Evidence for a charge-density wave or spin-density wave in the Cu-O chains in $YBa_2Cu_3O_{7-x}$

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The Doppler-broadened positron annihilation spectra of polycrystalline samples of $YBa_2Cu_3O_{7-x}$ have been measured and analyzed. By studying the difference between the normal-state (room-temperature) and superconducting-state (liquid-nitrogen temperature) spectra, we have deduced that the valence electrons undergo a significant redistribution in momentum states when the material becomes superconducting. We present evidence to demonstrate that this redistribution is consistent with the formation of a static charge-density wave or spin-density wave in the Cu-O chains either concurrent or very closely associated with the superconducting transition.

I. INTRODUCTION

Positron annihilation is a powerful tool for mapping out the momentum distribution of the valence electron in solids.[1] The method is particularly useful when sizable high-purity single crystals are not available so that more detailed magneto-oscillation measurements are not possible. For this reason, the method has been widely applied to investigate the high-temperature copper oxide superconductors.[2–10] In a typical experiment one measures the Doppler-broadened annihilation radiation (DBAR) spectrum and look for either evidence for momentum cutoff at the Fermi level or for any change in the spectrum between normal and superconducting states. Since superconductivity affects the momentum distribution of conduction electrons in an energy range $\pm kT_c$ around the Fermi energy μ, any change in the DBAR spectrum between normal and superconducting states is measured by the ratio $(kT_c/\mu)^2$, which is of the order 10^{-4} for high-temperature superconductors.[6] Changes in the DBAR spectrum of this size are impossible to observe. Nevertheless, many groups have reported fractions of 1% differences in the shape parameter between normal and superconducting states in copper oxides. In an effort to ascertain whether this change in momentum distribution is indeed due to superconductivity, we have measured the DBAR spectra of several polycrystalline samples of 1:2:3 material at room temperature, as well as liquid-nitrogen temperature. A new method to analyze the data is also proposed. The result shows that the change in the DBAR spectra associated with the superconducting transition is not a consequence of Cooper pair formation, but is consistent with the formation of a static charge-density-wave (CDW) or spin-density-wave (SDW) state in the Cu-O chains, concurrent with or very closely tied to the superconducting transition.

II. EXPERIMENT

A single phase powder sample of $YBa_2Cu_3Y_{7-x}$ ($x \cong 0.15$) was prepared in the usual manner and pressed into pellets of about 6 mm in diameter and 1 mm in thickness. A ^{22}Na source with an activity of about 50 μCi was enveloped in a Mylar film of $\frac{1}{4}$ mil thickness and sandwiched between two pellets of identical sample material. The assembly of source and sample was mounted on a high-resolution gamma spectrometer for the measurements of DBAR spectra. The spectrometer consists of a planar HPGe detector (Princeton Gamma Tech) having a full width resolution of 1.22 keV measured at half maximum of the 514-keV line of ^{85}Sr. The total number of counts collected under a DBAR spectrum was more than 4×10^6. For every specimen the measurement was first made in the normal state at room temperature and then in the superconducting state after the sample was cooled rapidly to liquid-nitrogen temperature. We chose to quench the sample to the superconducting state rather than cooling it in a cryostat because the former procedure minimizes the loss of oxygen that takes place when the sample is kept in a vacuum for a prolonged period of time.

The DBAR spectrum consists of contributions from all occupied electron states, core states as well as the occupied part of band states. Unlike simple metals, the bonds in copper oxide systems are highly covalent, and it remains unclear whether the normal-state spectrum gives any indication of Fermi surface effects.[9,10] We propose to study the effect of superconductivity on the electron system by taking the difference spectrum between normal and superconducting states. In this manner the subtle change that may take place at the Fermi level is highlighted and all other contributions are cancelled. We first apply a point by point deconvolution process to the

DBAR spectra to eliminate the line broadening due to instrumental resolution. The detail of the deconvolution process is given in the Appendix. The deconvoluted spectra of one sample are shown in Fig. 1. There is no sharp cutoff in the spectra to indicate a Fermi momentum, probably because the sample is polycrystalline and that the Fermi surface has complicated geometry. The normal-state spectrum exhibits shoulders near the points of half maximum, as was first noticed by Manuel *et al.*[11] In the superconducting state the shoulders are less pronounced. The best way to visualize this change in shape is to take a point by point subtraction of the normalized spectra at the two temperatures, as shown in Figs. 2 and 3 for two different materials. Since the difference is small, we chose not to deconvolute the spectra in order to avoid undue accumulation of errors. The difference spectrum in Fig. 2 was found for several different samples prepared under identical conditions, all with $T_c \cong 92$ K. Figure 3 was found for a partially vacuum-annealed sample with $T_c \cong 83$ K. Upon further annealing, the sample ceased to be superconducting at the nitrogen temperature, and the difference spectrum is reduced to the noise level.

For the purpose of comparing our results with other experimental findings, we have calculated the shape or S parameter for the two types of samples. The exact value of the S parameter depends on its definition, and this is not always stated explicitly by most authors. Nevertheless, our difference spectrum for the 92 K material corresponds to an approximately 1% increase in S parameter when going from room to liquid-nitrogen temperatures, and the 82 K material shows a 0.3% increase. The latter is consistent with what was reported in Refs. 3 and 6, and the former is somewhat larger. One investigation reported a decrease in the S parameter of the order of a few tenths of 1% when the sample was cooled below 250 K,[12] but this transition was not observed by other investigators. We feel that the shape parameter is not a precise way to characterize the subtle difference in the DBAR spectra in the two states. Accordingly, we propose in Sec. III a new way to analyze the spectra and show that it gives much better insight into the underlying physics.

III. THEORY

The authors of Ref. 3 have reported that the positrons sample preferentially the electron distribution in the Cu-O chains. Band structure calculations have shown the presence of delocalized electrons in these chains.[13] Consequently, we seek to understand the experimental observation by studying what effects superconductivity may have on a one-dimensional electron gas. In the normal state at zero temperature, the energy levels are filled between $-p_F$ and p_F, where p_F is the Fermi momentum. Consider a chain that makes an angle θ with the line joining the sample to the detector. Given a Doppler momentum p for the photon, it comes from the annihilation of an electron whose momentum along the chain was 2 psecθ. Thus, the counting rate is proportional to

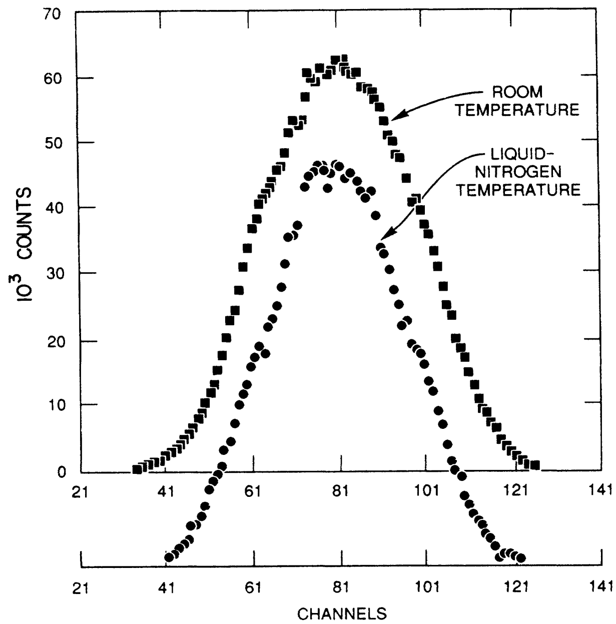

FIG. 1. Deconvoluted Doppler-broadened spectra of one sample of $YBa_2Cu_3O_{7-x}$ in normal (upper) and superconducting (lower) states.

$$N_n(p,\theta)=1 \quad \text{for} \quad |p|<p_F\cos(\theta/2)$$
$$=0 \quad \text{for} \quad p>p_F\cos(\theta/2) \; . \qquad (1)$$

Since the sample is polycrystalline with Cu-O chains in all possible directions, we must average over θ to obtain

$$N_n(p)=1-2p/p_F \quad \text{for} \quad |p|<p_F/2$$
$$=0 \quad \text{for} \quad p>p_F/2 \; . \qquad (2)$$

In the superconducting state the momentum distribution is not cut off sharply at the Fermi momentum. Instead, the distribution is given by the coherence factor[14]

$$N_s(p,\theta)=\frac{1}{2}\left[1-\frac{\varepsilon-\mu}{[(\varepsilon-\mu)^2+\Delta^2]^{1/2}}\right] , \qquad (3)$$

where ε is the energy of the annihilated electron with momentum 2 psecθ, μ is the Fermi energy, and Δ is the superconducting order parameter. Since Δ is a small fraction of μ, we may expand the energy around μ, i.e.,

$$\varepsilon=(2\ p\sec\theta)v_F \; , \qquad (4)$$

where v_F is the Fermi velocity, and $\mu=p_F v_F$. The angular average can be carried out, with the result

$$N_s(p)=\tfrac{1}{2}[1-g(p)] \; , \qquad (5)$$

where $g(p)$ is given by

$$g(p)=\frac{p\cos\alpha}{[(p_F/2)^2+(\Delta/v_F)^2]^{1/2}}\left\{\cos\alpha\left[\ln\tan\left[\frac{\pi}{4}+\frac{\alpha}{2}\right]-\ln\tan\left[\frac{\eta}{2}+\frac{\alpha}{2}\right]\right]+\sin\alpha[\sec\alpha-\sec(\eta+\alpha)]\right\} . \qquad (6)$$

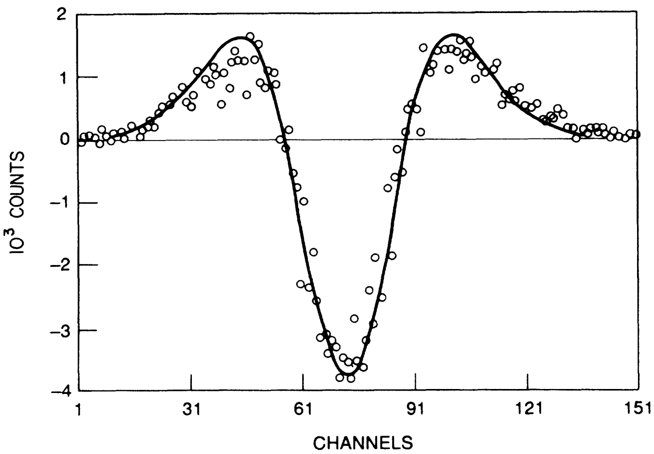

FIG. 2. The difference between the Doppler-broadened spectra of normal and superconducting states of one sample with $T_c = 92$ K. Each channel corresponds to a Doppler momentum of 1.37×10^{-4} m c.

The quantities η and α are defined by

$$\tan\eta = (2|p| - p_F)v_F/\Delta \ ,$$

$$\tan\alpha = v_F p_F/\Delta \ . \tag{7}$$

The difference spectrum

$$\Delta N(p) = N_n(p) - N_s(p)$$

is readily calculated. The difference is positive at the center of the zone and negative around p_F. For a hole band the entire difference spectrum reverses sign such that it is negative at the zone center and positive around p_F. We then convolute the calculated difference spectrum with the known resolution function and fit the result to the experimental data.[15]

Since the measured difference spectrum is negative at the center and positive further out, it indicates that the electrons are in a hole band. The calculated hole band on the chains is not centered at the Γ point,[13] but it hardly matters because the small occupied pocket around Γ makes a very small contribution to the spectrum. We expect the Fermi momentum of the hole band measured in the extended zone scheme to enter the expression of the difference spectrum. The position of the positive peak is sensitive to the choice of p_F, and for the best fit to the difference spectrum in Fig. 2, we find

$$p_F = 5.2\times 10^{-3} \text{ m}c \ .$$

The calculated value when converted to the same unit is

$$p_F = 5.5\times 10^{-3} \text{ m}c \ .$$

The magnitude of the difference spectrum is sensitive to the choice of Δ/v_F, and for the best fit we find

$$\Delta/v_F = 2.3\times 10^{-3} \text{ m}c \ .$$

Assuming $v_F = 10^7$ cm/sec for a typical d-band metal, we find $\Delta = 0.4$ eV, which is much larger than that estimated from the critical temperature

$$\Delta = 1.75\ kT_c = 13 \text{ meV} \ .$$

The fact that the change in the Doppler spectrum shape function gives hint to a very large order parameter was noticed by Smedskjaer *et al.*[6] and von Stetton *et al.*[3] An order parameter of this size cannot be associated with superconductivity. Before we discuss possible causes of the electron momentum redistribution, we present the result of our analysis of the difference spectrum in Fig. 3 for a slightly vacuum-annealed sample with $T_c = 83$ K. This sample contains less oxygen, so it is expected to have fewer holes in the band and a smaller Fermi momentum. The best fit to the data gives $p_F = 2.5\times 10^{-3}$ m c, which is much smaller than that for the 92 K sample. The order parameter turned out to be also much smaller,

$$\Delta/v_F = 1.1\times 10^{-3} \text{ m}c \ .$$

It is clear that for the two samples the order parameters do not scale with T_c, and this fact is another indication that the momentum redistribution is not due to superconductivity.

The Cu-O chains, being one-dimensional electron systems, can readily support charge-density-wave or spin-density-wave states, both of which are stabilized by the strong Coulomb interaction and can have order parameters as large as those observed by our DBAR spectra. The associated electron momentum redistribution for both states can be written approximately in the same form as in Eq. (3).[16] Therefore, we tentatively ascribe the difference in DBAR spectra between normal and superconducting states to the formation of CDW or SDW states in the Cu-O chains. We may also add at this point that we have analyzed the spectra using 2D and 3D electron gas models, but the fits are not nearly as good as the 1D model.

At present we are not capable of taking the spectra over a sequence of temperatures to see whether the observed momentum redistribution occurs abruptly at T_c. However, we believe that we are probing the same effect reported earlier by Smedskjaer *et al.*[6] and von Stetton

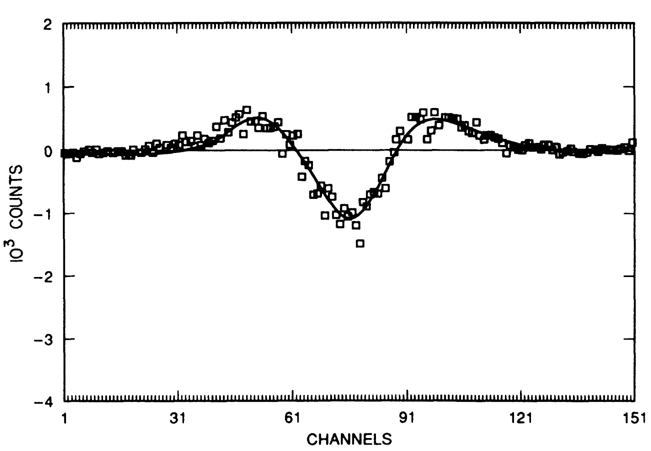

FIG. 3. The difference between the Doppler broadened spectra of normal and superconducting states of a slightly vacuum-annealed sample with $T_c = 83$ K.

et al.,[3] and both studies showed that the shape parameter undergoes a sharp change at T_c. Our suggestion that the change is associated with a CDW or SDW state in the Cu-O chains raises the immediate question why should the state form at the same temperature as superconductivity? A recent paper by Hertel, Appel, and Swihart provides an interesting clue.[17] It is shown that the electron-electron scattering between charge carriers in the chains and those in the Cu-O planes causes a temperature dependent pair-breaking effect which prevents the CDW state from forming in the chains until the Cu-O planes become superconducting. This scenario describes well the change in DBAR spectrum at T_c. Since electron-electron scattering affects CDW and SDW states in the same manner, the observed effect can also be due to SDW. We are not aware of any direct evidence for CDW or SDW in the Cu-O chains. There may be two reasons for this. Most neutron or x-ray scattering experiments are done at room temperature, and these experiments would miss the CDW or SDW state in the chains because they are only expected to be stable in the superconducting state. It is also possible that the Cu-O chains only achieve short-range order that can be detected by positron annihilation but not by neutron or x-ray scattering. This question can only be resolved through further experimentation.

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APPENDIX

The deconvolution process we have used to deduce the curves in Fig. 1 is described in the following.[18] We first let

$$F_i = \sum_{j=1}^{n} R_{i-j} U_j \ ,$$

where F_i is the datum point from the DBAR spectrum and R is the detector resolution function, defined over $2n-1$ channels and determined by using the 514 keV gamma line from ^{85}Sr. U is the unknown function we are searching. Both F and U are defined over n channels.

An iteration process uses the form

$$F_i^{(m)} = \sum_{j=1}^{n} R_{i-j} U_j^{(m)} \ ,$$

where $m = 1,2,3,\ldots$ denotes the order of iteration. For the initial estimate of U, we let

$$U_j^{(1)} = F_i \ ,$$

and subsequent U's are determined by using

$$U_i^{(m+1)} = U_i^{(m)} \left[\left(\sum_{j=i-8}^{j=i+8} F_j \right) \Big/ \left(\sum_{j=i-8}^{j=i+8} F_j^{(m)} \right) \right]^2 .$$

The quality of fit is measured by the parameter

$$\chi^2(m) = n^{-1} \sum_{i=1}^{n} (F_i - F_i^{(m)})^2 \ .$$

The process is repeated by letting $m \rightarrow m+1$ until a minimum χ^2 is reached. Our minimum values of χ^2 thus determined are all in the neighborhood of 1.20.

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[1]For a general survey of positron annihilation techniques, see R. W. Siegel, Annu. Rev. Mater. Sci. **10**, 393 (1980).

[2]Y. C. Jean, J. Kyle, H. Nakanishi, P. Turchi, R. H. Howell, A. L. Wachs, M. J. Fluss, R. L. Meng, H. P. Hor, J. Z. Huang, and C. W. Chu, Phys. Rev. Lett. **60**, 1069 (1988).

[3]E. von Stetten, S. Berko, X. S. Li, R. R. Lee, J. Brynestad, D. Singh, H. Krakauer, W. E. Pickett, and R. E. Cohen, Phys. Rev. Lett. **60**, 21 (1988).

[4]A. L. Wachs, P. Turchi, D. R. Harshman, Y. C. Jean, R. H. Howell, M. J. Fluss, J. Remeika, A. Cooper, and R. M. Flemming, APS Bulletin **33**, 804 (1988).

[5]S. G. Usmar, P. Sferlazzo, K. G. Lynn, and A. R. Moodenbaugh, Phys. Rev. B **36**, 8854 (1987).

[6]L. C. Smedskjaer, B. W. Veal, D. G. Legnini, A. P. Paulikas, and L. J. Nowicki, Phys. Rev. B **37**, 2330 (1988).

[7]S. J. Wang, S. V. Naidu, S. C. Sharma, D. K. De, D. Y. Jeong, T. D. Black, S. Krichene, J. R. Reynolds, and J. M. Owens, Phys. Rev. B **37**, 603 (1988).

[8]D. E. Farrell, J. D. McGervey, Y. Kobayashi, W. Zheng, B. S. Chandrasekhar, D. Boyne, and N. Bansal, Bull. Am. Phys. Soc. **33**, 804 (1988).

[9]P. Turchi, A. L. Wachs, Y. C. Jean, R. H. Howell, K. H. Wetzler, and M. J. Fluss, Lawrence Livermore National Laboratory Report No. UCRL 98202, 1988 (unpublished).

[10]L. C. Smedskjaer, J. Z. Liu, R. Benedek, D. G. Legnini, D. J. Lam, M. D. Stahulak, H. Claus, and A. Bansil, Physica C **156**, 269 (1988).

[11]L. Hoffmann, A. A. Manuel, M. Peter, E. Walker, and M. A. Damento, Europhys. Lett. **6**, 61 (1988).

[12]A. G. Balogh, W. Puff, L. Liszky, and B. Molnár, Phys. Rev. B **38**, 2883 (1988).

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

[14]J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964), Chap. 2.

[15]The resolution function is a Gaussian with $\mathrm{FWHM}=2.4\times10^{-3}$ mc. The best fit was obtained by $\mathrm{FWHM}=3.6\times10^{-3}$ mc. The extra width may be due to finite-temperature and other broadening effects.

[16]See the review by B. I. Halperin and T. M. Rice, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 21, pp. 116–192.

[17]P. Hertel, J. Appel, and J. C. Swihart, Phys. Rev. B **39**, 6708 (1989).

[18]S. Dannefaer and D. Kerr, Nucl. Instrum. Methods **131**, 119 (1975).