Phonons and Superconductivity in $Bi_2Sr_2CaCu_2O_8$

H. A. Mook, B. C. Chakoumakos, and M. Mostoller
Oak Ridge National Laboratory, Solid State Division, P.O. Box 2008, Oak Ridge, Tennessee 37830

A. T. Boothroyd[a] and D. McK. Paul
Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom
(Received 20 April 1992)

Detailed neutron scattering measurements have been made for selected phonons for $Bi_2Sr_2CaCu_2O_8$. The temperature dependence of the linewidths indicates large anharmonic effects particularly for the oxygen modes. The superconductivity induced change in width below T_c of the two highest energy oxygen modes is found to be nearly 2% of the phonon energy suggesting a large electron-phonon coupling.

PACS numbers: 74.70.Vy, 63.20.Dj, 63.20.Kr, 63.20.Ry

A number of measurements now show that the lattice dynamics of the high-T_c superconductors have unusual effects, particularly near T_c. Large changes are found in the ion channeling in $YBa_2Cu_3O_7$ and $ErBa_2Cu_3O_7$ in the vicinity of the transition T_c [1,2]. Neutron resonance absorption spectroscopy (NRAS) for Cu in $Bi_2Sr_2CaCu_2O_8$ shows that the kinetic energy (KE) drops rapidly slightly above T_c, but then remains temperature independent as the temperature is reduced further [3]. Cu K-edge x-ray absorption data indicate that there is an instability in the motion of the axial oxygen at the superconducting transition in $YBa_2Cu_3O_7$ [4], and dynamic changes in the local structure at T_c have been observed for $Tl_2Ba_2CaCu_2O_8$ by neutron scattering [5]. Although dispersion curves have been established for $YBa_2Cu_3O_{7-\delta}$ [6,7], no neutron scattering measurements are available for high-T_c superconductors showing the change in phonon linewidths resulting from superconductivity. Here, we report neutron scattering measurements on $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) undertaken to study the interaction between the lattice dynamics and superconductivity. Raman scattering and infrared spectroscopy can be used to study $q=0$ phonons; however, phonons at general points in the zone would be expected to behave very differently than the $q=0$ phonons. This may be particularly true for materials like 2:2:1:2 because an important length scale for superconductivity, the coherence length, is very short. Our measurements made for the high-energy oxygen vibrations in the region of the zone boundary demonstrate that considerable anharmonic effects are present in the material, and that sizable increases in the phonon widths occur below T_c.

Because of the complex structure of the material, the phonon dispersion curves have many branches close together in energy, and it is difficult to establish the positions of all the branches. Since the KE measurements for 2:2:1:2 showed the most unusual behavior for motion in the Cu-O planes, it was decided to concentrate on the phonons propagating in the planes. It is difficult to grow large high-quality crystals of 2:2:1:2, although rods of the material can be grown by the floating-zone technique in which the a and b axes alternate in being well oriented along the growth direction. The material is orthorhombic with $a=5.408$ Å, $b=5.413$ Å, and $c=30.87$ Å; however, since a is nearly equal to b, we will neglect this difference and consider the tetragonal cell only. Calculations for phonon dispersion relations made with the orthorhombic cell showed little difference from those made with the tetragonal cell for the modes of present interest. Six rods, about 0.75 cm in diameter and 4 cm long, were aligned together to make the sample. The sample thus had only the $a(b)$ axis aligned and had a mosaic spread of 13° (FWHM). T_c was measured by ac susceptibility for each of the rods. The transition showed an onset at 83 K and was rather broad with a tail extending to 75 K. The large mosaic spread of the sample restricted the types of modes we could measure; however, the modes of most interest are the longitudinal zone-boundary modes, and these are affected little by the sample mosaic spread. Our measurements were made using triple-axis spectrometers at the High-Flux Isotope Reactor at Oak Ridge National Laboratory and the MARI time-of-flight spectrometer at the ISIS facility at the Rutherford Appleton Laboratory.

Calculations were made for the 2:2:1:2 material using a shell model with short-range Born-Mayer interactions [$V(r)=Ae^{-r/\rho}$]. A fuller description of the model as applied to La_2CuO_4 may be found in Ref. [8]. We have established the zone-boundary energies of modes propagating in the (π,π) direction, in terms of square lattice notation. These measurements along with previous Raman data for the A_{1g} and B_{1g} modes provide fewer than twenty experimental guidelines to adjust roughly forty parameters. In this circumstance, starting values for parameters were taken from Ref. [8] and other sources in the literature and varied to move calculated and measured energies closer. It is found, as with other perovskites, that there is a tendency for instability, signaled by negative eigenvalues. For the 2:2:1:2 structure, shear along z is a particular problem. For the current calculation, parameters were determined so that there are no negative eigenvalues along major symmetry directions. Good agreement (10–20)% is found between the neutron scattering measurements and the energies obtained from the calculation. The calculation can thus be used to iden-

tify the atomic displacement patterns associated with the measured energies. No evidence in our measurements is found for the large sharp bosonic peak at 10 meV found by Arnold, Mueller, and Swihart [9], with either the sample discussed above or with oriented powdered samples made to examine the phonon density of states for the *a-b* planes.

Because of the large number of closely spaced phonon modes, it is, in general, almost impossible to isolate individual phonon modes to study. However, our measurements and calculations show that for most of the zone the top two oxygen modes are sufficiently far above the other modes in energy that they can be studied individually. We will first discuss measurements for the highest energy mode in the spectrum, made at the $0.8(\pi,\pi)$ position using a triple-axis spectrometer. The triple-axis spectrometer utilized a Be monochromator and a pyrolitic graphite analyzer with collimations of 40 min before and after the monochromator and 40 and 80 min before and after the analyzer. The measurement was made at the (1.6,1.6,0) position in reciprocal space rather than the (1.5,1.5,0) zone boundary (π,π) because kinematical constraints of the scattering geometry for the optimum initial and final spectrometer energies prevent closing of the scattering triangle at the (1.5,1.5,0) position. The increasing ratio of multiphonon to single-phonon scattering precludes using larger zone-boundary reciprocal-lattice positions. The motion of the oxygen is essentially the breathing mode in which the oxygen motion is directly toward the Cu atoms. We find that this mode is very broad and is difficult to distinguish from the highly sloping multiphonon background above 150 K. As the temperature is lowered, the mode sharpens and the background disappears with the minimum width found near 70 K. The large linewidths and large multiphonon scattering at the higher temperatures are a signature of anharmonic effects. As the temperature is lowered below 70 K, the peak broadens again. Measurements at ISIS were made only at 120 and 70 K and are in good agreement with the triple-axis measurements at these temperatures. Figure 1 shows triple-axis measurements for this mode made at several temperatures.

The second phonon mode examined is the next highest mode where spectra were obtained at the (2.3,2.3,0) reciprocal-lattice position $0.6(\pi,\pi)$. This position was chosen to take maximum advantage of the focusing conditions of the three-axis spectrometer. A higher momentum value could be used in this case as the multiphonon scattering is not as large at this somewhat reduced energy. This mode also samples the in-plane oxygen motion, with the motion this time being along the $a(b)$ direction. Measurements for three temperatures are shown in Fig. 2. The results are similar to those found before as the minimum width is found near the superconducting temperature. Measurements at ISIS revealed that differences in the phonon line shape between 120 and 70 K are

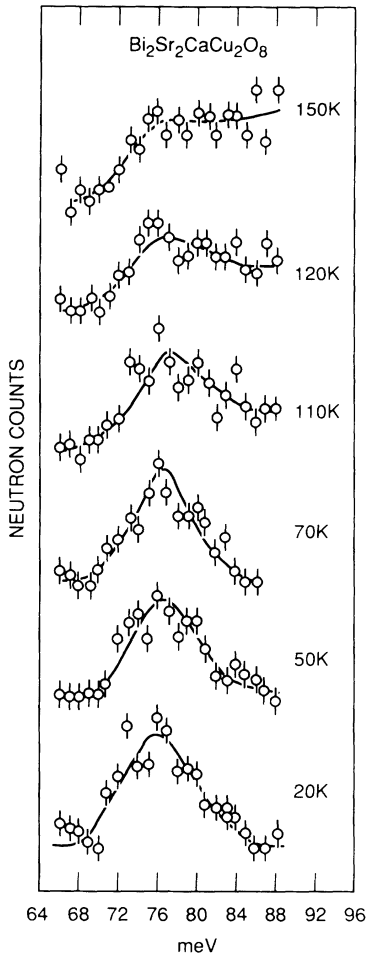

FIG. 1. Triple-axis measurements at the $0.8(\pi,\pi)$ position for the oxygen mode centered near 76 meV.

not restricted to $0.6(\pi,\pi)$ but occur over much of the branch. We note that the phonon energy is slightly reduced at 70 K relative to 120 or 10 K. The top curves in Fig. 3 show the phonon widths for these modes obtained by least-squares fitting a Gaussian line shape to the data, plotted as a function of temperature. Our Gaussian fit included a sloping background although the background is nearly flat below T_c, which is the temperature region important for determining the electron-phonon coupling.

It takes too much spectrometer time to make complete scans at closely spaced temperature intervals; however, a good indication of the phonon widths of the two highest energy modes can be obtained by picking an energy between them and counting at that energy as a function of temperature. The count rate will be high when the phonons are broad so that they overlap to some degree, and low when the phonons are narrow. Some of the background is multiphonon in nature and this will also reduce as the phonons become narrow. The third plot in Fig. 3 shows the temperature dependence of a measurement

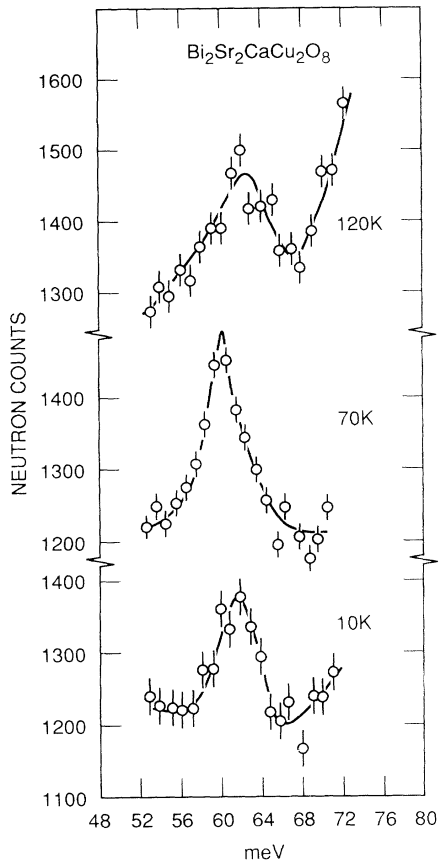

FIG. 2. Triple-axis measurements at the $0.6(\pi,\pi)$ position for the oxygen mode centered near 62 meV. A number of runs have been averaged together to achieve the error bars shown.

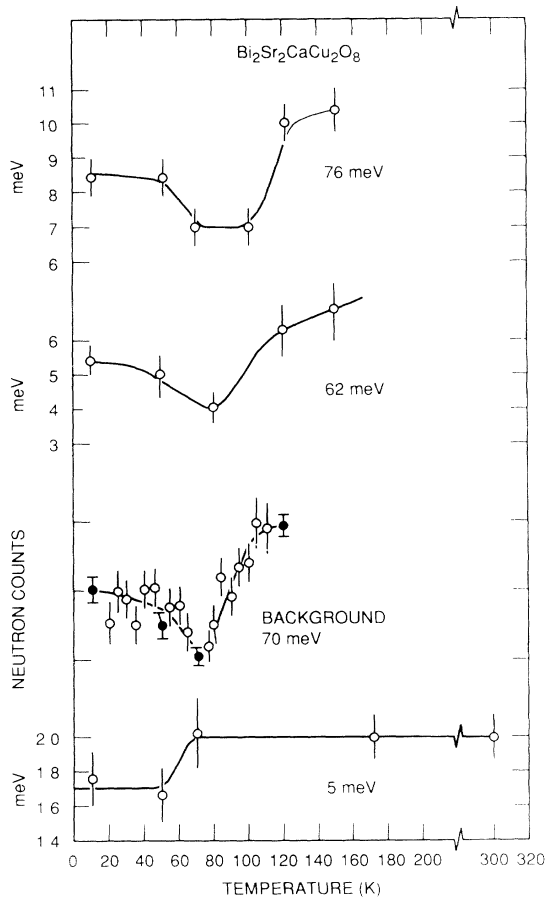

FIG. 3. The first two curves show the measured widths for the 76- and 62-meV modes for temperatures above and below T_c. The third graph is a measurement of the scattered intensity at $0.6(\pi,\pi)$ and 70 meV made as a function of temperature. The solid points with the smaller errors were counted for a longer time period. The bottom graph shows the width of the longitudinal-acoustic branch at 5 meV and $0.5(\pi,\pi)$ for temperatures above and below T_c.

made at (2.3,2.3,0) at the energy of 70 meV, which is between the two oxygen modes. The solid points with the reduced errors were counted for longer times. The result shows the strong anharmonic behavior at the higher temperatures, and that the phonon linewidth is a minimum near the superconducting transition temperature.

We found one low-energy position where an intense phonon peak could be clearly isolated. This is at an energy of 5 meV on the longitudinal-acoustic branch at the $0.5(\pi,\pi)$ position. The behavior here is different as the linewidth is quite temperature independent between 70 K and room temperature. A slight narrowing seems to take place below 70 K, but this narrowing is near the uncertainty of the measurement. The widths are shown in the lowest plot in Fig. 3. The linewidths at all temperatures are considerably wider than the instrumental resolution of 0.65 meV, perhaps because of the Bi-O plane disorder.

A number of other modes have been studied, and, while well-defined isolated spectra were not obtained, it is clear that considerable anharmonicity also exists for the modes in which the Cu is in motion. It appears that the rapid loss of anharmonicity for the Cu-O modes as the temperature is lowered toward T_c contributes to the sudden drop in Cu KE found in the NRAS measurement. The KE of a phonon is given by an integral over its spectral line shape weighted by the square of the energy. A broad phonon centered at the same energy thus has a much higher KE than a narrow one. We note that the normalized minimum yield for oxygen from ion channeling by Haga *et al.* [1] for $YBa_2Cu_3O_7$ looks very similar to our width measurements shown in Fig. 3, suggesting that the modes examined in the present experiment may be similar to the modes in $YBa_2Cu_3O_7$ responsible for much of their observed effect. Their results do not show quite as large a change in anharmonicity above T_c, which is consistent with recent NRAS measurements made for the KE for Cu in $YBa_2Cu_3O_7$ [10]. It is not clear how the sudden loss of anharmonicity near T_c is related to superconductivity.

The broadening of the oxygen linewidths below T_c

seems directly related to superconductivity as the broadening appears to follow the superconducting order parameter. This is to be expected as phonons above the gap have extra decay channels from the breaking of Cooper pairs. This has been documented for the case of Raman scattering and infrared spectroscopy for the near $q=0$ phonons in $R\mathrm{Ba_2Cu_3O_7}$ for various rare earths R [11]. Data analysis based on calculations by Zeyher and Zwicknagl [12] yielded values of the electron-phonon coupling constant λ_q for each phonon branch. It is not such a simple matter to obtain λ_q for the $q\neq 0$ phonons. Zeyher [13] has made a strong-coupling calculation of the phonon widths resulting from superconductivity for various positions in the zone using a model Fermi surface. This calculation suggests that the phonon width changes due to superconductivity would generally be small for phonons near the zone boundary, which in turn implies that a large λ_q would be needed to account for observations.

We can obtain the extra phonon width observed below T_c from our Gaussian fits and a knowledge of the spectrometer resolution by using the technique of Wertheim *et al.* [14]. The increase in width is found to be 1.0 ± 0.5 meV or 1.6% for the 62-meV mode and 1.5 ± 0.5 meV or 2% for the 76-meV mode. We note that this is larger than the $q=0$ value of about 0.5% found by Litvinchuk, Thomsen, and Cardona [11] for $R\mathrm{Ba_2Cu_3O_7}$ for the highest energy oxygen mode. This would suggest that the present measurements support a reasonably large λ_q for these modes.

The average value of λ for (2:2:1:2) can only be obtained by comparing our results to a calculation that incorporates the correct Fermi surface for this material. Also, the observation of a large λ_q at one point in the zone does not imply a large overall electron-phonon coupling. Crespi and Cohen [15] have shown that anisotropic Fermi-surface nesting can result in large electron-phonon effects for particular modes even though transport measurements suggest a much smaller electron-phonon interaction.

We find it very interesting that the high-energy phonon modes have such a dramatic change in width at temperatures just above T_c. As seen in Fig. 1, the 76-meV mode changes from being almost unobservable at 150 K to being well defined at 70 K. This suggests anharmonic effects that are associated in some manner with the superconductivity. It would thus seem necessary to consider anharmonic potentials in calculations that address the problem of phonon-mediated pairing in high-T_c superconductors.

The authors acknowledge helpful discussions with P. B. Allen, G. D. Mahan, and W. E. Pickett. We also appreciate the help of A. D. Taylor and M. Arai with the ISIS experiments. This research was supported in part by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

[a]Present address: Clarendon Laboratory, Oxford University, Oxford, United Kingdom.

[1] T. Haga, K. Yamaya, Y. Abe, Y. Tajima, and Y. Hidaka, Phys. Rev. B **41**, 826 (1990).
[2] R. P. Sharma, L. E. Rehn, P. M. Baldo, and J. Z. Liu, Phys. Rev. Lett. **62**, 2869 (1989).
[3] H. A. Mook, M. Mostoller, J. A. Harvey, N. W. Hill, B. C. Chakoumakos, and B. C. Sales, Phys. Rev. Lett. **65**, 2712 (1990).
[4] S. D. Conradson, I. D. Raistrick, and A. R. Bishop, Science **248**, 1394 (1990).
[5] B. H. Toby, T. Egami, J. D. Jorgensen, and M. A. Subramanian, Phys. Rev. Lett. **64**, 2414 (1990).
[6] L. Pintschovius, N. Pyka, W. Reichard, A. Yu. Rumiantsev, N. L. Mitrofanov, A. S. Ivanov, G. Collin, and P. Bourges, Physica (Amsterdam) **185C**, 156 (1991).
[7] W. Reichard, Neutron News **1**, 20 (1990).
[8] M. Mostoller, J. Zhang, A. M. Rao, and P. C. Eklund, Phys. Rev. B **41**, 6488 (1990).
[9] G. B. Arnold, F. M. Mueller, and J. C. Swihart, Phys. Rev. Lett. **67**, 2569 (1991).
[10] N. Hecker *et al.* (to be published).
[11] A. P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **80**, 257 (1991).
[12] R. Zeyher and G. Zwicknagl, Z. Phys. B **78**, 175 (1990).
[13] R. Zeyher, Phys. Rev. B **44**, 10404 (1991).
[14] G. K. Wertheim, M. A. Butler, K. W. West, and D. N. E. Buchanan, Rev. Sci. Instrum. **45**, 1369 (1974).
[15] V. H. Crespi and M. L. Cohen, Solid State Commun. **81**, 187 (1992).