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Pressure-induced tuning of phase transition and role of disorder in electrical transport properties of β-Sr$_x$V$_6$O$_{15}$

Ana Akrap,[*] Neven Barišić, Richard Gaal, and László Forró
Institut de Physique de la Matière Complexe, EPFL, CH-1015 Lausanne, Switzerland

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We report the resistivity and thermoelectric power of β-Sr$_x$V$_6$O$_{15}$, for various stoichiometries, $0.6 \leqslant x \leqslant 1$, and under pressures up to 1.7 GPa. The pristine system ($x=1$) exhibits a semiconductor-insulator transition at 155 K, which is evidenced in both resistivity and thermopower and is probably induced by charge ordering. We observe a pronounced change in the nature of the phase transition under pressure and we attribute it to the tuning of the nearest neighbor Coulomb interaction V. At ambient pressure, as the system moves away from stoichiometry to $x<1$, disorder is introduced into the strontium sublattice and the phase transition is immediately suppressed. The temperature dependence of the thermoelectric power gradually weakens as the system moves away from $x=1$, indicating the importance of disorder. While for $x<1$ compound thermoelectric power shows evidence of a localized contribution to the conduction, which may involve polaronic effects, the activation energies speak against small polarons in the pristine $x=1$ compound. We explain our results in a model of conduction through localized states in the off-stoichiometric systems and of thermally activated conduction in the pristine system.

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I. INTRODUCTION

Vanadium atoms surrounded by oxygen polyhedra build a multitude of different low-dimensional structures, which exhibit an impressive variety of electronic and magnetic phenomena. For example, β-NaV$_6$O$_{15}$ undergoes a metal-insulator transition at ambient pressure and becomes superconducting under high pressure.[1] This compound belongs to the family of quasi-one-dimensional β-vanadium bronzes, AV$_6$O$_{15}$, also referred to as β-$A_{1/3}$V$_2$O$_5$. A metal-insulator or a semiconductor-insulator transition seems to be a generic feature in both monovalent ($A=\mathrm{Na}, \mathrm{Ag}, \mathrm{Li}$), and divalent ($A=\mathrm{Sr}, \mathrm{Ca}$) cations,[2] and despite many experimental and theoretical efforts, its nature is still under debate. As opposed to the low-pressure phase transition, the high-pressure superconducting phases appear only if the intercalated cations are monovalent, while they are absent in the case of divalent cations.[3] To understand the interactions which lead to the presence or absence of high-pressure superconductivity in the A^+/A^{2+} vanadium bronzes, it is important to learn what is the driving force behind the ambient-pressure phase transition and what is the nature of the low-pressure insulating state.

The highly anisotropic electronic structure and quasi one-dimensional behavior of β-A_xV$_6$O$_{15}$ compounds stem from their crystallographic properties. The crystal structure is monoclinic with a twofold crystallographic b axis, as shown in Fig. 1. There are three different sites for vanadium atoms: V1, V2, and V3. V1 and V3 form zigzag chains made of edge-sharing VO$_6$ octahedra and VO$_5$ pyramids, respectively. V2 sites form two-leg ladders, whose rungs consist of corner-sharing VO$_6$ octahedra. Various monovalent (A^+) or divalent (A^{2+}) cations can be intercalated in the channels formed by the V$_2$O$_5$ framework. They occupy one of the two different sites in the unit cell and donate their valence electrons to the vanadium d bands. In the one-dimensional β phase, the two cation sites are so close that only one of them can be occupied at a time. A stoichiometric β system is the one with the maximum possible intercalated cations, $x=1$. In such a compound, exactly half of the places in the channels are filled and the cations form a zigzag chain, which leads to the doubling of the lattice periodicity along the b axis. The crystal structure of the β-A_xV$_6$O$_{15}$ is dominated by the two zigzag chains formed by V1 and V3 atoms and the V2-V2 ladders. However, the tight binding calculations[4] show that the electronic structure of the β-A_xV$_6$O$_{15}$ is based on two kinds of weakly interacting two-leg ladders: V1-V3 and V2-V2.

To learn about the dominant interactions in A_xV$_6$O$_{15}$ compounds, it is important to understand the nature of the low-pressure insulating ground state. It seemed fairly established that this is a charge ordered state between V^{4+} and V^{5+} sites.[5,6] However, some of the recent experimental data have hung a question mark over the charge order in β-AV$_6$O$_{15}$.

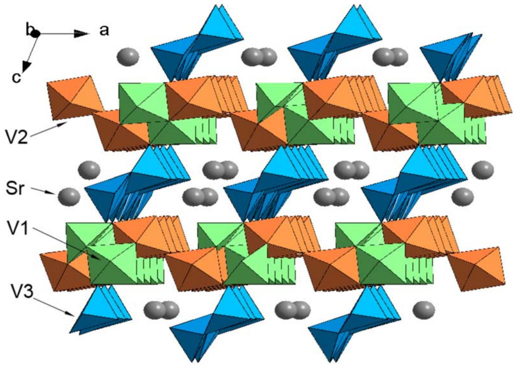

FIG. 1. (Color online) The crystal structure of the stoichiometric β-SrV$_6$O$_{15}$ compound. The V$_2$O$_5$ skeleton consists of chains formed by VO$_6$ and VO$_5$ polyhedra, running along the b axis. The three crystallographically different vanadium sites, V1, V2, and V3, are indicated by green, red, and blue (online). The gray balls represent the intercalated strontium atoms.

The neutron diffraction experiments on NaV_6O_{15} indicated that the ambient-pressure ground state cannot be understood in terms of a simple V^{4+}/V^{5+} site separation and may be better explained by a charge density wave (CDW).[7] Moreover, there seems to be evidence of a coherent charge transport in NaV_6O_{15}, pointing again to a CDW instability as a possible ground state.[8]

The phase transition in $A_xV_6O_{15}$ is extremely sensitive to any off-stoichiometry in the cation content. It is very quickly destroyed even by a small deviation from $x=1$. It is therefore important to understand the role of doping and disorder in $A_xV_6O_{15}$ compounds. If $x<1$, the electron doping of the vanadium *d* bands is decreased. This may imply moving away from the commensurability. Moreover, since for $x<1$ there is less then one cation per unit cell, the cation sublattice can no longer undergo a zigzag arrangement and it remains disordered. The cation disorder seems to have a decisive role, probably because the aperiodic potential produced by the donor atoms introduces disorder into the electronic subsystem.[9]

In this paper, we present a detailed study of the temperature, pressure, and stoichiometry dependence of the transport coefficients in β-$Sr_xV_6O_{15}$ compounds. We focus on two main issues: (1) the nature of the phase transition and how it develops under pressure and (2) the role of cation disorder in the electric transport. By applying pressure, we can change the order of the transition, as is clearly seen in both resistivity and thermopower. The temperature dependence of the transport coefficients sheds light on the possible mechanisms of conductivity, providing evidence against the previously suggested small polaron model. Moreover, our results seem to agree better with a charge ordered ground state than with a CDW scenario. The influence of pressure probably happens primarily through the nearest neighbor Coulomb interaction *V*, which makes the phase transition evolve from second order to a first order kind. The studies on off-stoichiometric compounds look into the effect of disorder on the transport coefficients. As the system moves away from stoichiometry, in the thermopower, we see a signature of conduction by hopping, implying that the conduction happens through a set of localized states.

II. EXPERIMENTAL DETAILS

The single crystals of β-$Sr_xV_6O_{15}$ were grown by a method similar to the one reported in Ref. 10. For electrical transport measurements, we used several needle-shaped crystals of typical dimensions $0.4\times0.05\times0.01$ mm^3. A sample with four silver paint contacts was mounted on a homemade thermopower sample holder, fitting into a clamped pressure cell. We could simultaneously measure the resistivity and the thermopower. Small metallic heaters installed at both ends of the sample generated the temperature gradient, measured with a Chromel-Constantan differential thermocouple. The pressure medium used in this study was kerosene, and the maximum pressure was 1.7 GPa. The pressure was measured using a calibrated InSb pressure gauge. The measurements presented here were performed on several samples, with all the important features confirmed.

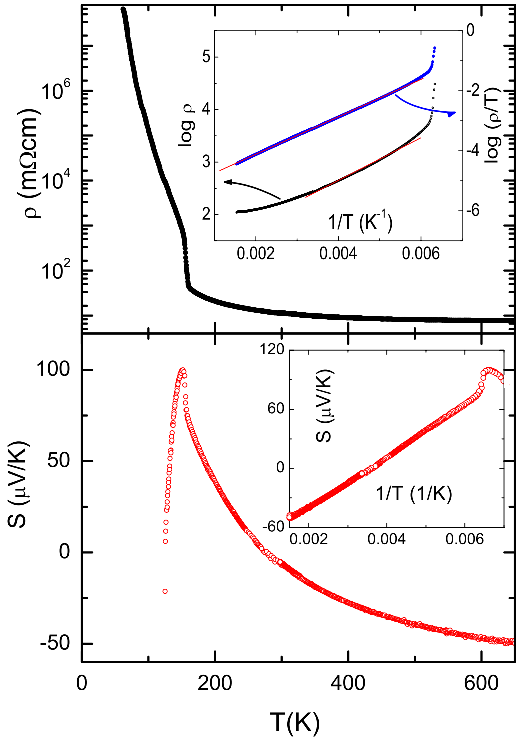

FIG. 2. (Color online) Resistivity (top) and thermoelectric power (bottom) under ambient pressure. The top inset shows the fit of the resistivity data, in the temperature range above the phase transition, to the activated model (left axis) and to the small polaron model (right axis). The bottom inset shows the high-temperature ($T>155$ K) $1/T$ dependence of the thermopower.

III. STOICHIOMETRIC SYSTEM

A. Ambient-pressure transport properties

The temperature dependencies of resistivity and thermopower of SrV_6O_{15} at ambient pressure are shown in Fig. 2. The room temperature value of the resistivity (10 mΩ cm) indicates that the system is either a semiconductor or a bad metal. However, even up to 650 K, there is not a trace of a metallic temperature dependence of resistivity. On the contrary, the resistivity can be reasonably well described by the activated behavior from room temperature down to the transition to an insulating phase at $T_c\approx155$ K,

$$\rho(T)=\rho_0 e^{\Delta_\rho/k_BT}. \qquad (1)$$

This equation, fitted to the temperature range between 165 and 300 K, yields a gap $\Delta_\rho\approx420$ K, as shown in the upper inset of Fig. 2. However, the analogous sodium-intercalated compound NaV_6O_{15} shows a *metallic* resistivity down to the transition, with a similar room temperature value of resistivity, $\rho\approx10$ mΩ cm.[5] From the resistivity measurement alone, it is not clear whether the nonmetallic behavior is an inherent property and SrV_6O_{15} is an intrinsic semiconductor or whether the nonmetallicity arises from the imperfections in the crystal structure. A slight off-stoichiometry causes disorder in the strontium sublattice, which may induce a gap along the chains. Another possibility would be that a nonmetallic conductivity is caused by strong one-dimensional (1D) fluctuations, as it is the case, for example, in the CDW system $(\mathrm{TaS}_4)_2\mathrm{I}$.[11]

However, neither of the two latter assumptions is able to explain the observed temperature dependence of the thermopower. In the case of a gap produced by ionic disorder, the thermopower would be small and weakly temperature dependent. We would expect something similar to happen in the case of 1D fluctuations. Quite on the contrary, the thermopower of $\mathrm{SrV}_6\mathrm{O}_{15}$ shows a clear $1/T$ behavior in the whole $T>T_c$ range, up to high temperatures ($T>650$ K). We can analyze the data using the expression for the thermopower of semiconductors,[12]

$$S(T) = -\frac{k_B}{|e|}\left(\ln\frac{m_h}{m_e} + \frac{b-1}{b+1}\frac{\Delta_\rho}{k_B T}\right). \tag{2}$$

Here, b is the ratio of electronic to hole mobility, μ_e/μ_h, and m_e and m_h are electron and hole effective masses. The room temperature value of thermoelectric power is small and negative, $S\approx -7$ μV/K. The thermopower crosses zero for $T\sim 280$ K. The thermopower gap is given by a fraction of the resistivity gap,

$$\Delta_S = \frac{b-1}{b+1}\Delta_\rho. \tag{3}$$

At high temperatures, the thermopower extrapolates to about -90 μV/K, which leads to the effective mass ratio of $m_e/m_h \approx 2.8$. The extracted value of the gap is $\Delta_S \approx 315$ K, from which we may calculate the ratio of the mobilities: $1/b=\mu_h/\mu_e\approx 7$.

A clear delineation between the high- and low-temperature phases is given by the semiconductor-insulator transition at 155 K. Since no hysteresis is observed in the resistivity, the phase transition seems to be of second order. On the contrary, the x-ray measurements seem to indicate that the transition is of the first order,[13] with a rather elevated change of volume at the transition. In the thermopower, the transition corresponds to a clearly defined change of slope at the T_c, which marks the beginning of a fluctuation regime. The faster increase in thermopower just below the transition could be due to the fact that the carriers couple to the phonons which appear below the phase transition.[14,15] The peak is followed by a strong downturn of thermopower at lower temperatures. This implies that the system is brought from holelike to electronlike conduction.

The above results, particularly the temperature dependence of the thermopower, show that it is not very likely that the phase transition is followed by an establishment of a CDW. As a further check of the CDW hypothesis, we have performed measurements of field-dependent resistivity, both by a dc method and by applying short current pulses through the sample. We found no strong increase in conductivity, that is, no signs of coherent transport up to electric fields as high as 150 V/cm and in a range of temperatures from 300 down to 65 K. We did, however, observe an appearance of switching between states of different resistivities, below 130 K, which will be discussed elsewhere.[16]

Several of the experimental results obtained on $\mathrm{NaV}_6\mathrm{O}_{15}$ have suggested a role of small polarons in the physics of β-vanadium bronzes. A peak in the midinfrared region in the optical conductivity[14] has been observed, and there have been indications of a significant electron-phonon coupling.[17] Analogously, one might expect to find small polarons in the strontium system, although the electron doping is twice higher. Indeed, the high-temperature resistivity data are very well fitted by an adiabatic small-polaronic model, where

$$\rho(T) = \rho_0 \frac{T}{T_0} e^{E_\rho/k_B T}, \tag{4}$$

as shown in the upper inset of Fig. 2. The resulting gap value of $E_\rho=620$ K is somewhat larger than Δ_ρ extracted by a fit to the activated behavior. This model seems to fit our data much better than the activated model of Eq. (1). One may be tempted to conclude that small polarons indeed do play a role in the electronic transport in β-$\mathrm{SrV}_6\mathrm{O}_{15}$. However, it should be noted that in both A^{+} and A^{2+} compounds, the density of charge carriers concluded from doping is relatively high, and the values of resistivity appear to be too low for a system with small-polaronic hopping.

Although the resistivity measurements may provide useful information about the presence or absence of small polarons, the thermoelectric power is a more helpful tool to check this hypothesis in $\mathrm{SrV}_6\mathrm{O}_{15}$. For a small polaron, it is assumed that its energy depends linearly on the atom's displacement from its carrier-free position. The thermopower measures the entropy transfer as a carrier is displaced from one atom to another. The energy difference between the two lattice distortions, on different lattice sites, corresponds to E_S, the chemical potential of the self-trapped polaron. The characteristic energy is related to the Seebeck coefficient as in the semiconducting case, $S\propto E_S/T$. In the case of small polaron hopping, E_S is much smaller than the energy E_ρ needed to activate a carrier across the gap. In fact, it has been shown[18] that a large difference between the two energies, $E_\rho \gg E_S$, may be taken as evidence of small-polaronic motion. In our case, the difference between the ambient-pressure activation energies in $\mathrm{SrV}_6\mathrm{O}_{15}$ extracted from the resistivity and thermopower, $E_\rho\approx 620$ K and $E_S\approx 315$ K, is too small to allow for a small-polaronic model. As we have seen above, such a difference in the two gaps within a two-band model implies that the hole mobility is several times larger than the electronic one. Whereas the possibility of polaronic hopping is suggested by the temperature dependence of the resistivity, the Seebeck coefficient seems to exclude the presence of small polarons. Finally, the peak which appears in the thermopower below the phase transition confirms the existence of strong electronic coupling to the lattice phonon modes, which has been demonstrated by other experimental techniques.

B. Tuning the phase transition with pressure

The temperature and pressure dependence of the transport coefficients is shown in Fig. 3. As we apply pressure, the value of ρ at room temperature linearly decreases, and $d\rho/dT$, which is negative at ambient pressure, increases. The

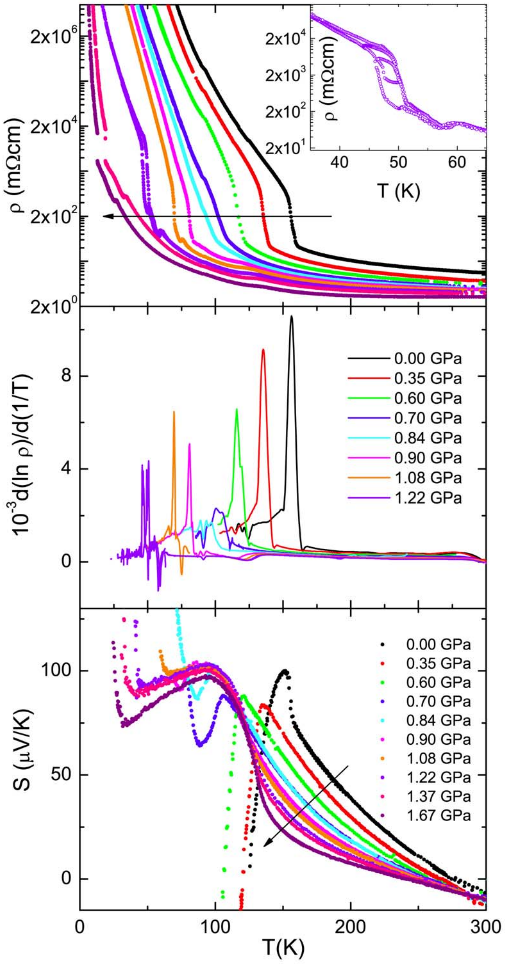

FIG. 3. (Color online) Temperature dependence of the resistivity (upper panel), the logarithmic derivative of resistivity (middle panel), and the thermoelectric power (lower panel) is shown under various pressures. The logarithmic derivative of resistivity clearly indicates an evolution from second to first order phase transition. The top inset displays the hysteresis in the resistivity for $p = 1.22$ GPa. The arrows indicate the direction of increasing pressure.

system is therefore progressively approaching a metallic state. Under pressure, the T_c rapidly shifts to the lower temperatures, which is shown in Fig. 4.

Intriguingly, the pressure brings about a very clear separation between two distinct regimes of the phase transition. While the sharp transition in the resistivity below $p \approx 0.7$ GPa is devoid of any hysteretic behavior, we observed hysteresis curves for $p > 1.0$ GPa. An example of such a hysteresis is shown in the inset of Fig. 3, depicting a blowup of the resistivity curve for 1.22 GPa. The second order phase transition, which takes place at $p < 0.6$ GPa, is replaced by a first order transition for $p > 1.0$ GPa. In the intermediate range, the transition seems to resemble a crossover. This can be seen from the wide and low profile of the logarithmic derivative of the resistivity, which is displayed in the Fig. 3.

The change in the character of the transition, which is quite evident from the logarithmic derivative of resistivity, is consistently followed by a change in the character of the thermopower. In the low-pressure phase, where the transition in resistivity is very sharp, the thermopower shows a sudden drop to negative values below the T_c. A large difference between the high and low-temperature resistivity gaps is another characteristic of the low-pressure phase. Moving onto slightly higher pressures, in the intermediate pressure region, at 0.7 and 0.8 GPa, the transition in the resistivity is considerably widened. For those pressures, in the Seebeck coefficient, we observe a markedly different behavior: immediately after the transition, it decreases and reaches a local minimum, followed by an upturn and a steep increase. There is no change of the dominant carrier sign, as the thermopower is positive in the whole low-temperature range. The position of the local minimum approximately corresponds to the temperature of the transition concluded from the resistivity. The thermopower keeps this new form under higher pressures, but as the pressure is increased, the height of the peak grows. The position of the local minimum shifts to lower temperatures, following the phase transition. In the resistivity, above ~1 GPa, we clearly observe a hysteresis at the transition. Additionally, several fine features appear in the resistivity in the same pressure region, such as a wide hump at about 120 K and a small peak at a temperature just above the phase transition. However, these features seem to be slightly sample dependent, so we shall not discuss them further. Pressures higher than 1.2 GPa make the transition more difficult to follow by measuring resistivity since it seems to depend significantly on the excitation current.[16] Therefore, we position the T_c somewhat arbitrarily at the temperature of the break in the resistivity curve. A more consistent estimate of the T_c is given by the temperature of the upturn in the thermopower.

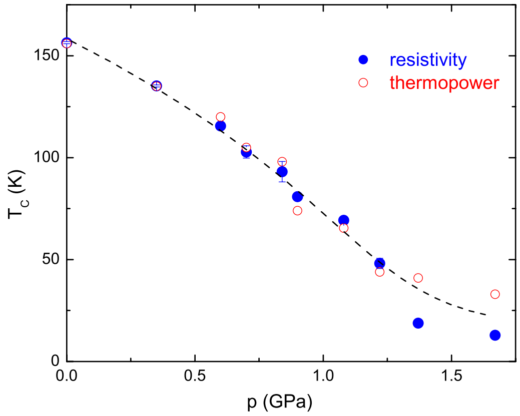

FIG. 4. (Color online) The temperature of the phase transition, as determined from the resistivity (closed circles), and the thermopower (open circles) shows remarkable sensitivity to the applied pressure. In the high-pressure phase, we determine the T_c from the thermopower as the temperature of the local minimum. The error bars are smaller than the size of symbols, unless indicated otherwise. The dashed line is a guide for the eyes.

The behavior of the high- and low-temperature activation energies under pressure, shown in Fig. 5, goes hand in hand with the enhanced metallicity of the system under pressure. The resistivity data were fitted by an activated model de-

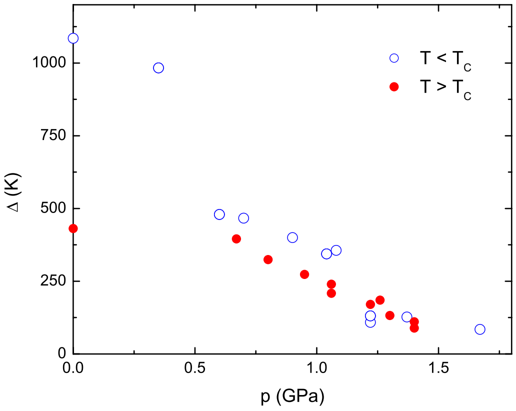

FIG. 5. (Color online) The energy gaps extracted from the resistivity of SrV_6O_{15} under different pressures, fitted to an activated behavior. Whereas the difference between the high- and low-temperature gaps is large at low pressures, above 0.6 GPa, the two values of the gap are very close.

scribed by Eq. (1). We note that, while in the low-pressure phase there is a significant difference between the high- and low-temperature gaps, this difference is comparatively small at higher pressures, $p > 0.6$ GPa. This infers that, whereas at low pressures, gap widens significantly below the phase transition, at higher pressures, the principal difference between the high and low-temperature phases should be in the carrier mobility or the number of the carriers. The pressure-dependent comparison between the activation energy for the resistivity and the characteristic gap from the thermopower measurements, shown in Fig. 6, gives further evidence against the small polaronic model. As the pressure increases, the difference between the two characteristic energies diminishes.

To summarize, all of the observed changes in the character of the phase transition confirm that the two well-separated regimes exist. Pressure induces a passage from a second to a first order phase transition. We note that similar results for resistivity under pressure were recently obtained by Yamauchi *et al.*[19] Based on their measurements of resistivity and susceptibility under pressure, the authors suggested a complex phase diagram for β-SrV_6O_{15}.

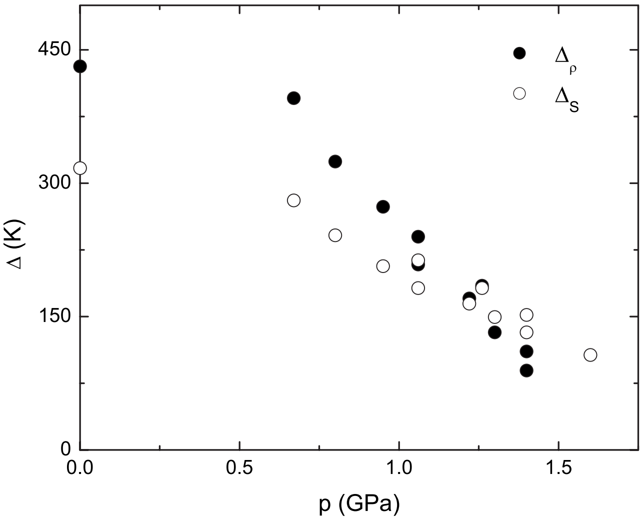

FIG. 6. The pressure dependence of the high-temperature energy gaps extracted from the resistivity (Δ_ρ), fitted to an activated behavior, and thermoelectric power (Δ_S), fitted to Eq. (2). The Δ_S is smaller than Δ_ρ because the presence of both electrons and holes leads to their partial compensation in the thermopower.

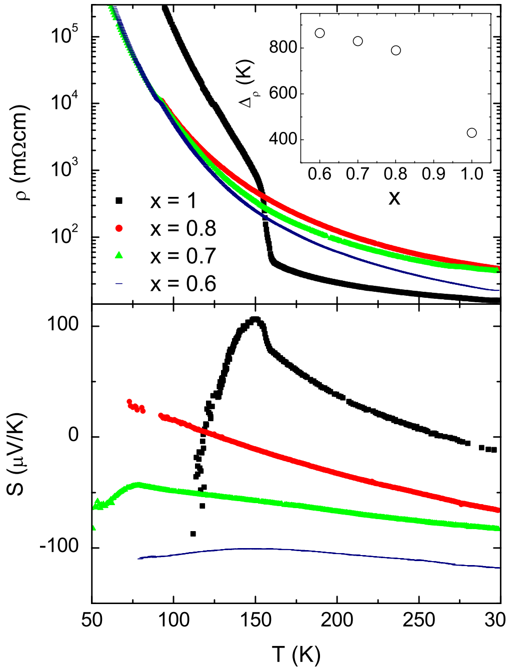

FIG. 7. (Color online) The ambient-pressure resistivity and thermoelectric power for various stoichiometries. The inset shows the dependence of the high-temperature phase activation energy Δ_ρ on stoichiometry.

IV. OFF-STOICHIOMETRY: THE ROLE OF DISORDER

A. Ambient-pressure transport for $x < 1$

The principal changes introduced with nonstoichiometry are a decrease in electron doping and an increase of the disorder in the strontium sublattice. The latter disorder is related to the occupancy of the available cation positions. Namely, the number of strontium atoms in the $x = 1$ compound exactly corresponds to the quantity of occupiable spaces in the tunnels between the vanadium polyhedra. However, when $x < 1$, this is not the case. Therefore, in the off-stoichiometric compounds, the strontium atoms no longer form regular zigzag chains, and we can speak of disorder.

On decreasing x, there is a systematic change in the transport properties of $Sr_xV_6O_{15}$, which is shown in Fig. 7. In the resistivity, the sharp phase transition, which is characteristic of the $x = 1$ compound, is immediately suppressed as $x < 1$ because it is very sensitive to the order in the cation sublattice. Still, both the high-temperature and the low-temperature values of the resistivity for all the doping levels are of similar magnitude as the ones for the stoichiometric system. This may suggest that even in the nonstoichiometric compounds, a similar transition from a semiconducting to an insulating phase takes place, but it is completely smeared by the static cation disorder.

Although no conclusion can be drawn from either the high or the low-temperature values of resistivity as stoichiometry is changed, the energy gaps point to a clear trend. If we compare the values of the energy gap calculated for the high-temperature resistivity phase, resulting from a fit to the thermally activated behavior, we see that the gap shows an important increase as doping is decreased. The gap Δ_ρ doubles as x changes from 1 to 0.8. With the further decrease of x, it continues to grow, albeit less dramatically.

In the thermopower, it is fairly straightforward to follow the progression from the pristine state to disordered states with $x<1$. This transport coefficient typically increases as the carrier density decreases. Logically, the absolute value of the thermopower at room temperature grows as we lower the strontium doping and thus moves away from the stoichiometric system. For the stoichiometries below $x=0.8$, the thermopower becomes negative in the whole temperature range, which corresponds to electrons being the dominant charge carriers. It is interesting to note that in NaV_6O_{15}, which by electron doping corresponds to $Sr_{0.5}V_6O_{15}$, the old transport measurements by Perlstein and Sienko[20] showed that the thermopower is similarly negative in the whole accessible temperature range.

Away from the stoichiometry, the thermopower no longer shows the $\propto 1/T$ behavior, characteristic of the high-temperature behavior of the stoichiometric compound. Instead, it becomes progressively less temperature dependent as x decreases. Such behavior stresses the importance of disorder in the electrical transport. The lack of a strong temperature dependence in the disordered systems can be caused by localized contributions to the conduction. Entropy terms originating from the hopping of the carriers at high temperatures may produce an approximately thermally independent contribution to the thermopower.

At a high enough temperature, $k_BT \ll E_F$, we can consider the possibility of a single-particle hopping motion. For this kind of hopping, the thermopower is determined only by the carrier concentration $c=N/N_a$, where N is the number of carriers and N_a the number of available sites. If the spin degree of freedom is also taken into account, the thermopower is given by a generalization of the Heikes formula,[21]

$$S = -\frac{k_B}{|e|}\ln \beta \frac{1-c}{c}, \tag{5}$$

where β counts the number of possible spin states. When we extract the values of c using the room temperature value of the thermopower and putting $\beta=2$ or 1, we get a series of values shown in Table I. The nominal carrier concentration is calculated per vanadium site, using the known doping: $c=N/N_a=2x/6$. Comparing the values calculated from the generalized Heikes formula with the formal values of c, we see that the thermopower overestimates the carrier concentration. If we ignore the spin degree of freedom ($\beta=1$), the agreement becomes much better, especially for the $x=0.6$ compound. Neglecting the spin degree of freedom may be grounded in the case of a strong on-site Coulomb interaction U or if the carriers really are spinless, e.g., in the case of bipolarons. Apart from the Heikes term, which is very likely to be present in the $x=0.6$ compound, there may be an additional term in the thermopower, due to another weakly thermally dependent mechanism. A possible reason why the Heikes term overestimates the total thermopower of $x=0.7$ and $x=0.8$ compounds would be that the temperatures we are looking at are simply not high enough for the Heikes formula to be applied.

TABLE I. Values of the carrier concentration c calculated from the nominal doping and from the thermoelectric power at 300 K, using the generalized Heikes formula, as described in the text.

Compound	d electrons/V atom	c ($\beta=2$)	c ($\beta=1$)
$Sr_{0.8}V_6O_{15}$	0.27	0.48	0.32
$Sr_{0.7}V_6O_{15}$	0.23	0.43	0.28
$Sr_{0.6}V_6O_{15}$	0.20	0.34	0.20

B. $Sr_{0.6}V_6O_{15}$: Disorder under pressure

The resistivity of $Sr_{0.6}V_6O_{15}$, for different pressures, is shown in Fig. 8. The room temperature value decreases as pressure is applied, and so does the resistivity gap.

Among all the systems studied here, the $Sr_{0.6}V_6O_{15}$ compound presumably contains the most disorder in the cation sublattice. Expectedly, if we envisage the thermopower as entropy per charge carrier, this system shows the largest thermopower. Additionally, the thermopower shows a very little temperature dependence, which means that the number and the mobility of charge carriers are approximately thermally independent. We should therefore expect that at least a part of the thermopower can be described by the generalized Heikes formula, Eq. (5).

In that sense, it is surprising that the absolute value of the thermopower significantly *decreases* with pressure, as shown in Fig. 9, instead of being pressure independent. If we attribute the thermopower to the pure entropy terms, this decrease in thermopower would suggest that under pressure, either the number of available sites decreases or that the

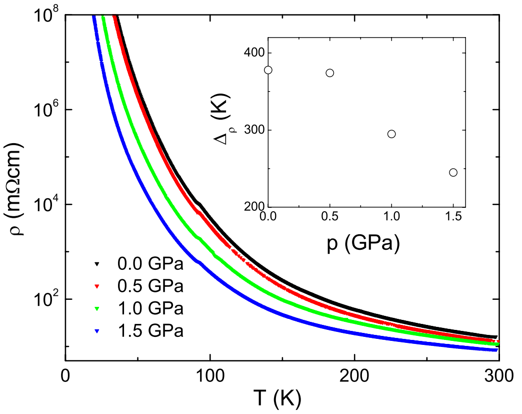

FIG. 8. (Color online) Electrical resistivity under pressure for the $x=0.6$ compound. The inset shows activation energies obtained from a fit to an activated behavior.

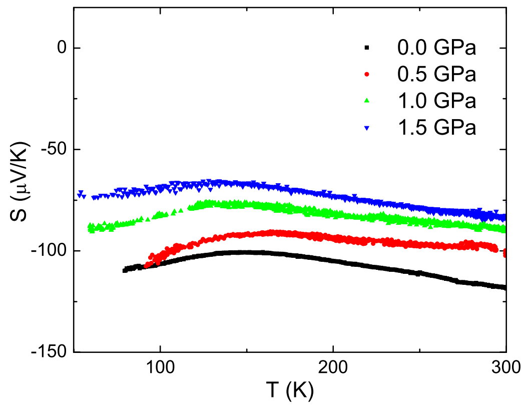

FIG. 9. (Color online) Thermoelectric power for the $x=0.6$ compound, under various pressures. While the weak temperature dependence of the thermopower is not much influenced by pressure, its absolute value decreases significantly.

carrier concentration increases. Indeed, employing the Heikes formula with $\beta=1$, we get an increase in the number of carriers per number of available sites c from 0.20 at ambient pressure to 0.28 at 1.5 GPa. Alternatively, we may suppose that apart from the electronic hopping, there is an additional polaronic contribution. We have already seen that it may not be possible to explain the thermopower of $x<1$ compounds only by single-electron hopping. Mott[22] showed that as polarons approach each other, their polarization clouds start to overlap, which in turn reduces the energy required for hopping. Therefore, if we suppose that besides the Heikes term there is another polaronic contribution to the total thermopower, this may provide an explanation for the observed pressure-induced decrease of the Seebeck coefficient.

V. DISCUSSION

Although many experiments were performed to investigate the origin of the phase transition in β-$A_xV_6O_{15}$ compounds, it still presents an enigma. Several different scenarios were proposed to account for the origin of the phase transition: a CDW instability, charge ordering, and the suggested presence of small polarons means that a polaron ordering may be an additional possibility.[14,17] Our results seem to show a disagreement with the picture in which the phase transition in SrV_6O_{15} is followed by an establishment of a CDW. For example, the conductivity is gapped already above the transition. While this also appears in some compounds that do exhibit a CDW and is attributed to strong 1D fluctuations, we observe a clear $1/T$ dependence of the thermopower, which is characteristic of semiconductors and at variance with the existence of such fluctuations. Besides, we found no trace of coherent transport even in very high electric fields. The absence of any coherent transport may be due to a commensurate CDW, which would be very strongly pinned. However, it should be noted that although the nature of the transition is very sensitive to pressure, even under pressure no depinning was observed.[16]

Another possibility, which is related to the small-polaronic conjecture,[14,17] could be that the phase transition is caused by polaron ordering. In such a picture, at the transition, the electrons would become trapped and localized by spatially incoherent lattice deformations. However, our thermopower data demonstrate that the presence of small polarons in SrV_6O_{15} is quite unlikely. It is also not clear whether the sharp resistivity upturn below the transition temperature would be possible in such a picture.

Hence, it seems more plausible that the phase transition originates from charge ordering. The filling of the vanadium d bands is presently unknown, which makes it difficult to speculate how charge order could take place or what the exact pattern of the charge disproportionation may be. However, according to the recent NMR measurements on SrV_6O_{15},[23] electronic charge strongly alternates in the V2-V2 ladders already in the high-temperature phase. This proves that the electronic system has a tendency toward charge disproportionation, which is probably due to its highly polarizable V_2O_5 skeleton. The NMR measurements also show that the d electrons are distributed quite uniformly over all the three unit chains. This, in turn, corroborates the results of the tight binding calculations, which suggest that in the strontium compound, both V1-V3 and V2-V2 ladders are populated by d electrons.[4] In addition, from the point of view of the field-dependent conductivity, a charge ordered phase would be very difficult to depin by an applied electric field, which is consistent with what we observe.

When the pressure is applied to SrV_6O_{15}, the phase transition continuously becomes less pronounced, and under ~0.7 GPa, it almost smoothes out. This can be followed in the temperature derivative of the resistivity. Finally, above 0.9 GPa, the transition suddenly sharpens again, only to abruptly disappear around 1.4 GPa. The change from a low-pressure second order to a medium-pressure first order phase transition is further supported by the fact that the thermopower indicates an accompanying change in the band structure: the sign of the dominant carriers below the phase transition changes upon entering the higher pressure region. In the pressure range above 0.7 GPa, we observe an upturn in the thermopower below the phase transition. This upturn indicates a possibility that there is a competition between two states of different conductivity. A confirmation of such an idea is a resistivity-switching behavior under an applied electric field, which we have recently observed.[16]

Yamauchi *et al.*[19] have published x-ray oscillation photographs taken on SrV_6O_{15} samples under several pressures up to ~1.6 GPa. They have shown that the strontium zigzag ordering persists at least up to the highest pressure reached. Therefore, the application of pressure does not cause disorder in the strontium sublattice. Their results also demonstrate that the superspots with the modulation vector $q=1/6b^*$, which appear at the phase transition under ambient pressure, exist only up to ~0.5 GPa. This corresponds to the pressure region where we observe an abrupt change in the character of the thermopower. Therefore, both transport and x-ray measurements point to the fact that pressure induces a fundamental change in the character of the phase transition and the ground state of the system. In the case of a CDW instability, one could suppose that such a tuning of the transition may come from a modulation of the value of $2k_F$. However, at pressures above 0.5 GPa, Yamauchi *et al.* observed the superspots with $q=1/10b^*$, which disappear above ~1.0 GPa. Since SrV_6O_{15} is a 1/6-filled compound, such a periodicity is not compatible with a CDW instability and clearly suggests a charge ordered phase instead.

To understand why the phase transition evolves under pressure in the way described here, the existence of a strong nearest neighbor Coulomb interaction V may be of paramount importance. If one takes into account the Coulomb interactions between the electrons on the vanadium chains, an extended Hubbard model can explain charge ordering or disproportionation.[24,25] The magnitude of these interactions is governed by the ratio V/t, where t is the effective intrachain transfer integral. At specific commensurate fillings, when the nearest neighbor Coulomb interaction exceeds a critical value, $V>V_c$, charge disproportionation occurs among sites with alternating "charge rich" and "charge poor" sites.[26] The overlaps between the chains may be changed by the application of pressure. In this way, we can tune the value of V/t, in turn modifying the condition for the charge ordering.

Concerning the $x<1$ samples, an obvious change introduced by off-stoichiometry is to decrease the electronic doping of the vanadium ladders. The optical measurements on $Sr_xV_6O_{15}$ polycrystals[27] and extended Hückel tight binding calculations[4] suggest that the difference between the $x=1$ and the $x<1$ systems lies in the occupation of the V2-V2 ladders. However, our measurements show that the most prominent effect of strontium off-stoichiometry is to induce the site occupancy disorder into the strontium sublattice. Disorder brings the system to a conduction through localized electronic states. This is particularly clearly evidenced in the progressive absence of temperature dependence in the thermopower as the system moves from $x=1$ to $x=0.6$. A localization of the electronic states may also be concluded from the comparatively high values of the energy gaps, with respect to the pristine compound.

VI. CONCLUSIONS

In summary, we have measured the resistivity and the thermoelectric power in the series of compounds $Sr_xV_6O_{15}$, for $x=1$, 0.8, 0.7, and 0.6, under various pressures. Thermopower turned out to be a particularly sensitive probe for the doping and pressure dependence of electrical transport in these systems. In the pristine compound, $x=1$, two different regimes of the phase transition could clearly be separated under pressure. Our results suggest that the semiconductor-insulator transition may be due to a charge ordering. The off-stoichiometric systems, $x<1$, exhibit no phase transition in resistivity. As x decreases, the charge gap grows and the thermal dependence of the thermopower steadily diminishes. This indicates that the conduction is mediated by hopping between localized states produced by disorder. Whereas we could eliminate small-polaronic conduction in the case of $x=1$ compound, based on the thermopower results, the decrease of thermopower in the $x=0.6$ compound under pressure indicates that there may be a polaronic contribution to the conduction.

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*ana.akrap@epfl.ch

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