PHYSICAL REVIEW B VOLUME 41, NUMBER 1 1 JANUARY 1990

Measurement by EPR of the penetration depth in the high-T_c superconductors $Tl_2Ba_2Ca_2Cu_3O_x$ and $Bi_2Ca_2SrCu_2O_x$

B. Rakvin,* T. A. Mahl, A. S. Bhalla,† Z. Z. Sheng,‡ and N. S. Dalal§
Chemistry Department, West Virginia University, Morgantown, West Virginia 26506

(Received 27 July 1989)

Using a newly developed EPR spin-probing methodology, we have measured magnetic penetration depth λ for $Tl_2Ba_2Ca_2Cu_3O_x$ and $Bi_2Ca_2SrCu_2O_x$. The temperature dependence of λ is found to follow the relationship $\lambda = \lambda_0[1-(T/T_c)^4]^{-1/2}$, with $\lambda_0 = 2520 \pm 100$ Å and $T_c = 119$ K for $Tl_2Ba_2Ca_2Cu_3O_x$ and $\lambda_0 = 2700 \pm 100$ Å with $T_c = 84$ K for $Bi_2Ca_2SrCu_2O_x$.

This paper reports the temperature dependence of the magnetic penetration depth λ in the high-temperature superconductors $Tl_2Ba_2Ca_2Cu_3O_x$ and $Bi_2Ca_2SrCu_2O_x$. The λ measurements were made using electron paramagnetic resonance (EPR) spectroscopy. This study was undertaken first, because λ represents one of the fundamental properties of superconductors; accurate measurements of its temperature dependence provide clues to the nature of the elementary excitations in these materials.[1-6] Second, although the use of EPR spectroscopy has been suggested recently,[7] the measurements were made only on $YBa_2Cu_3O_{7-\delta}$, and only over a narrow temperature range (≈ 15 K) below T_c. In the present work we have made some improvements in the methodology by making detailed measurements over a wider temperature range by applying it to two new compounds, and analyzing the data with a more accurate theoretical model.[8] The results obtained support the proposal made earlier that the EPR technique can be complementary to the data obtained by standard techniques for measuring λ, such as muon spin rotation (μ^+SR), neutron diffractometry, and magnetic susceptibility. This appears to be a significant advantage because two recent reports[5,6] suggest that each of the above-mentioned procedures has its advantages and disadvantages. In particular, the EPR methodology is more accessible than μ^+SR and neutron diffractometry. Moreover, it is quick and essentially a surface technique, which is particularly useful for the granular superconductors.

The principle of the newly introduced EPR methodology is similar to that proposed earlier by Pincus *et al.*[9] in 1964 for NMR for type-II superconductors. In NMR, the linewidth or second moment of a resonance signal is broadened by the inhomogeneous magnetic field due to the emergence of the magnetic flux lattice[10] below T_c, as long as the Zeeman field H_0 satisfies the condition $H_{c1} < H_0 < H_{c2}$. The same amount of inhomogeneous broadening is expected to influence an EPR line also since this broadening is field independent within the limit $H_{c1} < H_0 < H_{c2}$. Thus the EPR method is based on the measurement of the second moment of an EPR line of a paramagnetic probe adsorbed on the surface of a type-II superconductor.[7] The second moment is found to increase rapidly as the temperature is lowered below T_c and yields a direct measure of the flux distribution in the superconducting (mixed) state for type-II superconductors.

The above procedure was used for measuring the temperature dependence of λ for $Tl_2Ba_2Ca_2Cu_3O_x$ (Refs. 11 and 12) and $Bi_2Ca_2SrCu_2O_x$ (Ref. 13) prepared by solid-state reactions. The transition temperatures were also measured via magnetically modulated microwave absorption,[14] found to be 119 K for $Tl_2Ba_2Ca_2Cu_3O_x$ and 82 K for $Bi_2Ca_2SrCu_2O_x$. The paramagnetic probe used was the stable free radical diphenylpicryl hydrazyl (DPPH). In order to absorb the probe on the surface, the superconductor samples were immersed in an acetone solution of ($\approx 10^{-2}$ M) DPPH and dried in air. The EPR measurements were made using a Bruker ER 200D EPR spectrometer, operating at 9.5 GHz (*X* band), $H_0 \approx 3500$ Oe. The temperature was controlled to ±0.1 K using an Oxford Instrument model DTC2 temperature controller. All measurements were performed with magnetic-field modulation amplitudes in the range of 0.8–4 Oe at a frequency of 100 kHz. The microwave power level used was kept low (about 1 mW) in order to minimize power saturation and broadening.

Generally, EPR spectra of solid DPPH are characterized by strong electron-spin exchange which results in an exchange-narrowed spectrum.[15] The signal exhibits only a small (1–2 Oe) monotonic broadening from room temperature down to ≈ 30 K.[16] Figure 1 shows some typical EPR spectra of DPPH adsorbed on $Tl_2Ba_2Ca_2Cu_3O_x$ and $Bi_2Ca_2SrCu_2O_x$. It can be noted that the spectra exhibit no significant change in the line shape for temperatures $T > T_c$, but a rapid broadening below the T_c's for each sample. Figures 2 and 3 show the temperature dependence of the second moment $\langle \Delta H^2 \rangle$ for both samples.

The second moment data (Figs. 2 and 3) were analyzed by using Brandt's recently reported[8] formula for a perfect triangular lattice:

$$\langle \Delta H^2 \rangle = 0.00371 \Phi_0^2/\lambda^4 , \tag{1a}$$

$$\lambda = \frac{\lambda_0}{(1-t^4)^{1/2}} . \tag{1b}$$

Here Φ_0 is the flux quantum, λ_0 is the penetration depth at $T = 0$ K, and t is the reduced temperature T/T_c. The temperature variation of λ is assumed to be described with the standard two-fluid form[17] [Eq. (1b)]. In the superconducting phase ($T < T_c$), the data are fitted to Eq. (1) by subtracting the background contribution estimated

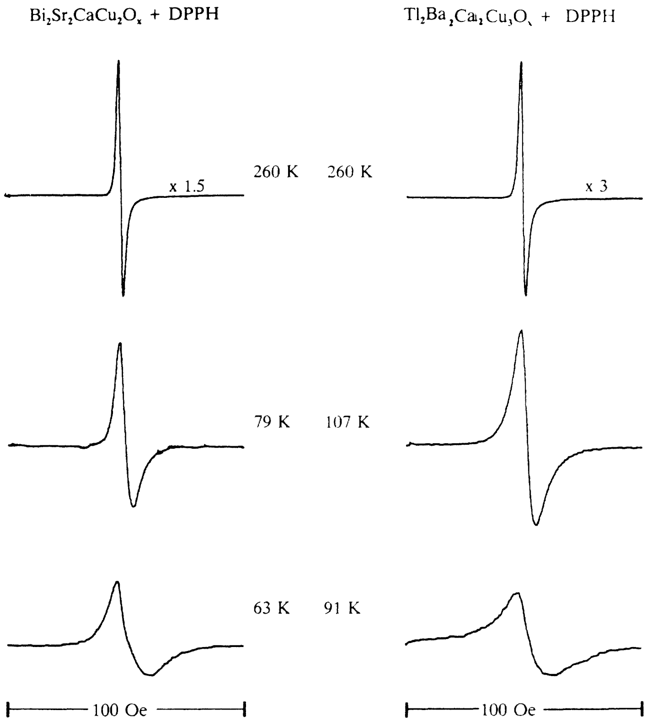

FIG. 1. Typical EPR spectra of the spin probe DPPH adsorbed on $Bi_2Ca_2SrCu_2O_x$ and $Tl_2Ba_2Ca_2Cu_3O_x$. A significant line broadening can be noted in the spectra below T_c, 82 K for $Bi_2Ca_2SrCu_2O_x$ and 119 K for $Tl_2Ba_2Ca_2Cu_3O_x$.

from the $T > T_c$ data

$$\langle \Delta H^2 \rangle = \langle \Delta H^2 \rangle_{T<T_c} + \langle \Delta H^2 \rangle_{T>T_c} . \qquad (2)$$

The best-fit curves are obtained with parameters $\lambda_0 = 2520$ Å and $T_c = 119$ K for $Tl_2Ba_2Ca_2Cu_3O_x$ and $\lambda_0 = 2700$ Å and $T_c = 84$ K for $Bi_2Ca_2SrCu_2O_x$, respectively. The dashed lines correspond to the same fit but with the change of λ_0 by ± 100 Å. As can be seen, all experimental data lie within these dashed curves. These results indicate that this method can yield an estimate of λ_0 to within ± 100 Å and that within this accuracy the variation of λ follows the BCS model for both compounds.

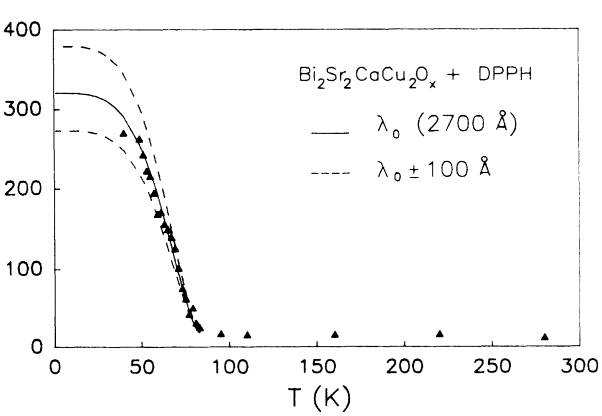

FIG. 2. Temperature dependence of the second moment $\langle \Delta H^2 \rangle$ of the EPR signal of DPPH adsorbed on $Bi_2Ca_2SrCu_2O_x$. The solid line is a fit to Eq. (1) in the text, yielding $\lambda_0 = 2700$ Å with $T_c = 84$ K. Dashed lines are curves with $\lambda_0 = 2700 \pm 100$ Å and a $T_c = 84$ K.

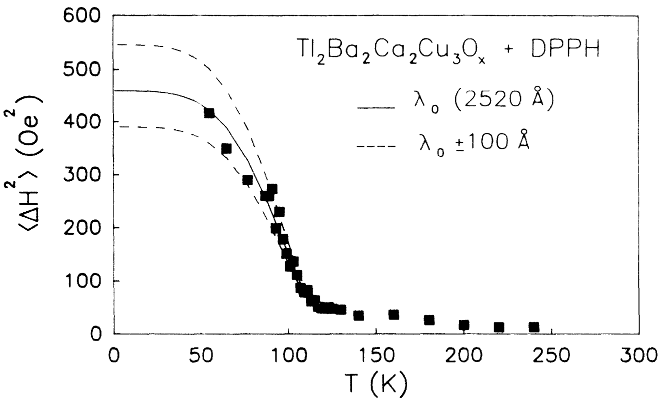

FIG. 3. Temperature dependence of the second moment $\langle \Delta H^2 \rangle$ of the EPR signal of DPPH adsorbed on $Tl_2Ba_2Ca_2Cu_3O_x$. The solid line is a fit to Eq. (1) in the text, yielding $\lambda_0 = 2520 \pm 100$ Å and a $T_c = 119$ K.

At present, accurate measurement of λ_0 for these samples by established methods such as μ^+SR or polarized neutron diffractometry are not available. However, for $Bi_2Ca_2SrCu_2O_x$ the presently deduced value (2700 Å) is in the range of the values of 1585 and 3650 Å, deduced from critical-field measurements for the related compound $Bi_4Ca_3Sr_3Cu_4O_{16}$.[18] Similarly, for $Tl_2Ba_2Ca_2Cu_3O_x$ Hentsch *et al.*[19] measured the temperature dependence of $\langle \Delta H^2 \rangle$ for the related compound $Tl_2Ba_2Ca_2Cu_3O_x$ via ^{205}Tl NMR. The ^{205}Tl NMR lines also exhibited a sharp increase in $\langle \Delta H^2 \rangle$ in the superconducting phase. However, in this case the experimental data do not seem to follow Eq. (1), and perhaps this is why λ_0 was not evaluated quantitatively. We thus have no literature values to compare with our results for $Tl_2Ba_2Ca_2$ Cu_3O_x but our data appear to be well described by Eq. (1).

In conclusion, while the present results are still preliminary the EPR spin-probe methodology appears to be an easily accessible, inexpensive, quick, and sensitive method which yields λ_0 with an accuracy of within 100 Å. Our data on the temperature dependence of λ for $Tl_2Ba_2Ca_2Cu_3O_x$ and $Bi_2Ca_2SrCu_2O_x$ can be described by conventional BCS theory, similar to what was found by μ^+SR experiments[1,2] for $YBa_2Cu_3O_{7-\delta}$. The present work also has implications for other EPR studies (such as those on Cu^{2+} or Gd^{3+}) in which the broadening of signals due to the magnetic flux lattice formed by the vortices should be considered in any line-shape analysis.

A shortcoming of the method appears to be the decreases in the signal-to-noise ratio due to the nonresonant microwave absorption phenomenon.[20-23] Moreover, DPPH is not a suitable probe below 30 K because it undergoes an antiferromagnetic phase transition around this temperature. Further investigations aimed at improving this shortcoming via a better probe (which does not undergo a phase transition) and which utilizes higher measurement frequencies are in progress.

[*] Permanent address: Ruder Bošković Institute, University of Zagreb, P.O. Box 1016, 41001 Zagreb, Croatia, Yugoslavia.

[†] Permanent address: Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802.

[‡] Permanent address: Physics Department, University of Arkansas, AR 72701.

[§] Address correspondence to this author.

[1] D. R. Harshman, G. Aeppli, E. J. Ansaldo, B. Batlogg, J. H. Brewer, J. F. Carolan, R. J. Cava, M. Celio, A. C. D. Chaklader, W. N. Hardy, S. R. Kreitzman, G. M. Luke, D. R. Noakes, and M. Senba, Phys. Rev. B **36**, 2386 (1987).

[2] D. R. Harshman, L. F. Schneemeyer, J. V. Waszczak, G. Aeppli, R. J. Cava, B. Batlogg, L. W. Rupp, E. J. Ansaldo, and D. Ll. Williams, Phys. Rev. B **39**, 851 (1989).

[3] L. Krusin-Elbaum, A. P. Malozemoff, Y. Yeshurun, D. C. Cronemeyer, and F. Holtzberg, Phys. Rev. B **39**, 2936 (1989).

[4] L. Krusin-Elbaum, L. R. Greene, F. Holtzberg, A. P. Malozemoff, and Y. Yeshurun, Phys. Rev. Lett. **62**, 217 (1989).

[5] A. F. Hebard, A. T. Fiory, and D. R. Harshman, Phys. Rev. Lett. **62**, 2885 (1989).

[6] L. R. Greene, L. Krusin-Elbaum, and A. P. Malozemoff, Phys. Rev. Lett. **62**, 2886 (1989).

[7] B. Rakvin, M. Požek, and A. Dulčić, Solid State Commun. (to be published).

[8] E. H. Brandt, Phys. Rev. B **37**, 2349 (1988).

[9] P. Pincus, A. C. Gossard, V. Jaccarino, and J. H. Wernick, Phys. Lett. **13**, 21 (1964).

[10] A. Abrikosov, Zh. Eksp. Teor. Fiz. **32**, 1142 (1957) [Sov. Phys. JETP **5**, 1174 (1957)].

[11] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 138 (1988).

[12] Z. Z. Sheng, W. Kiehel, J. Bennett, A. El Ali, D. Marsh, G. D. Mooney, F. Arammash, J. Smith, D. Viar, and A. M. Hermann, Appl. Phys. Lett. **52**, 1738 (1988).

[13] Prepared at the Materials Research Laboratory, the Pennsylvania State University. The oxygen stoichiometry x is close to 8; A. S. Bhalla (private communication).

[14] T. A. Mahl, J. P. DeLooze, P. H. Kahol, and N. S. Dalal, in *Proceedings of the Workshop on the Materials Science of High T_c Superconductors: Magnetic Interaction, Gaithersburg, Maryland, 1988,* edited by L. H. Bennet, Y. Flom, and G. C. Vezzoli (World Scientific, Singapore, 1989), Vol. 17, p. 293.

[15] See, for example, C. P. Poole, Jr., *Electron Spin Resonance* (Wiley, New York, 1982).

[16] C. S. Singer and E. G. Spencer, J. Chem. Phys. **21**, 939 (1953).

[17] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[18] M. G. Alexander, Phys. Rev. B **38**, 9194 (1988).

[19] F. Hentsch, N. Winzek, M. Mehring, Hj. Mattausch, and A. Simon, Physica C **158**, 137 (1989).

[20] S. V. Bhat, P. Ganguly, T. V. Ramakrishnan, and C. N. R. Rao, J. Phys. C **20**, L559 (1987).

[21] J. Stankowski, P. K. Kahol, N. S. Dalal, and J. S. Moodera, Phys. Rev. B **36**, 7126 (1987); K. W. Blazey, K. A. Müller, J. G. Bednorz, W. Berlinger, G. Amoretti, E. Buluggiu, A. Vera, and F. C. Matacotta, *ibid.* **36**, 7241 (1987).

[22] A. Dulčić, B. Leontić, M. Perić, and B. Rakvin, Europhys. Lett. **4**, 1403 (1987); M. Perić, B. Rakvin, M. Prester, N. Brničević, and A. Dulčić, Phys. Rev. B **37**, 522 (1988).

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