

The power factor of Cr-doped V_2O_3 near the Mott transition

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We have measured the Seebeck coefficient, S , of nominally 1.1% Cr doped V_2O_3 as a function of both temperature and pressure. Large variations of S are found at the Mott insulator-metal transition. A combination of our data with resistivity data allows us to estimate the power factor. Contrary to thermopower and resistivity, the power factor is not strongly modified upon crossing the first order phase transition. Such a behavior is in sharp contrast with standard semiconductors.

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Thermoelectric energy conversion, where thermal energy is directly transformed into electrical energy, has attracted much interest in recent years. The efficiency of a thermoelectric device is defined by its material properties with the thermoelectric power factor $P_F = S^2\sigma$ and the figure of merit $ZT = \frac{S^2\sigma T}{\kappa}$, where S is the Seebeck coefficient, T is the temperature, σ is the electrical and κ the thermal conductivity. For e.g., environmentally friendly electric-power generators, materials with high efficiency (i.e., $ZT \approx 1$) are one of the current main interests in research on thermoelectric materials. As P_F is a combination of S^2 , which is large in an insulator, and σ , which is large for a metal, materials that undergo a metal to insulator transition (MIT) are promising candidates for a large power factor.

Among such candidates, doped Mott insulators such as the cobaltates^{1,2} or doped $SrTiO_3$ (Ref. 3) appear to be promising. Surprisingly, the thermoelectric properties of the archetype of the Mott insulator, V_2O_3 , have not yet been studied extensively. Indeed, since the pioneering work of McWhan *et al.*,⁴ V_2O_3 has been the subject of research in order to gain insights into its high temperature MIT from a paramagnetic metallic to a paramagnetic insulating phase. This transition can be induced either by hydrostatic or chemical (e.g., doping with chromium) pressure. As it occurs without any change in the crystal symmetry, it is the canonical example of the Mott transition.⁵ The first order transition line terminates at a second order critical point above which it becomes a crossover. In a single band model, the thermopower of a Mott insulator should be zero. Nevertheless, first experiments⁶ have shown that this is not the case and thermoelectric properties of V_2O_3 might be revisited. By combining our results with literature data for the electrical conductivity,^{7,8} which were carried out under the same experimental conditions, we get information about the power factor. We use the pressure as the control parameter as it allows to sweep the entire phase diagram with only one sample.

A single crystal of V_2O_3 with a nominal doping of 1.1% Cr was prepared using the skull melter technique.⁹ This Cr concentration ensures that the sample is on the insulating

side of the transition at ambient pressure, but that a moderate pressure of a few kilobars (or, alternatively, a decrease in temperature) drives the system into the metallic state. The sample was oriented along the hexagonal c -axis by X-ray diffraction using the Laue method and then cut into bars of a typical length of 5 mm along the c -axis with a cross-section of $1 \times 0.2 \text{ mm}^2$. The experiments were performed in a pressure cell using isopentane as pressure medium and the thermopower was measured at temperatures between 300 and 500 K and pressures between 0.5 and 5 kbar following the experimental procedure described in Ref. 10. A schematic drawing of the experimental setup is shown in insert of Fig. 1. The absolute temperature and the temperature gradient were measured using chromel/constantan thermocouples. The aspect ratio of the sample allows us to consider that the thermal gradient is applied essentially along the c -axis. The voltage contacts were glued with silver paste on small gold pads evaporated near the ends of the sample. The differential thermocouple was thermally connected to these pads through

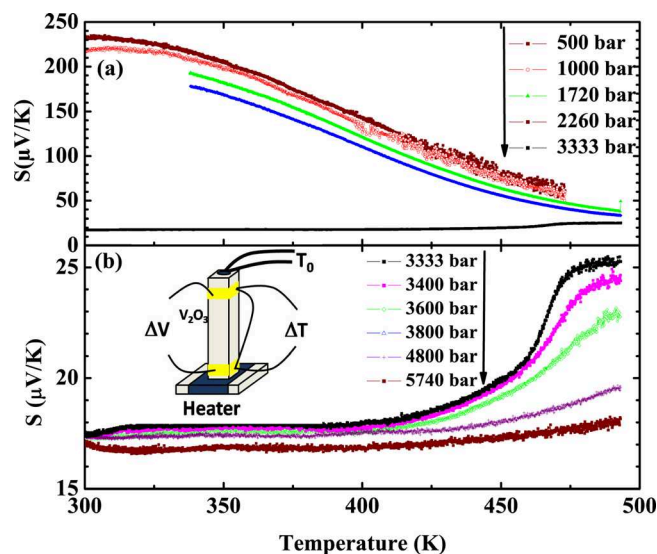


FIG. 1. (Color online) Thermopower of 1.1% Cr doped V_2O_3 as a function of temperature for different applied pressures: (a) in the insulating phase. (b) in the metallic phase. Note that in (a), the curve at 3333 bar has been added for a better comparison. Insert: schematic experimental set-up for the measurement of thermopower. ΔV and ΔT represent, respectively, the voltage and temperature variation throughout the sample when a pulse of current is applied on the heater. The base temperature, T_0 , is measured with a chromel/constantan thermocouple.

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a thin layer of varnish. The thermal gradient, $\Delta T = 1\text{ K}$, was much lower than the temperature range under study which allowed to remain in the linear region of the $\Delta V(\Delta T)$ curve, where ΔV is the measured voltage across the sample. We consider anyway that a few percent error is possible on the absolute value of S which is essentially due to a misalignment of ΔV and ΔT lead wires and a possible thermal link at the gold pad-differential thermocouple interface especially at such high temperatures. All measurements were performed on the same V_2O_3 single crystal. However, preliminary experiments carried out on several samples under ambient pressure have proved that the absolute value of S is reproducible within $\pm 10\ \mu\text{V/K}$ and in good agreement with previous experiments.⁶ Thermopower was measured at several constant pressures in variable temperature experiments up to 500 K and at several fixed temperatures in pressure sweeps near the critical point of the Mott transition. We had to avoid to cross the first order transition line around room temperature, because of a discontinuous volume change of about 1% occurring at the transition,¹¹ which would imply an irreversible harm to the sample. This volume change becomes smaller at higher temperatures¹² and allows to cross the transition safely at temperatures not too far from T_c .

In Fig. 1, the absolute thermopower is plotted against temperature for several pressures in the insulating (a) and metallic (b) phases. At low pressures, in the insulating phase, S decreases with increasing temperature and is similar for all pressures. At high pressures, we observe quite different temperature profiles for the various pressures in the metallic phase. This is awaited if a crossover line is crossed, as expected from dynamical mean field theory (DMFT) calculations¹³ and has been already seen in conductivity measurements.^{7,8} Far from the transition line in the metallic phase, S only slightly increases between 300 and 500 K.

Fig. 2 shows the thermopower in the mixed region where the transition is actually crossed. At low pressures, a large hysteresis upon heating and cooling and a large discontinuity at the transition are observed.

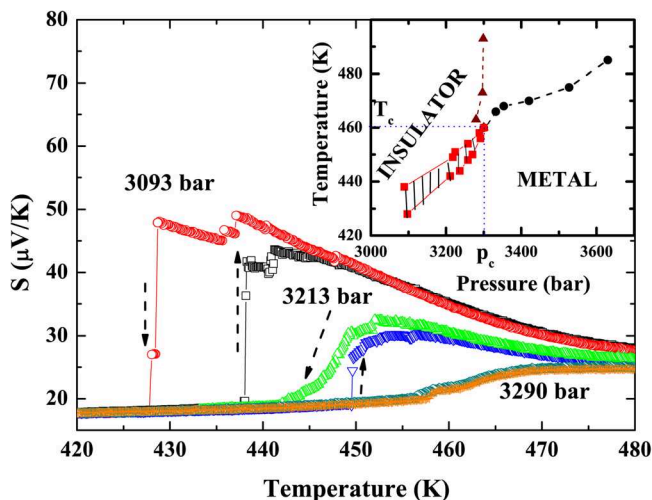


FIG. 2. (Color online) Thermopower of 1.1% Cr doped V_2O_3 as a function of temperature near the critical point. Insert: temperature-pressure phase diagram of 1.1% Cr doped V_2O_3 . The hatched region indicates the region of the hysteresis in S . The dashed lines represent the cross-over lines where S present an inflexion point upon cooling (circles) or increasing pressure (triangles). The dotted lines are guides to the eyes.

At higher pressures, the discontinuity and the hysteresis become smaller and finally vanish at the critical point. At pressures above the critical pressure p_c , it is possible to define a crossover line from the inflection point of the curves of Figs. 1(b) and 2. Similar data (not shown) can be obtained by measuring S as a function of pressure at fixed temperature. A second crossover line is then determined which allows the establishment of the pressure-temperature phase diagram shown in the insert of Fig. 2. Then, we were able to define the critical point by $T_c \approx 460\text{ K} \pm 2\text{ K}$ and $p_c \approx 3300\text{ bar} \pm 5\text{ bar}$. Within the experimental errors, the critical temperature is in agreement with the one found in electrical conductivity experiments,⁸ despite a different value for p_c which is attributed to a difference of Cr doping: a small difference in doping of 0.1% results in a difference of approximately 400 bar in p_c . Using the critical point (p_c, T_c) as the reference to correct for small shifts of doping from one sample to the other, we are able to calculate the power factor by using resistivity data of Ref. 7 provided a pressure correction is made. We note that no temperature correction is needed which confirms the similar quality of the samples from one batch to an other. With this in mind, it is possible to estimate the power factor (P_F) near the critical point where it may reach its maximum as a competition between (large) conductivity and (large) Seebeck coefficients.

As a first example, we calculated the power factor in the metallic phase at 400 K and 5000 bar. S measured in this work is $S \approx 20\ \mu\text{V/K}$ and the conductivity is $\sigma \approx 1200\ \Omega^{-1}\text{ cm}^{-1}$ deduced from Refs. 7 and 8 which gives a power factor of $P_F \approx 0.48\ \mu\text{W.K}^{-2}\text{ cm}^{-1}$ with an error of about 10% considering the possible errors in pressure shifts and measurements of the absolute values associated to geometrical factors. This value is quite small when compared to values obtained for other compounds such as $37.1\ \mu\text{W.K}^{-2}\text{ cm}^{-1}$ in TiS_2 ,¹⁴ $\approx 50\ \mu\text{W.K}^{-2}\text{ cm}^{-1}$ in Bi_2Te_3 (Ref. 15) or $10\ \mu\text{W.K}^{-2}\text{ cm}^{-1}$ in cobaltates¹⁶ but similar to values obtained in underdoped cuprates. The low value of P_F found here is related to the fact that V_2O_3 is the canonical example for the half-filled band Mott insulator where S should remain zero.¹ The existence of a finite thermopower is already the signature of an electron-hole band asymmetry which is not taken into account in single band models. Due to missing data for the thermal conductivity of V_2O_3 , it is only possible to calculate the factor of merit at one exemplary point. The only available value in the literature for pure V_2O_3 is $\kappa \approx 6\text{ Wm}^{-1}\text{ K}^{-1}$ at 400 K,¹⁷ which yields an approximate value for the metallic phase (e.g., $(\text{V}_{0.9}\text{Cr}_{0.1})_2\text{O}_3$ at 5000 bar) of $ZT = 3.2 \times 10^{-3}$ at 400 K. In the following, we will limit the discussion to the power factor.

In the insulating phase, at 400 K and 1000 bar we have $S \approx 150\ \mu\text{V/K}$ and $\sigma \approx 20\ \Omega^{-1}\text{ cm}^{-1}$ so $P_F \approx 0.45\ \mu\text{W.K}^{-2}\text{ cm}^{-1}$, which is equally small. The power factor in the region near the MIT can be found in Fig. 3. In Fig. 3(a), P_F is plotted against temperature just above the critical pressure at 3333 bar and further in the metallic region at 4050 bar. Both curves show very similar decrease of P_F between 300 and 500 K. Furthermore, in Fig. 3(b), P_F is plotted versus pressure at two different temperatures. Both curves at fixed temperatures, 458 and 473 K, exhibit a monotonous decrease of P_F with pressure. The sharp step

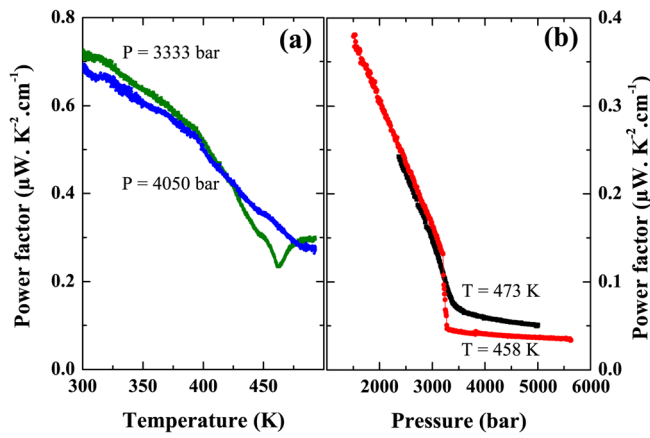


FIG. 3. (Color online) Power factor of 1.1% Cr doped V₂O₃ (a) at fixed pressure and variable temperature and (b) at fixed temperature and variable pressure.

observed at the lowest temperature is the manifestation of the transition from the insulating to the metallic phase. Finally, according to this analysis, it appears that the highest P_F can be found in the low temperature region in the metallic phase and not in a region where metallic (large σ) and insulating (large S) properties are competing. Our results also demonstrate the weak influence of the MIT on P_F despite a strong variation of both the conductivity (several orders of magnitude) and the thermopower (about one decade) when crossing this transition.

The theoretical approaches of the thermopower (TEP) in this material require including both e-e interactions and phonons, and such a theory is not available at this time. Here, we give some general qualitative arguments to show why such a behavior is expected to occur near a Mott transition. The transport coefficients in a material can be defined from the Boltzmann's equation approach.¹⁸ The electrical conductivity, $\sigma \propto K_0$ and the Seebeck coefficient, $S \propto K_1/(K_0T)$ so $P_F \propto K_1^2/(K_0T^2)$ with

$$K_n = -\frac{2}{3} \int \tau_k v_k v_k \left(-\frac{\partial f_0}{\partial \varepsilon} \right)_{\varepsilon=\mu} (\varepsilon(k) - \mu)^n d^3k,$$

where μ is the chemical potential, f_0 is the Fermi distribution function, $\varepsilon(k)$ is the band dispersion, $v(k)$ is the group velocity, and τ_k is the quasiparticle lifetime. K_1 is sensitive to the electron-hole asymmetry which varies weakly near the Mott transition. Indeed, the band structure is fixed by the electron-electron interactions: the bare band structure is replaced by a more complex structure with the existence of a quasiparticle

peak at the chemical potential energy which disappears at the Mott transition.¹³ Thus, the asymmetry of the band structure varies smoothly with pressure or temperature and is related only to the interactions and not to the bare band structure. Such evolution is in sharp contrast with doping in standard semiconductors which directly induces a change of the electron-hole asymmetry by shifting the position of the chemical energy with respect to the conduction and valence bands.

In conclusion, we presented the temperature and pressure dependent study of the thermoelectric power of the canonical Mott insulator, chromium doped V₂O₃, in the vicinity of its MIT. It is found that the strong electron-electron interactions at the Mott transition of V₂O₃ lead to a weak modification of the power factor at the transition in sharp contrast with both conductivity and thermopower variations. Finally, the largest value for P_F is found in the metallic state at low temperatures far from the Mott transition. The evolution of P_F with pressure (or equivalently chemical doping) is in sharp contrast with semiconductors where it is maximum for heavily doped semiconductors.¹⁹

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