Eur. Phys. J. B **16**, 205–208 (2000)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Rapid Note

Transport and optical conductivity in Na_xWO_3

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Received 28 March 2000

Abstract. We present the results of a dc transport and optical investigation of WO_3 and Na_xWO_3 with $x = 0.01$. Upon Na-doping we find a (Drude) metallic component in the optical conductivity, while the transport data display a crossover from an activated to a variable range hopping regime around 210 K. We suggest the possible formation of polarons (and bipolarons) and speculate that superconductivity could be induced, provided the dc percolation threshold is achieved.

PACS. 78.20.-e Optical properties of bulk materials and thin films – 74.25.Fy Transport properties (electric and thermal conductivity, thermoelectric effects, etc.)

Recently high-temperature superconductivity in WO_3 samples doped with sodium was reported [1,2]. According to the authors, in this system superconductivity seems to develop on the surface only, without propagating in the bulk. It is well known that in high-T_c superconducting perovskite cuprates (HTCS) superconductivity is quasi two-dimensional (2D) in character and is essentially confined to the CuO planes perpendicular to the c-axis [3]. The possibility of obtaining a system, where the structure is modulated so that superconductivity only develops at the surface, is very intriguing. While superconductivity in the WO_3 system is not new [4], a critical temperature of 91 K (*i.e.*, in the HTCS range) in the Na_xWO_3 system, which does not contain CuO planes or magnetic ions, is very interesting and could have important implications for the development of theories in high-T_c superconductors.

Reich *et al.* [1] observed on the surface of an insulator – the bulk of the WO_3 crystal – a transition from a semiconducting to a superconducting state in the high-T_c range upon surface doping with sodium. With a four point contact resistance measurement the authors found a semiconductor response above 100 K and a sharp drop towards a metallic or a superconducting state below 100 K, corresponding to the temperature of a diamagnetic transition [1]. This result seems to be quite robust since the depth of the diamagnetic step has decreased considerably when the surface of the crystals was covered by gold [1]. The resistance was also found to be dependent on the applied magnetic field. Moreover, electron spin resonance (ESR) measurements confirmed the first observation of superconductivity by showing that the ESR relaxation rate decreases significantly and it quantitatively follows the BCS theory [2]. Indeed, $1/T_1$ decreases in the same fashion as is known to occur in NMR when a gap opens in the superconducting state [2]. The gap was estimated to be $\Delta = 160$ K or $2\Delta/k_BT_c \sim 3.5$ [2]. Susceptibility measurements in field cooled and zero-field cooled modes suggest superconductivity of type II.

Further experiments are certainly needed in order to elucidate the quite intriguing superconductivity behaviour in Na-doped WO_3. Here we present transport and optical experiments as a function of temperature and magnetic field performed on $Na_{0.01}WO_3$ as well as on WO_3 pressed pellet samples. Transport data are expected to reveal the dominant scattering mechanism, while optical measurements are a powerful contactless measurement technique capable of revealing the intrinsic transport mechanisms and dynamical properties of the sample.

The Na_xWO_3 powder mixtures were prepared from WO_3 (Ventron, 99.7%), and Na_2CO_3 (Riedel de Haen, p.a.). Batches of 20 g were homogenized, pressed into pellets (diameter 12 mm) and calcined in closed alumina crucibles on Pt foil at 950 °C for 4 hours in air. This procedure was then repeated twice. The resulting samples were milled for 4 hours in planetary mill in acetone medium. From this powder, pressed pellets (diameter of about 8 mm) were obtained and annealed at 950 °C for 4 hours in flowing argon atmosphere. From other experiments [1] it is known that for $x \geq 0.05$ the presence of $Na_2W_4O_{13}$ is detected in the X-ray analysis and SEM microstructure photographs reveal the presence of a secondary phase in between the grains in Na_xWO_3. Consequently, we did not investigate samples with $x > 0.01$ to avoid problems with impurity phases. No impurities of any

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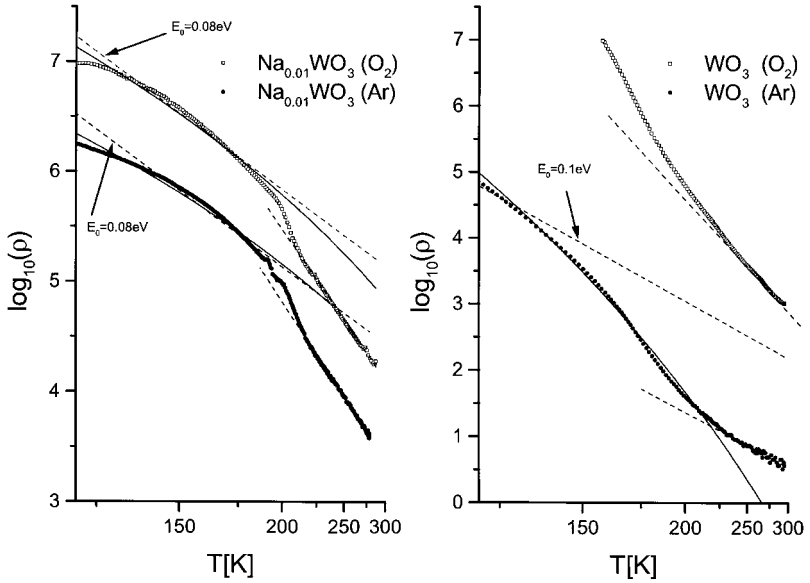

Fig. 1. Temperature dependence of the resistivity in WO_3 and $Na_{0.01}WO_3$ annealed in Ar and oxygen. Note the abscissas are plotted using a reciprocal scale. The solid lines are calculated using the VRH model. The dashed lines are exponential fits (see text).

kind were detected for our measured samples with $x = 0$ and 0.01.

The resistance of the ceramic pellets was measured using the standard 4-probe technique with gold paste contacts using either a Keithley 237 current source measuring unit or a combination of current source (Keithley 237)/electrometer (Keithley 2000). Linear I-V characteristics were found to be intrinsic at all temperatures measured. Non-linear I-V characteristics, which were sometimes obtained, were determined to be a sign of either sample degradation or bad contacts. Great care was taken to ensure that the measurement time for each point was substantially longer than the electrometer integration time in order to avoid possible artifacts in the resistivity at high values of resistance. Some slight changes in the resistance of the order of a few percent were observed on thermal cycling, and since exposure to light strongly influenced the value of the resistance [5], the samples were held in the dark during the measurements.

The reflectivity $R(\omega)$ was measured as a function of temperature between $T = 300$ K and $T = 6$ K over a broad spectral range from 5×10^{-3} up to 4 eV, using three different spectrometers with overlapping frequency ranges (see Ref. [6] for more technical details). In the far infrared (FIR) spectral range the reflectivity was also measured with a magnetic field of 6 T. The real part $\sigma_1(\omega)$ of the optical conductivity was obtained from Kramers-Kronig (KK) transformations of the measured reflectivity. Standard extrapolations were used above our highest frequency limit, while below the lowest measured frequency we performed either a Hagen-Rubens (HR) extrapolation for a metallic behavior or an extrapolation to a constant reflectivity value for the insulating case (see below).

In Figure 1 we show a semilogarithmic plot of the temperature dependence of the resistivity for the samples with $x = 0$ and $x = 0.01$ annealed in Ar and O_2. All samples appear to show exponentially activated behavior from room temperature to approximately $T_a \approx 210$ K, with a distinct break in the slope (activation energy) at this temperature. The measurements on undoped ($x = 0$) samples are in agreement with previous work on undoped WO_3 [7]. The activation energies determined from fits to the data using the simple activated hopping model $\rho = \rho_0 \exp[-E_0/kT]$ are shown in Table 1. Note that the activation energy E_0 is approximately twice as large in the Na-doped samples with $x = 0.01$ than in the Ar-annealed sample with $x = 0$. Below T_a, we find that the resistivity behaves more or less according to a power law of the form $\rho = \rho_0 \exp[-T_0/T]^n$ with $n \approx 1/4$. In Figure 1 we have plotted curves with the variable range hopping (VRH) model with $n = 1/4$ superimposed on the data. There is some deviation from the VRH law, though not so remarkable. There appears to be very little difference between the two differently annealed samples with $x = 0.01$ below T_a. In the case of the $x = 0$ samples, the data for the O-annealed samples do not extend far enough to low temperatures to be able to make any firm statements about the behavior in the O-annealed WO_3 sample below 200 K, while the Ar-annealed sample data are in good agreement with data from Schirmer and Salje [4]. From the resistivity measurements we can conclude that both Na-doped and undoped samples appear to be semiconducting with an abrupt transition from simple activated hopping

Table 1. Activation energies obtained from the resistivity measurements for the different samples above 200 K.

Sample	$E_0(T > T_a)$ [eV]
WO_3 Ar	0.095 ± 0.01
WO_3 O_2	0.25 ± 0.03
Na_xWO_3 Ar	0.17 ± 0.01
Na_xWO_3 O_2	0.16 ± 0.01

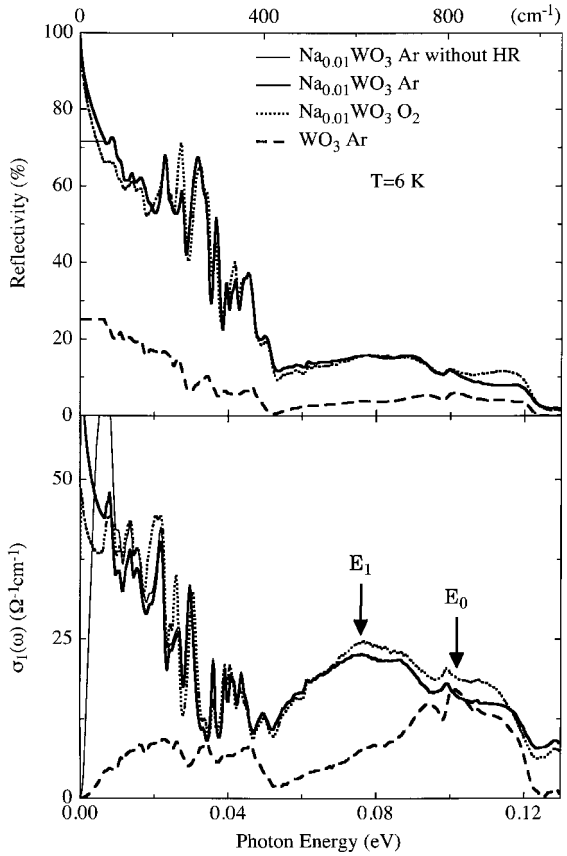

Fig. 2. Optical reflectivity (a) and conductivity (b) of WO_3 and $Na_{0.01}WO_3$. The arrows indicate E_0 and the (bi)polaron excitation E_1, the latter being ascribed to doped electrons. The results of the KK analysis for both HR and constant extrapolations of $R(\omega)$ towards zero-frequency in Na-doped WO_3 are shown for comparison. The difference only appears at very low frequency (*i.e.*, $\omega < 0.02$ eV).

to variable-range hopping near $T_a \sim 210$ K. It is somewhat puzzling that ρ_{dc} at 300 K for the Na-doped material is higher than for the pristine WO_3 compound. This is in contrast to the trend suggested by the optical data (see below). We can attribute this apparent discrepancy to the percolative nature of the dc resistivity, where inter-grain boundaries of the ceramic samples play an important role.

Our resistivity curves are in any case significantly different to the data reported by reference [1]. A significant result is the absence of any superconductivity transition. WO_3 is considered to be a representative material for the formation of polarons [4]. With this in mind, the fact that the high-temperature activation energy E_0 in the Na-doped samples is approximately twice of the Ar-annealed undoped sample suggests the formation of bound polaron pairs (bipolarons) in this temperature range. Indeed, preliminary SQUID susceptibility measurements on Na-doped samples show that the susceptibility of the Na-doped samples is significantly smaller than expected from the $x = 0.01$ doping concentration [8], implying the formation of spin-singlet bipolarons. Ar annealing is seen to result in a decrease in resistivity, which is consistent with oxygen deficiency resulting in increased electron doping [9].

Figure 2 shows the reflectivity spectra $R(\omega)$ and the corresponding real part $\sigma_1(\omega)$ of the optical conductivity below 0.12 eV for the two samples at 6 K and zero magnetic field. We did not find any temperature or magnetic field dependence in the optical spectra of either compound. Particularly for the Na-doped sample, there is no optical signature of any insulator-metal transition with lowering temperature, as suggested in $\rho(T)$ of reference [1], nor do we observe any detectable changes occurring near 210 K. The optical spectra are not sensitive to the quite strong temperature dependence of the dc resistivity $\rho(T)$, even though $\rho(T)$ increases by a few orders of magnitude between 300 K and low temperatures (Fig. 1). Indeed, the very low dc-conductivity values are beyond the precision of the optical measurements. Nevertheless, it is evident in the spectra that Na-doping strongly affects the optical properties of the WO_3 system. Indeed, the optical reflectivity (Fig. 2a) of WO_3 is very low and insulator-like, and is barely possible to perform a HR extrapolation. On the other hand, the Na-doped sample shows an increase in reflectivity in the FIR spectral range (Fig. 2a). Several sharp phonon-like absorptions are overlapped with an apparently overdamped plasma edge (*i.e.*, the scattering rate is larger than the plasma frequency) with onset around 0.06 eV. The reflectivity spectra are very similar for O_2 and Ar annealed samples. The increasing reflectivity with decreasing frequencies in $Na_{0.01}WO_3$ allows the use of a HR extrapolation for $\omega \to 0$. The σ_{dc} values used for the HR are low: $\sigma_{dc} = 90\,(\Omega\,\mathrm{cm})^{-1}$ for the argon annealed sample and 60 $(\Omega\,\mathrm{cm})^{-1}$ for the oxygen one. These values are higher than the ones obtained from transport measurements performed on the same samples (Fig. 1). As already mentioned, such a discrepancy can be due to the fact that the reflectivity measurement is a contactless technique and grain contacts play no role. However, since the reflectivity is so overdamped, we cannot completely rule out the possibility of a constant value extrapolation (instead of HR) which would be typical of an insulating behavior. It could be argued that, although we see the onset of (overdamped) metallic behavior, at energies beyond our measurable spectral range ($\omega < 0.002$ eV) the appropriate extrapolation might be a constant. However, the remarkable difference in the raw optical reflectivity spectra due to Na doping and particularly the clear enhancement of the FIR reflectivity for $Na_{0.01}WO_3$ supports our use of the HR extrapolation. In any case the main features of the optical conductivity above 0.02 eV are not affected by the choice of extrapolation in either case and for reference the optical conductivity using a constant value low-frequency extrapolation of $R(\omega)$ is also plotted in Figure 2.

In the FIR spectral range of the optical conductivity (Fig. 2b) one can recognize a small effective (Drude) metallic contribution for $Na_{0.01}WO_3$. In contrast, $\sigma_1(\omega)$ for WO_3 is insulating-like. There are several sharp absorptions in $\sigma_1(\omega)$ of $Na_{0.01}WO_3$. In WO_3, the FIR spectrum is mainly characterized by broader and less intense absorptions (with respect to the Na-doped sample). These modes can be most probably ascribed to the symmetry-breaking induced optically active phonons. The formation

of polarons can locally change the lattice symmetry activating new phonon modes, which may be otherwise Raman active or silent, and enhance the oscillator strength of the FIR active ones modes.

In the mid-infrared range a broad absorption band centered at about 0.1 eV dominates the spectra. In the undoped sample, the absorption near 0.1 eV in the optical conductivity of WO_3 could be considered as the optical counterpart of the energy gap E_0 in the transport measurements. Upon Na doping, a new broad feature around $E_1 = 0.08$ eV acquires considerable spectral weight (in addition to the low-frequency Drude-like feature in the FIR). We attribute this new feature to doped-electron (bi)polarons introduced by Na doping (see arrows in Fig. 2b). This feature in $Na_{0.01}WO_3$ cannot be directly identified with an activation energy in the dc resistivity measurements, where the transport is dominated by variable range hopping at low temperatures. Nevertheless, plotting in Figure 1 the expected T-dependence of the dc resistivity which would correspond to the activation energy of 0.08 eV and 0.1 eV in $Na_{0.01}WO_3$ and WO_3, respectively, we find that the two types of measurements (transport and optics) are not necessarily inconsistent below T_a.

In the infrared we also observe a peak (not shown here) at higher frequency (with an onset at about 1 eV) that most probably corresponds to an interband transition. The intensity of this absorption slightly depends on the extrapolation used for frequencies above the measured ones. Here we are more interested in the low frequency range and specifically in the doping dependence of the transport properties, which are not affected by the high frequency extrapolation. Summarizing the optical findings, we can say that in our spectra a weak metallic component can be recognized in the Na-doped specimen but we do not find any evidence of superconductivity and of a temperature-induced transition from insulating to metallic behavior [1].

Our results are not fully consistent with those reported on single crystals by Reich *et al.* [1] and Shengelaya *et al.* [2]. We can formulate several possibilities to explain this apparent discrepancy. The superconductivity in these materials was suggested to develop only on the surface of an otherwise semiconducting sample. As far as optics is concerned, the superconducting layer could be too thin for the penetration depth of infrared light which could essentially reveal the signal due to the (semiconducting) bulk of the WO_3 sample. If we model the expected response of a system composed of a thin superconducting layer on an insulating substrate, we find that the measured total reflectivity is dominated by the contribution of the insulating substrate. Moreover, Shengelaya *et al.* [2] indicated that in WO_3:Na superconductivity probably occurs in a small fraction of the sample and that the superconducting clusters of unknown phase should form a non-percolating network. The very low doping concentration of Na – which is apparently necessary to achieve superconductivity – makes the presence of several phases rather likely and recent measurements support this point of view [2]. The multiphase character and the absence of percolation of the samples could prevent transport and infrared measurements from revealing the superconducting signal of a small superconducting fraction of the sample in an insulating medium. This is particularly true for optical measurements where a weighted average of the optical response is obtained. This is quite similar to the situation encountered in measurements on HTCS pressed pellet samples (before the single crystals become available) which also did not show any clear sign of superconductivity [10]. Indeed, the non-superconducting material present on the surface of the specimens and the mixing of the c-axis and ab-plane contributions of a highly anisotropic material considerably affected the optical measurements of polycrystalline specimens [10].

In conclusion, we have found a Drude component in the optical conductivity which clearly develops upon Na-doping the WO_3 system, which is otherwise insulating. In addition, a mid-infrared feature near 0.08 eV attributed to polaron hopping can clearly be identified in the Na-doped samples. Transport measurements are found to show evidence for a transition from temperature-activated Arrhenius behaviour to VRH transport in the Na-soped material near $T_a = 200$ K, which, however, is not detected in the optical conductivity. The polycrystalline form of the samples and the fact that doping only occurs on the surface prevent any clear identification of a superconducting phase transition in the system. We might speculate that the onset of superconductivity in these compounds might be found to coincide with the achievement of the dc percolation threshold.

We wish to acknowledge useful discussions with V.V. Kabanov. The work in Zurich has been supported by the Swiss National Foundation for the Scientific Research.

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