundary of the metal-insulator transition. Contrary to the results reported on related systems, we find a transition from the conducting state to an insulating state and a decrease of T_C with increasing pressure while the lattice structure remains unchanged. We show that this unusual behavior is driven by a gradual change of the spin state of Co^{3+} ions from magnetic intermediate-spin ($t_{2g}^5 e_g^1; S=1$) to a nonmagnetic low-spin ($t_{2g}^6 e_g^0; S=0$) state.

DOI: 10.1103/PhysRevB.69.140403 PACS number(s): 75.30.−m, 71.27.+a, 62.50.+p, 71.30.+h

The study of the electronic and magnetic properties of strongly correlated transition metal oxides (TMO), such as perovskites of the type RMO_3 ($R =$ rare-earth ion, $M =$ transition metal) near the metal-insulator (MI) transition has recently attracted considerable attention. This is due to the fact that in this class of systems the MI transition is driven by strong correlation effects associated with electron-electron interaction and the interplay between charge, orbital, and spin degrees of freedom. The MI transition can be induced by varying the carrier concentration, temperature, magnetic field, and internal or external pressure.[1] Thus, studying such an interplay is a fundamental issue for a better understanding of the nature of the MI transition as well as the unique phenomena observed in these systems, e.g., colossal magnetoresistance or even high temperature superconductivity.

In this respect, external pressure can be very effective, e.g., by modifying the effective bandwidth (W) of the transition metal by changing the M-O bond length ($d_{M\text{-}O}$) and/or the M-O-M bond angle (θ), thereby providing a unique tool to tune electronic and magnetic properties by "bandwidth control" of these systems. In manganese perovskites $R_{1-x}A_x$MnO$_3$ ($A =$ Ca,Sr,Ba), for example, it has been shown that increasing pressure decreases $d_{\text{Mn-O}}$ and increases θ. Both variations lead to an increase of W and thereby stabilize the ferromagnetic metallic state.[2–4] Regarding the charge degree of freedom, recent high pressure studies on Sr$_{2/3}$La$_{1/3}$FeO$_3$ show a pressure-induced transition from the charge-disproportionate antiferromagnetic insulating state to a charge-uniform ferromagnetic metallic state.[5]

Transition-metal oxides containing the Co^{3+} ion are of special interest, because in addition to the usual charge, spin, and orbital degrees of freedom they possess an extra degree of freedom, namely the possibility to change the spin state of the Co^{3+} ion. This can occur in Co^{3+} TMO compounds if the crystal-field energy Δ_{CF} and the intraatomic exchange energy E_{ex} (Hund's rule coupling) are comparable. Such a delicate energy balance leads to spin-state transitions which can be induced by changing the temperature or composition [e.g.,6–8]. Among these systems, the rhombohedral perovskites La$_{1-x}$Sr$_x$CoO$_3$ ($0 \leqslant x \leqslant 0.5$) represent a unique system which allows one to investigate the interplay between the spin-state degree of freedom and electronic and magnetic properties particularly near the MI transition. In LaCoO$_3$ the ground state of Co^{3+} ions is, contrary to typical Mott insulators, nonmagnetic with a low-spin (LS) configuration ($t_{2g}^6 e_g^0; S=0$), and these ions can be thermally excited to an intermediate-spin (IS) state ($t_{2g}^5 e_g^1; S=1$) at $T \approx 100$ K.[9–11] At higher temperatures around 500 K the system undergoes a MI transition.[12] However, by doping with Sr^{2+}, the ground state becomes ferromagnetic for $x \geqslant 0.18$ (through a spin-glass-like region between $0 < x < 0.18$); at the same time the electrical conductivity increases with increasing x and for $x \approx 0.2$ the system undergoes a transition to a metallic state.[13–17] It is generally accepted that replacing La^{3+} by Sr^{2+} creates formally Co^{4+} ions and that the double exchange between Co^{4+} and the remaining Co^{3+} leads to a ferromagnetic coupling.[15,18] However, little is known about the correlation between the spin and charge degree of freedom near the MI transition, i.e., whether and to what extent these spin-state transitions affect the MI transition.

In the present work we have investigated the effect of pressure on the electronic, magnetic, and structural properties of a conducting, ferromagnetic single crystal of La$_{0.82}$Sr$_{0.18}$CoO$_3$ located near the boundary of the MI transition. We found, contrary to the results reported on related systems (La$_{1-x}$Sr$_x$MnO$_3$, La$_{1-x}$Sr$_x$FeO$_3$ and RNiO$_3$), a dramatic pressure-induced *increase* of the electrical resistivity (~4 orders of magnitude) and a decrease of T_C with increasing pressure, while the lattice structure remains unchanged. This is quite unusual because in all other correlated oxides pressure always leads to an increase of the 3d bandwidth and thereby to a transition to a more conducting state. The opposite effect observed in this work is rather unique and is apparently connected with different physical mechanisms. We explain this behavior as a consequence of a change of the Co^{3+} spin state from a magnetic IS configuration to a nonmagnetic LS configuration under pressure.

Single crystals of La$_{0.82}$Sr$_{0.18}$CoO$_3$ were grown by the traveling zone method in a 4-mirror image furnace under

©2004 The American Physical Society

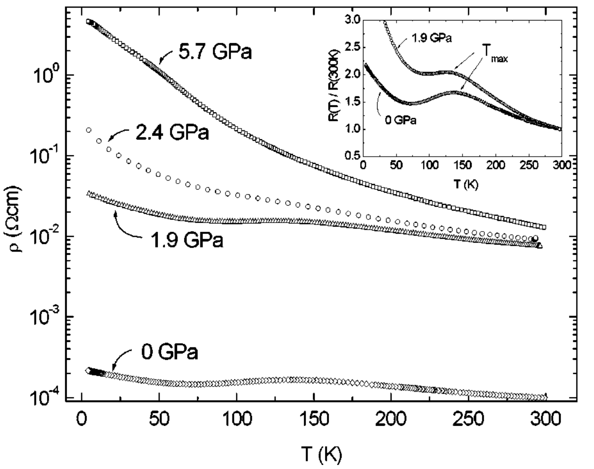

FIG. 1. Temperature dependence of the resistivity $\rho(p,T)$ of $La_{0.82}Sr_{0.18}CoO_3$ at different pressures up to 5.7 GPa. Inset shows the anomaly around T_C at ambient pressure and 1.9 GPa.

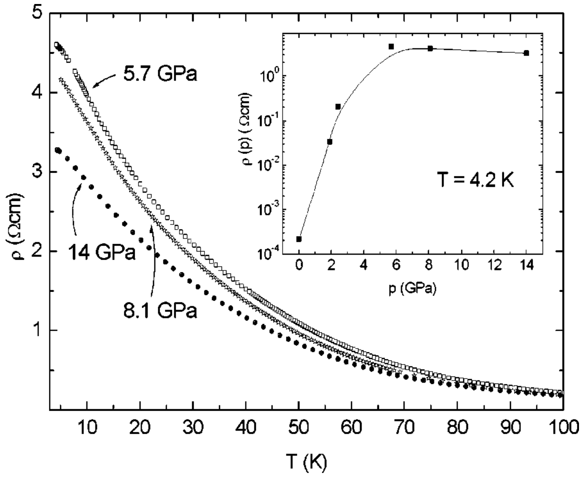

FIG. 2. Temperature dependence of the electrical resistivity $\rho(p,T)$ of $La_{0.82}Sr_{0.18}CoO_3$ in the pressure range $5.7\ \mathrm{GPa} \leqslant p \leqslant 14\ \mathrm{GPa}$. Inset shows the values of $\rho(p)$ at $T = 4.2$ K as a function of pressure in the whole pressure range.

oxygen pressure of 5 bar. Details of the preparation and characterization are published elsewhere.[17] The pressure dependence of the electrical resistivity up to 14 GPa and for $4.2\ \mathrm{K} < T < 300\ \mathrm{K}$ was measured in a Bridgman-type high pressure cell. This setup is basically similar to that described in Ref. 19. Sintered diamond anvils with a flat surface of 4 mm diameter were used to achieve pressure up to 14 GPa. A sample of $25 \times 140 \times 280\ (\mu\mathrm{m}^3)$ was measured by the conventional four-terminal method. Steatite was used as a pressure transmitting medium and the pressure gradient within the pressured cavity was between 5–7%. The pressure dependence of the magnetization up to 1.5 GPa was measured in an external magnetic field of 2 T and between $2\ \mathrm{K} < T < 300\ \mathrm{K}$ by means of a superconducting quantum interferometer device (SQUID) magnetometer. A miniature pressure clamp (Teflon cell) was used as described elsewhere.[20] The pressure dependence of the lattice parameters up to 15 GPa was measured on powdered samples by energy dispersive x-ray diffraction at HASYLAB using the diamond anvil cell technique.

Figure 1 shows the temperature dependence of the resistivity $\rho(p,T)$ at different pressures up to 5.7 GPa. The $\rho(T)$-curve at ambient pressure shows a local maximum at a temperature $T_{\mathrm{max}} \approx 138$ K (see the inset of Fig. 1) slightly below the transition temperature T_C to a ferromagnetic state ($T_C \approx 157$ K at ambient pressure) as deduced from magnetization measurements.[17] As is evident from Fig. 1, with increasing pressure up to 5.7 GPa the electrical resistivity *increases dramatically* by about 4 orders magnitude, indicating a strong reduction of electron hopping with increasing pressure. By increasing the pressure above 5.7 GPa (Fig. 2) we find no further increase of $\rho(T)$; instead at $T = 4.2$ K it decreases by about 30% at 14 GPa compared with the corresponding value at 5.7 GPa. The pressure dependence of $\rho(p)$ at 4.2 K is shown in the inset of Fig. 2. The maximum of $\rho(T)$, T_{max}, which is correlated with the value of T_C, is shifted to lower temperatures with increasing pressure (Fig. 2). We obtain a decrease of T_{max} of about 8 K between $p = 0$ and 1.9 GPa.[21] Assuming that this decrease of T_{max} is equal to that of T_C, we estimate a pressure-induced relative decrease of T_C which amounts to $\partial \ln T_C / \partial p \approx -2.6 \times 10^{-2}\ \mathrm{GPa}^{-1}$.

The observation of a strong increase of the electrical resistivity (i.e., suppression of electron hopping), and the reduction of T_C with increasing pressure is unexpected and opposite to the results reported on related TMO $La_{1-x}Sr_xMnO_3$ (Ref. 3) [and $La_{1-x}Sr_xFeO_3$ (Ref. 5)]. For example, in $La_{0.75}Sr_{0.25}MnO_3$ one finds an enhancement of electron hopping with increasing pressure that stabilizes the ferromagnetic metallic state via "double exchange." The relative increase of T_C with pressure in this system amounts to $\partial \ln T_C / \partial p \approx +6.4 \times 10^{-2}\ \mathrm{GPa}^{-1}$.

In the following we discuss two possible explanations for the observed suppression of electron hopping and the reduction of T_C in $La_{0.82}Sr_{0.18}CoO_3$ with increasing pressure for $p \leqslant 5.7$ GPa. The first possibility could be a pressure-induced structural phase transition and/or an unusual change of the

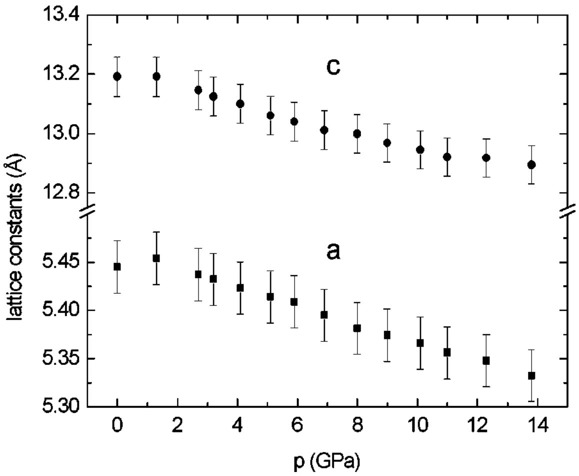

FIG. 3. Pressure variation of the lattice parameters a and c of the hexagonal unit cell of $La_{0.82}Sr_{0.18}CoO_3$ as obtained from energy dispersive x-ray diffraction at 300 K.

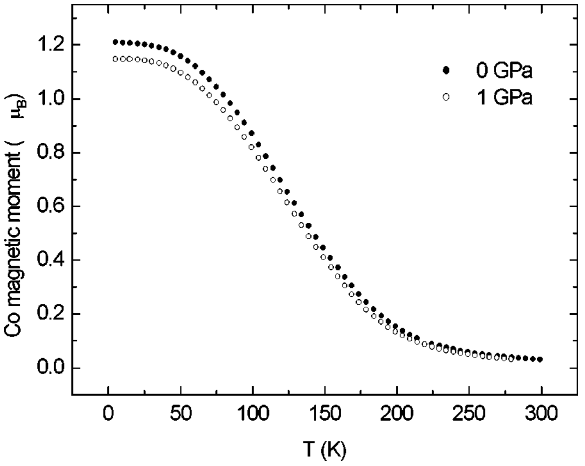

FIG. 4. Temperature dependence of the Co magnetic moment of $La_{0.82}Sr_{0.18}CoO_3$ in an external magnetic field of 2 T at ambient pressure and 1.0 GPa as deduced from magnetization measurements.

Co-O-Co bond angle and Co-O bond length. In Fig. 3 we show the pressure dependence of the lattice parameters *a* and *c* of the hexagonal unit cell as obtained from our diffraction measurements at 300 K. As shown in Fig. 3, we find within the accuracy of measurements no discontinuity in the pressure dependence of the lattice parameters *a* and *c* (and the volume), thus showing no indication of a structural phase transition. The value of the bulk modulus (B_0) and its derivative (B_0') as obtained from the fit of the equation of state using the Birch-Murnaghan equation, $B_o = 158(8)$ GPa and $B_0' = 5(1)$, are found to be close to the values for $LaCoO_3$, $B_o = 150(2)$ GPa, and $B_0' = 4$.[22]

From our x-ray diffraction data it is difficult to deduce information about the pressure dependence of the Co-O bond length and Co-O-Co bond angle. However, such information can be obtained from recent high resolution angle dispersive x-ray diffraction data on $LaCoO_3$.[22] Here, it is shown that with increasing pressure the Co-O bond length decreases more rapidly than that of La-O, resulting in a large increase of the Co-O-Co bond angle (from 166° to $\approx 177°$ at ≈ 4 GPa). The increase of the bond angle with increasing pressure is the usual structural response of TMO with perovskite structure and is known to enhance electron hopping, thereby stabilizing the metallic state. We observe exactly the opposite response to pressure, finding instead a pressure-induced suppression of electron hopping and the reduction of T_C with elevated pressure. Therefore, we have to discuss another explanation, not based on structural changes: the possibility of a pressure-induced spin-state transition from the magnetic IS Co^{3+} state to a nonmagnetic LS state. This is based on two experimental facts: first, the ionic radius of LS Co^{3+} (0.545 Å) is smaller than that of HS Co^{3+} (0.61 Å).[23,24] The second is the energy of the crystal-field splitting Δ_{CF} in $LaCoO_3$, which has been found to increase remarkably with increasing pressure.[25] Thus, pressure is expected to favor the population of the LS state at the expense of depopulation of the IS state. A direct consequence of such a pressure-induced transition from the magnetic IS to a nonmagnetic LS state in $La_{0.82}Sr_{0.18}CoO_3$ would be a reduction of the magnitude of the Co saturation moment with increasing pressure. As the LS $LaCoO_3$ compound is known to be an insulator, one can expect that this pressure-induced IS to LS transition in $La_{0.82}Sr_{0.18}CoO_3$ would also suppress the conductivity. This is what we observed experimentally.

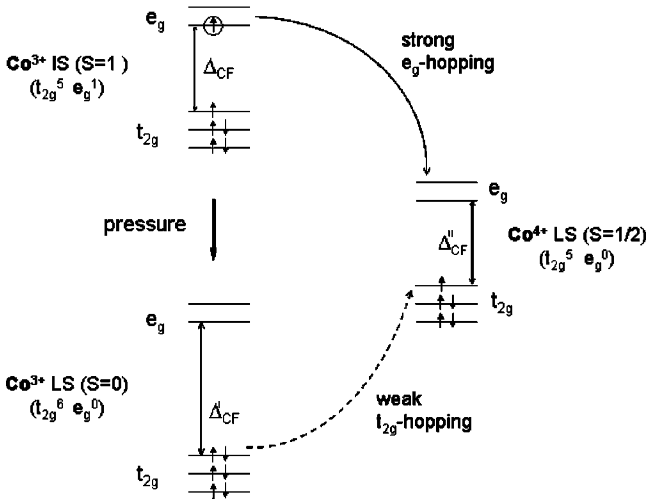

FIG. 5. Schematic representation of the interplay between spin-state transition and electron hopping in $La_{0.82}Sr_{0.18}CoO_3$: at ambient pressure conductivity occurs by hopping of an e_g electron from IS Co^{3+} to LS Co^{4+}. With increasing pressure, the crystal-field splitting Δ_{CF} of IS Co^{3+} increases ($\Delta'_{CF} > \Delta_{CF}$) (Ref. 25). Consequently, the IS Co^{3+} will be gradually depopulated and the ground state of Co^{3+} is then predominantly a LS state. As a result, the strong e_g hopping between Co^{3+} and Co^{4+} is strongly suppressed and only a weak t_{2g} hopping remains.

In order to verify this interpretation we have measured the pressure dependence of the saturation magnetization of Co (μ_{Co}) in $La_{0.82}Sr_{0.18}CoO_3$. Figure 4 displays the temperature dependence of the magnetization in an external magnetic field of 2 T for ambient pressure and 1.0 GPa. The decrease of the magnetization at low temperatures with increasing pressure is evident from this figure. We obtain from the experimental data a decrease of μ_{Co} (at 5 K) from $1.11(1)\mu_B$ at ambient pressure to $1.05(1)\mu_B$, i.e., 5.4(2) % at 1 GPa. This corresponds to a decrease of μ_{Co} by more than 30% at 5.7 GPa, if one assumes a linear decrease of μ_{Co} with increasing pressure. In addition, we find a decrease of T_C (≈ 4 K/GPa) which is similar to that estimated from our high pressure resistivity data (see above). It is clear that the observed decrease of T_C with increasing pressure is a consequence of the reduction of the Co magnetic moment. These experimental findings strongly support our suggestion of a pressure-induced IS to LS transition in $La_{0.82}Sr_{0.18}CoO_3$.

In the following we present a qualitative model explaining why such a spin-state transition results in a suppression of electron hopping. Assuming that at ambient pressure the ground state of $La_{0.82}Sr_{0.18}CoO_3$ is a homogeneous mixture of IS Co^{3+} and LS Co^{4+} ions,[15,17,18] we see that the conduction occurs predominantly through hopping of an e_g electron from Co^{3+} ($t_{2g}^5 e_g^1$) to Co^{4+} ($t_{2g}^5 e_g^0$). Furthermore, this transport process can account for the magnetic coupling of the localized t_{2g} electrons (double exchange), resulting in a ferromagnetic conducting state. This is demonstrated in Fig. 5. With increasing pressure the energy of the crystal-field splitting increases ($\Delta'_{\mathrm{CF}} > \Delta_{\mathrm{CF}}$) which results in a gradual depopulation of the IS Co^{3+} state and its crossover to a LS state. At sufficiently high pressures ($p \approx 5.7$ GPa) the IS state will be largely depopulated and a large part of the ground state of Co^{3+} is then predominantly a LS state $t_{2g}^6 e_g^0$ configuration. Consequently, the relatively strong e_g hopping at ambient pressure between Co^{3+} and Co^{4+} would be strongly suppressed and only a very weak t_{2g} hopping would remain. Thus, the gradual depopulation of the IS Co^{3+} state with increasing pressure can explain the observed suppression of electron hopping in $\mathrm{La}_{0.82}\mathrm{Sr}_{0.18}\mathrm{CoO}_3$.

In this context we would like to emphasize that the effect of the pressure-induced IS to LS transition on the electron hopping *prevails over* the opposite effect of an increase of the Co-O-Co bond angle with increasing pressure. This clearly shows that the strong correlation between the spin-state and charge degrees of freedom in $(\mathrm{La,Sr})\mathrm{CoO}_3$ dominates the MI transition.

Finally, we discuss the observed decrease in the electrical resistivity with increasing pressure above 5.7 GPa (Fig. 2). As mentioned before, the resistivity decreases by about 30% at 4.2 K between 5.7 and 14 GPa. This decrease can be explained in the following way: above ≈ 5.7 GPa a large part of the Co^{3+} is already transformed from the IS to the LS state, so that this mechanism is not efficient any more and the usual tendency due to broadening of the effective bandwidth with increasing pressure prevails. This leads to a consequent decrease of the electrical resistivity.

In conclusion, we have investigated the effect of pressure on electronic, magnetic and structural properties of the ferromagnetic conducting perovskite $\mathrm{La}_{0.82}\mathrm{Sr}_{0.18}\mathrm{CoO}_3$. We observed a quite unusual effect: a transition from the *conducting state to an insulating state*, which is contrary to expectations. We explain this unusual behavior as a consequence of a pressure-induced transition from the magnetic intermediate-spin state to a nonmagnetic low-spin state of Co^{3+}. This interpretation is supported by the observed reduction of the Co saturation magnetic moment with increasing pressure and provides a natural explanation of the observed effect. Our results demonstrate the very important role of spin-state degree of freedom for the MI transition in materials with correlated electrons.

M. M. A., D. I. K., and T. L. thank L. H. Tjeng for fruitful discussions. This work was supported by the Deutsche Forschungsgemeinschaft through SFB 608.

---

[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1988) and references therein.

[2] H. Y. Hwang, T. T. M. Palstra, S-W. Cheong, and B. Batlogg, Phys. Rev. B **52**, 15 046 (1995).

[3] Y. Moritomo, A. Asamitsu, and Y. Tokura, Phys. Rev. B **51**, 16 491 (1995).

[4] C. Meneghini, D. Levy, S. Mobilio, M. Ortolani, M. Nuñez-Reguero, A. Kumar, and D. D. Sarma, Phys. Rev. B **65**, 012111 (2002).

[5] T. Kawakami, S. Nasu, T. Sasaki, K. Kuzushita, S. Morimoto, S. Endo, T. Yamada, S. Kawasaki, and M. Takano, Phys. Rev. Lett. **88**, 037602 (2002).

[6] C. Martin, A. Maignan, D. Pelloquin, N. Nguyen, and B. Raveau, Appl. Phys. Lett. **71**, 1421 (1997).

[7] S. Tsubouchi, T. Kyômen, M. Itoh, P. Ganguly, M. Oguni, Y. Shimojo, Y. Morii, and Y. Ishii, Phys. Rev. B **66**, 052418 (2002).

[8] S. Roy, M. Khan, Y. Q. Guo, J. Craig, and N. Ali, Phys. Rev. B **65**, 064437 (2002).

[9] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **54**, 5309 (1996).

[10] T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B **55**, 4257 (1997).

[11] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüninger, T. Lorenz, P. Reutler, and A. Revcolevschi, Phys. Rev. B **66**, 020402(R) (2002).

[12] Y. Tokura, Y. Okimoto, S. Yamaguchi, H. Taniguchi, T. Kimura, and H. Takagi, Phys. Rev. B **58**, R1699 (1998).

[13] M. Itoh, I. Natori, S. Kubota, and K. Motoya, J. Phys. Soc. Jpn. **63**, 1486 (1994).

[14] R. Caciuffo, D. Rinaldi, G. Barucca, J. Mira, J. Rivas, M. A. Señarís-Rodríguez, P. G. Radaelli, D. Fiorani, and J. B. Goodenough, Phys. Rev. B **59**, 1068 (1999).

[15] D. Louca, J. L. Sarrao, J. D. Thompson, H. Röder, and G. H. Kwei, Phys. Rev. B **60**, 10 378 (1999).

[16] J. Wu and C. Leighton, Phys. Rev. B **67**, 174408 (2003).

[17] M. Kriener, C. Zobel, A. Reichl, J. Baier, M. Cwik, K. Berggold, H. Kierspel, O. Zabara, A. Freimuth, and T. Lorenz, Phys. Rev. B **69**, 094417 (2004).

[18] D. Louca and J. L. Sarrao, Phys. Rev. Lett. **91**, 155501 (2003).

[19] D. Jaccard, E. Vargoz, K. Alami-Yadri, and H. Wilhelm, Rev. High Pressure Sci. Technol. **7**, 412 (1998).

[20] S. S. Saxena, P. Agarwal, K. Ahilan, F. M. Grosche, R. K. W. Haselwimmer, M. J. Steiner, E. Pugh, I. R. Walker, S. R. Julian, P. Monthoux, G. G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, and J. Flouquet, Nature (London) **406**, 587 (2000).

[21] The values of T_{max} for 0 GPa (138 K) and 1.9 GPa (130 K) were estimated from the first derivative of $\rho(T)$, where $\partial\rho(T)/\partial T = 0$.

[22] T. Vogt, J. A. Hriljac, N. C. Hyatt, and P. Woodward, Phys. Rev. B **67**, 140401(R) (2003).

[23] R. D. Shannon and C. T. Prewitt, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **25**, 925 (1969).

[24] The radius of the Co^{3+} IS state is expected to be close to that of the HS state since in both states the e_g orbitals are occupied.

[25] K. Asai, O. Yokokura, M. Suzuki, T. Naka, T. Matsumoto, H. Takahashi, N. Môri, and K. Kohn, J. Phys. Soc. Jpn. **66**, 967 (1997).