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LETTER TO THE EDITOR

Sheet superconductivity in twin walls: experimental evidence of WO_{3-x}

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Abstract. Single crystals of WO_3 that contain ferroelastic twin walls have been chemically deoxygenated using a gas transport reaction with Na vapour. The reaction product consists of a non-superconducting matrix of tetragonal WO_{3-x} and superconducting twin boundaries. The superconducting transition temperature is 3 K. The upper critical field has been measured; its temperature dependence shows BCS type behaviour at $T < 2.5$ K and a weak tail near T_c.

Tungsten oxide, WO_3, which has been weakly reduced to WO_{3-x} with $3-x$ typically in the order of 2.95, shows the formation of bi-polarons in its structural ε-phase [1]. Illumination with light leads to a polaronic photoeffect in which bi-polarons are split into pairs of polarons. These polarons were analysed by optical spectroscopy and EPR techniques [2, 3].

The obvious prediction for high bi-polaron density systems is that Bose condensation should lead to superconductivity below the condensation temperatures. Salje *et al* [1] have tested a sample with a carrier concentration of 0.33×10^{18} cm^{-3} in a temperature range down to 9×10^{-5} K. No superconductivity was found; instead bi-polarons were localized near structural defects.

In this letter we report the results of a new experimental study in which the carrier concentration was increased by vapour phase reaction with sodium. In order to reduce WO_3 to WO_{3-x}, the orthorhombic sample was heated at 730 K for variable time lengths, along with metallic sodium. A U-shaped silica tube was used, in which the sample and the metallic sodium were placed in opposite ends. The tube was evacuated and heated, so that sodium vapour was transported onto the sample, reducing the surface under the formation of Na_2O. Parts of the sample further from the surface subsequently became reduced due to the high oxygen mobility in WO_3. This resulted in a bluish–black coloured final product which is distinct from the yellow–green of the starting material. The reflected light microscope image showed that the regions along the original orthorhombic–tetragonal twin boundaries [4] were more highly reduced. This can be seen directly via the colour change in a cleaved sample. In figure 1, a sample with two domain walls is shown. The increased levels of reduction caused the crystal to change colour to dark yellow, then to red, as occurs towards the edge of the crystal, which is the bottom right area of the photograph. This is in marked contrast with the bluish appearance of the bulk. The walls of the domains appear dark yellow, shown as dark grey in the photograph, indicating their decoration with the superconducting phase.

Various orientations of walls were found. Their orientation is perpendicular to the cleavage plane with two sets of nearly orthogonal ferroelastic walls. The two sets are

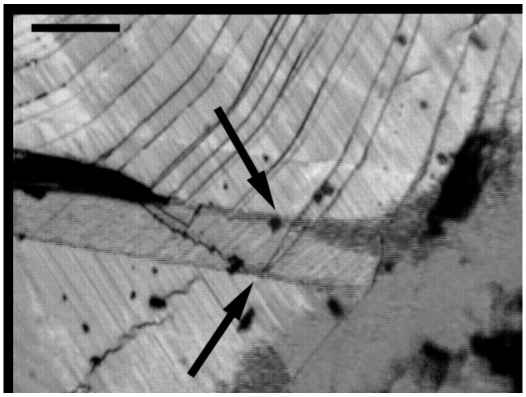

Figure 1. A twinned crystal of reduced WO_3, showing the superconducting phase along the domain boundaries (marked by black arrows). The scale bar in the top left corner is 50 μm.

oriented at 45° with respect to each other. The orientations of the walls correspond to the ferroelastic transformation of the tetragonal–orthorhombic and orthorhombic–monoclinic transition in WO_3. In many samples only one wall orientation is observed; these parallel walls transverse the entire sample, i.e. the crystal has a ‘stripe’ domain pattern.

Structure analysis using single crystal x-ray diffraction of uniformly reduced material showed that the reduced bulk material appears as a tetragonal phase similar to the orthorhombic structure [5] and not as the more common CS phases [6]. This tetragonal phase was found to remain stable for large grains (typically 1 mm diameter), but fine grained material was found to convert to CS phases after a few days at room temperature. No sodium was found inside the sample using repeated analysis with a secondary electron microprobe, although some contamination was sometimes seen at the surface.

The superconducting phase transition was found by measurements of the d.c. conductivity using the four-probe technique. Figure 2(a) shows the temperature dependence over an extended temperature range. At temperatures well above T_c semiconducting behaviour is found. For zero field, the transition temperature is 3 K (figure 2(a)). With increasing magnetic field the transition temperature is suppressed. The temperature dependence of $H_{c2}(T)$ shows surprisingly high absolute values and strong similarity to BCS behaviour at $T \ll T_c$. A slight positive curvature near 3 K may be due to magnetic impurities or due to the sheet nature of superconductivity. In order to test for bulk superconductivity, several samples were measured using a SQUID magnetometer which was previously calibrated using an indium sample with transition temperature of 3.4 K [7]. No SQUID signal was found on any weakly reduced sample which we take as an indication that the bulk of our crystals is not superconducting in the range of chemical composition considered in this study.

No magnetic screening is expected in these samples with parallel superconducting domain walls. In much more highly reduced material (with possibly more complex wall structures) a weak SQUID signal has been observed which could be estimated to relate to a superconducting fraction of $\approx$2%. This feature is subject to further investigation. Within the context of this letter it is important to note that samples with parallel domain walls show dc superconductivity along the walls but no screening effect in magnetic measurements. We understand this observation as an indication that superconductivity exists only in the domain walls and not in the embedding matrix.

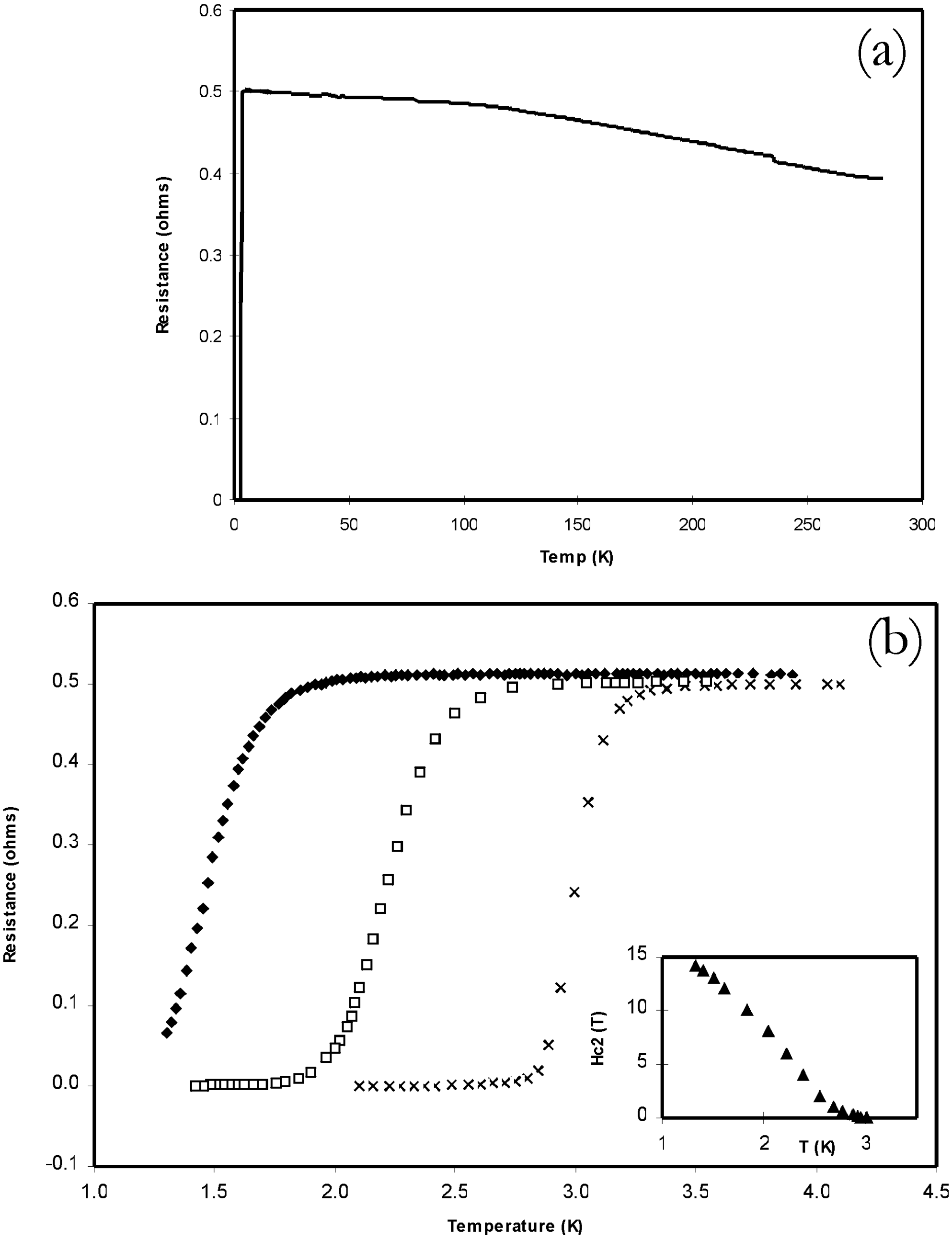

Figure 2. Resistivity of a reduced WO$_{3-x}$ sample with mainly parallel domain walls over an extended temperature interval (a). The field dependence of the resistivity is shown for low temperatures in (b). The fields are 0 T (×), 6 T (□) and 13 T (◆). The inset shows the temperature dependence of H_{c2}.

To our knowledge, this result is the first in which sheet superconductivity on domain walls was reproducibly generated in any superconducting material. The significance of this discovery is obvious for potential device applications with high densities of active and passive components. High values of H_{c2} give us hope that the critical currents J_c may be sufficient for such device applications. From a purely scientific view, this sheet superconductivity could lead to better in-depth studies of correlation effects, weak links, Andreev mirrors, 2D vortex motion etc [8–10]. A detailed description of the crystallographic characterization of the bulk and the wall structures will be published separately.

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