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Electrical transport in charge-ordered Fe_2OBO_3: Resistive switching and pressure effects

Ana Akrap,[1,2,*] Manuel Angst,[3,4] Peter Khalifah,[5] David Mandrus,[3,6] Brian C. Sales,[3] and László Forró[1]
[1]*Institut de Physique de la Matière Complexe, EPFL, CH-1015 Lausanne, Switzerland*
[2]*Condensed Matter Physics and Materials Sciences Department, Brookhaven National Laboratory, Upton, New York 11973, USA*
[3]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[4]*Institut für Festkörperforschung, JCNS, and JARA-FIT, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*
[5]*Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA*
[6]*Department of Materials Science and Technology Division, The University of Tennessee, Knoxville, Tennessee 37996, USA*

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The pressure-temperature-electric field phase diagram of Fe_2OBO_3 is studied under ambient and high pressure using resistivity and thermoelectric power measurements. The onset of the incommensurate charge order at $T_{CO}=340$ K does not depend on pressure up to at least 2 GPa. The temperature of the transition to the commensurate charge order is increased by ~ 10 K/GPa. High pressure stabilizes the commensurate phase. We find evidence for resistive switching in the incommensurate phase, which may be linked to the dynamics of the charge-order domain boundaries.

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I. INTRODUCTION

Charge-ordered (CO) states may occur in strongly correlated systems as a way to minimize the repulsive energy between the electrons at the expense of their kinetic energy.[1] In the mixed-valence compounds this often happens due to strong on-site and intersite Coulomb interactions which originate from the localized nature of *d* orbitals. CO is usually commensurate with the underlying lattice but geometrical frustration[2] or other competing interactions may lead to incommensurability and eventually suppress charge order.[3]

Some charge-ordered oxides show resistive switching: if a sufficiently high electric field is applied, it induces an abrupt change in the resistivity. Resistive switching has been observed in the semiconducting or insulating phases of many transition-metal oxides, in different structures: thin films, polycrystalline materials, single crystals, and nanostructures.[4–6] Although the origin of the resistive switching is still an unsettled issue, one of the possible mechanisms leading to resistive switching seems to be related to the modification of the CO.[4,7] For example, in magnetite a sufficiently high electric field may melt the CO and cause a transition into a low-resistance state.[4,8] This phenomenon may be of technological interest for implementation in devices.[9,10]

The low-temperature phase of iron oxoborate Fe_2OBO_3 presents the clearest example of ionic CO found so far;[11,12] a nearly integer iron valence separation into Fe^{2+} and Fe^{3+} has been demonstrated by Mössbauer spectroscopy, structural refinement, and electronic-structure calculations.[12] Recent resonant x-ray diffraction measurements support an unusually large charge disproportionation.[13] At intermediate temperatures the compound features an incommensurately charge-ordered phase, which is probably related to the geometrical frustration of the structure.[14]

The warwickite crystal structure of Fe_2OBO_3 is based on ribbons built by four edge-sharing infinite chains of FeO_6 octahedra, along the crystallographic *a* axis, as shown in Fig. 1. The ribbons share corners and are linked by trigonal planar BO_3 groups. Such arrangement of the ribbons in the *bc* plane, perpendicular to the chain direction, leads to geometrical frustration for interactions between chains.[14] At low temperatures, $T<280$ K, the electronic system is commensurately charge ordered, with its basic charge ordered units being chains of alternating Fe^{2+} and Fe^{3+} sites.[12] Because of the energy degeneracy of various configurations, the total CO is established over domains.[14] An unprecedented phase with an incommensurate, temperature-dependent charge-ordered superstructure has recently been found in the intermediate-temperature range, $280<T<340$ K. The incommensurate phase was proposed to arise due to the easy creation of antiphase domain walls, which results most likely from a compromise between the tendency toward charge ordering and the geometrical frustration.[14] The proposed antiphase structures have recently been directly observed by high-resolution transmission electron microscopy, confirming this scenario.[15] One way of addressing the connection between the geometrical frustration and CO is by applying pressure, which may tune the interatomic distances. At the same time, due to the clearly established presence of CO in Fe_2OBO_3, this compound seems like a good candidate to explore the possible existence of the resistance switching.

In this paper we study the influence of pressure on the charge-ordered phases in Fe_2OBO_3 by means of electrical transport measurements. Our results show that while the temperature of the incommensurate charge-ordering transition, $T_{CO}\approx 340$ K, shows very little pressure dependence, the temperature of the commensurate transition increases with pressure. Hence, pressure shrinks the temperature window of the intermediate incommensurate phase and stabilizes commensurate CO. In addition, we observe that the resistance of the system can be switched by a sufficiently large excitation current in the incommensurately charge-ordered phase. This occurs in a wide temperature range, including room temperature. We interpret this effect as evidence that the charge distribution is at least partly mobile in the incommensurate phase, in agreement with Mössbauer spectral results.[14] Switching is not observed above T_{CO} or in the commensurately ordered phase, below 260 K. Our results are consistent

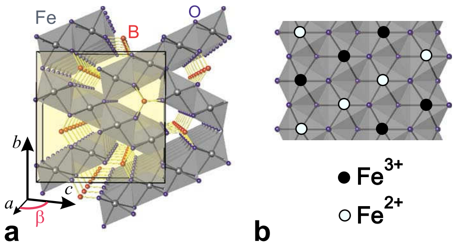

FIG. 1. (Color online) (a) The crystal structure of Fe_2OBO_3 at 355 K with a shaded unit cell. (b) A four-chain ribbon with an indicated possible ground-state CO configuration (after Refs. 12 and 14).

with a picture in which the high-temperature (HT) phase transition is related to the on-site Coulomb repulsion U and the intrachain Coulomb repulsion, whereas the commensurate ordering results from the competition of interchain interactions.

II. EXPERIMENTAL DETAILS

The needle-shaped crystals used in this study were prepared using the method described in the work of Angst *et al.*,[12] and their size was typically $2\times0.2\times0.2$ mm^3. A sample was equipped with four electrical contacts, made by evaporating thin layers of chromium and gold (thickness 50 nm each) and attaching golden wires by silver epoxy. The resistivity was measured along the needle, which corresponds to the chain direction. The E-j characteristic was determined by varying the current through the sample and recording the produced voltage. The measurements were repeated on several different samples from two distinct growth batches; all the observed effects were qualitatively and quantitatively reproduced. For the thermoelectric power measurement, a sample was attached to a ceramic surface. Two heaters produced a temperature gradient along the needle, which was measured by a Chromel-Constantan thermocouple located parallel to the sample. High-pressure resistivity measurements were performed in a clamped piston cylinder pressure cell using kerosene as a hydrostatic pressure medium. The pressure was determined by an InSb pressure gauge.

III. RESULTS AND DISCUSSION

A. Ambient pressure transport

Figure 2 shows the temperature dependence of the resistivity and thermopower up to 800 K at ambient pressure. The resistivity in the HT phase, above ~400 K, shows a very clear activated behavior,[16]

$$\rho=\rho_0 \exp\frac{\Delta}{k_B T} \tag{1}$$

with an activation energy $\Delta_{HT}=179\pm1$ meV. The thermopower at high temperatures assumes relatively small values. Between ~370 and ~500 K, the thermopower may be approximately described by the semiconductor formula,[16,17]

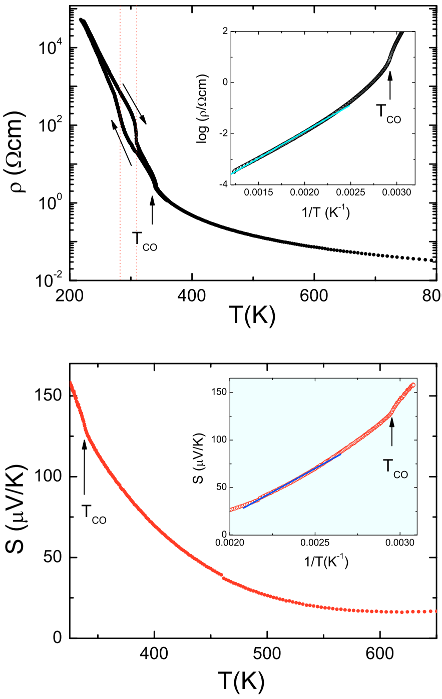

FIG. 2. (Color online) Top panel: temperature dependence of the resistivity at ambient pressure, measured at high bias. The inset shows the activated behavior of the resistivity at high temperatures. Dotted lines mark the incommensurate-commensurate phase transition. Bottom panel: temperature dependence of the thermoelectric power with a ~$1/T$ dependence shown in the inset. The small jump in S around 460 K is an experimental artifact. The arrows mark the incommensurate charge-ordering transition.

$$S(T)\sim-\frac{k_B}{|e|}\cdot\frac{\Delta_S}{2k_B T}. \tag{2}$$

The above simple formula is insufficient to describe the data at higher temperatures. The activation energy extracted from the thermopower data is very close to the value from the resistivity, $\Delta_S=186\pm2$ meV. The positive sign of the thermopower and the close values of Δ_{HT} and Δ_S indicate that the majority of the carriers are holelike. The reported orthorhombic-monoclinic phase transition, where the incommensurate charge ordering takes place,[14] is seen in both transport coefficients as an abrupt increase in the slope at $T_{CO}\approx340$ K. The sign, the absolute value, and the temperature dependence of the thermopower are very different from what has previously been reported.[18] In their study, Rivas-Murias *et al.* found that the thermopower was negative and only weakly temperature dependent above 200 K, albeit with a change in slope at T_{CO}. It may be worth noting that our measurement was performed on single crystals, whereas the previous study used polycrystalline material.

Below the charge-ordering transition, the resistivity exhibits hysteretic behavior in a wide temperature range, in good agreement with the previously reported results.[14] We note that the present measurements were performed at high bias, applying a current density of typically $j\sim10^{-2}$ A/cm^2 above 250 K. On cooling, the transition from

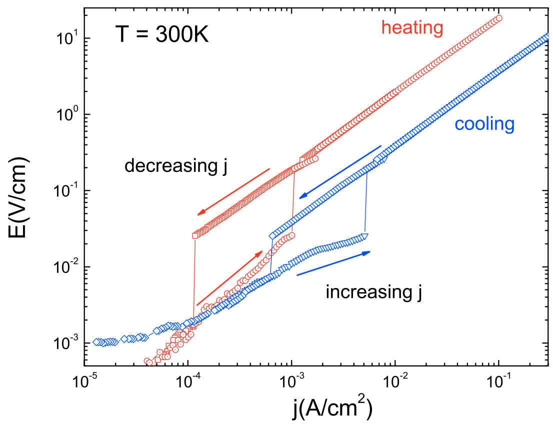

FIG. 3. (Color online) The dependence of electrical field E between the voltage contacts of the sample on the current density j injected into the sample. The shown two sets of E-j curves were taken under ambient pressure, at 300 K, while heating the sample (top curves) and while cooling it (bottom curves). The arrows mark the direction of decreasing and increasing current.

incommensurate to commensurate CO occurs at 280 K, and on warming up this temperature is somewhat higher, 308 K. The first-order nature of the transition, evidenced by the ~30 K wide hysteresis in the resistivity, is currently understood in terms of the existence of charge-ordered domains in this intermediate range. Extracting the value of the resistivity activation energy in the commensurate CO phase from the resistivity data below ~260 K gives $\Delta_{LT}=375\pm2$ meV, twice the value of the high-temperature activation energy. Although the intermediate, incommensurate charge-ordered phase is too narrow to obtain a reliable value of Δ through the Eq. (1), a crude estimate gives a value close to the low-temperature Δ_{LT}. The resistivity of the intermediate phase is larger than in the high-temperature charge-disordered phase, and so is the activation energy. However, the difference between the two activation energies describing the incommensurate and the low-temperature commensurate charge-ordered phase seems relatively small. This suggests that the main reason that the conductivity decreases as the CO becomes commensurate is the diminishing of the number and the mobility of the carriers. Such a conclusion is consistent with the Mössbauer spectral results,[12] which indicate the presence of hopping electrons in the incommensurate phase.

B. Resistive switching

Interestingly, we observe distinct nonlinearities in the E-j dependence in the incommensurately charge-ordered phase of Fe_2OBO_3. Increasing the current density over a certain temperature-dependent threshold value induces switching from a low-current low resistivity to a high-current high resistivity state. The switching effect was repeatable after several current cycles and was seen in three different samples which belong to two distinct growth batches. The resistive switching occurs in a wide temperature range, and it is shown in Fig. 3 for $T=300$ K. The two pairs of curves represent the electric field in the sample as a function of increasing and decreasing current while heating and cooling the sample. As an illustration we focus on the top set of curves (squares and circles in Fig. 3), which were obtained when the sample is heated until its temperature is stabilized at 300 K. If the current density through the sample is increased from 30 μA/cm^2, the electric field measured on the voltage contacts increases linearly until it reaches the critical value of ~0.025 V/cm; at this point the electric field exhibits an abrupt increase to a metastable state with ~0.2 V/cm. After a small increase in current there is another, albeit much smaller jump from ~0.26 to ~0.35 V/cm. This corresponds to the resistivity changing from 26 Ω cm (low-field low current state) through 182 Ω cm (intermediate metastable state) to 198 Ω cm (high-field high current state). Conversely, if the current density is gradually decreased from 0.1 A/cm^2, the electric field at first linearly decreases but then it suddenly drops from ~0.026 to ~2 mV/cm. This translates into a drop in the resistivity from ~218 Ω cm at high bias to 15 Ω cm at low bias. The curves taken at 300 K form closed hysteretic loops with a feature of double threshold biases.

From E-j dependencies at various temperatures, some of which are shown in the top panel of Fig. 4, we can extract the values of critical electric fields where the resistivity suddenly changes. The temperature dependence of these critical fields is shown in the bottom panel of Fig. 4. Below 340 K, the first threshold develops at ~0.03 V/cm. At lower temperatures, $T<300$ K, another threshold field appears at ~0.3 V/cm. Although these fields show a certain sample dependence, they remain in the vicinity of ~0.01 and ~0.1 V/cm.

Similar switching effects have been observed in a number of transition-metal oxides.[5,19–22] The interest in resistive switching is spurred by its possible relevance for electroresistivity memory applications.[23] In Fe_2OBO_3 switching occurs at room temperature, a fact which may enhance the technological applicability of this phenomenon. However, the high-resistance state has no remanence: after the current is removed, the system reverts to its low-resistance state.

The phenomenon of resistive switching is in general not clarified, although it seems clear that it occurs in the vicinity of contact areas.[19] It has been proposed that the resistance switching occurs as a result of charge accumulation induced by electric field.[20] One possibility is that the crystalline defect creation, involving movement of the ions, causes charge to accumulate and induces resistive switching, in which case the switching effect is said to be ionic.[21,24,25] Another possibility is that the origin of the charge accumulation and consequently of the switching is electronic,[22] for example, caused by the carrier hopping through a spatial network of inhomogeneities when an electric field is applied. In the latter case, the resistive switching would occur on a shorter time scale. In addition, in some charge-density-wave systems a moderate electric field may depin the charge modulation and cause a coherent transport, leading to a large decrease in the resistivity.[26] Finally, resistive switching may also be caused by a more trivial effect: Joule heating. This was shown to be the case, for example, in $LuFe_2O_4$,[6,27] and several stripe-ordered cuprates,[28] nickelates,[29] and manganites.[30]

In magnetite, where a critical electric field causes a sudden drop in the resistance, it was observed that a drop in the contact resistances precedes the resistive switching;[4,8] this

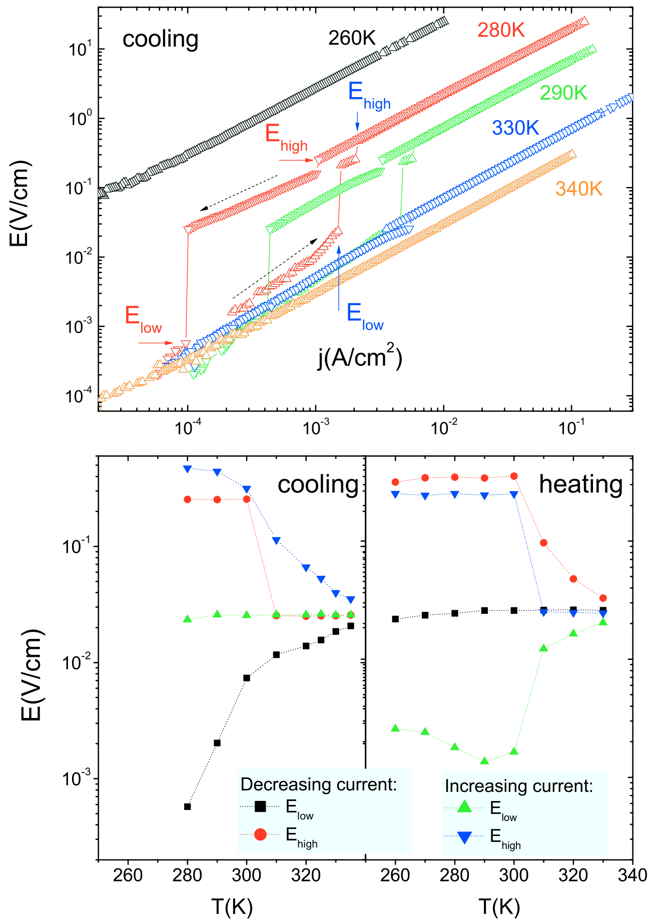

FIG. 4. (Color online) Top panel: the dependence of electrical field E between the voltage contacts of the sample on the current density j injected into the sample. The shown sets of E-j curves were taken under ambient pressure while cooling the sample. For the E-j dependencies taken at 280 K, we marked four characteristic electrical fields which delimit the regions where switching takes place. Horizontal (red) arrows denote switching fields for decreasing current; vertical (blue) arrows mark the switching fields for increasing current. Bottom panel: the temperature dependence of the limiting values of electrical field (E_{low} and E_{high}), extracted for the cooling (left) and the heating (right) data. The connecting lines are guide for the eyes.

was brought into connection with Joule heating of the contacts. In Fe_2OBO_3, there is a small change in ρ when current is increased to just below the critical current value, right before the switching takes place. While we cannot exclude the possibility that the contacts (50-nm-thick layers of Cr and Au) play a role in the observed switching, it does not seem plausible that thermal effects could be responsible for the switching. We have verified that the switching in Fe_2OBO_3 is not caused by Joule heating by applying microsecond-long current pulses; the change in the resistance does not depend on the duration of the current pulse. In addition, Joule heating may be excluded on the grounds that it would lead to a higher current causing a decrease in the resistivity, opposite of what we observe. Moreover, it is important to note that no switching is observed either above the incommensurate charge-ordering transition, for $T \gtrsim 340$ K, or when the CO is commensurate, below ~ 260 K. As it is illustrated in Fig. 4, switching is only observed in the incommensurate CO phase. This asserts that the resistive switching is an inherent property of this intermediate phase. The fact that switching is restricted to the incommensurate CO phase indicates that it is probably not related to ion migration but rather that it is electronic in origin.

An electronic mechanism leading to switching seems to be at work in the related system, nanocrystals, and thin films of magnetite.[4,8] It has been shown that a strong electric field can break the Mott insulator phase and induce metallization in the one-dimensional Hubbard model.[31] Similarly, field may induce melting of the CO.[7] While such a scenario is plausible for magnetite, in Fe_2OBO_3 the resistivity discontinuity happens in the opposite direction—high electric field corresponds to the state of lower conductivity. This fact also excludes the possibility that resistive switching is caused by the depinning of the charge modulation.

In Fe_2OBO_3, it is only in the incommensurate CO phase that a critical current density may abruptly change the conductivity. This suggests that the charge distribution in the incommensurate phase is soft and becomes more rigid in the low-temperature phase, when the switching is no longer observed. In the intermediate phase, the CO is incommensurate with respect to the underlying lattice. The incommensurability likely appears because the interchain Coulomb interactions are frustrated. The CO in Fe_2OBO_3 is established on the level of microdomains. Because of frustration, the domain boundaries can be created and moved very easily in the intermediate-temperature range, which is also indicated by the analysis of Mössbauer spectra.[12] This mobility of domain boundaries is probably at the origin of the enhanced electrical conductivity of the incommensurate phase, as the flow of a current can be accompanied by domain-wall motion. An alternative possibility may be that the switching involves transition between the incommensurate and the commensurate CO. However, it is not clear that this would lead to such a strong rise in the resistivity as observed: Fig. 2 shows that the difference in the resistivity between the two CO phases is too small to account for the switching. Although further work is necessary to elucidate the details, we think that the strong resistivity increase upon surpassing a threshold current density indicates an inherent limitation of the domain-wall mobility.

Finally, the low critical electric fields suggest that the current flow may be filamentary. Filamentary conduction has been invoked in several other oxides where switching occurs at similarly low values of electric field.[5,21] Mesoscopically inhomogeneous current distribution would lead to a much larger local current density and electric field than the measured average value. Evidently, microscopic techniques will be necessary to address this issue.

C. High-pressure transport

Pressure offers a clean way of modifying the interatomic distances and accordingly tuning the ground state of a compound. Figure 5 shows the temperature dependence of the resistivity in Fe_2OBO_3 under pressures up to 2.0 GPa. The

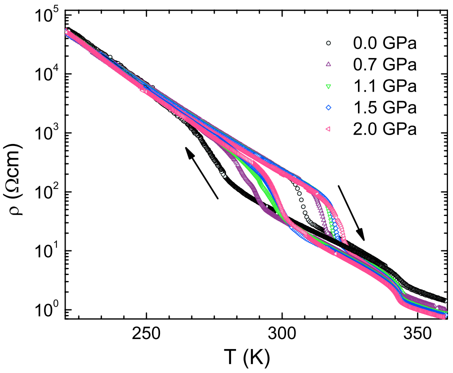

FIG. 5. (Color online) The temperature dependence of resistivity for different pressures. The arrows denote increasing and decreasing the temperature.

conduction is enhanced in the high- and intermediate-temperature regions; as pressure reaches 2.0 GPa, the resistivity drops by ~50% above 320 K. On the contrary, there seems to be no important change in the resistivity of the commensurately charge-ordered, low-temperature phase. Due to the limited range of the high-temperature phase data, a reliable activation energy cannot be extracted. Estimating trends as a function of pressure is, however, still possible and indicates no significant pressure dependence of the high-temperature activation energy. The resistivity decrease is probably related to an increase in the mobility of carriers. Similarly, the low-temperature activation energy is virtually pressure independent, $\Delta_{LT} \approx 400$ meV. The effect of pressure on Fe_2OBO_3 is small compared, for example, to the organic compounds.[32] We attribute this to the hardness of the system, resulting in relatively weak compressibility.

Figure 6 shows the progression of all the charge-ordering temperatures under applied pressure. Pressure has virtually no influence on T_{CO}, the temperature where incommensurate CO is established. In contrast, the phase transition from the incommensurate to the commensurate charge-ordered state is strongly affected. The temperature of the commensurate ordering increases monotonically at a rate of ~10 K/GPa, both for the data collected in the cooling and in the heating cycles. As a result, the most important effect of applying pressure to Fe_2OBO_3 is to narrow the temperature window of the incommensurate phase. The switching behavior occurs at high pressure again only in the incommensurate phase, consistent with our ambient pressure results.

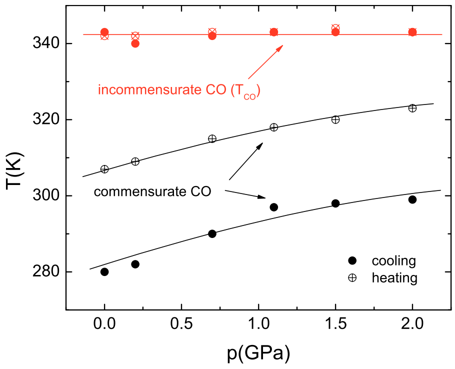

FIG. 6. (Color online) Pressure dependence of the transition temperatures at which incommensurate and commensurate charge ordering take place. The lines are guide to the eyes.

The lack of pressure dependence of T_{CO} indicates that the incommensurate CO is governed by interactions which do not change under pressure. Coincidentally, the atomic distances within an Fe chain are not expected to vary considerably under pressure, compared to the atomic distances between the ribbons. The logical conclusion is that at T_{CO} charge order is established along the Fe chains; caused by a large on-site Coulomb interaction U and the Coulomb repulsion V between the nearest neighbors along the chain direction.[33] The band-structure calculations performed for Fe_2OBO_3 showed that the electron-electron correlations in the 3d shell of Fe cations indeed play a significant role in the physics of the compound.[34] Only if a strong U of 5.5 eV is included does an insulating charge-ordered solution appear.[12,14] The calculated corresponding gap[34] amounts to approximately 400 meV, which is in good agreement with our experimental data for Δ_{LT}. With $U=0$, a metallic solution would persist down to low temperatures, without CO.

Contrary to T_{CO}, the incommensurate-commensurate phase transition is considerably pressure dependent, leading to a decrease in the thermal span of the incommensurate CO phase. This may be understood from the perspective of the compound structure. At ambient pressure, the unit-cell volume at 325 K (incommensurate CO phase) is about 0.05% lower than the volume at 355 K (no CO); the cell volume at 295 K (commensurate CO) is 0.15% lower than at 325 K.[12,35] Although pressure and temperature do not necessarily act in the same way, it appears that a strong decrease in volume would be consistent with high pressure favoring the low-temperature commensurate phase over the incommensurate phase. A good characterization of the incommensurate phase may be given by starting from the commensurate CO and introducing a high density of domain boundaries. The domain boundaries are perpendicular to one crystallographic direction, b. Of all the three lattice parameters, it is b that shrinks the most upon cooling: a decrease of 0.07% in b between 325 K and 295 K may be compared to smaller changes in a and c, 0.05% and 0.04%, respectively.[35] This gives an indication that pressure, too, may disfavor the creation of domain walls. However, if the volume reduction is the cause for the shift of the low-temperature phase transition, a smaller effect on T_{CO} would be expected as well; this seems not to be the case.

A valid general starting point for a theoretical description of charge ordering is given by the extended Hubbard model.[33] Besides the kinetic term, it includes on-site interaction characterized by U and the nearest-neighbor Coulomb repulsion, parametrized by V. A strong on-site interaction U favors charge disproportionation but in order to account for a long-range CO one must also consider the intersite Coulomb repulsion.[1] The existence of an incommensurate phase in Fe_2OBO_3 indicates the presence of competing Coulomb interactions. There is evidence that in this intermediate phase the interribbon and intraribbon interactions are approximately frustrated, which is the probable cause of the incommensurability of the CO.[14] This is similar to the case of quarter-filled square lattice, for which it has been shown that geometrical frustration can entirely suppress charge ordering even in the presence of very strong Coulomb repulsions, and lead to so-called quantum melting.[3] The underlying idea is that the frustration of the structure produces a competition between Coulomb interactions, which stabilizes a metallic, charge-disordered state as long as no particular interaction dominates.

When Fe_2OBO_3 is in the intermediate incommensurate phase, reducing the temperature helps establish a dominant interchain interaction and the CO steadily becomes commensurate with the underlying lattice. The existence of the two charge-ordered phases, commensurate and incommensurate, and their distinct pressure dependence implies that to describe this system, the above-mentioned extended Hubbard Hamiltonian needs to include minimally two different parameters for intersite Coulomb interaction. One is needed to account for the intrachain repulsion, V_1, and the other, V_2, to represent an effective interchain interaction. Based on the independence of T_{CO} on pressure, we assume that V_1 is similarly pressure independent. An increase in V_2 under pressure would then lead to the shrinking of the incommensurate phase. To identify V_2 and to verify our conjecture about its pressure dependence, we would have to know the structure of Fe_2OBO_3 under pressure. However, relying on the above discussion about the temperature dependence of the lattice parameters, we may tentatively associate V_2 with the Coulomb repulsion between the neighboring sites in b direction. If pressure favors a decrease in b, this leads to an increase in V_2 and consequently reduces the range of the incommensurate CO.

IV. CONCLUSIONS

We have shown that the properties of the incommensurate charge-ordered phase in Fe_2OBO_3 may be tuned through external parameters, such as electric field and pressure. The application of pressure reduces the temperature range of the incommensurate phase. In the incommensurate charge-ordered phase, the resistivity may be tuned depending on the applied current. Bistable resistive switching also occurs at room temperature and for this reason may be interesting for applications; however, the high-resistivity state has no remanence. The behavior of the transport coefficients in the incommensurate phase is probably closely related to the dynamics of the domain walls. The domain boundaries are perpendicular to the direction of the lattice parameter b, which presumably depends on pressure. By reducing b, pressure enhances the intersite repulsion along this direction, which eliminates the domain boundaries and stabilizes commensurate CO. The understanding of the origin of the resistivity switching requires further investigation, for example, high-resolution structural studies in external electric field or real-space conductivity mapping.

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*ana.akrap@gmail.com

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