Valence states of Cr and the insulator-to-metal transition in Cr-doped SrTiO₃

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Resistivity measurements and x-ray absorption near-edge structure spectroscopy were performed on single crystals of 0.2 mol % Cr-doped SrTiO₃, which exhibit an electrical-field-induced insulator-to-conductor transition with a resistive memory effect. The electrically conducting state is shown to be metallic. The insulator-to-metal transition is accompanied by an increase of the Cr valence underneath the anode from Cr³⁺ to approximately Cr⁴⁺. This indicates that the insulator-to-metal transition is associated with internal doping due to a change of the Cr valence, thereby providing free carriers to the Ti 3d band.

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Transition-metal perovskites exhibit a fascinating variety of electronic properties, ranging from insulating, semiconducting, and metallic to superconducting behavior. SrTiO₃ is a prototypical perovskite with a cubic structure at room temperature ($a=3.905$ Å). The nominal valence of Ti in this compound is 4+ with a 3d⁰ ($S=0$) configuration. SrTiO₃ has a charge gap $\Delta \sim 3.2$ eV between the empty Ti 3d states and the O 2p band, implying that SrTiO₃ is a band rather than a Mott-Hubbard insulator. The insulating state is easily transformed to a metallic state by electron doping, thereby injecting carriers into the Ti 3d band. This is realized, for example, in La_{1-x}Sr_xTiO₃, SrTi_{1-x}Nb_xO₃, and SrTiO_{3-δ}.¹⁻⁴ The insulator-to-metal transition occurs at a small critical density of electron doping of $\sim 10^{18}$ e/cm³, several orders of magnitude lower than typical values for doped transition-metal oxides.^{5,6}

Recently, Cr-doped SrTiO₃ has attracted renewed interest because it exhibits an insulator-to-conductor transition with a resistive memory effect.⁷⁻⁹ Exposed to an electrical field, the resistance of the initially insulating Cr-doped SrTiO₃ is reduced by several orders of magnitude. Consecutive electrical current pulses of opposite polarity switch the resistance of the perovskite reversibly between a high-resistance and a low-resistance state. These two different states persist after removal of the applied electrical bias. Because of its very long retention time, Cr-doped SrTiO₃ is an interesting candidate for nonvolatile memory applications, for example, as a possible replacement for conventional flash memory. A phenomenological model for this resistive memory effect was proposed based on an insulating medium containing nonpercolating metallic domains.¹⁰ The microscopic origin of the insulator-to-conductor transition and the nature of the bistable resistance state, however, are unknown. For Cr-doped SrTiO₃, the Cr dopant may play a crucial role in these processes. Cr can have several valence states, some of which

might be accompanied by a Jahn-Teller distortion.⁵ One could think of a scenario in which internal doping of the Ti 3d band occurs owing to a valence change of Cr. This would profoundly affect the resistivity of SrTiO₃.

In this report, we focus on the Cr valence state through the insulator-to-conductor transition in Cr-doped SrTiO₃. Electrical resistance data and x-ray absorption near-edge structure (XANES) spectra at the Cr K edge of 0.2 mol % Cr-doped SrTiO₃ single crystals are presented. XANES measurements provide information on the formal valence and coordination geometry of the Cr dopant in SrTiO₃. The XANES measurements are compared with density functional theory (DFT) band structure and *ab initio* real-space multiple scattering calculations. The conducting state is shown to be metallic. It was found that the insulator-to-metal transition is accompanied by a significant increase in the valence of Cr in SrTiO₃ underneath the anode electrode. This reveals that the insulator-to-metal transition is associated with internal doping due to a change of the Cr valence, thereby providing free carriers that drive the transition.

Single crystals of 0.2 mol % Cr-doped SrTiO₃ (diameter ~ 5 mm) were melt grown in a N₂/O₂ atmosphere by floating-zone melting. The precursors were prepared using a stoichiometric mixture of SrO, TiO₂, and Cr₂O₃ sintered at 1350 °C in air. The crystals were postannealed for 6 h at 1150 °C in a reducing Ar/H₂ atmosphere. The oxygen stoichiometry of Cr-doped SrTiO_{3-δ} was determined to be $\delta \leq 0.001$ using thermal gravimetric analysis. The [001]-oriented surfaces were polished using chemical-mechanical polishing. Using standard photolithography, 100-nm-thick Pt electrodes 400×200 μm² in size and separated by 200 μm were patterned in planar geometry along the [010] axis on the [001] surface of the single crystals. The resistance was measured with a Quantum Design Physical Property Measurement System (PPMS). X-ray absorption spectroscopy

FIG. 1. Temperature dependence of the resistance of a 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$ single crystal after electrical forming. Inset is the resistance versus T^2 .

data were collected at the High-Brilliance X-ray Spectroscopy Beamline ID26 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France, and the LUCIA French/Swiss Beamline of the Swiss Light Source (SLS), Paul Scherrer Institut, Switzerland. The measurements were performed in fluorescence-yield mode using a multielement Ge or a single Si drift diode detector. The x-ray spot size on the sample at an incident beam angle of 45° was $150 \times 100 \mu\text{m}^2$ with an attenuation length of $\sim 5 \mu\text{m}$ at $E = 6 \text{ keV}$. The incident beam is linearly polarized along $[100]$. The x-ray transmission of the 100-nm-thick Pt electrodes is $\sim 90\%$ at $E = 5.4$ to 6 keV . The electrodes, therefore, act as an excellent reference for the beam position on the crystal.

As-prepared 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$ crystals are insulating (resistivity $\rho > 100 \text{ G}\Omega \text{ cm}$), transparent, and orange in color. The bistable resistance state is obtained only after the crystal has been exposed to an electrical bias for a certain period of time, which we will call “electrical forming” hereafter. This electrical forming causes the resistance to degrade. Finally, after an extended exposure to the electrical field, a conducting state is obtained. The temperature dependence of the resistance of a 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$ single crystal that was exposed to an electrical field of $E \sim 10 \text{ kV/cm}$ for $t \sim 10 \text{ h}$ at $T = 293 \text{ K}$ is displayed in Fig. 1. The decrease of the resistance upon cooling indicates that a metallic path now exists between the electrodes. This shows that the electrical forming caused an insulator-to-metal transition. In the inset of Fig. 1, the resistance is plotted versus the square of the temperature. The measured resistance is well described by a quadratic temperature dependence. This T^2 dependence indicates that the electron-electron scattering dominates the electron-phonon scattering processes, resembling the situation for electron-doped SrTiO_3 observed, for example, in $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$.¹

Cr K -edge XANES measurements were performed on 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$ to investigate the formal valence and coordination geometry of the Cr dopant through the insulator-to-metal transition. For x-ray absorption at the Cr K edge, the dipole transition promotes an electron from the Cr $1s$ core state to an empty $4p$ band state. The energy position

FIG. 2. Cr K -edge XANES of a 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$ single crystal after electrical forming underneath (a) anode and (b) cathode. The dashed lines are Cr K -edge XANES prior to electrical forming. The insets show schematic the position of the x-ray beam on the crystal with the Pt anode (A) and cathode (C). The crystal orientation is indicated.

of the Cr K edge provides information on the valence, whereas the absorption fine structure is characteristic for the spatial environment of the absorbing atom. Figure 2 displays the Cr K -edge XANES of 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$. The dashed line is the Cr K -edge XANES spectrum prior to electrical forming. The solid line in Figs. 2(a) and 2(b) is the Cr K -edge XANES after electrical forming underneath the anode and cathode, respectively. No electrical field was applied while an x-ray absorption spectrum was collected. Underneath the anode, the position of the Cr K edge (measured at half the edge jump) shifted by $1.9 \pm 0.2 \text{ eV}$ after electrical forming. This binding-energy shift is proof that the Cr valence underneath the anode is increased. Moreover, the significant change in the absorption features in the near-edge region indicates an additional modification of the spatial environment of the absorbing Cr atom. On the other hand, underneath the cathode no change of the binding energy occurs. The electronic state and coordination of Cr remain essentially unchanged in the volume probed by the beam after electrical forming.

It is illustrative to compare the K -edge XANES of Cr with different valences and spatial environments. The solid line in Fig. 3(a) displays the Cr K -edge spectra of a fully oxidized 0.2 mol % Cr-doped SrTiO_3 single crystal that was annealed for 6 h at 1150°C in O_2 . For comparison the spectrum of reduced 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$ prior to electrical forming is also included as a dashed line. The position of the Cr K edge (measured at half the edge jump) shifted by $1.6 \pm 0.2 \text{ eV}$ after oxidation. Figure 3(b) displays the Cr K -edge XANES of LaCrO_3 and SrCrO_4 . Cr is coordinated octahedrally in the perovskite LaCrO_3 . In monoclinic SrCrO_4 , Cr is coordinated tetrahedrally and is not a center of symmetry. This causes a strong O $2p$ -Cr $3d$ hybridization, resulting in a highly localized molecular orbital state that gives rise to the isolated pre-edge peak at $E \sim 5990 \text{ eV}$ below the main absorption edge.^{11,12}

The Cr K edge of Cr-doped $\text{SrTiO}_{3-\delta}$ prior to electrical forming resembles the K edge of octahedrally coordinated

FIG. 3. (a) Cr K -edge XANES of 0.2 mol % Cr-doped SrTiO_3 single crystals annealed in O_2 (solid line) and Ar/H_2 (dashed line). (b) Cr K -edge XANES of SrCrO_4 (solid line) and LaCrO_3 (dashed line).

Cr^{3+} in LaCrO_3 . The energy positions of the absorption edges coincide, proving that the valence state of Cr in Cr-doped $\text{SrTiO}_{3-\delta}$ prior to electrical forming is Cr^{3+} . The absence of the strong pre-edge peak in the Cr K -edge XANES shows that the Cr^{3+} ion is surrounded by O atoms with a fully occupied Cr-O_6 octahedron configuration. Consequently the oxygen vacancies in Cr-doped $\text{SrTiO}_{3-\delta}$ are introduced in the oxygen octahedra of Ti and not in those of Cr^{3+} .

After electrical forming, the Cr K -edge XANES underneath the anode, displayed in Fig. 2(a), resembles the K -edge XANES of Cr in the fully oxidized Cr-doped SrTiO_3 reference crystal. Both spectra exhibit a small prepeak at an energy position that coincides with the strong prepeak in SrCrO_4 . This could be an indication that the inversion symmetry at the Cr site is broken. However, the small intensity of this prepeak implies that the deviation from the regular cubic Cr-O_6 octahedron symmetry is small. To quantify the increase of Cr valence, a comparison can be made with the K -edge shift data collected for various Cr compounds with different Cr valences studied in Ref. 12. A linear dependence of the K -edge shift as a function of the Cr valence of 1.6 eV/ e was found. Using this, the 1.9-eV Cr K -edge shift indicates that the formal Cr valence underneath the anode is increased from Cr^{3+} to $\text{Cr}^{4+\epsilon}$, with $\epsilon \sim 0.2$, i.e., to approximately Cr^{4+} .

To obtain more detailed information on the changes of the electronic states and spatial environment of Cr through the insulator-to-metal transition, density functional theory (DFT) band structure calculations and *ab initio* real-space multiple scattering XANES calculations were performed using the DMOL³ (Ref. 13) and the FEFF8 (Ref. 14) codes, respectively. *Ab initio* real-space multiple scattering XANES calculations were performed on clusters of 119 atoms. For the DFT calculations $3 \times 3 \times 3$ SrTiO_3 super cells, containing 1 Cr atom among a total of 135 atoms, were treated with a $6 \times 6 \times 6$ mesh in k space. An extended variational basis set was used which includes 5p functions for the Cr ion.

Figure 4 compares the DFT calculation of the density of Cr 4p states for Cr^{3+} in SrTiO_3 [Fig. 4(a)] with the experi-

FIG. 4. DFT calculation of density of Cr 4p states for (a) Cr^{3+} in SrTiO_3 and (b) Cr^{4+} in SrTiO_3 . (c) Cr K -edge XANES of Cr-doped $\text{SrTiO}_{3-\delta}$ single crystal prior to electrical forming.

mental K -edge XANES of Cr^{3+} in Cr-doped $\text{SrTiO}_{3-\delta}$ [Fig. 4(c)]. Qualitatively, the experimental Cr K -edge XANES is described well by the DFT calculation. A small prepeak labeled A, the main absorption edge B with “shoulder” C, and increased absorption D are all obtained. The Cr–O bond length is calculated to be 1.921 Å (Ti–O bond length is 1.953 Å). Figure 4(b) displays the DFT calculation for Cr^{4+} in SrTiO_3 . A 1.6 eV shift of the density of Cr 4p states is found, consistent with the value obtained experimentally from the Cr valence standards in Ref. 12. Moreover, the Cr–O bond length decreased to 1.882 Å. However, the individual features A to D in the density of Cr 4p states remain essentially unchanged. Therefore, the valence change cannot account for the significant change in the absorption features in the near-edge region of $\text{Cr}^{4+\epsilon}$; hence, also a structural distortion of the Cr–O₆ octahedron must take place.

Ab initio real-space multiple scattering XANES calculations are used to trace a possible origin of the change in the absorption features in the near-edge region of $\text{Cr}^{4+\epsilon}$. The dashed line in Fig. 5 is the calculated Cr K -edge XANES for an undistorted $\text{Cr}^{3+}\text{-O}_6$ octahedron in a SrTiO_3 matrix. Good agreement with the Cr K -edge XANES of Cr-doped $\text{SrTiO}_{3-\delta}$ prior to electrical forming is found. For transition-metal oxides, partially filled orbitals would generally lead to a degeneracy of the ground state that is broken by the Jahn-Teller effect.⁵ Cr^{5+} and Cr^{4+} in an octahedral structure have 1 and 2 electrons in the t_{2g} orbitals, respectively, implying that a Jahn-Teller effect can be expected. This Jahn-Teller effect significantly affects the local spatial environment of Cr and, therefore, could be the origin of the change in the absorption features in the near-edge region of $\text{Cr}^{4+\epsilon}$. The solid line in Fig. 5 is the calculated spectrum for a Jahn-Teller-distorted $\text{Cr}^{4+\epsilon}\text{-O}_6$ octahedron for which two Cr–O bonds along the $d_{3z^2-r^2}$ orbital elongated by 0.15 Å, whereas the other four Cr–O bonds along $d_{x^2-y^2}$ contracted by 0.15 Å. The flattening of the experimental Cr K edge is reproduced very well. This

FIG. 5. *Ab initio* real-space multiple scattering calculation of Cr *K*-edge XANES for an undistorted $\text{Cr}^{3+}\text{-O}_6$ octahedron (dashed line) and a Jahn-Teller-distorted $\text{Cr}^{4+\epsilon}\text{-O}_6$ octahedron (solid line) in SrTiO_3 matrix.

gives evidence for the Jahn-Teller effect in $\text{Cr}^{4+\epsilon}\text{-O}_6$ octahedra.

How do we interpret the observed changes in the valence states of Cr in Cr-doped $\text{SrTiO}_{3-\delta}$ through the insulator-to-metal transition? The stoichiometry of the as-grown crystal is $\text{SrTi}_{0.998}^{4+}\text{Cr}_{0.002}^{4+}\text{O}_3$; the valence of Ti and Cr is 4+. The Cr *K*-edge XANES measurements showed that during the Ar/H₂ annealing oxygen vacancies are introduced in the Ti-O₆ octahedra and that the valence of Cr changes to 3+, leading to $\text{SrTi}_{0.998}^{4+}\text{Cr}_{0.002}^{3+}\text{O}_{3-\delta}$ with $\delta \sim 0.001$. Essentially all electrons created by introducing oxygen vacancies in the Ti-O₆ octahedron are trapped at the Cr site, reducing its valence from Cr^{4+} to Cr^{3+} . Therefore, no electrons are introduced in the Ti 3*d* band, and the crystal remains electrically insulating.

During electrical forming, the valence of Cr was shown to increase from Cr^{3+} to approximately Cr^{4+} underneath the anode. Two scenarios can account for this increase of valence. (i) Electrical forming leads to “detrapping” of electrons previously localized at the Cr sites. A charge transfer of electrons from Cr^{3+} sites to the Ti 3*d* band occurs. This leads to $\text{SrTi}_{0.998}^{4-\Delta}\text{Cr}_{0.002}^{4+}\text{O}_{3-\delta}$ with ~ 0.2 mol % Ti^{3+} ($3d^1$). (ii) Alternatively, electromigration of oxygen vacancies^{15,16} could explain an increase of the valence of Cr at the anode, leading to

a stoichiometry $\text{SrTi}_{0.998}^{4+}\text{Cr}_{0.002}^{4+}\text{O}_3$ with ~ 0 mol % Ti^{3+} . Only scenario (i), in which free electrons are introduced into the Ti 3*d* band, can account for the observed metallic conduction of the formed crystal. This leads us to favor the interpretation that the insulator-to-metal transition is associated with internal doping due to an increase of the Cr valence, thereby providing free carriers that drive the transition. An electron doping of $\sim 3 \times 10^{19} \text{ e/cm}^3$ would be expected for 0.2 mol % Cr-doped $\text{SrTiO}_{3-\delta}$, which is significantly more than is required to drive the insulator-to-metal transition in SrTiO_3 .⁶

The increase of Cr valence with the concomitant reduction of Cr-O bond length profoundly affects the local strain in SrTiO_3 . The DFT calculations predict a tensile strain on the SrTiO_3 lattice of 1% and 3% for Cr^{3+} and Cr^{4+} , respectively. A Jahn-Teller distortion of the $\text{Cr}^{4+\epsilon}\text{-O}_6$ octahedron might further increase the strain. Such a large strain would favor a (local) ferroelectric polarization,¹⁷⁻¹⁹ as is corroborated by the recent finding of strain-induced ferroelectricity in SrTiO_3 at room temperature for a strain exceeding 1%.²⁰ Therefore, one could speculate that the two memory states might be due to such a locally present ferroelectric polarization. However, a detailed extended x-ray-absorption fine structure (EXAFS) study is required to confirm such a scenario.

In summary, we studied the insulator-to-metal transition in Cr-doped $\text{SrTiO}_{3-\delta}$ induced by an electrical field. Resistivity measurements showed that during electrical forming a metallic path is introduced in the crystal. Cr *K*-edge XANES revealed that electrical forming is accompanied by an increase of the Cr valence underneath the anode from Cr^{3+} to $\text{Cr}^{4+\epsilon}$, with $\epsilon \sim 0.2$, i.e., to approximately Cr^{4+} . This supports the interpretation that the insulator-to-metal transition is associated with internal doping of the Ti 3*d* band due to a change of the Cr-dopant valence. DFT and *ab initio* real-space multiple scattering XANES calculations predict that a significant (local) strain in the SrTiO_3 lattice is induced by Cr^{3+} and Cr^{4+} , possibly combined with a Jahn-Teller distortion of the $\text{Cr}^{4+\epsilon}\text{-O}_6$ octahedron.

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¹Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima, T. Arima, K. Kumagai, and Y. Iye, *Phys. Rev. Lett.* **70**, 2126 (1993).

²H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, *Phys. Rev.* **134**, A442 (1964).

³J. F. Schooley, W. R. Hosler, and M. L. Cohen, *Phys. Rev. Lett.* **12**, 474 (1964).

⁴G. Binnig, A. Baratoff, H. E. Hoenig, and J. G. Bednorz, *Phys. Rev. Lett.* **45**, 1352 (1980).

⁵M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039

(1998).

⁶P. Calvani, M. Capizzi, F. Donato, S. Lupi, P. Maselli, and D. Peschiaroli, *Phys. Rev. B* **47**, 8917 (1993), and references therein.

⁷A. Beck, J. G. Bednorz, Ch. Gerber, C. Rossel, and D. Widmer, *Appl. Phys. Lett.* **77**, 139 (2000).

⁸Y. Watanabe, J. G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck, and S. J. Wind, *Appl. Phys. Lett.* **78**, 3738 (2001).

⁹C. Rossel, G. I. Meijer, D. Bremaud, and D. Widmer, *J. Appl.*

- Phys. **90**, 2892 (2001).
- ¹⁰M. J. Rozenberg, I. H. Inoue, and M. J. Sanchez, Phys. Rev. Lett. **92**, 178302 (2004).
- ¹¹A. Bianconi, E. Fritsch, G. Calas, and J. Petiau, Phys. Rev. B **32**, 4292 (1985).
- ¹²A. Pantelouris, M. Modrow, M. Pantelouris, J. Hormes, and D. Reinen, Chem. Phys. **300**, 13 (2004).
- ¹³B. Delley, J. Chem. Phys. **113**, 7756 (2000).
- ¹⁴A. L. Ankudinov, C. E. Bouldin, J. J. Rehr, J. Sims, and H. Hung, Phys. Rev. B **65**, 104107 (2002).
- ¹⁵J. Blanc and D. L. Staebler, Phys. Rev. B **4**, 3548 (1971).
- ¹⁶R. Waser, T. Baiatu, and K.-H. Härdtl, J. Am. Ceram. Soc. **73**, 1654 (1990), and references therein.
- ¹⁷H. Uwe and T. Sakudo, Phys. Rev. B **13**, 271 (1976).
- ¹⁸N. A. Pertsev, A. K. Tagantsev, and N. Setter, Phys. Rev. B **61**, R825 (2000).
- ¹⁹O. Tikhomirov, H. Jiang, and J. Levy, Phys. Rev. Lett. **89**, 147601 (2002).
- ²⁰J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, Nature (London) **430**, 3758 (2004).