

Pressure-Induced Insulator-to-Metal Transition in $\text{TbBaCo}_2\text{O}_{5.48}$

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(Received 4 May 2009; published 15 September 2009)

$\text{TbBaCo}_2\text{O}_{5.48}$ has been studied by high-pressure synchrotron x-ray diffraction together with resistivity measurements as a function of temperature and pressure. It was found that under pressure a structural phase transition takes place corroborating with a sluggish insulator-to-metal transition. An onset of the metallic state was deduced from a gradual drop of resistivity at the range 3–10 GPa culminating into the change in sign of dR/dT , from negative to positive, at $P \geq 10$ GPa; at the same pressure range there is a change of lattice strain components calculated from the unit cell dimensions. The changes in structural and transport properties are very similar to those found on heating at ambient pressure implying a common mechanism.

DOI: 10.1103/PhysRevLett.103.125501

PACS numbers: 81.40.Vw, 61.05.cp

$\text{RBaCo}_2\text{O}_{5.5}$ complex oxides, where R stands for a rare-earth metal, contain Co^{3+} ions with octahedral or pyramidal coordination of oxygen atoms (Fig. 1). Each Co^{3+} ion can be found in low-, intermediate-, or high-spin state (LS, IS, or HS) having different ionic radii and deformation patterns characteristic for an orbital ordering [1].

$\text{RBaCo}_2\text{O}_{5.5}$ shows insulator-to-metal (I - M) transition on heating. At the same temperature (T_{I-M}), there is a structural change; T_{I-M} varies as a function of rare-earth element. Single crystal studies available for $R = \text{Gd}$ [2], Dy [3], Tb [4], and Nd [4] indicate that insulator-to-metal transition takes place together with $Pmma$ ($2a_c \times 2a_c \times 2a_c$) to $Pmmm$ ($a_c \times 2a_c \times 2a_c$) structural transformation; here and below a_c stands for the cell dimension of the prototype primitive cubic perovskite. In agreement with $Pmma$ ($2a_c \times 2a_c \times 2a_c$) single crystal structure, neutron powder diffraction for Tb and Ho also points to 4 independent cobalt ions in the asymmetric cell below T_{I-M} [1,5]. All 4 cobalt ions have different distortions of the oxygen polyhedrons indicating an ordering of Co^{3+} spin and orbital states [4].

A general analysis shows [4] that the perovskite cell doubling in different directions results from different structural mechanisms. The mechanism relevant to the orthorhombic c -parameter doubling ($\mathbf{c} = 2\mathbf{a}_c$) includes ordering R or Ba ions, randomly distributed in the position 1(a) of the cubic perovskite structure, as well as displacement of Co and O ions (order parameter X_1^c). The cell multiplication in the b direction ($\mathbf{b} = 2\mathbf{a}_c$) occurs along with establishing the order in the Co sublattice disordered in the perovskite structure (OP X_4^c). Finally, ($a_c \times 2a_c \times 2a_c$) \rightarrow ($2a_c \times 2a_c \times 2a_c$) cell modification is induced by the displacements of the positions of R or Ba and oxygen ions (OP X_{10}^c).

There are few reasons to expect a change in structural and transport properties of insulating oxides of $3d$ metals as a function of pressure. Mott transition found in some

oxides is one of them, the others are more specific to the Co system considered here, $\text{TbBaCo}_2\text{O}_{5.5}$. On heating there is a change in orbital structure (correlated static Jahn-Teller distortions become uncorrelated) accompanied with a decrease of the unit cell volume [6,7], the transition is therefore predominantly of the order-disorder type. Pressure could favor the orbitally disordered low volume phase [6,8,9] thus giving an increase of conductivity. On the other hand, change of spin state for Co ions from HS or IS to LS is also accompanied by a decrease of ionic radius, thus pressure could also favor the spin conversion toward spin states with smaller ionic radii. However, in the latter case one would not expect an increase of conductivity under pressure since LS states effectively block electron mobility via a so-called “spin blockade” mechanism [10,11] suggested for the temperature induced insulator-to-metal transition. One more possible mechanism may be foreseen from symmetry analysis [4] and links the structural phase transition to the insulator-to-metal transition via a change in the electron transfer integral through Co-O-Co path [6]; for this mechanism one would expect a symmetry change under pressure and a displacive mechanism.

However, as no change in physical and structural properties has been found so far between ambient pressure and 1.2 GPa [12], this observation supported “spin blockade” as a primary mechanism for the temperature induced metal-to-insulator transition.

In this report we show, by combining diffraction and transport measurements, that there is an insulator-to-metal transition but at the pressure higher than probed before, at ~ 10 GPa. In terms of corresponding lattice strains this transition is similar to one induced by temperature, thus suggesting a common mechanism for both insulator-to-metal transformations.

Powder diffraction experiment has been done at Swiss-Norwegian Beam Lines at the European Synchrotron Radiation Facility. A tiny amount of powder was loaded

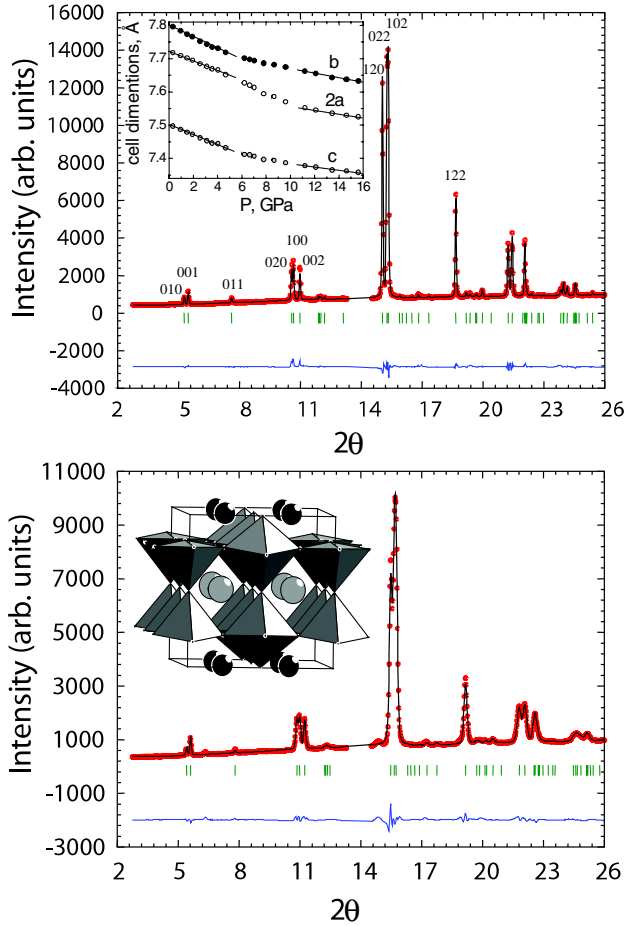


FIG. 1 (color online). Diffraction patterns for $\text{TbBaCo}_2\text{O}_{5.48}$ with experimental points, fitted profile, difference curve (bottom), and positions for Bragg reflections (vertical bars). Top panel: $P = 1.48$ GPa, bottom panel: $P = 16.55$ GPa. Unit cell dimensions as a function of pressure are shown in the insert of the top panel. Insert for the bottom panel shows the high temperature/high-pressure orthorhombic $Pmmm$ ($a_c \times 2a_c \times 2a_c$) structure. Color code: Tb (black), Ba (gray), Co ions are coordinated by oxygen forming octahedrons and pyramids.

in a diamond anvil cell (DAC) together with Ruby single crystal for pressure calibration, and with 4:1 Methanol-Ethanol mixture as a pressure transmitting media. Powder data were collected using MAR345 Image Plate detector with the sample-to-detector distance ~ 220 mm and with the wavelength 0.71136 Å. The beam was slit down to about 100 microns. In total, 21 diffraction patterns were measured covering the pressure range from 0.3–16.6 GPa, all at room temperature. A powder from the same sample has been loaded into a glass capillary and diffraction data were collected with the same setup as a function of temperature at ambient pressure. CryoStream 700+ nitrogen blower was used to control the temperature. 2D MAR images were converted in powder patterns using Fit2D software [13].

The data for all data sets were refined against the average $a_c \times 2a_c \times 2a_c$ $Pmmm$ model with the Rietveld

method using Fullprof [14], because of a limited information content of powder patterns [4]. Profile parameters, cell dimensions, overall B -factor and atomic coordinates were refined together with the background parameters. The patterns for low and high pressure are shown at Fig. 1. Ratios of unit cell dimensions for both temperature and pressure experiments are shown in Fig. 2.

For resistance measurements the sample–metal-gasket cavity was coated with an insulating mixture of Al_2O_3 and NaCl combined with epoxy. Quasi-four-probe DC electrical resistance measurements as a function of pressure and temperature, $R(P, T)$ were carried out with 5–7- μm thick Pt-foil electrodes. For $R_P(T)$ measurements over the 80(5)–290 K range the DAC was slowly and gradually immersed in a liquid N_2 - and He-filled Dewar in which the gas temperature varied with height. Temperature was measured using a Si-diode thermometer (for more details see [15]).

The temperature-dependent resistance studies, $R(P, T)$, provide the definitive experimental evidence for the onset of the I - M transition with pressure increase (see Fig. 3). The onset of a metallic state was deduced from a gradual drop of resistivity at the range 3–10 GPa culminating into the change in sign of dR/dT , from negative to positive, at $P \geq 10$ GPa. This pressure evolution of resistivity may be related to a fast drop of transition temperature for pressures around 10 GPa. As far as we are aware of, such a transition has not been seen yet for $\text{REBaCo}_2\text{O}_{5.5}$ complex oxides and corresponding phase diagram has not yet been mapped.

At a fixed pressure and over the 80–240 K range the resistivity data fairly accurately obey the relation of $\ln\sigma = \ln\sigma_0 - (T_0/T)^{1/4}$ with some deviations at higher T [16] (Fig. 4). With increasing of applied pressure the conductivity increases markedly, and the slope of the straight line diminishes. The data are consistent with the Mott *variable-range hopping* law [17]; $k_B T_0$ values extracted from those data range from 1.2×10^4 eV at 0.4 GPa to 0.37×10^4 eV for $P = 8$ GPa (k_B is Boltzmann’s constant).

From T_0 values we can estimate a localization length α^{-1} using the relation [18]

$$\alpha^{-1} = [k_B T_0 N(E_F)/16]^{-1/3} \quad (1)$$

and the ratio of the localization length to the intersite distance a [15]:

$$(a\alpha)^{-1} \propto 5[k_B T_0 N^*(E_F)]^{-1/3}, \quad (2)$$

where $N(E_F)$ and $N^*(E_F)$ are the density of states and the normalized density of states at the Fermi level. Assuming that $N^*(E_F)$ is in the range of 1–10 $(\text{eV})^{-1}$ (see for example [19]) we will get the value 0.1–0.22 of $(a\alpha)^{-1}$ at 0.4 GPa which does not seem to be indicative of a simple variable-range hopping process. At $P = 8$ GPa $(a\alpha)^{-1} \sim 0.15$ –0.32 corresponding to a more significant overlap of the original localized wave functions under compression

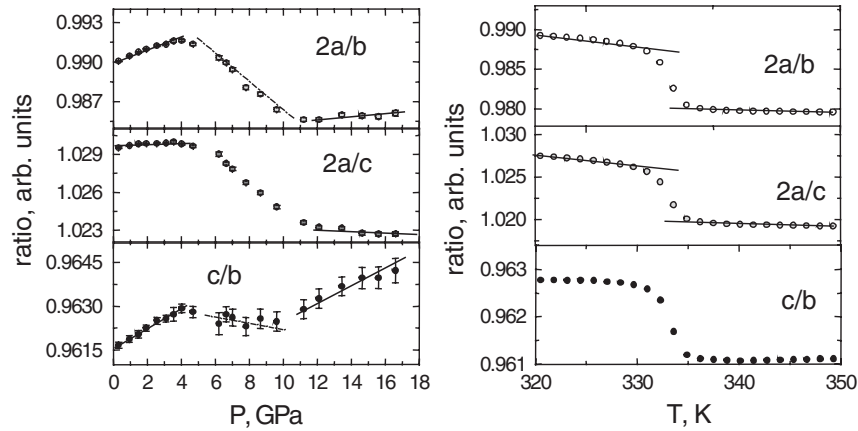


FIG. 2. Ratio of unit cell dimensions as a function of pressure (left) and temperature (right). Error bars are smaller than symbol, except for c/b ratio as a function of pressure.

but still unrealistic for “pure” $T^{1/4}$ behavior. It is noteworthy that the extremely large T_0 could be due to incipient polaron formation, which according to Emin [20] can be confused with variable-range hopping.

At the pressure range 4–10 GPa there is also a change of the ratio of the lattice constants of the average orthorhombic $Pmmm$ ($a_c \times 2a_c \times 2a_c$) cell; the same behavior follows for the spontaneous strains. The change in the ratio of the lattice constants is very similar to what is observed as a function of temperature (Fig. 2). All the ratios show the same dependence as a function of temperature indicating nearly isotropic thermal expansion. The difference in pressure response may be related to elastic anisotropy.

Single crystal diffraction data evidence that there is the structural phase transition [4] on heating with change of symmetry from $Pmma$ ($2a_c \times 2a_c \times 2a_c$) to $Pmmm$ ($a_c \times 2a_c \times 2a_c$); in powder diffraction, due to the limited information content relative to single crystal data, this phase transition manifests itself only via deformation of the average $Pmmm$ ($a_c \times 2a_c \times 2a_c$) structure [6]. The similarity of temperature and pressure responses depicted at Fig. 2 suggests that alike structural transformation happens also under pressure.

The similarity also suggests a common mechanism of the insulator-to-metal transition taking place on heating and, as follows from Fig. 3, as a function of pressure as well. A model explaining I - M transition on heating invokes a conversion of Co ions toward their HS states, that is the necessary component for a so-called spin blockade [10]. Because of higher ionic radius of HS ions this mechanism assumes bigger unit cell volume and should therefore be suppressed under pressure. A change of the Co spin state observed for LaCoO_3 under pressure may serve as an example of such expectations [21].

Considering possible character of temperature-pressure dependences of critical parameters one should remember that from the point of view of a general theory (see above and Ref. [4]), $Pmmm$ structure is a result of

distortion of the parent perovskite structure by two OP X_1^c and X_4^c . Lowering symmetry from $Pmmm$ to $Pmma$ is induced by an additional order parameter X_{10}^c . Without losing in generality, we can consider the latter transition in the framework of a local theory for a single $Pmmm(1)$ - $Pmma(2)$ transformation. The $Pm3m$ -to- $Pmmm$ symmetry lowering reduces a six-dimensional X_{10}^c to six one-dimensional irreducible representations (IRs): $X_{10}^c \rightarrow [X_{-2}^- + X_{-4}^- + \Gamma_{-2}^- + \Gamma_{-3}^- + \Gamma_{-3}^+ + \Gamma_{-4}^-]_{\text{ortho}}$. The representation X_{-2}^- corresponds to the order parameter for the $Pmmm(1)$ - $Pmma(2)$ transformation. The corresponding nonequilibrium energy (Landau potential) contains only even-order terms. This allows the phase transition to be continuous (second order) with gradual evolution of critical parameters. X_{10}^c IR primarily involves a displacement of oxygen atoms, i.e., a deformation of Co-O-Co valence angle, together with a

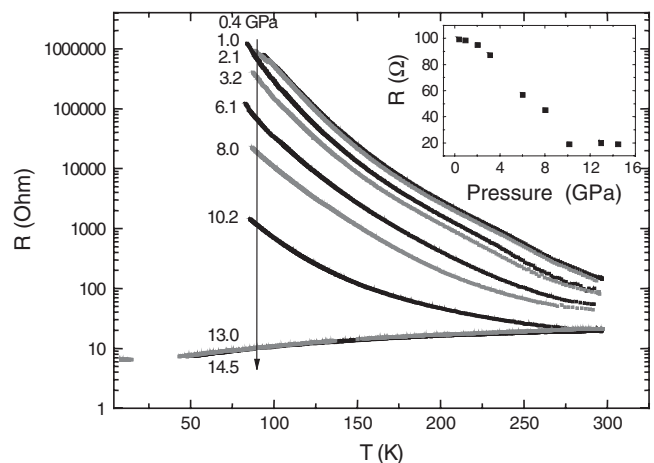


FIG. 3. Temperature dependence of the resistivity measured at different pressures. The inset shows the pressure dependence of the resistance at 298 K. Note a change in $R(T)$ behavior between 10 and 13 GPa and the preceding gradual decrease in R from 3 to 10 GPa.

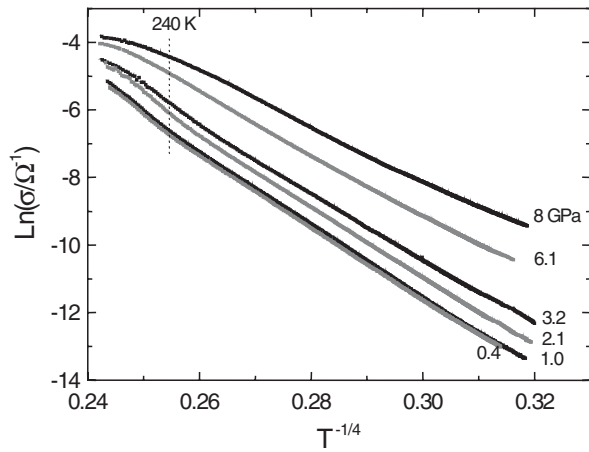


FIG. 4. Temperature dependences of the electrical conductivity σ of $\text{TbBaCo}_2\text{O}_{5.5}$ at various pressures in the temperature range 90–290 K. Note the linear relationship of $\ln(\sigma)$ versus $T^{-1/4}$ below 240 K.

partial ordering of Co spin and orbital states over 4 independent Co sites. Close similarity of temperature and pressure induced transitions does not suggest that entropy and therefore an ordering are primary reason for the metal-to-insulator transition. On the other hand, within a small polaron model [6], a change of Co-O-Co angle affects the electron transfer integral, e_g bandwidth, and, as a result, the conductivity.

One would expect an oxygen isotope effect for the mechanism involving X_{10}^c critical phonon; the shift of the T_{I-M} as a function of the oxygen isotope composition has indeed been observed for the Pr, Dy, Ho, Y analogs [22].

However, to get an experimental proof of the suggested mechanism, one needs to follow the temperature and pressure evolution of weak superstructure reflections signifying $Pmma$ ($2a_c \times 2a_c \times 2a_c$) to $Pmmm$ ($a_c \times 2a_c \times 2a_c$) transition. Temperature evolution has been published by us before [4], we are not aware of similar diffraction study as a function of pressure. A pressure dependent single crystal diffraction experiment is therefore highly desirable in order to clarify the way structural phase transition affects transport properties.

This research was supported in part by Israeli Science Foundation Grant No. #36/05 and by the Swiss National Foundation through NCCR program MaNEP. We thank also R. Arielly and E. Porat for assisting with the resistivity measurements, and SNBL team for their friendly support.

[1] V.P. Plakhty, Yu.P. Chernenkov, S.N. Barilo, A. Podlesnyak, E. Pomjakushina, E.V. Moskvina, and S.V. Gavrillov, Phys. Rev. B **71**, 214407 (2005).

[2] Y.P. Chernenkov, V.P. Plakhty, V.I. Fedorov, S.N. Barilo, S.V. Shiryayev, and G.L. Bychkov, Phys. Rev. B **71**, 184105 (2005).

[3] Y. Chernenkov, V. Plakhty, A. Gukasov, S. Barilo, S. Shiryayev, G. Bychkov, V. Hinkov, V. Fedorov, and V. Chekanov, Phys. Lett. A **365**, 166 (2007).

[4] D. Chernyshov, V. Dmitriev, E. Pomjakushina, K. Conder, M. Stingaciu, V. Pomjakushin, A. Podlesnyak, A.A. Taskin, and Y. Ando, Phys. Rev. B **78**, 024105 (2008).

[5] J.-E. Jørgensen and L. Keller, Phys. Rev. B **77**, 024427 (2008).

[6] E. Pomjakushina, K. Conder, and V. Pomjakushin, Phys. Rev. B **73**, 113105 (2006).

[7] H. Kusuya, A. Machida, Y. Moritomo, K. Kato, E. Nishibori, M. Takata, M. Sakata, and A. Nakamura, J. Phys. Soc. Jpn. **70**, 3577 (2001).

[8] T. Chatterji, F. Fauth, B. Ouladdiaf, P. Mandal, and B. Ghosh, Phys. Rev. B **68**, 052406 (2003).

[9] S. Margadonna and G. Karotsis, J. Mater. Chem. **17**, 2013 (2007).

[10] A. Maignan, V. Caignaert, B. Raveau, D. Khomskii, and G. Sawatzky, Phys. Rev. Lett. **93**, 026401 (2004).

[11] A.A. Taskin and Y. Ando, Phys. Rev. Lett. **95**, 176603 (2005); A.A. Taskin and Y. Ando, J. Magn. Magn. Mater. **310**, 969 (2007).

[12] A. Podlesnyak, S. Streule, K. Conder, E. Pomjakushina, J. Mesot, A. Mirmelstein, P. Schützendorf, R. Lengsdorf, and M.M. Abd-Elmeguid, Physica (Amsterdam) **378B**, 537 (2006).

[13] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, and D. Hausermann, High Press. Res. **14**, 235 (1996).

[14] J. Rodriguez-Carvajal, Physica (Amsterdam) **192B**, 55 (1993).

[15] G.Kh. Rozenberg, G.R. Hearne, M.P. Pasternak, P.A. Metcalf, and J.M. Honig, Phys. Rev. B **53**, 6482 (1996).

[16] According to N.F. Mott, Philos. Mag. **34**, 643 (1976) in the case of many-electron hops a deviation from $T^{1/4}$ behavior is expected at higher temperature due to the interaction of electrons on localized states. Another reason for such deviation could be a sequence of the PM \rightarrow FM \rightarrow AFM transitions observed at this temperature range [see A. Podlesnyak *et al.*, J. Magn. Magn. Mater. **316**, e710 (2007)].

[17] N.F. Mott, *Metal-Insulator Transitions* (Taylor & Francis Ltd., London, 1990); Festkörperprobleme **XIX**, 331 (1979).

[18] J.G. Austin and N.F. Mott, Adv. Phys. **18**, 41 (1969).

[19] V.A.M. Brabers, Physica (Amsterdam) **205B**, 143 (1995).

[20] D. Emin, Adv. Phys. **22**, 57 (1973); Phys. Rev. Lett. **32**, 303 (1974).

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

[22] K. Conder, E. Pomjakushina, V. Pomjakushin, M. Stingaciu, S. Streule, and A. Podlesnyak, J. Phys. Condens. Matter **17**, 5813 (2005).