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Dielectric breakdown and current switching effect in the incommensurate layered compound $(\mathrm{LaS})_{1.196}\mathrm{VS}_2$

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A current switching effect of several orders of magnitude was observed in the incommensurate misfit layered compound $(\mathrm{LaS})_{1.196}\mathrm{VS}_2$. This effect involves correlated vanadium t_{2g} states in a hexagonal $[\mathrm{VS}_2]$ layer. Application of moderate electric fields (~ 50 V/cm) induces a dielectric breakdown and restores a metallic state. The large pretransitional nonlinearities are consistent with a Poole-Frenkel mechanism which highlights the role of Coulomb interactions. This behavior and the strong modulation of the vanadium atom positions, revealed by single crystal x-ray structure determination, are in favor of a heterogeneous charge distribution. With respect to recent theoretical works, we suggest that the current switching effect observed in $(\mathrm{LaS})_{1.196}\mathrm{VS}_2$ is related to the breakdown of a remaining Mott insulator state.

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Transition metal oxides have been extensively studied in the last decades and they have led to a renewed interest in metal insulator transition (MIT) in correlated electron systems[1] where fascinating properties such as high temperature superconductivity can be encountered. The application of large external fields can affect the ground state of these systems as exemplified by the magnetic field induced MIT observed in manganites and that leads to colossal magnetoresistance.[2] Recently experimental evidence of electric field induced MIT was observed in Mott insulators $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{NiO}_4$ (Ref. 3), $\mathrm{Sr}_2\mathrm{CuO}_3$ (Ref. 4), and $\mathrm{Pr}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ (Ref. 5). These important current switching effects may originate from the peculiar charge, spin and/or orbital ordering taking place in these compounds. For example, a field induced stripe depinning was proposed for $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{NiO}_4$ (Ref. 3), while a field induced melting of the charge ordered state was proposed in $\mathrm{Pr}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ (Ref. 5). Recent theoretical works[6] have shown that a strong enough electric field could break the Mott-insulator phase and explain the MIT. So far, a dielectric breakdown was mainly observed in transition metal oxides that involve e_g orbital in a MO_2 square plane. In this paper we report a similar dielectric breakdown for a transition metal sulfide with hexagonal packing and a t_{2g} orbital.

$(\mathrm{LaS})_{1.196}\mathrm{VS}_2$ is a material with partially filled t_{2g} shells in hexagonal packing.[7] It is a member of the misfit layered chalcogenide family $(\mathrm{LnX})_{1+x}\mathrm{TX}_2$ (Ln=rare earth; X=S, Se; T=Ti, V, Cr) which has been extensively studied during the last decade.[8] These systems have a typical two-dimensional (2D) structure shown in Fig. 1 where incommensurability occurs along one of the in-plane axes (the a direction). The mismatch between both sublattices, (LnX) and (TX_2), is defined by the term $1+x$; its value is equal to the ratio $2a_2/a_1$ [a_2 and a_1 being the unit cell parameters of (TX_2) and (LnX) parts, respectively]. Band structure calculations indicate that the d bands of the transition element are incompletely filled which should favor a metallic character.[7] In fact, the transport properties strongly depend on the nature of the transition metal and on the strength of the electronic correlations. For instance, $(\mathrm{CeS})_{1.19}\mathrm{TiS}_2$ is a conventional metal without any sign of electronic correlations[9] while $(\mathrm{LaS})_{1.20}\mathrm{CrS}_2$ is believed to be a Mott insulator with fully polarized t_{2g} orbitals.[10] $(\mathrm{LaS})_{1.196}\mathrm{VS}_2$, the compound of interest here, shows a complex behavior with both metallic and nonmetallic characteristics.[7,11,12] The band structure suggests that it should be a metal with the Fermi level located near a minimum of the density of states,[7] and the magnetic susceptibility is Pauli-like with a strong enhancement. Reflectivity measurements[9] suggest as well the existence of free carriers. However, the electrical resistivity is hoppinglike without any

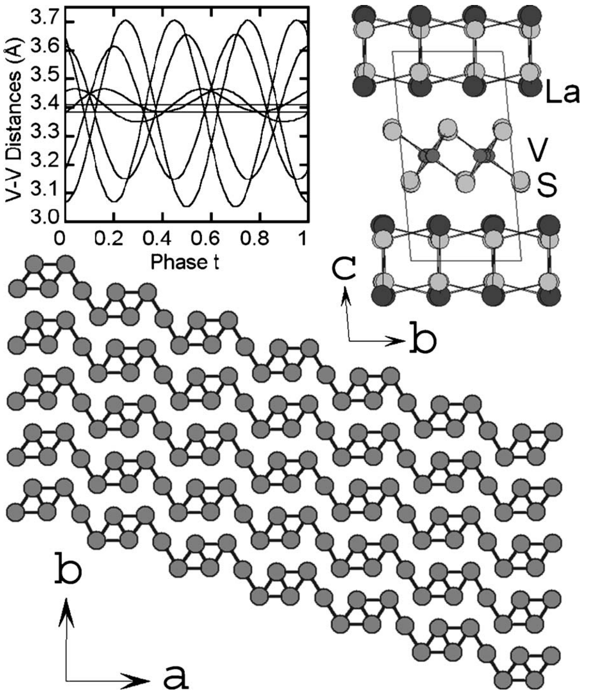

FIG. 1. Structure of LaVS_3. Right upper panel: sketch of the structure in the b,c plane. Left upper part: Modulation of the V-V distance as a function of the phase t of the modulation. Lower panel: projection of the VS_2 layer in the a,b plane. V atoms are in grey. The V-V lines correspond to a V-V distance smaller than the average 3.38 Å distance.

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sign of metallicity. It was recently argued[13] that this compound is a Mott insulator or at least close to the Mott insulating state. Here we report on large nonlinear effects in $(LaS)_{1.196}VS_2$ which lead to large current switching effects and allow the return to a metallic state. This phenomena bears some analogy with the dielectric breakdown observed in Mott insulator oxides.[2–4] It suggests that the breakdown of Mott insulators can also be realized in material with hexagonal packing and t_{2g} orbitals.

Two new batches of $(LaS)_{1.196}VS_2$ single crystals, abbreviated as $LaVS_3$ in the following, have been freshly synthesized as described elsewhere.[7] They were characterized and tested for quality (intensity and shape of the spots) with a Stoe image plate system (IPDS). X-ray diffraction patterns (not shown) clearly revealed the composite character of the structure with a triclinic symmetry. Since only the average structure of $LaVS_3$ was reported in the literature,[14] we made use of the $(3+1)$ *D* superspace formalism[15] to obtain an accurate description of the modulation.[16] $(LaS)_{1.196}VS_2$ was found to be isostructural to $(La_{0.95}Se)_{1.21}VSe_2$ (Ref. 17). We did not find evidence of the presence of a large amount of La vacancies. The structure of $LaVS_3$ is shown in the right upper part of Fig. 1. It consists of $[LaS]$ and $[VS_2]$ slabs regularly stacked along the *c* direction. The $[LaS]$ slabs are built from two atomic layers with a $(100)_{NaCl}$ structure. The hexagonal $[VS_2]$ part is similar to the one observed in TiS_2 with vanadium atoms located in the octahedra of sulfur atoms. Our refinement revealed that the vanadium positions are strongly modulated with V-V nearest neighbor distances which cover a very wide range from 3.05 Å to 3.71 Å as shown in the left panel of Fig. 1. This strong modulation leads to the formation of linear vanadium clusters in real space which extend over more than several tens of Å as schematically drawn on the lower panel of Fig. 1 where we consider only the V-V distances smaller than the average distance of 3.38 Å. The strength of this modulation and the shape of the vanadium clusters are quite puzzling. The V-V distance modulation is surprisingly large by comparison with what is observed in the Ti or Cr based misfit compounds.[18] The mismatch (responsible for the incommensurability) between the $[LaS]$ and the $[VS_2]$ layers seems to be insufficient to explain such a strong effect. Conversely it suggests that it could originate or at least be enhanced by electronic effects. Charge density waves (CDW) or charge and/or orbital ordering are possible candidates. Most of these effects are associated with large nonlinear field effects that we have tried to evidence.

DC resistivity in the ohmic regime was measured on large plateletlike crystals in the planar four probe configuration (in plane resistivity) with gold evaporated electrodes between 4.2 K and 300 K. It was checked that measurements within a same batch give essentially the same results. We did not observe any significative anisotropy along the in-plane *a* and *b* crystallographic directions as well. Figure 2 shows the resistivity ρ versus $T^{-1/4}$ for two crystals (sample 1 and sample 2) from two different batches.[7] While the resistivity curves are quite different, their functional temperature dependence is not. A slight variation in the La content (i.e., presence of La vacancies) can easily account for this discrepancy. It was previously shown[7] that our synthesis route may produce $(La_{1-\delta}S)_{1.196}VS_2$ crystals with a different rate δ of La vacancies $(0 \leqslant \delta \leqslant 0.04)$. Because it modifies the amount of charge transfer, it affects the electronic properties. Here, energy dispersive x-ray (EDX) chemical analysis shows that both crystals have the expected composition with δ close to 0 in agreement with our structure refinement. Still some differences in δ due to the limited accuracy of EDX cannot be disregarded and are likely responsible for the differences in the ohmic transport properties. Below 75 K, the resistivity nicely follows the Mott's law with $\rho = \exp(T_0/T)^{1/4}$. $T_0^{1/4} = 19\ K^{1/4}$ and $53\ K^{1/4}$ are found for sample 1 and sample 2, respectively.[19] It suggests a three-dimensional (3D) variable range hopping (VRH) transport mechanism. As already mentioned, it contrasts with local density approximation (LDA) band structure calculations which predict a metallic behavior. The clusterized structure described previously may be a clue to understand this VRH behavior. While it seems likely that carriers are delocalized within the clusters, they have to hop when long V-V distances occur. VRH transport is thus expected with a low resistivity at room temperature as observed here $[\rho(300\ K) \sim 2-5\ m\Omega\ cm]$.

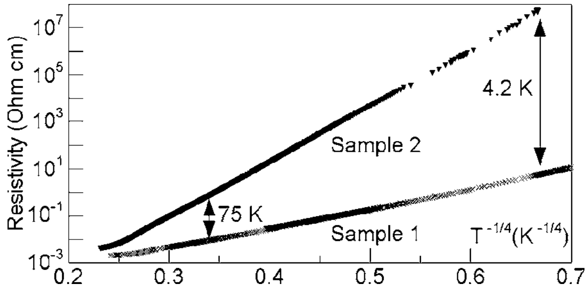

FIG. 2. Resistivity curves of $(LaS)_{1.196}VS_2$ single crystals sample 1 and sample 2 versus $T^{-1/4}$.

Nonlinear I(V) characteristics are observed when the voltage is increased. Measurements are performed in the four probe configuration by applying DC current pulses. The pulse time is setup between 10 ms and some seconds in order to obtain a steady state but to avoid sample overheating. Figure 3(a) shows the current density *J versus* the electric field *E* characteristics for sample 1 in the temperature range 1.6 K to 150 K. In both samples, strong nonlinear effects are observed depending on the field strength: first, deviations from Ohm's law appear then a dielectric breakdown at which the current density increases dramatically occurs for a threshold field E_{th}. For sample 1, $E_{th} \sim 50\ V/cm$ is found and the dielectric breakdown is clearly apparent up to 40 K [see Fig. 3(a)].

A second set of experiments was conducted on sample 2 in which a 1 kHz AC voltage of 10 mV is applied on top of DC bias pulses. The current is measured through a Solartron 1260 impedance analyzer. Results are shown on Fig. 3(b) where the sample 2 differential resistivity $(\rho = V_{ac}/I_{ac})$ is plotted *versus* the DC bias. They allow to characterize the electrical behavior close to and above the transition more carefully. (i) For both samples, the dielectric breakdown results in a resistivity jump which can be as large as six orders of magnitude at low temperature. (ii) For sample 2, ρ

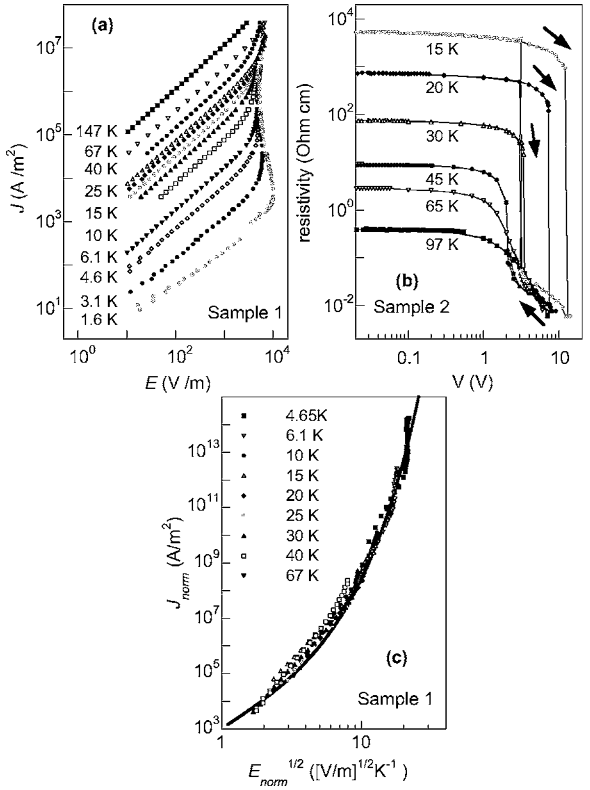

FIG. 3. (a) Current density/electric field $J(E)$ characteristics for sample 1 between 1.6 K to 147 K. The threshold field occurs at 50 V/cm. (b) Hysteretic behavior of the differential resistivity $\rho = V_{ac}/I_{ac}$ of sample 2 with the applied DC bias voltage. Upon increasing the bias and above E_{fw}, a transition to a metallic state is observed. When decreasing the bias, the insulating state is recovered below $E_{th} \sim 40$ V/cm. (c) Master plot for the pretransition behavior of sample 1. J_{norm} and E_{norm} refer to the nonohmic contributions which are temperature normalized (see the text). The thick line corresponds to a fit with $\alpha^2 \sinh \alpha$.

$\sim 10^{-2}$ Ω cm in the low resistive state, i.e., it is of the same order of magnitude as the room temperature resistivity and it is essentially temperature independent as shown when $V \sim 10$ V. It suggests that the dielectric breakdown results in a metalliclike state. (iii) Below 45 K, the breakdown is hysteretic between a forward voltage V_{fwd} and a backward voltage threshold V_{th} which does not depend on the frequency in the 0.1 to 10 kHz range. It is worth noting that between each measurement point of Fig. 3(b) the electric circuit is left open which suggests that the field induced metallic state remains stable over long periods of time (in the range from 1 s to several mn). For sample 2, V_{th} is temperature independent and it corresponds to an electric field $E_{th} \sim 42$ V/cm, i.e., it is comparable to sample 1 E_{th}. E_{fwd} decreases when the temperature increases as $\exp(-T/T_{fwd})$ with $T_{fwd} \sim 12$ K. $E_{fwd} \sim E_{th}$ is above 45 K where the hysteretic behavior is lost and the transition becomes very smooth. The same trend is observed for sample 1 where the onset of the negative resistance [see Fig. 3(a)] is due to E_{fwd} and decreases when T increases while E_{th} is temperature independent.

The observation of a field induced metallic state that is reached after the transition supports our previous discussion about a possible electronic nature of the modulation. The dielectric breakdown as well as the nonlinearities are reminiscent of collective transport properties such as field induced depinning and the sliding motion of CDW. Charge density waves have been widely observed in chalcogenide materials[20] and we have tried to find evidence for such an instability in $LaVS_3$. We have extended our resisitivity measurements up to 700 °C without finding any evidence of metallicity up to this temperature. We have also looked for changes in the diffraction pattern in the (a,b) plane between 300 K and 10 K. We did not find any difference (except for a lattice thermal contraction) which confirms that the material does not experience a phase transition in this temperature range and that CDW are not present in our compound. In addition, the E_{th} magnitude found here is significantly larger than typical threshold fields observed in CDW systems (0.01–0.1 V/cm), and the nonlinearities do not obey the Zener tunneling law. In fact, the appearance of the metallic state induced by the electric field in $LaVS_3$ is likely accompanied by the release of a large number of mobile charge carriers that might be initially localized in the vanadium clusters schematically drawn in Fig. 1.

The pretransition behavior gives some clues to understanding the origin of the pinning forces of these carriers. As already noticed, large nonlinearities are observed before the dielectric breakdown [see Fig. 3(a)]. For sample 1, where the effect is the clearest, the separation of the current density into an ohmic part J_{ohm} and a nonohmic one J_+ shows that $J_+ \propto \exp(E^{1/2})$ at high field. Attempts to invoke Zener tunneling were unsuccessful. The $\exp(E^{1/2})$ dependence is encountered in the Poole-Frenkel mechanism, i.e., field assisted thermal emission of carriers from Coulombic centers. As shown by Hill,[21] such a mechanism should result in a renormalization of both current and field with the temperature leading to a master plot. When defining $J_{norm} = J_+ \times \exp(82/T)$ and $E_{norm}^{1/2} = E^{1/2} \times (1/T + 1/12) = E^{1/2}/T_{eff}$, Fig. 3(c) shows that all of the field dependencies fall on a unique curve (shown as a thick line) $J_{norm} \propto \alpha^2 \sinh \alpha$ where $\alpha = \beta E^{1/2}/k_B T_{eff}$ and $\beta = e^{3/2}(\pi\epsilon)^{-1/2}$ is the Poole-Frenkel constant.[22] It suggests that a Poole-Frenkel-like mechanism is responsible for the nonlinearities. Note however, that T_{eff} is used instead of T which indicates that the pinned carriers experience an effective temperature lower than the phonon one. T_{eff} is limited to 12 K, i.e., amazingly the same characteristic temperature as T_{fwd}. The normalization of the parameters gives an activation energy required to extract a charge carrier from the Coulombic center $E_a/k_B \sim 82$ K with an effective dielectric constant close to 1. It is quite interesting to note that this mechanism emphasizes the role of the Coulomb interactions in this material which may also play a role in the enhancement of its Pauli susceptibility.[7]

From this analysis, the following picture emerges. An heterogeneous charge distribution exists in the material with two kind of carriers: conventional carriers with hopping conduction and pinned carriers in Coulombic centers. The application of a moderate electric fields allows the depinning of later charges while exceeding E_{fwd} results in a dielectric breakdown. A metalliclike state is thus obtained. This heterogeneous charge distribution is likely related to the modulation of the vanadium-vanadium distances that was revealed by the single crystal x-ray structure determination. Such a nonuniform distribution of V atoms in the VS_2 plane will also strongly modulate the transfer integrals as well as the magnitude of the onsite Coulomb interactions. On the other hand, recent photoemission studies have revealed that $La_{1.17-x}Pb_xVS_{3.17}$ is a classical Mott-Hubbard system for $x=0.17$ while long range Coulomb interactions seems to remain in the undoped compound ($x=0$).[13] All these ingredients—the proximity of a Mott-insulating state, the importance of the Coulomb interactions, the very strong modulation of the V-V distance which modulates as well the energy integrals—lead us to suggest that the criteria for a Mott-insulator state may be realized locally. This is presumably at the origin of the heterogeneous charge distribution. As proposed by recent theoretical works, strong enough electric fields may break the local Mott-insulating state restoring thus the metallicity.

In summary, a current switching effect of several orders of magnitude is observed in an inorganic and nonoxide material, namely $(LaS)_{1.196}VS_2$. The electric field induced metal insulator transition involves correlated vanadium t_{2g} states in a hexagonal $[VS_2]$ layer. The analysis of the transitional and pretransitional behavior reveals a heterogeneous charge distribution with conventional carriers and pinned carriers in Coulombic centers. We found that a Poole-Frenkel-like mechanism can account for the pretransitional nonlinearities. Indeed, it means that Coulomb interactions play a key role in this compound. The heterogeneous charge distribution is likely related to the modulated structure of the compound that was elucidated from x-ray diffraction. Our results are reminiscent of dielectric breakdown effects that were recently observed in Mott insulator compounds such as $La_{2-x}Sr_xNiO_4$ (Ref. 3), Sr_2CuO_3 (Ref. 4) or $Pr_{1-x}Ca_xMnO_3$ (Ref. 5). We suggest that the current switching effect observed here in $(LaS)_{1.196}VS_2$ is related to a similar phenomenon with a destruction of locally realized Mott-insulator phases by the electric field.[6]

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