

May 01, 1990

Electron-spin-resonance in single-crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_{4/3}\text{Pb}_{2/3}\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$

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Recommended Citation

Karim, R.; Seed, R.; How, H.; Widom, A.; Vittoria, C.; Balestrino, G.; and Paroli, P., "Electron-spin-resonance in single-crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_{4/3}\text{Pb}_{2/3}\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ " (1990). *Electrical and Computer Engineering Faculty Publications*. Paper 41.
<http://hdl.handle.net/2047/d20002211>

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Citation: *J. Appl. Phys.* **67**, 5064 (1990); doi: 10.1063/1.344671

View online: <http://dx.doi.org/10.1063/1.344671>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v67/i9>

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Electron-spin resonance in single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_{4/3}\text{Pb}_{2/3}\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$

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We report on electron-spin resonance on single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_{4/3}\text{Pb}_{2/3}\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ at 9 GHz. While in the YBCO there was no observable ESR signal in the normal state (above T_c) or in the superconducting state (below T_c), we did observe a large microwave nonresonant absorption below T_c at low field values ($H < 200$ Oe). We attribute this form of absorption to fluxoid formation below T_c . In the BiPbSrCaCuO single crystals, a significantly different result was found in that an electron-spin-resonance signal was measured both above and below T_c , besides the low-field absorption occurring only below T_c . The g value was found to be 2.055 and reasonably constant with temperature from 300 to 4 K with H parallel to the c axis. We attributed the ESR line to Cu^{++} ion excitation. The ESR signal increased as T decreased from 300 K to T_c and the variation with temperature fits a Boltzmann statistics law. Below T_c the ESR signal remained constant as T was decreased below T_c . We explained this result in terms of two competing statistical effects. One effect is due to the fact that the ESR signal in the fluxoid region increases as the Boltzmann factor, but the fluxoid density decreases by the same factor. The net effect is that the ESR signal is constant with temperature below T_c . Hence, this is a clear demonstration of statistics involved in the formation of fluxoids.

INTRODUCTION

Conventionally, electron-spin resonance has been used to detect energy absorption at magnetic resonance in paramagnetic materials. Since the discovery of high-temperature superconductors, nonresonant microwave absorption at low field has also been observed using ESR techniques.¹ In this case, the absorption is due to the normal regions which are present in type-II superconductors. The size of the signal is proportional to the ratio of the normal to the superconducting volumes. Many authors have emphasized the role of Cu^{++} ions in the new high T_c superconductors. Some authors have suggested that these ions are coupled via Heisenberg exchange interaction.² Susceptibility measurements indicate the YBCO single crystals are paramagnetic above T_c . Thus, ESR should provide a good method to characterize these new superconductors. However, the most direct method of detecting the Cu^{++} ion (i.e., the ESR technique) has failed to give any signal on YBCO and other related compounds.

The complete absence of ESR signals in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, and Bi and Tl (2212, etc.) compounds is not clearly understood at this time. We report in this paper on ESR measurements on PbBiSrCaCuO single-crystal platelets. In these platelets, in addition to the low-field nonresonant absorption signal (which has been observed in all new high T_c superconductors, below T_c , so far), an ESR signal was observable both above and below T_c . Unlike previous reports of broad ESR lines (linewidth ~ 600 Oe) reported on polycrystalline YBCO compounds previously,³⁻⁶ which most probably come from impurity phases of Y_2BaCuO_5 or BaCuO_2 , we observe a sharp line (linewidth ~ 55 Oe) on single-crystal platelets of PbBiSrCaCuO . The g

value of 2.055 obtained for this line leads us to believe it is due to Cu^{++} ion excitation.

The variation with temperature of this line shows a dependence which can be traced to Boltzmann statistics above T_c . By observing the temperature dependence of this line below T_c we conclude that the growth of fluxoid areas in the high T_c materials must obey Boltzmann statistics.

EXPERIMENT

Single-crystal platelets of YBCO measuring $1 \text{ mm} \times 1 \text{ mm} \times 50 \mu\text{m}$ were grown using the flux melt technique. The sample preparation and characterization for these samples have been reported elsewhere.⁷ The BiPbSrCaCuO samples were also grown by a flux method.⁸ The starting molar composition was PbO 11.5%, Bi_2O_3 11.5%, SrCO_3 23%, CaCO_3 23%, CuO 31%, and the total charge was 93 g. The above powders were mixed, placed in a 55 cc Pt crucible, and subjected to the following thermal cycle: 20–500 °C at 100 °C/h, 500–900 °C at 30 °C/h, 900–700 °C at 0.5 °C/h, then quenched to 20 °C. On the lower part of the crucible, a number of bulky agglomerates were obtained, which could be easily separated from the flux. From them, single-crystal platelets, several millimeters wide and about 50 μm thick, could be easily cleaved out. Measured lattice constants are $a \approx b = 5.43 \text{ \AA}$, $c = 30.77 \text{ \AA}$.

ESR measurements in the temperature range 300–4 K were carried out using a Varian E-line spectrometer fitted with an Oxford ESR900 continuous flow cryostat, operating at 9.32 GHz. Microwave absorption experiments were carried out in a microwave cavity resonating in the TE_{102} rectangular mode. Microwave power levels of approximately 2 mW and field modulation of 4 G at 100 kHz were typical

settings for the experiments. For the low-field measurements, a pair of Helmholtz coils were wound to negate the residual field in the large magnets and thus the field could be varied from -100 to 100 G.

RESULTS AND DISCUSSION

Typical low-field absorption signals were observed for YBCO and BiPbSrCaCuO single crystals below T_c (Fig. 1). The temperature dependence of these signals has been reported elsewhere.⁹ The low-field curve is somewhat hysteric and its angular dependence with H parallel and perpendicular to the c axis is shown in Fig. 2, with the field held at the peak value (~ 7 Oe). Angular variation experiments on the BSCCO (2212) samples indicate a lesser degree of anisotropy as compared to the YBCO samples. (This is indicated by the ratio of the signal level with H parallel and perpendicular to the c axis.)

The YBCO sample showed no detectable ESR signal either above or below T_c with H being swept from 0 to 20 kG. ESR measurements on single-crystal BiPbSrCaCuO exhibited a sharp line centered around $H = 3225$ Oe at 9.32 GHz ($g = 2.055$) (Fig. 3). We believe the source of this line to be the Cu^{++} ion excitation. The g value of 2.055 remains almost constant for temperature ranges from 300 down to 4 K with negligible change in linewidth (≈ 55 G for the whole range). The temperature-independent line broadening suggests this broadening is due to spin-spin interaction. An estimate of inhomogeneous line broadening due to magnetic dipole-dipole interaction can be calculated using¹⁰

$$\Delta H = \mu/a^3 \approx 118 \text{ (Oe)}, \quad (1)$$

as compared to the experimental value of 55 Oe. Here μ is the

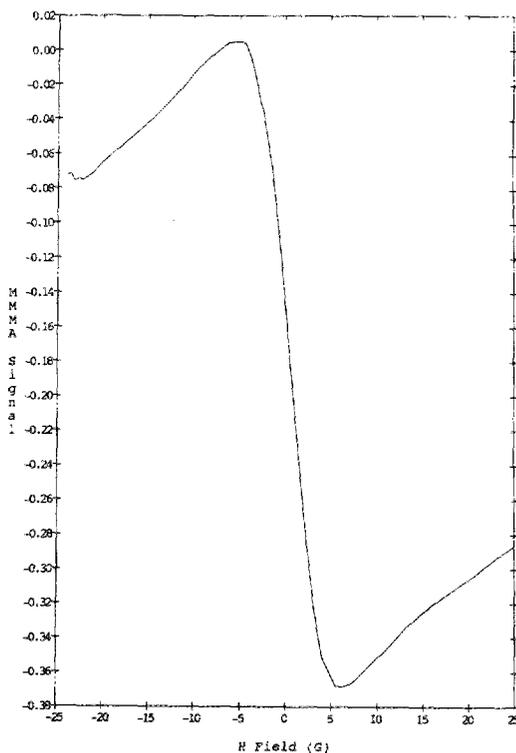


FIG. 1. Typical low-field magnetically modulated microwave absorption (MMA) signal vs H is displayed for single-crystal YBCO at $T = 75$ K.

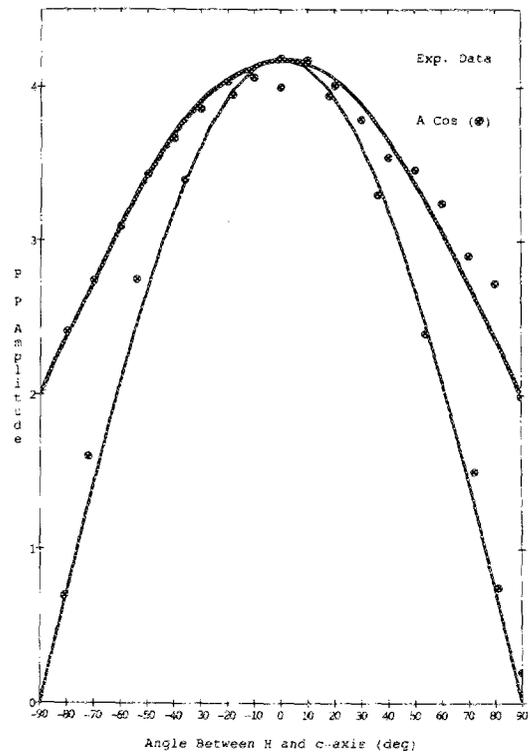


FIG. 2. Peak-to-peak signal amplitude vs angle between H and the c axis for single-crystal YBCO and BiPbSrCaCuO at $T = 75$ K. In YBCO, the signal almost goes to zero, but in the BiPbSrCaCuO, the signal falls to some constant amplitude. This is due to the greater anisotropy of YBCO.

electron-spin magnetic moment and equals

$$\mu = g e \hbar / 2m,$$

and $a = 5.43 \text{ \AA}$ is the distance between nearest neighbors.

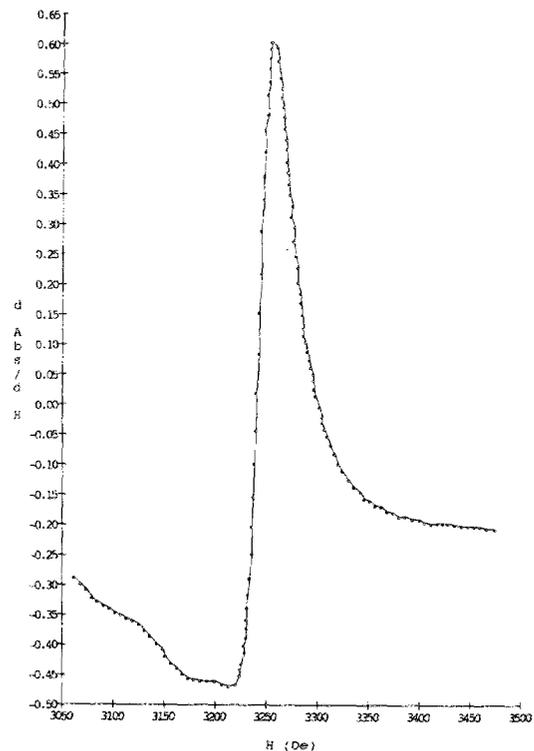


FIG. 3. Typical ESR signal for BiPbSrCaCuO single crystal. ($H_{\text{res}} = 3225$ Oe, $\Delta H = 55$ Oe, $g = 2.055$).

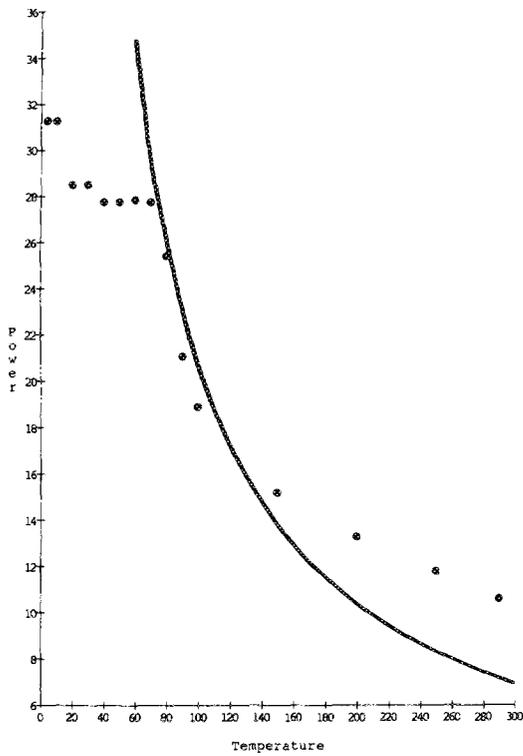


FIG. 4. Temperature dependence of peak-to-peak absorption signal. Solid line represents theoretical curve.

The somewhat reduced broadening may be as a result of exchange narrowing which becomes effective for ion separation around 5 \AA .¹¹

The interesting feature about this line is its dependence on temperature. Since the amplitude of an ESR signal is proportional to the number of available spins, one would expect the signal amplitude to roughly obey Boltzmann statistics. The ESR signal is proportional to the number of spins involved in the magnetic transitions. In thermal equilibrium, this can be approximately calculated using Boltzmann statistics and is given by the relation¹¹

$$n = N \left(\frac{e^{kv/kT} - 1}{e^{kv/kT} + 1} \right), \quad (2)$$

where N is the total number of spins. The calculated curve using the above equation and the experimental data points

are plotted in Fig. 4. Above T_c , the calculated and experimental observed signal levels are in good agreement. Below T_c , the signal level is almost a constant. To explain this effect we recall that flux penetration below T_c creates regions of normal electrons. These electrons are responsible for the ESR signal observed below T_c . As the temperature is decreased, the number of available spins should increase according to Eq. (2), giving rise to a corresponding increase in the signal amplitude. However, the area of fluxoid regions decrease proportionately and exactly compensate the increase in the signal level due to the increase in difference of spins between the energy states. This demonstrates that fluxoid formation obeys the Boltzmann statistics in the high T_c materials.

CONCLUSION

Low-field nonresonant absorption is present in all the new superconductors we have tested. EPR signals from YBCO and most of the related compounds are absent even though susceptibility tests indicate that they are paramagnetic above T_c . From the temperature variation of the EPR data in BiPbSrCaCuO compounds, we conclude that the signal is mainly due to inhomogeneously broadened Cu^{++} line. Furthermore, the signal amplitude provides information in the fluxoid formation process below T_c . Its constant magnitude indicates fluxoids decrease in area with temperature in accordance with Boltzmann statistics.

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