RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 1 1 JANUARY 1989

130-K superconductivity and microwave absorption in Tl-Ba-Ca-Cu-O

Zhao Min-Guang*
Center of Theoretical Physics, Chinese Centre of Science and Technology (World Laboratory), Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China

Yan Qi-Li
Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China
(Received 6 July 1988; revised manuscript received 19 September 1988)

In a Tl-Ba-Ca-Cu-O oxide, prepared by means of conventional ceramic technique, the zero-resistance temperature was found to be 127 ± 0.5 K and the diamagnetic transition temperature to be 130 ± 1 K. An ESR measurement shows that there is an intense low-field microwave-absorption peak below T_c ($R=0$) in the sample. This means that the superconductivity of Tl-Ca-Ba-Cu-O is either associated with the glass feature or with the spin-triplet state of Cu^{2+}-Cu^{2+} pairs via the exchange interaction mediated by an O^- ion, as is indirectly supported by the similar microwave absorption measurement on single-crystal $LiNbO_3:Cu^{2+}$.

INTRODUCTION

The recently discovered high-temperature superconductors A-Ba-Cu-O (with A=Y, La, Eu, etc.) have polycrystalline structure. Owing to the presence of grains in such ceramic materials, one expected to observe a large number of Josephson junctions between these grains. In the works of Stankowski, Kahol, Dalal, and Moodera,[1] Khachaturyan *et al.*,[2] Durny *et al.*,[3] and Blazey *et al.*,[4] the low-field microwave absorption in the ESR spectrum was interpreted as a superconducting-glass feature in the high-T_c oxides. We report here ESR and microwave absorption measurements on the Tl-Ca-Ba-Cu-O systems and on single-crystal $LiNbO_3:Cu^{2+}$.

EXPERIMENT

Similar to the previous procedure by Sheng and Herman,[5] Hazen *et al.*,[6] Zhao *et al.*,[7] and Zhao *et al.*,[8] appropriate amounts of Tl_2O_3, CaO, CuO, and BaO oxide powder with a certain nominal composition $Tl_3Ba_2Ca_3Cu_4O_x$, $Tl_2BaCa_2Cu_2O_x$, and $TlBaCaCu_2O_x$ were completely mixed and ground, and pressed into a pellet. A boat containing the pellets was then put into a tube furnace, which had been heated to 830 °C, was heated for 8 h in flowing O_2, and quenched in air to room temperature.

Resistance and ac susceptibility were measured by a four-probe technique and by a mutual inductance method, respectively. Figures 1(a) and 1(b) show the variations of resistance and susceptibility with temperature. The resistance decreases almost linearly with decreasing temperature to just above the superconducting onset temperature, and then sharply drops. The sample of $Tl_2Ba_1Ca_2Cu_3O_x$ has an onset temperature of 136 ± 1 K and reaches zero resistance at 127 ± 0.5 K. The ac susceptibility curve clearly shows the diamagnetic transition temperature to be 130 ± 1 rather than 120 K.

An ESR spectrum, typical for a polycrystalline sample of $Tl_3Ba_2Ca_3Cu_4O_x$, was observed using a Bruker ER-200D spectrometer at temperatures of 220, 120, and 100 K [see Figs. 2(a), 2(b), and 2(c)]. Additional features appear clear when the temperature drops down to 120 K, as shown in Fig. 2(b). Below this temperature, these features dominate the ESR spectra; when $T \leq 105$ K [below 105 K x reaches a constant value (see Fig. 1)], a

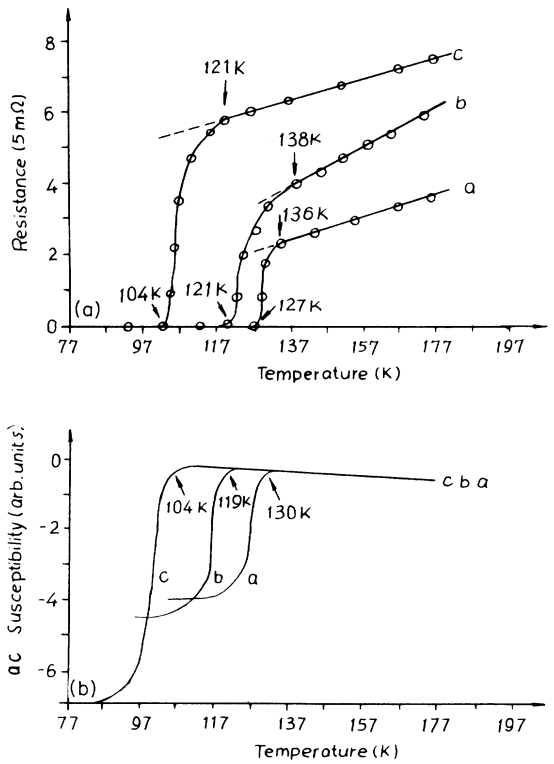

FIG. 1. (a) Temperature dependence of the resistivity and temperature dependence of the ac susceptibility. Curve a, $Tl_2BaCa_2Cu_3O_x$; curve b, $Tl_3Ba_2Ca_3Cu_4O_x$; curve c, $TlBaCaCu_2O_x$. For (b), the driving field frequency was 295 Hz.

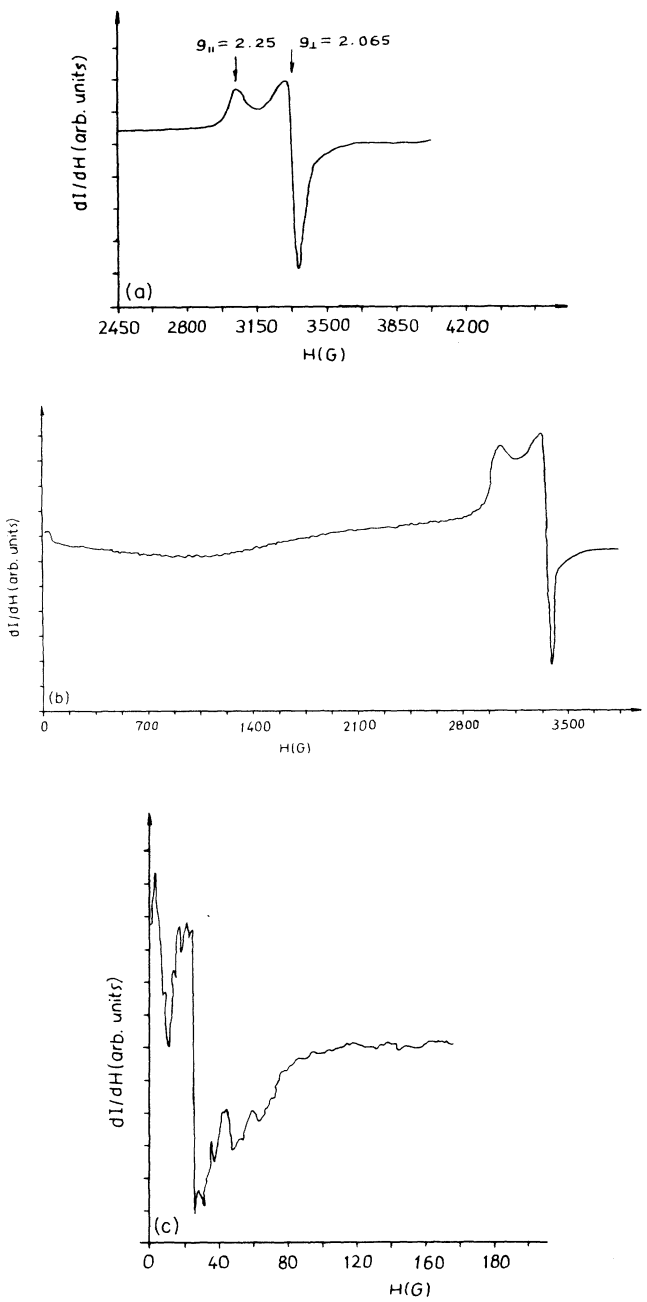

FIG. 2. ESR spectrum of the sample of $Tl_3Ba_2Ca_3Cu_4O_x$. (a) At 220 K; gain, 2.5×10^4; microwave frequency, 9.607 GHz. (b) At 120 K; gain, 4×10^4; microwave frequency, 9.61 GHz. (c) At 100 K; gain, 1.25×10^2; microwave frequency, 9.61 GHz. I is the absorption intensity in all panels.

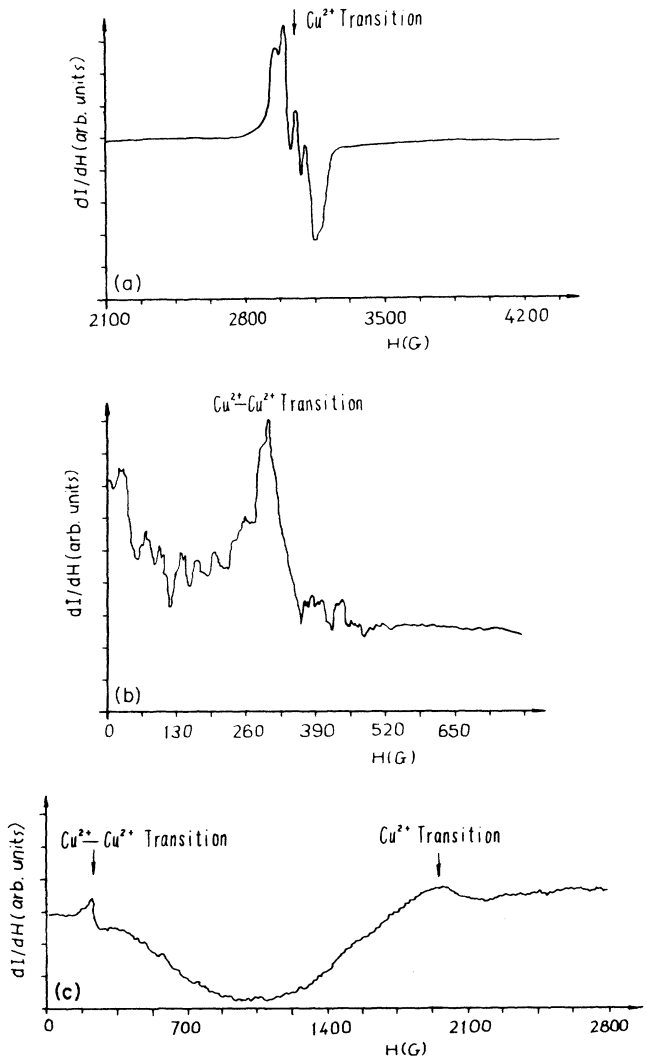

FIG. 3. (a) ESR spectrum of various samples. Size of all samples was the same, $0.3\times0.5\times1$ cm^3, and $\mathbf{H}\|c_3$. (a) $LiNbO_2$:Cu^{2+} at 77 K; gain, 4×10^4; microwave frequency, 9.76 GHz. I is the absorption intensity. (b) LiNbO:Cu^{2+} at 77 K; gain, 5×10^4; microwave frequency, 9.765 GHz. (c) $LiNbO_3$:Cu^{2+} at 300 K; gain, 4×10^4; microwave frequency, 9.75 GHz.

strong peak appears at about 20 G. Above T_c, however, only a microwave absorption resulting from the paramagnetic Cu^{2+} centers remains and $g_{\parallel}=2.25\pm0.005$ and $g_{\perp}=2.065\pm0.005$.

We think that there are two possible interpretations of the low-field absorption of Tl-Ba-Ca-Cu-O. (a) It is associated with the Josephson oscillations, as shown by Stankowske *et al.*,[1] Khachaturyan *et al.*,[2] Durny *et al.*,[3] and Blazey *et al.*,[4] or (b) it is associated with the spin-triplet transition of Cu^{2+}-Cu^{2+} pairs via the exchange interaction mediated by the O^- ions. In the latter case, the pair-transition condition is given by Ref. 9,

$$\nu=|D|+g\beta H,$$

where ν denotes the absorption frequency of microwaves, D the zero-field splitting parameter of Cu^{2+}-Cu^{2+}, g the ESR g factor of Cu^{2+}-Cu^{2+} pairs, β the Bohr magneton, and H the applied magnetic field.

In order to indirectly test our viewpoint, we have prepared a single crystal to $LiNbO_3$ (3 wt.% Cu^{2+}), measured its ESR spectrum, and found $g_{\parallel}=2.258\pm0.005$ and $g_{\perp}=2.155\pm0.005$. As can be seen from Fig. 3, low-field

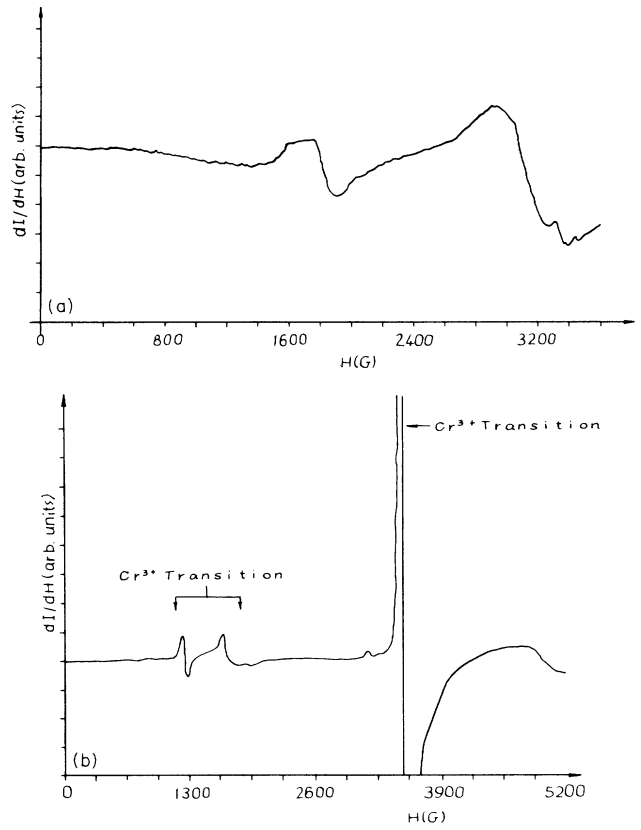

FIG. 4. ESR spectrum of two samples, with $H \| C_3$ and a gain of 4×10^4. Sample sizes are $0.3\times0.5\times1$ cm^3. (a) $LiNbO_3$: 0.5 wt.% Cr^{3+} at 300 K, with a microwave frequency of 7.65 GHz. (b) $LiNbO_3$: Cr^{3+} at 77 K, with a microwave frequency of 9.61 GHz.

microwave absorption exists at about 250 G (test temperatures: 300 and 77 K), as a result of the spin-triplet transition of Cu^{2+}-Cu^{2+} pairs with spin of unity ($s=1$) via the exchange interaction.

It is interesting to note that if we utilize the formula of D, and take $J=260\pm50$ cm^{-1} (see Ref. 9), we get

$$D=\frac{J}{8}\left[\frac{(g_{\|}-2.0023)^2}{4}\right]-(g_{\perp}-2.0023)^2$$

$$=-7.22\ \text{GHz},$$

$\nu=9.67$ GHz, $J=300$ cm^{-1} for $LiNbO_3$:Cu^{2+},

and

$D=9.484$ GHz,

$\nu=9.61$ GHz, $J=220$ cm^{-1} for Tl-Ba-Ca-Cu-O.

The results are in agreement with the experimental frequencies of 9.761 GHz for $LiNbO_3$:Cu^{2+} and of 9.61 GHz for Tl-Ba-Ca-Cu-O, respectively.

$LiNbO_3$ has a high dielectric constant, which helps to disturb the microwave fields. It is a piezoelectric single crystal with normal modes of mechanical vibration, which may be strongly driven by microwaves, that reacts back on the ESR cavity to produce potentially strange, geometry-dependent absorptions. Thus, the similarity in response between the superconductor and $LiNbO_3$:Cu^{2+} may be fortuitous. In order to determine whether this was the case, we have also measured the low-field microwave absorptions of $LiNbO_3$ (0.5 wt.% Cr^{3+}), but found nothing (see Fig. 4). Thus we can believe that the low-field microwave absorption in the single crystal of $LiNbO_3$:Cu^{2+} is associated with the absorption of Cu^{2+}-Cu^{2+} pairs with spin unity ($s=1$) via the Cu^{2+}-Cu^{2+} exchange interaction. Because $D>0$ the ground state is $S_z=0$. That the low-field microwave absorption in the high-T_c superconducting oxides arises from the spin-triplet transition of Cu^{2+}-Cu^{2+} pair via the exchange interaction mediated by the O^- ion contradicts the various spin-pairing singlet superconductivity mechanisms.[10] Our results are in agreement with the results by Su, Yu, Dong, and Tosatti[11] and Liang.[12]

The project was supported by National Natural Science Foundation of China.

*Permanent address: Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China.

[1]J. Stankowski, P. K. Kahol, N. S. Dalal, and J. S. Moodera, Phys. Rev. B **36**, 7126 (1987).

[2]K. Khachaturyan, E. P. Weber, P. Tejedor, A. M. Stacy, and A. M. Portis, Phys. Rev. B **36**, 8309 (1987).

[3]R. Durny, J. Hautala, S. Ducharme, B. Lee, O. G. Symko, P. C. Taylor, and D. J. Zeng, Phys. Rev. B **36**, 2361 (1987).

[4]K. W. Blazey, K. A. Muller, J. G. Bednorz, W. Berlinger, and G. Amoretti, Phys. Rev. B **36**, 7241 (1987).

[5]Z. Z. Sheng and A. M. Hermann (unpublished).

[6]R. M. Hazen, L. W. Finger, R. S. Angel, C. T. Prewitt, N. L. Ross, C. G. Hadidacos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, A. El Ali, and A. M. Hermann, Phys. Rev. Lett. **60**, 1657 (1988).

[7]Z. X. Zhao, L. Q. Chen, Z. H. Mai, Y. Z. Huang, Z. L. Xiao, X. Chu, D. N. Zheng, Z. L. Jia, J. H. Wang, G. H. Wang, Y. M. Ni, J. Q. Bi, Q. S. Yang, and D. H. Shen, J. Mod. Phys. B **2**, 479 (1988).

[8]Zhao Min-Guang, Zhao Xiao-Ning, and Zeng Xiao-Lan, Z. Phys. B (to be published).

[9]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), pp. 23 and 506.

[10]Zhao Min-Guang, Zhao Xiao-Ning, and Zeng Xiao-Lan, Z. Phys. B (to be published).

[11]Z. B. Su, L. Yu, J. M. Dong, and E. Tosatti, J. Mod. Phys. B **1**, 269 (1987).

[12]W. Y. Liang, J. Phys. C **20**, 571 (1987).