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Rapid Note

Electron spin resonance and magnetic susceptibility suggest superconductivity in Na doped WO_3 samples

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Abstract. In WO_3 doped with Na (WO_3:Na) an Electron Spin Resonance (ESR) signal with unresolved fine and/or hyperfine structure is detected and used as a probe for the state of the carriers. Using the saturation method we determined the spin-lattice relaxation rate $1/T_1$ of these paramagnetic centers. Upon cooling below 100 K, $1/T_1$ decreases markedly, as known to occur in NMR when a gap opens in the superconducting state. At low temperatures, $1/T_1$ quantitatively follows BCS behavior with a gap $\Delta = 160$ K or $2\Delta/kT_c = 3.5$. The magnetic susceptibility exhibits a strong difference between magnetic-field cooled and zero-field cooled regimes below T_c which also supports a so far unknown superconducting phase resulting from Na doping.

PACS. 74.72.-h High-T_c compounds – 76.30.-v Electron paramagnetic resonance and relaxation

Recently, two of the present authors (S. R. and Y. T.) have reported susceptibility and resistivity measurements in WO_3 surface doped with Na [1], from which they inferred the onset of high-temperature superconductivity at $T_c = 91$ K. In contrast to the high-temperature cuprate superconductors, WO_3 does not have an antiferromagnetic (AFM) Mott-insulator background when undoped. In the cuprates the strong AFM fluctuations prevent the detection of intrinsic ESR signals [2]. Only recently has the ESR signal from the trapped Jahn-Teller (JT) polarons been observed in $La_{2-x}Sr_xCuO_4$ [3]. Therefore we have undertaken the search for ESR signals in WO_3:Na, and met with success. As shown hereafter, a signal with unresolved structure is detected around a g-factor of $g \sim 2$. In this Note, we present the temperature dependence of the spin-lattice relaxation of this signal. Below the range of the reported T_c, the ESR relaxation rate decreases significantly, and it quantitatively follows BCS theory as was first observed in the classical NMR relaxation experiments [4]. *This is the first ESR observation of this kind in any superconductor, be it classical or non-classical.* In the course of the present experiments, it was also observed that the field cooled and zero-field cooled dc susceptibilities differ strongly below T_c, as it was first found in the cuprate superconductors [5]. This observation quite strongly supports the ESR indications for superconductivity in the WO_3:Na samples.

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The ESR measurements were performed at 9.4 GHz using a BRUKER ER-200D spectrometer. The WO_3:Na samples used here are the same as those studied by Reich and Tsabba [1], who reported a surface composition of $Na_{0.05}WO_3$. We studied several samples obtained in different thermal cycles. In all the samples studied, a complex ESR spectrum is observed around $g \sim 2$ (see inset of Fig. 1). This spectrum is probably due to the unresolved fine and/or hyperfine structure, as the samples consist of a large number of small single crystals with random orientations in the magnetic field. The exact description of the paramagnetic center responsible for the observed ESR signal has to await the availability of large Na-doped WO_3 single crystals. The linewidths and positions of the ESR lines were temperature independent. The spectra can easily be saturated, especially at low temperatures, which allowed to extract the spin-lattice relaxation time T_1 from the dependence of the signal amplitude on the microwave power [6]. We used the method developed for inhomogeneously broadened lines because the ESR linewidth was found to be independent of microwave power [7]. An absolute value of T_1 requires the knowledge of the rf magnetic field amplitude H_1 inside the sample, which is not easy to determine because of the high dielectric constant of WO_3. Therefore we consider only the relative change of T_1 with temperature. Figure 1 shows the temperature dependence of the spin-lattice relaxation rate $1/T_1$ in a WO_3:Na sample. One can see that below about 100 K, $1/T_1$ decreases markedly without the Hebel-Slichter coherence peak [8].

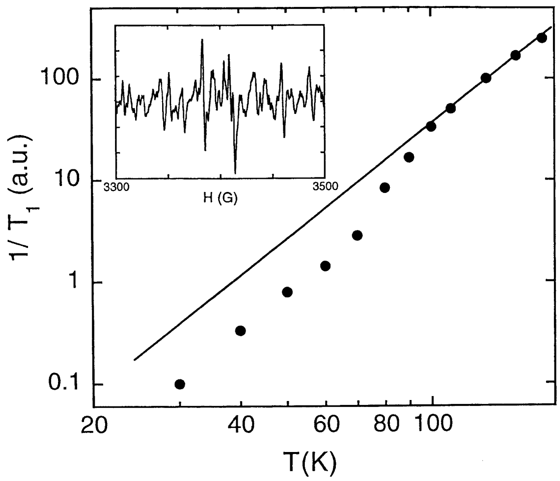

Fig. 1. Relative temperature dependence of $1/T_1$ in WO_3:Na on a log-log scale. The solid line represents a T^4 dependence above 100 K. The inset shows a part of the ESR spectrum observed in WO_3:Na at $T = 80$ K.

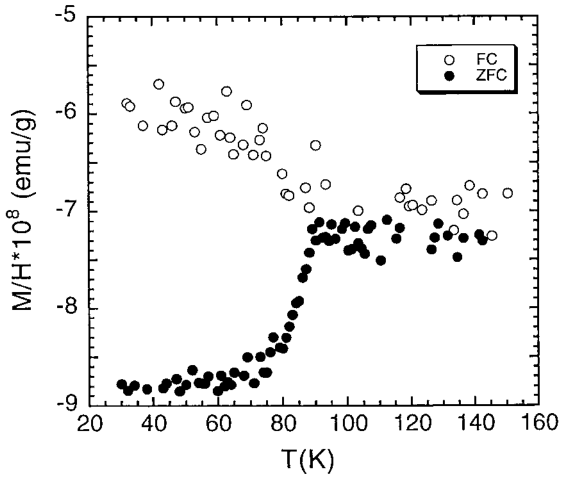

Fig. 3. Field cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibilities of WO_3:Na. Both measurements are performed in a magnetic field $H = 100$ Oe.

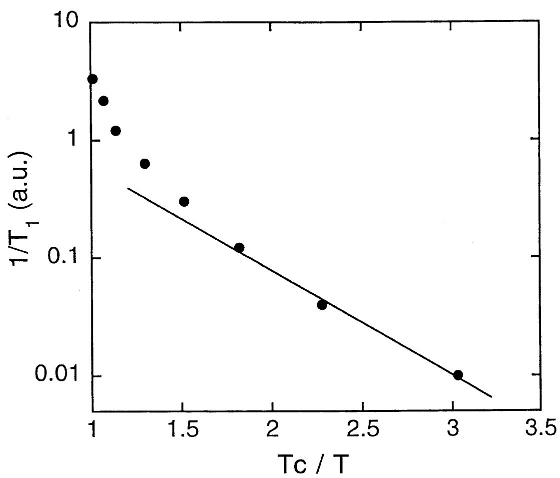

Fig. 2. A plot of the variation of the $1/T_1$ *versus* T_c/T on a semilog scale. The solid line is a fit to the low-temperature region using equation (1).

It is interesting to note that the Hebel-Slichter peak is also absent in NMR studies of cuprate high-T_c compounds [9] or heavy-fermion superconductors [10]. We attribute the steep decrease of $1/T_1$ below 100 K to an electronic gap opening in the superconducting state. For temperatures far below T_c, this gap in the electronic excitation spectrum should lead to a relaxation rate of the form

$$1/T_1 \propto \mathrm{e}^{-\Delta/kT}, \tag{1}$$

where Δ is the value of the electronic gap. In Figure 2 we plotted the relaxation rate *versus* T_c/T on a semilog plot taking $T_c = 91$ K. The solid line is a fit to the low-temperature region using equation (1). Below about $T = 0.6T_c$, $1/T_1$ is seen to vary exponentially as described in equation (1). From the fit we obtained $2\Delta/\mathrm{k}T_c = 3.5$, in good agreement with the prediction of the weak-coupling BCS theory, $2\Delta/\mathrm{k}T_c = 3.52$.

We also observed that the field cooled (FC) and zero-field cooled (ZFC) dc susceptibilities measured using a SQUID magnetometer differ strongly below T_c (see Fig. 3). The existence of the difference between the two susceptibility curves for the ZFC and FC modes would indicate a type-II superconductor. Such a behavior was first found in high-T_c copper oxides [5] and it is due to the glassy nature. These data make an assignment of the electronic gap in terms of charge-density wave opening as rather unlikely. In WO_3:Na the superconductivity probably occurs in a small fraction of the sample, the superconducting clusters of unknown phase forming a nonpercolating network [1]. If the size of the superconducting clusters is much smaller than the penetration depth, there will be no flux exclusion in the FC mode according the Shoenberg formula [11] because the field completely penetrates the clusters. This can be another reason for the observed strong difference between the FC and ZFC magnetizations. The complete field penetration also allows the present ESR observation.

The obtained ESR and magnetic susceptibility results, together with earlier resistivity measurements [1], suggest the presence of high-T_c superconductivity. The ESR relaxation and the resistivity start to decrease below 100 K, while the transition in the susceptibility occurs at 91 K. It is interesting to note that such a behavior was observed in LaBaCuO high-T_c cuprates just after their discovery, the onset of the resistive transition occurring higher than the susceptibility [12]. This behavior is characteristic of a *percolative transition.* Moreover, the semiconducting-like behavior of the resistivity above T_c and the finite resistivity below T_c found in WO_3:Na [1], were also often observed in the early days of high-T_c superconductivity, and are due to the multiphase character of the samples [13]. We expect that with improving sample synthesis and increasing superconducting volume fraction these spurious effects will decrease.

We would like to emphasize that for $YBa_2Cu_3O_{7-x}$ compounds no ESR signal such as reported here for WO_3:Na is known. This seems to exclude a possible contamination of the WO_3:Na samples by YBCO as origin for the superconducting signatures with a $T_c = 91$ K.

The experiments reported here indicate the opening of an electronic, possibly superconductivity gap. However, they cannot tell whether it is a single or multi-phase system as it was also the case in the first report on the Ba-La-Cu-O system [12,13]. The very low doping concentration of Na makes the presence of several phases rather likely. The extremely small diamagnetic signals shown in [1] and in Figure 3 support this view. If this is the case, the ESR signal can arise from a region next to the superconductive phase. Actually, it would have to be so because, owing to the gap opening seen in the data of Figures 1 and 2, there must exist a relaxation path between the carriers that become superconducting and the ESR centers. The latter cannot become paired as the signal remains unchanged at T_c. A microscopic investigation of the material homogeneity and of the possibly new phase in WO_3 is clearly needed.

Upon doping tetragonal or hexagonal WO_3 with various alkali metals, superconductivity was observed with T_c increasing from 0.6 K for a concentration of 33% to over 6 K for an unknown, but lower, concentration [14]. The T_c of 91 K found for approximately 5% surface doping with Na clearly follows this trend. It points to an overdoped situation for the higher alkali-metal concentrations, as it is also known for the cuprates by now [15].

In summary, in WO_3:Na an ESR signal from a paramagnetic center is detected whose spin-lattice relaxation rate decreases markedly below $\sim$ 100 K and follows BCS behavior with a gap $\Delta = 160$ K. However, any electronic gap opening, for example charge-density waves, can explain such an observation. On the other hand the irreversible susceptibility behavior and the earlier resistivity measurements [1], rather support the presence of high-T_c superconductivity with the possible presence of another unknown phase in WO_3.

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