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Rapid Note

Possible nucleation of a 2D superconducting phase on WO_3 single crystals surface doped with Na^+

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Abstract. WO_3 crystals with a surface composition of $Na_{0.05}WO_3$ were grown. These crystals exhibit a sharp diamagnetic step in magnetization at 91 K, and a magnetic hysteresis below this temperature. As the temperature is lowered below 100 K in transport measurements, a sharp metal to insulator transition is observed, this is followed by a sharp decrease in the resistivity when the temperature is lowered to about 90 K. When the surface of the crystals was covered by gold the depth of the diamagnetic step had decreased considerably. These results indicate a possible nucleation of a superconducting phase on the surface of these crystals. This is a non cuprate system exhibiting a critical temperature in the HTS range.

PACS. 74.70.-b Superconducting materials (excluding high-T_c compounds) – 74.20.-z Theories and models of superconducting state – 74.60.Ec Mixed state, critical fields, and surface sheath

Two dimensional and quasi 2D superconductivity are common phenomena. The first example goes back to 1963 when Saint-James and de Gennes [1] showed that in an ideal sample with anhomogenous order parameter the nucleation of superconducting regions in decreasing field should always occur near the surface of the sample. For a superconductor of the second kind this implies that in fields $H : H_2 < H < H_3$ there remains a superconducting sheath on some parts of the sample confined to a thickness of the order of the correlation length ξ. In HTS perovskite cuprates the order parameter is spatially modulated along the c axis as the superconductivity is quasi 2D in character and is confined to the CuO planes coupled by Josephson junctions. A question arises about a possible system in which the structure is modulated in such a way so that superconductivity will develop on the surface only, not a type III superconductivity, and will not propagate into the bulk. In this short paper we suggest that WO_3 single crystals doped on the surface with sodium may constitute such a superconductor. This is a non cuprate system with a critical temperature of 91 K.

The $5d$-transition-metal oxides WO_3 and Na_xWO_3 are similar in electronic structure to $3d$ oxides. They have nearly the ABO_3 perovskite crystal structure, with the W ions occupying the octahedral B cation sites. In WO_3 the A cation site is vacant, while in Na_xWO_3 the Na^+ ions occupy that site. Stoichiometric WO_3 is an insulator, since the W $5d$ band is empty; when Na ions are added to WO_3, they donate their $3s$ electron to the W $5d$ band, resulting in bulk metallic behavior for $x \geq 0.3$ [2,3]. These materials in tetragonal or hexagonal form exhibit also bulk superconductivity at sub-liquid helium temperature [4,5]. Sheet superconductivity at 3 K in twin walls of a non superconducting tetragonal WO_{3-x} was reported by Aird *et al.* in 1998 [6,7]. For $x < 0.3$ the Na_xWO_3 sodium tungsten bronzes, formed by doping the insulating host WO_3 with Na^+ ions, are n-type semiconductors.

We prepared single crystals in which the surface is doped with Na^+ ions following the method described in reference [8]. We introduced WO_3 powder, which contains 0.5% atomic concentration of sodium, into platinum tubes 10 cm long and 0.5 cm in inner diameter.

These tubes were sealed at both ends and introduced into a tube furnace. They were kept at 1370 °C for 30 hours and then cooled at 2 °C/h to 1230 °C. In the last step of the temperature cycle they were cooled to R.T. at a rate of 80 °C/h. The temperature gradient in the furnace at 1370 °C was ≈ 5 °C/cm. The resulting crystals have cubic morphology, see Figure 1, and are a few hundred μm in size. These crystals exhibit a deep olive green color. X-ray and XPS show the WO_3 perovskite-like structure and composition with a surface enrichment of sodium to 5% atomic concentration. The surface composition is thus $Na_{0.05}WO_3$. In ternary materials such as sodium tungsten bronzes there is the possibility that the chemical composition close to the surface differs significantly from that of the bulk. In particular, one can envisage surface sodium depletion or enrichment without major structural upheaval [9]. The 4f (1/2); 4f (5/2) tungsten spectra observed on the surface by XPS show W^{6+} valence

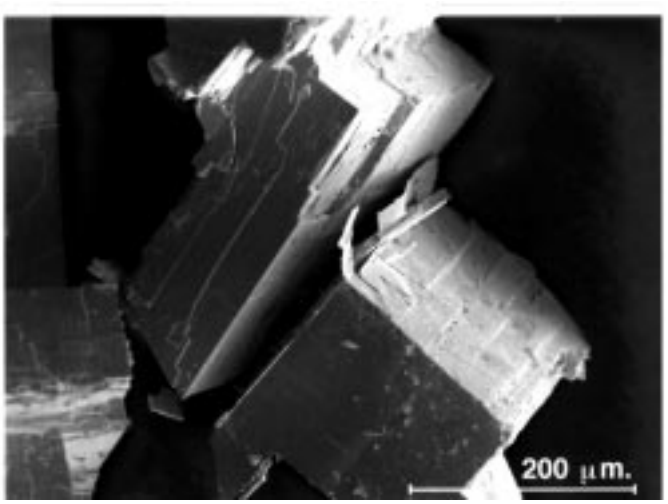

Fig. 1. STM micrograph of WO_3 crystals coated with gold.

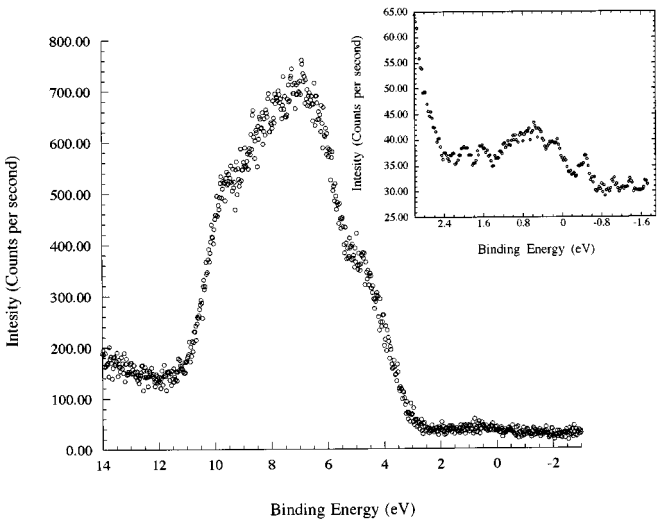

Fig. 2. XPS spectrum of the valence band. Inlay: finite density of states near the Fermi level.

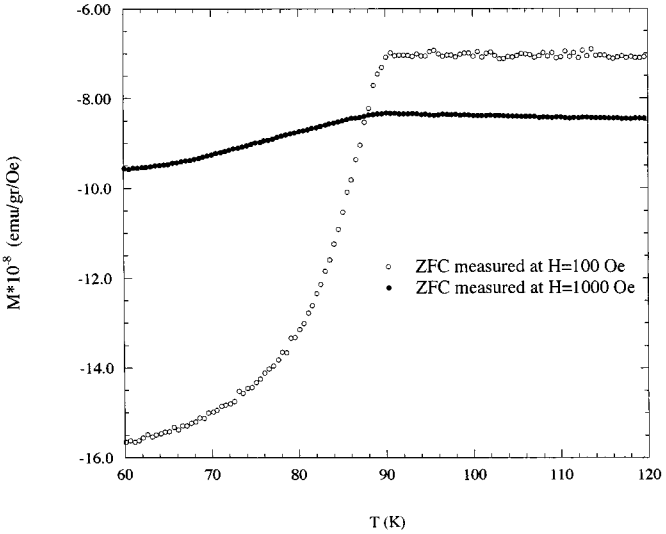

Fig. 3. Zero field cooled magnetic moment *vs.* temperature curves normalized by the magnetic field: (○) measured at 100 Oe; (●) measured at 1000 Oe in a heating cycle.

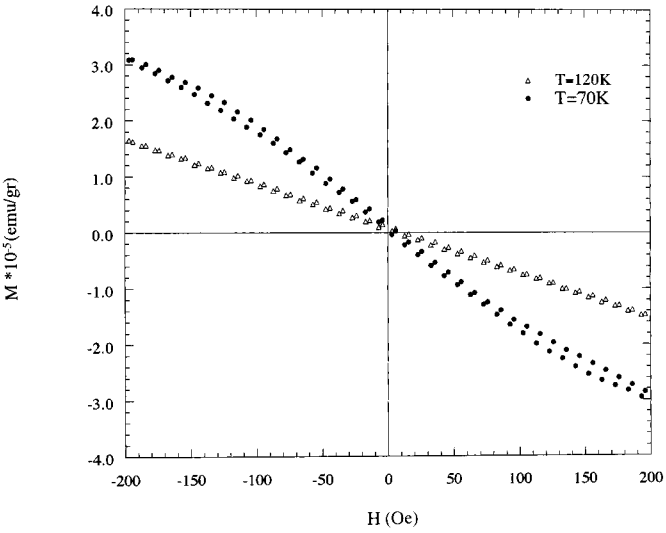

Fig. 4. Magnetization loops measured at $T = 70$ K and $T = 120$ K.

state. A finite electron density is observed near Fermi level due to the sodium doping, see Figure 2.

Zero fields cooled (ZFC) magnetic moment, normalized by the field, *vs.* temperature curves are shown in Figure 3. These curves were measured with a $MPMS_2$ SQUID magnetometer at 100 Oe and at 1000 Oe in a heating cycle. The crystals are diamagnetic and a sharp diamagnetic transition step at 91 K is observed in the low field run. (This value coincides with the T_c of YBCO. We performed therefore the necessary experiments to exclude the possibility of YBCO contamination in the instrument or in the samples.) At 1000 Oe the diamagnetic step is diminished and the transition is lowered by one degree. For $T > 91$ K the curves do not coincide because of the non-linear field response, see inlay in Figure 5. This diamagnetic step was observed in eleven samples derived from crystals prepared in three independent thermal cycles. In the low temperature range five phase transitions [8] were identified in tungsten trioxide. At 40, 65, 130, 220, and 260 K, none of those coincides with the 91 K diamagnetic step observed in our measurements, in a magnetization *vs.* temperature run we identify only the 260 K transition.

In Figure 4 we show magnetization loops *vs.* field for $T = 70$ K, below the diamagnetic transition step, and for 120 K, above the step. At 120 K a linear non- hysteretic response is observed in the measured range. At 70 K the response is non-linear and the loops are open. To observe the above signals with a good signal to noise ratio; 20:1 in the 10^{-7} emu range, it is necessary to use a well tuned SQUID preferably with a magnetic shield.

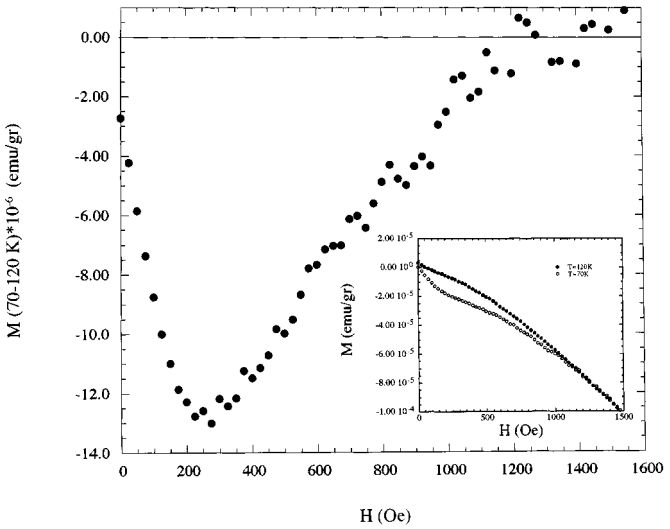

Fig. 5. Difference in magnetic moment between 70 K and 120 K as function of external magnetic field. Inlay: Magnetic moment *vs.* field for two virgin isotherms: $T = 120$ K and $T = 70$ K.

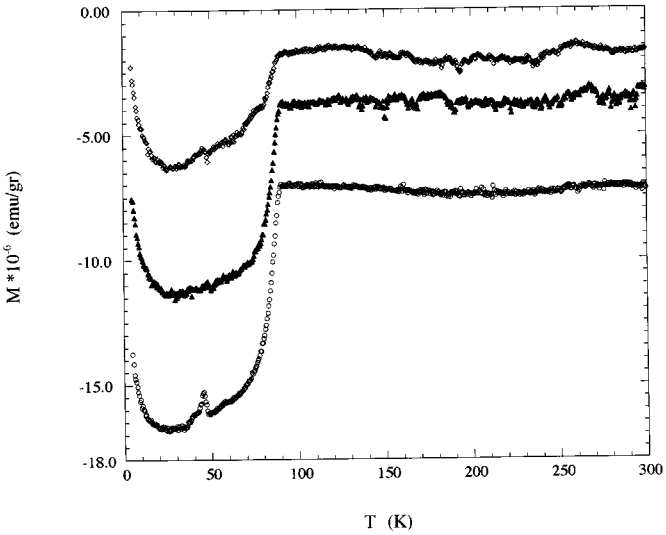

Fig. 7. Magnetic moment *vs.* temperature (ZFC) measured at 100 Oe in a heating cycle. (○) Bare crystals, (▲) crystals coated with gold after first sputtering process, (◇) after second sputtering process.

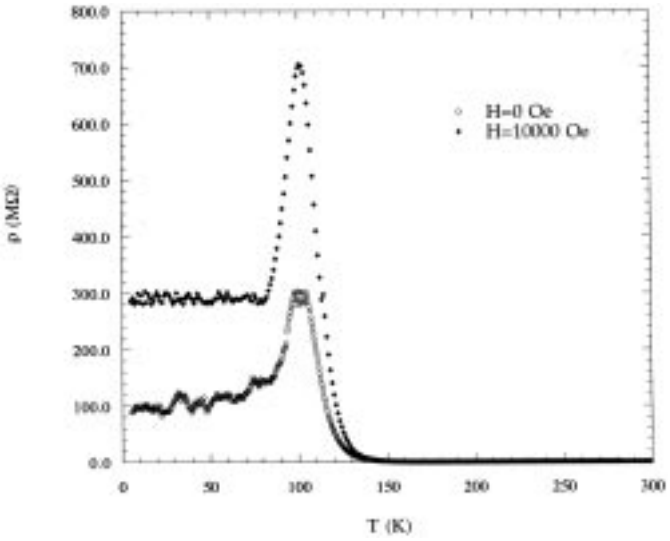

Fig. 6. Four point resistance measurement in a WO_3 , Na^+ doped on the surface, single crystal as function of temperature: (♦) H = 10^4 Oe, (○) H = 0.0 Oe.

In Figure 5 we show the difference in magnetic moment between a virgin magnetization curve measured at 70 K and a virgin curve measured at 120 K, see inlay $0 \leq H \leq 1500$ Oe. The difference curve which shows the temperature dependence of the additional diamagnetism below the transition step is reminiscent of a curve characteristic of a type II superconductor with $H^* = 230$ Oe.

A transport four point measurement on a single crystal using a current of 10 nA, in a voltage limiting mode of 10 V, is shown in Figure 6 for $H = 0$ Oe and for $H = 10^4$ Oe. Above 100 K a semiconductor response is observed. Below 100 K a sharp drop in resistance is measured revealing the onset to a metallic or a superconducting transition. The center of this transition coincides with the diamagnetic transition. It is clear that if a superconducting phase nucleates it does not percolate and instability develops which causes the leveling of the resistivity. In this cryogenic temperature range we observe a noisy and unstable response, where resistance increases with magnetic field as the superconducting fraction is diminished. An incomplete percolation of superconducting regions, 3D case, was observed in the discovery of superconductivity in the Ba-La-Cu-O system by Bednorz and Muller in 1986, Figure 1, [10], our system is more 2D like. Note that on the semiconducting side a large magneto-resistance effect is observed.

In Figure 7 we show the ZFC magnetic moment *vs.* temperature dependence for the bare $Na_{0.05}WO_3$ (surface composition) crystals (bottom curve). These crystals were then coated with pure gold in two consecutive sputtering runs. In each run the spacial orientation of the crystals was randomized during sputtering. After each coating with gold the sample was remeasured. We observe that upon improvement of the gold cover the diamagnetic signal below 91 K is diminished. A twofold drop in the diamagnetic signal after two sputtering runs is observed. This experiment strongly suggests that the source of the additional diamagnetism below the transition temperature is the surface of the crystals. The leakage of the S.C. wave function from the surface of the crystal into the gold sheath is probably causing the decrease in the diamagnetic signal [11]. At cryogenic temperatures a considerable paramagnetic contribution is measured. This paramagnetic contribution is due to sub 0.1% atomic concentration of Cu^{++} impurities as detected by XPS.

We can estimate the lower limit for the width, d, of the non-continues sheath carrying the additional diamagnetism below 91 K. The measured additional susceptibility in small magnetic field is: $\chi^{\rm add} = -5.5 \times 10^{-7}$ emu/cm^3 Oe, see Figure 5. Modeling the single crystals as cubes with a characteristic size $l = 3 \times 10^{-2}$ cm. and assuming a uniformly random coverage, below the 2D site percolation threshold $p_{\rm c} \cong 0.7$, of the surface by the diamagnetic sheath we can write:

$$\chi^{\rm add} \frac{l^3}{6l^2 d} = -\frac{1}{4\pi} p_{\rm c}$$

which yields $d \geq 5$ Å.

If our interpretation is correct we observe on the surface of an insulator – the bulk of the WO_3 crystal – a transition from a semiconducting to a 2D superconducting state in the high $T_{\rm c}$ range upon surface doping with sodium.

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