Rapid Note

Transport and optical conductivity in Na\textsubscript{x}WO\textsubscript{3}

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Abstract. We present the results of a dc transport and optical investigation of WO\textsubscript{3} and Na\textsubscript{x}WO\textsubscript{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\textsubscript{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-temperature superconductors (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\textsubscript{3} system is not new [4], a critical temperature of 91 K (i.e., in the HTCS range) in the Na\textsubscript{x}WO\textsubscript{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\textsubscript{c} superconductors.

Reich et al. [1] observed on the surface of an insulator – the bulk of the WO\textsubscript{3} crystal – a transition from a semiconducting to a superconducting state in the high-T\textsubscript{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\textsubscript{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 \(2\Delta/k_B T_c \sim 3.5\) [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\textsubscript{3}. Here we present transport and optical experiments as a function of temperature and magnetic field performed on Na\textsubscript{0.01}WO\textsubscript{3} as well as on WO\textsubscript{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\textsubscript{x}WO\textsubscript{3} powder mixtures were prepared from WO\textsubscript{3} (Ventron, 99.7%), and Na\textsubscript{2}CO\textsubscript{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\textsubscript{0.2}W\textsubscript{4}O\textsubscript{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\textsubscript{x}WO\textsubscript{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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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 \( 5 \times 10^{-3} \) 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 \( \rho = \rho_0 \exp[-T_a/T]^n \) 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

![Figure 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).](image)

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_0(T &gt; T_a) [eV] )</th>
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<tbody>
<tr>
<td>( WO_3 ) Ar</td>
<td>0.095 ± 0.01</td>
</tr>
<tr>
<td>( WO_3 ) ( O_2 )</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>( Na_{0.01}WO_3 ) Ar</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td>( Na_{0.01}WO_3 ) ( O_2 )</td>
<td>0.16 ± 0.01</td>
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