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LETTER TO THE EDITOR

An electron paramagnetic resonance study of superconducting crystals from the Tl–Ca–Ba–Cu–O system

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Abstract. We present the results of electron paramagnetic resonance spectroscopy experiments on superconducting crystals from the Tl–Ca–Ba–Cu–O system. Fourteen crystals were examined. A resonant absorption attributable to Cu^{2+} was observed from two of these and was found to be similar to that observed from non-superconducting $Tl_2YBa_2Cu_2O_x$. None of the crystals studied showed a resonant absorption consistent with Tl^{2+}. We interpret the observed resonant absorptions as originating from currently unidentified occlusions of impurity within those crystals.

The role of magnetism in the mechanism of superconductivity in the lamellar CuO_2 materials is an area of current interest. Neutron scattering studies of $La_{2-x}Sr_xCuO_4$ [1] have shown antiferromagnetic spin correlations to occur and implied that the full Cu^{2+} moment is retained in the superconducting state. Analogous behaviour for the Néel transition and for the bulk susceptibility has been indicated by measurements on $YBa_2Cu_3O_{6+\delta}$ [2] and evidence for fluctuations has been inferred from 'two-magnon' Raman scattering experiments [3]. Magnetic resonance techniques yield information on the static and dynamic behaviour of spin systems within a material. The nuclear spin–lattice relaxation rate data recorded for the planar Cu(2) site in $YBa_2Cu_3O_7$ [4, 5] have been interpreted in terms of localised electronic moments at the Cu(2) site. Electron paramagnetic resonance (EPR) experiments on single-crystal $YBa_2Cu_3O_7$ [6, 7] and $Bi_2Sr_2CaCu_2O_8$ [8] have shown that no resonant absorption can be detected for these materials. Similar experiments on powdered materials are prone to misinterpretation due to the existence of closely associated paramagnetic impurity phases [9, 10]. In recent EPR absorption experiments on polycrystalline $Tl_3Ba_2Ca_3Cu_4O_x$ [11] resonant absorptions attributable to Cu^{2+} and Cu^{2+}–Cu^{2+} pairs have been observed and it has been concluded that superconductivity of the Tl–Ca–Ba–Cu–O system is associated either with the glass feature or with the spin-triplet feature of these pairs.

In this Letter we present the results of EPR experiments on superconducting single crystals from the Tl–Ca–Ba–Cu–O system. The measurements were carried out at

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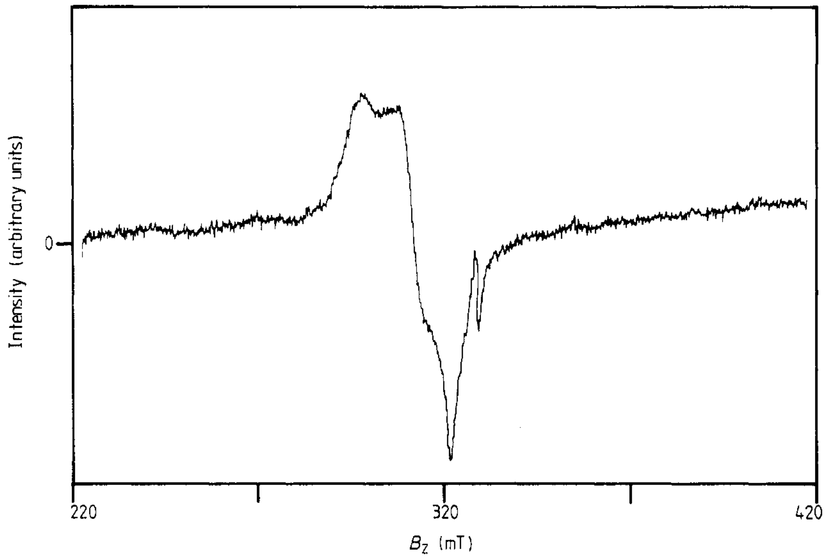

Figure 1. The room-temperature EPR spectrum recorded at 9.2 GHz for the $Tl_2CaBa_2Cu_2O_8$ crystal BMe1T-A with the Zeeman field perpendicular to the c axis.

9.2 GHz on a Varian E109 spectrometer equipped with a variable-temperature (4.2 to 300 K) facility. Fourteen crystals were examined, all grown at Sandia National Laboratories; the growth procedure has been detailed elsewhere [12]. Six crystals were of $Tl_2CaBa_2Cu_2O_8$ (2122) material, four were of syntactic 2122 : 2223 material, three were of polycrystalline 2223 material, and there was one 2223 sample. The crystals were typically of the order of $1 \times 1 \times 0.2$ mm^3 in dimension. Detailed temperature-dependent microwave absorption measurements were carried out on members of this group of crystals and confirmed the onset of superconductivity consistent with the known superconducting transition temperatures. The EPR experiments were carried using a Zeeman magnetic field range of 0 to 0.95 T. Data were recorded at room temperature and with the crystal c axis perpendicular to the Zeeman field for each crystal. Further studies were carried out on the 2223 crystal and on several members of the 2122 crystal set at various temperatures in the range 50 to 300 K and with the crystal c axis orientated both parallel and perpendicular to the Zeeman field. The room-temperature EPR spectrum of polycrystalline $Tl_2YBa_2Cu_2O_x$ was also recorded.

A resonant absorption was observed at room temperature from two (BMe1T-A[2122] and AMI-I[2122 : 2223]) of the fourteen crystals examined. The EPR spectrum recorded from BMe1T-A with the Zeeman field perpendicular to the c axis is shown in figure 1. The spectrum may be characterised by the g-values $g_1 = 2.226 \pm 0.011$ and $g_2 = 2.047 \pm 0.007$ derived from the low- and high-field extrema, respectively. The spectrum from AMI-I exhibited a similar linewidth and was consistent with the above g-values but was of weaker intensity. It should be noted that neither crystal was exceptional with regard to dimensions. The spectrum recorded from $Tl_2YBa_2Cu_2O_x$ is shown in figure 2. The g-values taken from the low- and high-field extrema are $g_1 = 2.171 \pm 0.022$ and $g_2 = 2.047 \pm 0.008$.

Consideration of the crystal structure of $Tl_2CaBa_2Cu_2O_8$ [13] shows that one Cu site exists within the unit cell and that the intra-plane Cu–Cu separation is 0.385 nm and the

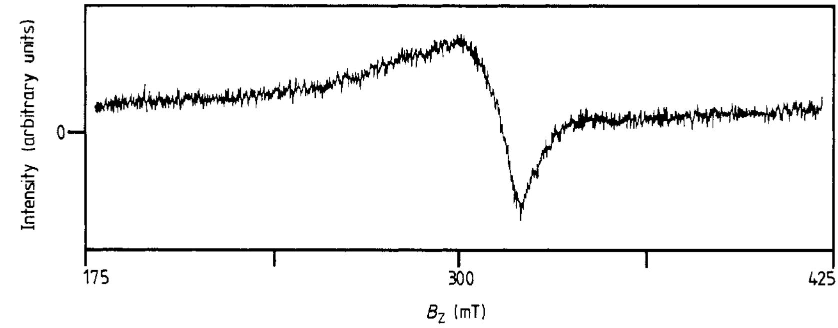

Figure 2. The room-temperature EPR spectrum recorded at 9.2 GHz for $Tl_2YBa_2Cu_2O_x$.

inter-plane distance is 0.316 nm. If one can indeed consider localised moments, then in the case of the Zeeman field applied perpendicular to the crystal *c* axis the root mean square fluctuating internal magnetic field due to the magnetic dipolar interactions of nearest neighbours would be of the order of 120 mT. With such Cu–Cu separations, however, exchange interactions can be expected to dominate dipolar terms. Values for the effective Cu–Cu exchange interaction inferred from the 'two-magnon' Raman experiments [3] are of the order of 0.1 eV. At the frequency of our present experiments this would be expected to have a drastic effect upon the Cu^{2+} EPR spectrum, given that the spin–lattice relaxation time is not so short as to preclude observation. If the ions are assumed similar and the anisotropic contributions to the exchange interaction neglected, appreciable exchange narrowing of the spectrum may be expected. This is clearly inconsistent with the results presented here.

The observation of resonant absorptions from only two of the fourteen crystals studied combined with the variation in intensity of the feature among the crystals leads us to conclude that the spectrum originates from Cu^{2+} in a currently unidentified occlusion of impurity phase. The similarity of the spectrum observed for the non-superconducting $Tl_2YBa_2Cu_2O_x$ material was also considered. Furthermore, it should be noted that no resonant absorption consistent with Tl^{2+} or Cu^{2+}–Cu^{2+} pairs was observed for the crystals studied. These results, together with similar studies on $YBa_2Cu_3O_7$ [6, 7] and $Bi_2Sr_2CaCu_2O_8$ [8], lend considerable weight to the conclusion that no EPR absorption attributable to either Cu^{2+} or Cu^{2+}–Cu^{2+} pairs is observable in the lamellar CuO_2 superconducting materials.

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