PHYSICAL REVIEW B VOLUME 37, NUMBER 4 1 FEBRUARY 1988

Positron-annihilation studies of the superconductivity transition in $YBa_2Cu_3O_{7-x}$

L. C. Smedskjaer, B. W. Veal, D. G. Legnini, A. P. Paulikas, and L. J. Nowicki
Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 10 August 1987)

Positron-annihilation studies, by Doppler broadening, of the superconducting transition in $YBa_2Cu_3O_{7-x}$ ($x \approx 0.1$) have been made. Below T_c a large positive temperature dependence of the line-shape parameter is observed, while at (or near) T_c an almost discontinuous increase in the line-shape parameter takes place. The behavior below T_c may be consistent with a Bardeen-Cooper-Schrieffer-like theory if an energy band with a small dispersion crosses the Fermi level. The discontinuity is not clearly understood, but may be due to a major change in the electronic structure taking place with the onset of superconductivity.

The original discovery of the new superconducting oxide materials with $T_c \approx 40$ K (Ref. 1) and the more recent discovery of materials with $T_c \approx 90$ K (Refs. 2–4) have stimulated an extensive research effort aimed at understanding the physical phenomena that cause the high-temperature superconductivity. A great deal of attention has been directed to the electronic structure of the high-T_c materials, since an understanding of the electronic structure clearly is a prerequisite for a detailed description of the mechanisms leading to the high values of T_c.

Recent theoretical band-structure calculations for the superconductor $YBa_2Cu_3O_{7-x}$ (Refs. 5–7) have provided a great deal of important insight into the nature of this material. However, direct observations of the electronic structure have not yet been made. Positron-annihilation studies are important in this regard, since they permit a direct experimental investigation of this structure. Such studies, when performed on large single crystals (not available at present), will lead to a detailed mapping of the Fermi surface. Studies of polycrystalline samples will provide important, although less detailed, information about changes in the structure due to the superconducting transition. Since the mechanism(s) responsible for superconductivity in the high-T_c materials is not understood, elucidation of the electron structure and any observation variation in the structure connected with the superconducting transition is vitally important.

In this paper we present Doppler-broadening positron-annihilation results for polycrystalline $YBa_2Cu_3O_{7-x}$ ($x \approx 0.1$) as a function of temperature. The magnitude of the line-shape parameter S changes abruptly near the superconducting transition temperature. For $T < T_c$, the functional dependence of S reflects changes in the band structure which are attributed to the formation of Cooper pairs. The present measurements provide the first direct observation of band-structure changes in the high-T_c oxides that are associated with pair formation.

The $YBa_2Cu_3O_{7-x}$ samples were made using a procedure described earlier.[8] The oxygen concentration was determined to be 6.9 ($x = 0.1$) by neutron-diffraction measurements on other samples prepared in the same way. The midpoint of the superconducting transition temperature for these samples was found to be $T_c = 92$ K with a width of 2 K. Positron lifetime and Doppler-broadening measurments were performed using a traditional spectrometer[9] having a full width at half maximum (FWHM) of 270 ps and 1.3 keV, respectively. The Doppler-broadening line-shape parameters were stabilized using the 497-keV γ line from ^{103}Ru (Ref. 10) and the line-shape parameter was obtained from a 2.2 keV-broad region under the center of the distribution.

Temperatures were measured using a chromel-constantan thermocouple calibrated at room temperature, at $-77\,°C$ in a dry ice/ethanol mixture, and at liquid-nitrogen temperature. We estimate the temperature gradient across the sample at low temperatures to be no more than 5 K.

The Doppler-broadening line-shape parameter is shown as a function of temperature in Fig. 1. We shall first discuss various possibilities for the positron states that might give rise to the effects seen in the figure. Two lifetimes were observed at room temperature (167 ps, 247 ps, $I_1 = 65\%$, $I_2 = 35\%$). In view of the short lifetimes and the absence of any long lifetime ($\tau \approx 1$ ns), it is unlikely that quasipositronium is formed in substantial amounts in the sample. Two-dimensional angular correlation spectra demonstrated the presence of a delocalized positron state

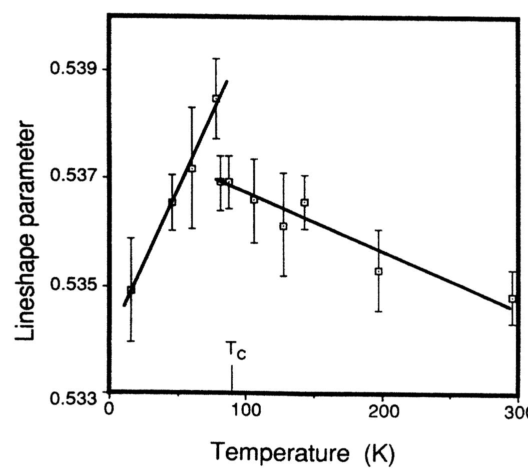

FIG. 1. Doppler-broadening line-shape parameter for $YBa_2Cu_3O_{6.9}$ vs temperature.

in the present polycrystalline sample.[11] In view of this we associate the 167-ps lifetime with the shortened lifetime of a free positron and the 247 ps lifetime with that of a positron in a trap, most likely an oxygen vacancy.[11] Assuming the validity of the two-state trapping model,[12-14] we find that the above observations are consistent with a trapping probability of $\approx 11\%$ for the positrons, and that the data in Fig. 1 are dominated by the annihilation of free positrons (89%).

It is appropriate to examine whether the effects in Fig. 1 might be due to minor changes in the positron trapping, or whether they are associated with changes in the electronic structure. One might speculate that the negative temperature dependence of S, observed for $T > T_c$, could be due to positron trapping in extended defects with a low binding energy $E_b \approx k_B T$.[15] The behavior for $T < T_c$ cannot, however, be explained in terms of trapping in extended defects alone, since the temperature dependence is positive. Furthermore, the trapping rate is considered to be temperature independent in more localized defects with larger binding energies ($E_b \gg k_B T$) (Refs. 16 and 17), and therefore trapping in such defects would not account for the observed effects. We suggest, therefore, that the effects seen in Fig. 1 are mainly due to changes in the electronic structure as sampled by a positron in the Bloch state.

Figure 1 exhibits a step in the line-shape parameter at or near T_c. Also, we observe that S increases with an amount $\Delta S/S \approx 6\times 10^{-3}$ between 11 K and T_c. These unexpected results are apparently a consequence of substantial changes in the electronic structure associated with the transition between the normal and superconducting states.

To estimate the order of magnitude of the change $\Delta S \equiv S(T = T_c) - S(T = 0)$ we shall make the fundamental assumption that the electron Hamiltonian has the same form as the Bardeen-Cooper-Schriefer (BCS) reduced Hamiltonian. This assumption does not by itself presume any specific coupling mechanism leading to superconductivity, but merely implies the existence of Cooper pairs and an energy gap $E_g = 2\times\Delta$. Thus, we assume that the system ground state may be written as

$$|\mathrm{BCS}\rangle = \prod_k (u_k + v_k a_k^\dagger a_{-k}^\dagger)\,|\mathrm{vac}\rangle \ , \quad (1)$$

where $|\mathrm{vac}\rangle$ is the vacuum state and $a^\dagger$ are creation operators. The occupation number for state k,

$$\langle n(k)\rangle_{\mathrm{BCS}} = v_k^2 = \frac{1}{2}\left[1 - \frac{\xi(k)}{[\Delta^2+\xi^2(k)]^{1/2}}\right] \ ,$$
$$\xi(k) \equiv E(k) - E_F \ , \quad (2)$$

where $E(k)$ is the energy dispersion and E_F is the Fermi energy. For $\Delta = 0$ it is seen that $n(k) = 1$ for $k < k_F$ and $n(k) = 0$ elsewhere. For $\Delta > 0$, $n(k)$ is smeared near k_F by an amount Δk:

$$\Delta k \approx \frac{m^*}{\hbar^2 k_F}\Delta \ , \quad (3)$$

where m^* is the effective electron mass. The smearing, Δk, increases the overall momentum of the electron population and therefore leads to a decrease in the Doppler-broadening parameter as the energy window Δ increases with decreasing temperature. Thus, for temperatures $T < T_c$ a positive temperature coefficient for the Doppler-broadening signal is anticipated, as it is also seen in Fig. 1.

The positron annihilates with the conduction electrons in the filled bands as well as with the conduction electrons in the partially filled bands. The electrons (in the partially filled bands) having momenta smeared with Δk are only a small fraction of the conduction electrons. The net effect on S will then be the smearing Δk weighted with this fraction. In calculating the effect we shall treat the Fermi surface as essentially two dimensional with ≈ 4 bands crossing E_F out of a total of ≈ 36 conduction bands.[6] Assuming a simple cylindrical Fermi surface with radius k_F one obtains that

$$\langle \Delta k\rangle_{\mathrm{BCS}} \approx \frac{4}{36}\frac{2\pi k_F \Delta k}{\pi k_{\mathrm{BZ}}^2}\Delta k \ , \quad (4)$$

where k_{BZ} is the Brillouin zone wave vector. From Eqs. (3) and (4) we get

$$\left|\frac{\Delta S}{S}\right| \approx \frac{2\langle\Delta\Theta\rangle}{\Theta_{\mathrm{FWHM}}} = \frac{4}{36}4\left[\frac{m^*}{m}\right]^2\left[\frac{\Delta}{mc^2}\right]^2(\Theta_F\Theta_{\mathrm{BZ}}^2\Theta_{\mathrm{FWHM}})^{-1} \ , \quad (5)$$

where $\Theta = \hbar k/mc$ is the dimensionless momentum. Further Θ_{FWHM} is the observed FWHM of the distribution, while $|\Delta S/S|$ is the fractional change in the line-shape parameter.

It is emphasized that Eq. (5) should only be considered to be an estimator. First, it is conceivable that the positron wave function is large near the negatively charged oxygen ions with the consequence that the positron may annihilate preferentially with electrons near the oxygen ions. However, we assume here that annihilation occurs with equal probability with all conduction electrons. (A detailed calculation of the positron and the electron states in the sample would be required to ascertain this effect.) Second, it has been assumed that the Fermi surface is simple and cylindrical and that the energy dispersion is free-particle-like. More complicated surfaces with multiple intersections between the surface and the bands, might increase $|\Delta S/S|$. Despite these approximation Eq. (5) is useful to estimate the expected $|\Delta S/S|$ due to the superconducting transition. In addition it should be noted that $|\Delta S/S|$ is proportional to the square of both the electron mass and the energy gap.

Using the values $\theta_F \approx 2$ mrad, $\theta_{\mathrm{BZ}} \approx 3$ mrad, and $\theta_{\mathrm{FWHM}} \approx 10$ mrad we get

$$\left|\frac{\Delta S}{S}\right| \approx 10^{-4}\left[\frac{m^*}{m}\right]^2\left[\frac{\Delta}{0.1\ \mathrm{eV}}\right]^2 . \quad (6)$$

If $m^* = m$ and $\Delta = 0.1$ eV one obtains $|\Delta S/S| \approx 10^{-4}$, which is below the fractional change that can normally be observed in a Doppler-broadening experiment. However, from Fig. 1 it is seen that $|\Delta S/S| \approx 6\times10^{-3}$ ($T=0$ to $T=T_c$) or about 60 times larger. The results shown in Fig. 1 thus cannot be explained in terms of the BCS ground state, while assuming $m^* \approx m$. However, the formulation of Eq. (6) suggests that if the average mass, m^*, of the electrons near E_F is $\approx 8-10$ m, then the expected $|\Delta S/S|$ would fall within the range observed. The present positron results could therefore indicate the presence of an electron band with small dispersion near the Fermi energy.

In Fig. 2 band calculations for $YBa_2Cu_3O_7$ are shown.[6] It is seen that the bands labeled 1, 2, and 3 are not expected to contribute significantly to $|\Delta S/S|$ while band 4 might do so. Indeed, using the results of Refs. 5 and 6 the estimate of $|\Delta S/S|$ might be considerably improved by using the calculated Fermi surface and energy-band dispersion. In this case we avoid the assumptions of a free-particle-like dispersion [Eq. (3)] and the assumption of a simple cylindrical Fermi surface [Eq. (4)]. Now one finds

$$\left|\frac{\Delta S}{S}\right| \approx \alpha \left(\frac{\Delta}{0.1\ \mathrm{eV}}\right)^2, \qquad (7)$$

where $\alpha=10^{-4}$ for the sum of bands 1, 2, and 3, while band 4 gives $10^{-3} < =\alpha= < 10^{-2}$. (The factor α is expressed as a range because varying masses in the band preclude making a precise estimate of the effect.) This suggests that band 4 is the heavy band causing the effects seen in Fig. 1. [Band 4 is mainly due to the $Cu(1)(d_{yz}) - O(1)(p_z) - O(4)(p_y)$ orbitals and has a charge density highly localized on the one-dimensional chains.[6]] The present results do not imply that only band 4 is superconducting, since bands 1, 2, and 3 would not contribute significantly to $\Delta S/S$ should they become superconducting. The results do suggest, however, that band 4 is intimately associated with the high-T_c superconductivity.

The introduction of oxygen vacancies into the chains is expected to raise the Fermi level with the possibility that band 4 would be below the Fermi surface in the present sample ($x \approx 6.9$).[6] In this case the band would not contribute to $\Delta S/S$. However, the calculations do not specifically include the effect on the bands of vacancies in the chains. In light of the present results one might speculate that band 4 indeed may not be entirely below the Fermi surface in a sample at $x=6.9$. Calculations that include the effect of vacancies now seem to be very important.

Finally, we discuss the apparently discontinuous behavior to S. The discontinuity cannot be accounted for by a simple BCS-like theory alone, since $\Delta(T_c)=0$ and thus $\Delta k(T_c)=0$. The discontinuity could be caused by a change in the band structure that occurs when the sample

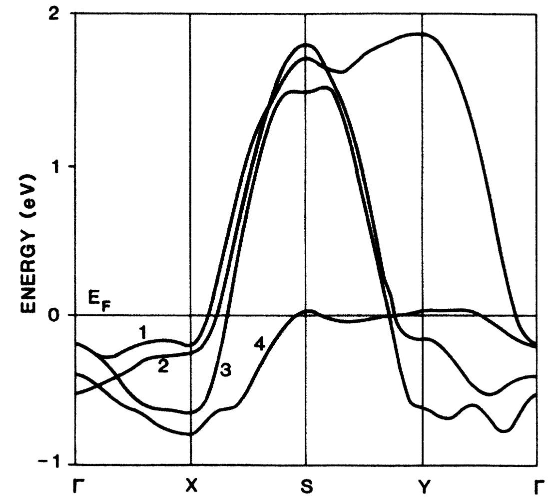

FIG. 2. Calculated band structure for $YBa_2Cu_3O_7$. Only the topmost bands are shown. The bands intersecting the Fermi level are labeled 1-4 (after Ref. 6).

becomes superconducting. For example, electrons with large momentum (at E_F) shifted closer to the Γ point would produce such an effect.

In conclusion, we have observed effects in the temperature dependence of the Doppler-broadening line shape for $YBa_2Cu_3O_{6.9}$ that are associated with the transition from the normal state to the superconducting state. An apparent discontinuity in S occurs near T_c that is not readily related to band-structure effects expected from a BCS-like theory. We have demonstrated, however, that the temperature dependence of the line-shape parameter S for $T<T_c$ may be accounted for by a simple BCS-like theory. Furthermore, the analysis predicts that a heavy band crosses E_F, a result consistent with band-structure calculations for $YBa_2Cu_3O_7$. The analysis further suggests that band 4, largely attributed to the one-dimensional chains, is intimately associated with high-T_c superconductivity.

These measurements represent the first observations of band-structure changes associated with a superconducting transition observed by positron annihilation. The present results suggest that future PAS studies will provide essential information about the electronic structure of the high-T_c oxides and its relation to the superconducting properties of these materials.

We are grateful to D. D. Koelling for helpful discussions. This work was supported by the U. S. Department of Energy, Basic Energy Sciences–Materials Sciences under Contract No. W-31-109-ENG-38.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B 64, 189 (1986).
[2]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. 58, 908 (1987).
[3]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. 58, 1676 (1987).

[4]D. G. Hinks, C. Soderholm, D. W. Capone II, J. D. Jorgensen, I. K. Schuller, C. U. Segre, K. Zhang, and J. D. Grace, Appl. Phys. Lett. **50**, 1688 (1987).

[5]S. Massida, J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. **A122**, 198 (1987).

[6]J. Yu, S. Massida, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 203 (1987).

[7]W. Y. Ching, Y. Xu, G. Zhao, K. W. Wong, and F. Zandiehnadem, Phys. Rev. Lett. **59**, 1333 (1987).

[8]J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, Phys. Rev. B **36**, 5731 (1987).

[9]L. C. Smedskjaer and M. J. Fluss, in *Methods of Experimental Physics*, edited by J. N. Mundy, S. J. Rothman, M. J. Fluss, and L. C. Smedskjaer (Academic New York, 1983), Vol. 21, p. 123.

[10]L. C. Smedskjaer, M. J. Fluss, and D. G. Legnini, Nucl. Instrum. Methods Phys. Res. Sect. B, **4**, 196 (1984).

[11]L. C. Smedskjaer, B. W. Veal, D. G. Legnini, A. P. Paulikas, and L. J. Nowicki (unpublished).

[12]W. Brandt, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), p. 155.

[13]B. Bergersen and M. J. Stott, Solid State Commun. **7**, 1203 (1969).

[14]D. C. Connors and R. N. West, Phys. Lett. **A30**, 24 (1969).

[15]L. C. Smedskjaer, M. Manninen, and M. J. Fluss, J. Phys. **10**, 2237 (1980).

[16]R. M. Nieminen, in *Positron Solid State Physics*, Proceedings of the International School of Physics "Enrico Fermi," Course LXXXIII, edited by W. Brandt and A. Dupasquier (North-Holland, New York, 1983), p. 359.

[17]T. McMullen, J. Phys. F **7**, 3041 (1977); **8**, 87 (1978).