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Instability of oxygen vacancy ordering at the metal–insulator transition in the iron-doped $\text{TbBaCo}_2\text{O}_{5.5}$ layered perovskite

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Abstract

The $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ layered perovskite, exhibiting a metal–insulator phase transition at $T_{MI} \sim 340$ K, has been investigated by the Mössbauer spectroscopy method. It was found that the Fe^{3+} ions have two different positions in the low-temperature insulator phase (at $T < T_{MI}$) and predominantly one position in the high-temperature metallic region above T_{MI} . X-ray diffraction experiments have revealed an orthorhombic-to-tetragonal crystal structure transformation taking place at T_{MI} . These results have been interpreted as favouring an oxygen vacancy order–disorder transition that occurs simultaneously with the metal–insulator one.

1. Introduction

The transition metal oxides are known to exhibit a wide variety of electrical properties from those of profound insulator to those of metal. Some of the oxide compounds show a temperature-induced metal–insulator transition (MIT). In some cases the MIT occurs as a first-order phase transition and the resistivity sharply decreases by several orders of magnitude at the temperature of the phase transition. Among different oxide compounds exhibiting a MIT, one finds $\text{RBaCo}_2\text{O}_{5.5}$ (R: rare-earth ions) layered-type perovskites which are insulators below $T_{MI} \sim 350$ K and metals above this temperature [1–3]. These oxygen-deficient perovskites have been obtained recently and attracted the attention of many investigators in the field of materials research. However, in spite of considerable efforts, the nature of the MIT in these

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compounds is still a matter of discussion. In some recent works [3, 4] this transition was suggested to be connected with oxygen vacancy ordering by analogy to the vacancy-ordered $\text{SrFeO}_{3-1/n}$ phases, where the compounds with $n = 8, 4$ and 2 show a first-order phase transition to their disordered structures at 523, 598 and 1103 K respectively [5]. However, the structural investigations [6, 7] of $\text{RBaCo}_2\text{O}_{5+\delta}$ have shown that although the MIT is accompanied by considerable crystal structural changes, the oxygen vacancies are kept ordered above T_{MI} . Several models have been proposed to explain the MIT in these compounds, most of them based on the idea of a spin state transition of Co^{3+} ions at T_{MI} [6–8].

Recently the effect of iron doping on the physical properties of the $\text{TbBaCo}_2\text{O}_{5.5}$ perovskite has been investigated [9]. In particular, it was established that a small Fe substitution (up to 5%) influences the magnetic properties quite strongly, whereas the temperature of the MIT is influenced only weakly. In this work we present results of a Mössbauer spectroscopy study of the MIT in the Fe-doped cobaltite $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$. It was established that the Fe^{3+} ions have two low-symmetry positions in the temperature range $T < T_{MI}$ and predominantly one position above T_{MI} . These results are interpreted on the assumption of an oxygen vacancy order–disorder transition that occurs simultaneously with the MIT in the iron-doped sample.

2. Experimental details

The sample of $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ was obtained using the standard ceramic method. After prefiring at 900 °C the pellets were reground and fired in air at 1180 °C for 10 h; this was followed by cooling down to room temperature at a rate of 100 °C h⁻¹. The purity of the phase obtained was confirmed by means of x-ray diffraction (XRD). High-temperature XRD structural analysis was carried out in air at temperatures of 290–360 K using a DRON-3M diffractometer with a high-temperature device, UVD-2000 (Cr K α radiation). The Mössbauer measurements were performed using a conventional constant-acceleration spectrometer with a source of ⁵⁷Co in Rh. The spectra were recorded in transmission geometry at temperatures ranging from 295 to 370 K. The Mössbauer spectra were fitted using the NORMOS program [10]. All isomer shifts are related to the α -Fe standard. The dc resistivity measurements were performed using the standard four-probe method.

3. Results and discussion

The electrical resistivity versus temperature curve for the $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ sample is presented in figure 1. One can see the pronounced insulator–metal transition occurring at around $T_{MI} = 335$ K on heating. This transition is accompanied by an exothermic effect, which is typical for a first-order phase transition (figure 1 inset). According to the XRD study, the $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ sample at room temperature has an orthorhombic crystal structure like the parent iron-free compound. Detailed description of the crystal structure of the $\text{RBaCo}_2\text{O}_{5+\delta}$ perovskites can be found in a number of works [6–8]. According to these data the $\text{RBaCo}_2\text{O}_{5+\delta}$ are characterized by a crystal structure similar to the layered-type structure typical for the YBaFeCuO_5 . This type of structure may be represented as being a consequence of the $[\text{CoO}_2]$ – $[\text{BaO}]$ – $[\text{CoO}_2]$ – $[\text{RO}_\delta]$ layers stacked along the c -axis. In the case of $\delta = 0$ the crystal structure is tetragonal and all cobalt ions are located within square pyramids with fivefold coordination. With increasing δ , additional oxygen ions occupy $[\text{RO}_\delta]$ layers providing an octahedral environment for some of the Co ions. For the samples with R = Gd and Tb slowly cooled in air, δ equals ~ 0.5 and both oxygen atoms and oxygen vacancies within the $[\text{RO}_{0.5}]$ layer are ordered in such a way that a consequent alternation of CoO_5 pyramids and

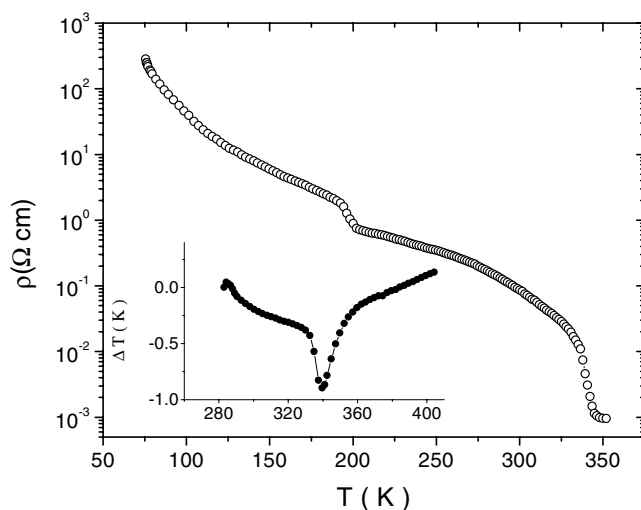


Figure 1. The temperature dependence of the resistivity of $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ measured on warming. The inset shows the DTA curve on warming around the metal–insulator phase transition.

CoO_6 octahedrons occurs along the b -axis. This kind of ordering leads to a reduction of the crystal symmetry from tetragonal to orthorhombic. The crystal structure transformation taking place at T_{MI} does not change the orthorhombic symmetry, and oxygen vacancy ordering is kept above T_{MI} in the $\text{Gd/TbBaCo}_2\text{O}_{5.5}$ perovskites [6, 7, 11].

The room temperature Mössbauer spectrum of the $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ consists of two well defined quadrupole doublets with splittings of $QS_1 = 0.925 \text{ mm s}^{-1}$, $QS_2 = 1.399 \text{ mm s}^{-1}$ and corresponding isomer shifts $IS_1 = 0.074 \text{ mm s}^{-1}$, $IS_2 = 0.068 \text{ mm s}^{-1}$ (figure 2). The values of the magnetic hyperfine fields $\sim 50 \text{ T}$ observed at low temperatures (rather lower than the temperature of the magnetic ordering $T_N \sim 285 \text{ K}$) are typical for the Fe^{3+} ($S = 5/2$) state. The charge state of Fe ions in the air-synthesized $\text{TbBaCo}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$ system has been discussed in the work [9] where a Mössbauer study over a wide temperature range, $T \leq 295 \text{ K}$, as well as thermogravimetric data were presented for samples with different Fe contents. On the basis of the results obtained, it has been concluded that Fe ions adopt 3+ charge states in the concentration range $0 < x < 1$. Two spectral components with fairly large quadrupole splittings suggest that iron atoms are located in two different low-symmetry positions in the $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ lattice. The relative spectral area of the quadrupole doublets allows the determination of the relative fractions of Fe atoms in the corresponding lattice positions. Assuming the same Debye–Waller factor for all Fe sites, the relative spectral area of a given subspectrum is proportional to the relative fraction of the Fe atoms located in the corresponding lattice site. From the fits shown in figure 2 one finds that in the $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ sample, about 60% of Fe atoms are located in sites with quadrupole splittings QS_1 and 40% in sites with splittings QS_2 . In our previous work [9] we have interpreted these two positions as two different positions with fivefold coordination. The first position corresponds to the regular square-pyramidal position in the crystal structure of $\text{RBaCo}_2\text{O}_{5.5}$. The second pyramidal position appears to result from the octahedral position on removing one oxygen atom from the $[\text{TbO}_{0.5}]$ layer. Thus the iron substitution leads to the decrease of the oxygen content according to the formula $\text{TbBaCo}_{2-2x}^{3+}\text{Fe}_x^{3+}\text{Co}_x^{2+}\text{O}_{5.5-x/2}$. TGA data are in agreement with this chemical formula [9]. The Mössbauer spectra recorded at increasing temperatures did not change up to

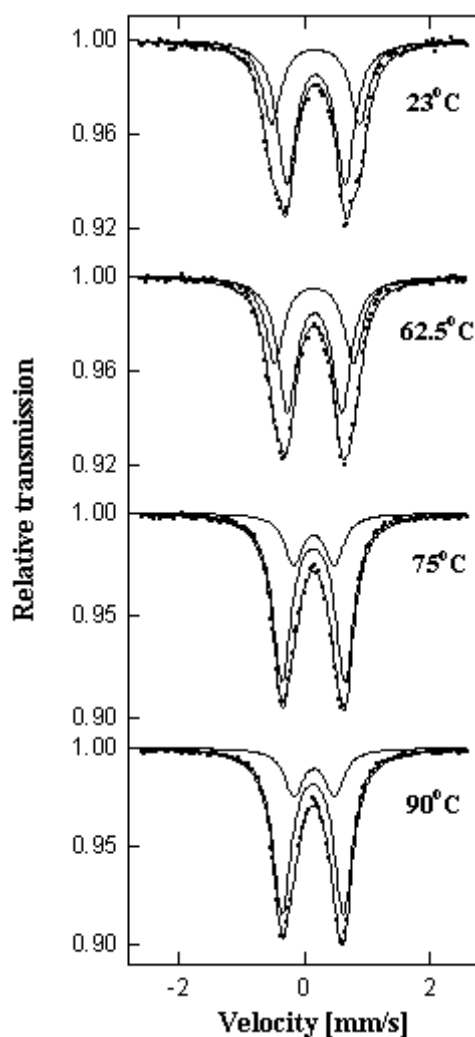


Figure 2. The Mössbauer spectra of $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ measured at different temperatures.

335 K. However, above T_{MI} the Mössbauer spectra changed sharply (figure 2). In the high-temperature spectra the main contribution is a spectral component with $QS_3 = 0.974 \text{ mm s}^{-1}$. The corresponding isomer shift and relative spectral area at 365 K are $IS_3 = 0.023 \text{ mm s}^{-1}$ and 82% respectively. But in addition to the component QS_3 , one can clearly see another component with $QS_4 = 0.641 \text{ mm s}^{-1}$, $IS_4 = 0.046 \text{ mm s}^{-1}$ and a spectral area of 18%. Thus, on the basis of these results, we can conclude that above T_{MI} the iron ions are located predominantly in one crystallographic position. Taking into account the above-mentioned interpretation of the two different positions of Fe ions below T_{MI} , we can conclude that above T_{MI} the oxygen vacancies in the $[\text{TbO}_{0.5}]$ layer are disordered. In order to check this assumption we have carried out a high-temperature XRD experiment, since in the case of random distribution of the oxygen vacancies in the $[\text{TbO}_\delta]$ layer the tetragonal structure is expected. The x-ray patterns of $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ at 293 and 360 K are presented in figure 3. Both spectra can be successfully indexed, in orthorhombic and tetragonal symmetry respectively. However, it

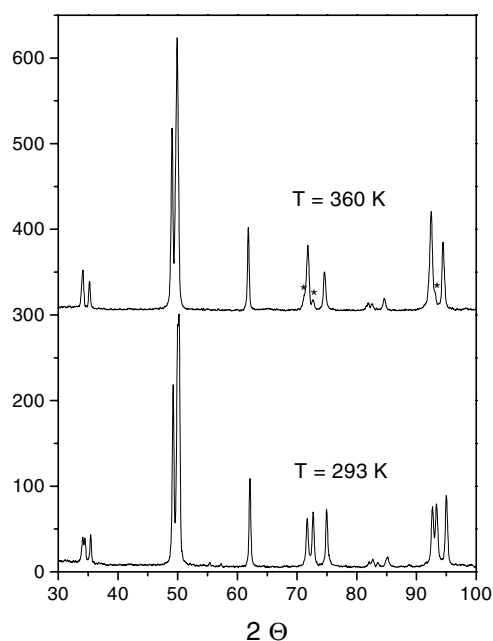


Figure 3. X-ray powder patterns for $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ at two different temperatures (Cr $K\alpha$ radiation). The reflections marked by asterisks relate to surviving orthorhombic phase.

can be clearly seen that above the MIT there is also a small content of an orthorhombic phase similar to that for the Fe-free compound (in the $\text{TbBaCo}_2\text{O}_{5.5}$ the orthorhombic symmetry does not change above T_{MI}), which is obviously caused by an inhomogeneous distribution of the iron ions. The presence of the orthorhombic phase above T_{MI} explains the second spectral component (QS_4) in the high-temperature Mössbauer spectrum.

According to these results, the high-temperature metallic phase of $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$ is characterized by a tetragonal structure with disordered oxygen vacancies in the $[\text{TbO}_\delta]$ layer. Therefore one can conclude that oxygen vacancy ordering does not play a key role in the formation of the metallic properties of $\text{RBaCo}_2\text{O}_{5.5}$ perovskites. Most of the works devoted to the investigation of the MIT in the $\text{RBaCo}_2\text{O}_{5.5}$ compounds conclude that the transition is induced by the spin state transition of Co^{3+} ions. The sharp increase of the effective paramagnetic moment at T_{MI} provides a satisfactory argument in favour of this assumption [6, 8]. However, two nonequivalent positions of cobalt ions in the $\text{RBaCo}_2\text{O}_{5.5}$ lattice (above/below T_{MI}) and three possible spin states of Co^{3+} ions (LS: low-spin states; IS: intermediate-spin states; HS: high-spin states) give a wide field for speculation. Thus, according to [6] all cobalt ions adopt the IS state below T_{MI} and the corresponding HS and IS states in the octahedral and pyramidal coordinations above T_{MI} . Another electronic transformation, $\text{LS} \rightarrow \text{IS}$, for cobalt in the octahedral position has also been proposed [7]. But it is difficult to envisage just cobalt in the pyramids causing the high magnetic ordering temperature of about 285 K and the transition from an antiferromagnetic state into a state with a spontaneous magnetization around 250 K. Recently, the RBaCo_2O_5 compounds containing all cobalt ions within square pyramids have been investigated by the neutron diffraction method, and it was found that Co^{3+} adopts the HS configuration [12]. We suggest a scenario for the MIT involving an $\text{IS} \rightarrow \text{HS}$ state transition for cobalt ions with octahedral environments and

invariance of the HS state for cobalt in the pyramids. In this model the high-temperature metallic phase contains all cobalt ions in the same spin state, which is more probable since there is only one position for cobalt ions above T_{MI} in $\text{TbBaCo}_{1.92}\text{Fe}_{0.08}\text{O}_{5+\delta}$.

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References

- [1] Martin C, Maignan A, Pelloquin D, Nguyen N and Raveau B 1997 *Appl. Phys. Lett.* **71** 1421
- [2] Troyanchuk I O, Kasper N V, Khalyavin D D, Szymczak H, Szymczak R and Baran M 1998 *Phys. Rev. Lett.* **80** 3380
- [3] Troyanchuk I O, Kasper N V, Khalyavin D D, Szymczak H, Szymczak R and Baran M 1998 *Phys. Rev. B* **58** 2418
- [4] Troyanchuk I O, Kasper N V, Khalyavin D D, Chobot A N and Szymczak H 1998 *J. Phys.: Condens. Matter* **10** 6381
- [5] Takeda Y, Kauno K, Takada T, Yamamoto O, Takano M, Nakayama N and Bando Y 1996 *J. Solid State Chem.* **63** 237
- [6] Moritomo Y, Akimoto T, Takeo M, Machida A, Nishibori E, Takata M, Sakata M, Ohoyama K and Nakamura A 2000 *Phys. Rev. B* **61** R13 325
- [7] Kusuya H, Machida A, Moritomo Y, Kato K, Nishibori E, Takata M, Sakata M and Nakamura A 2001 *J. Phys. Soc. Japan* **70** 2377
- [8] Maignan A, Martin C, Pelloquin D, Nguyen N and Raveau B 1999 *J. Solid State Chem.* **142** 147
- [9] Kopcewicz M, Khalyavin D D, Troyanchuk I O, Szymczak H, Logvinovich D J and Naumovich E N 2002 *J. Appl. Phys.* at press
- [10] Brand R A, Lauer J and Herlach D M 1983 *J. Phys. F: Met. Phys.* **13** 675
- [11] Frontera C, Garcia-Munoz J L, Llobet A, Aranda M A G, Rodriguez-Carvajal J, Respaud M, Broto J M, Ragué B, Rakoto H and Goiran M L 2001 *J. Alloys Compounds* **323–324** 468
- [12] Suard E, Fauth F, Caignaert V, Mirebeau I and Baldinozzi G 2000 *Phys. Rev. B* **61** R11 871