Phonon density of states of the $YBa_2Cu_3O_y$ superconducting ceramics

L. Mihály
Central Research Institute for Physics, H-1525 Budapest, POB 49, Hungary

L. Rosta
Laboratoire Leon Brillouin, Centre d'Études Nucléaires de Saclay, F-91191 Gif-sur-Yvette, France and Central Research Institute for Physics, H-1525 Budapest, POB 49, Hungary

G. Coddens
Laboratoire Leon Brillouin, Centre d'Études Nucléaires de Saclay, F-91191 Gif-sur-Yvette, France and University of Antwerp, B-2610 Wilrijk, Belgium

F. Mezei
Hahn-Meitner Institut, D-1000 Berlin 39, PF 390128, Federal Republic of Germany and Central Research Institute for Physics, H-1525 Budapest, POB 49, Hungary

Gy. Hutiray, G. Kriza, and B. Keszei
Central Research Institute for Physics, H-1525 Budapest, POB 49, Hungary
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Neutron scattering measurements were performed on polycrystalline Y-Ba-Cu-O ceramics to explore the relationship between structure, phonon spectrum, and superconductivity. No evidence was seen for soft phonon modes. The superconducting transition temperature of the compound was tuned by heat treatments. Although oxygen removal leads to changes in the lattice parameters and the time-of-flight spectrum indicates a general softening of the lattice, the characteristic features in the phonon density of states remain unchanged.

The copper-based superconducting oxide ceramics of very high critical temperatures[1-3] have attracted considerable attention recently. The prototype compound $YBa_2Cu_3O_y$ has a well-defined metal-ion stoichiometry,[2] but the oxygen content y may vary according to the preparation conditions.[4] X-ray and neutron-diffraction measurements indicate that the structure of the compound can be described as a distorted oxygen-deficient perovskite.[4-6] A feature common to both the La_2CuO_4-based superconductors[7] and the very-high-T_c materials is the existence of two-dimensional copper-oxygen planes, which are most likely responsible for the metallic conduction. Also, the valence state of the copper seems to be of fundamental importance; for $y=6.5$ when all the copper is divalent the superconductivity disappears.[8]

Attempts were made to explain the extraordinary high critical temperature in the framework of strong-coupling BCS theory[9,10] and by proposing novel mechanisms for electron-electron coupling.[11] Particularly strong electron-phonon coupling may arise in the vicinity of a soft phonon mode, and arguments were made to relate the high T_c to a Peierls-type structural instability.[10] From this point of view the study of the phonon spectrum or phonon density of states is of fundamental interest.

In this paper we report inelastic neutron scattering studies in the energy range 0–40 meV, complemented by neutron diffraction and dc resistivity measurements. For the high-T_c compound $YBa_2Cu_3O_y$ ($y\approx 7.0$, $T_c=91$ K) an enhancement in the phonon density of states (DOS) is observable around $\hbar\omega\approx 5$ meV, but no soft modes are visible. Heat treatment in argon flow decreased the oxygen content of the sample and reduced the critical temperature to $T_c\approx 20$ K. Although oxygen removal leads to changes in the lattice parameters and the time-of-flight spectrum indicates a general softening of the lattice, the characteristic features in the phonon DOS remain unchanged. In particular, the DOS enhancement at 5 meV does not vary in correlation with the critical temperature.

The samples were prepared by firing Y_2O_3, $BaCO_3$, and CuO in two steps. First the well-mixed powder was heated to 900 °C in air for 24 h. The product was reground, pressed into pellets, heated to 950 °C in oxygen atmosphere for 12 h, and cooled to room temperature in 5 h. Altogether 80 g of $YBa_2Cu_3O_y$ (referred to as "pristine sample") were obtained this way. X-ray powder diffraction indicated less than 5% of any other phase and the density of the porous material was about half of the theoretical value. 40 g of the pristine sample were further heat treated in argon flow at 480 °C for 10 h ("argon-treated sample"). The weight loss of 0.86% in this process corresponds to an oxygen loss of $\Delta y=0.36$. After completion of the neutron scattering experiment, the argon-treated sample was fired at 550 °C for 3 h in oxygen flow and cooled down in 12 h ("oxygen-treated sample"). An increase of oxygen content corresponding to $\Delta y=0.38$, slightly larger than the oxygen loss due to argon treatment, was calculated from the weight change. As discussed later in detail, the properties of the oxygen-treated sample were found to be practically identical to the pristine sample.

The superconducting transition temperatures of the samples were deduced from dc conductivity measurements (Fig. 1). While the critical temperature of the pristine and oxygen-treated samples is 91 and 94 K, respectively, the argon-treated sample has a substantially reduced and smeared transition ($T_{\text{onset}}=25$ K, $T_{\text{zero resistance}}=10$ K). The temperature dependence of the resistivity clearly demonstrates the change in the superconductivity properties due to oxygen loss.

The structure of the polycrystalline samples was investigated by neutron diffraction, performed on cold-neutron-guide triple-axis spectrometer G43 of LLB (Laboratoire Leon Brillouin) Saclay at the wavelength of $\lambda=4.00$ Å. At this wavelength the first few diffraction peaks are stretched out over the full $2\theta=0°-180°$ angle range resulting in an extremely good resolution. For example, the (003), (010), and (100) reflections are separated in our study, whereas they coincide in the diffraction measurements performed at shorter neutron wavelengths.[5,6] On the other hand, the relatively small number of reflections does not allow for a refinement of the structure. The results are summarized in Table I. The peaks can be indexed according to an orthorhombic structure with lattice constants depending on the oxygen content. For the argon-treated sample the structure is closer to tetragonal and the lattice is elongated in the c direction. The Bragg peak widths are resolution limited, indicating that the heat treatment affected the bulk of the material.

Inelastic neutron scattering experiments were made at the MIBEMOL time-of-flight spectrometer of LLB Saclay. The incident neutron energy was 3.4 meV ($\lambda=4.9$ Å) and the spectra were recorded at room temperature in up scattering (neutron energy gain). Sixteen detector columns of six counters each were arranged over scattering angles between 80° and 100°. The flight path

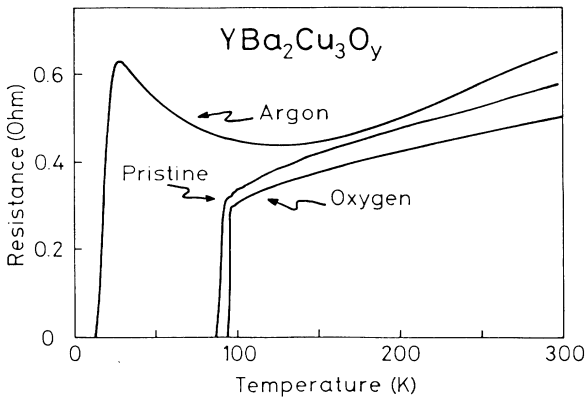

FIG. 1. Temperature-dependent resistivity of pristine, argon-treated, and oxygen-treated $YBa_2Cu_3O_y$ samples, oxygen contents, estimated from the weight of the samples, are $y=6.98$, $y=6.62$, and $y=7.00$, respectively. The pristine and oxygen-treated materials have a high transition temperature, the argon treatment suppresses T_c.

was 3.58 m and the time resolution was 14.7 μsec/channel. The choppers were operated at 130 Hz. Under these circumstances the time spread at the sample is 100 μsec, resulting in a time resolution of 140 μsec for elastic scattering and 100 μsec for energy exchange of 40 meV or higher. Since MIBEMOL is installed on a neutron guide viewing a cold source it is well suited at room temperature for the study of low-energy phonons in the energy range of 0–30 meV while the luminosity decreases sharply above 40 meV.

In Fig. 2, the time-of-flight spectra of the three samples are shown. The oxygen-treated sample was measured for

TABLE I. Neutron diffraction results on the three samples of different heat treatments. The Bragg peaks were indexed according to the orthorhombic structure of lattice constants shown in the last rows. The intensities, normalized to the intensity of the (111) reflection, are also shown.

	Pristine		Oxygen		Argon	
hkl	*d* [Å]	$I/I(111)$	*d* [Å]	$I/I(111)$	*d* [Å]	$I/I(111)$
002	5.84	0.26	5.83	0.22	5.86	0.08
003	3.89	0.93	3.89	0.80	3.90	0.11
010					3.87	0.16
100	3.82	1.00	3.82	1.10	3.84	0.55
011		< 0.05		< 0.05	3.67	0.10
101	3.63	0.73	3.63	0.78	3.65	0.33
012	3.23	0.17	3.23	0.16		< 0.05
004	2.92	1.06	2.92	0.89	2.93	0.66
013	2.75	1.15	2.75	1.68	2.75	1.00
103	2.72	4.32	2.72	4.64	2.74	1.43
110					2.72	1.50
111	2.65	1.00	2.65	1.00	2.65	1.50
112		< 0.05		< 0.05	2.47	0.13
a	3820		3820		3840	
b	3885		3885		3870	
c	11675		11660		11725	

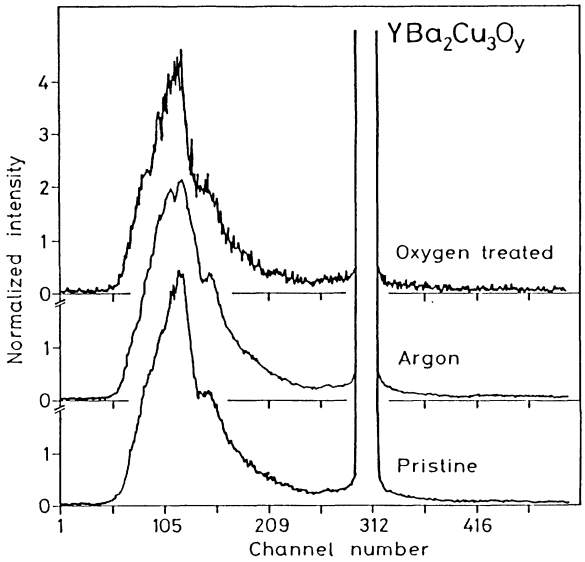

FIG. 2. Time-of-flight spectra of the pristine, argon-treated, and the oxygen-treated samples. For the oxygen-treated sample the data collection time was shorter, resulting in a larger statistical error.

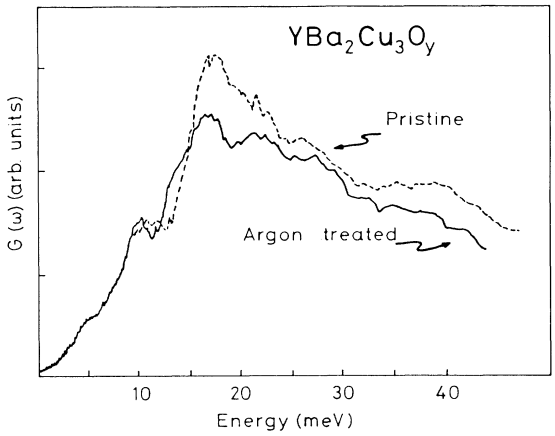

FIG. 3. Generalized phonon density of states $G(\omega)$ for the pristine- and argon-treated samples. The two spectra coincide for energies lower than 8 meV.

a shorter time, resulting in a larger statistical error in the data. Nevertheless, the spectra of the pristine- and oxygen-treated samples are practically identical. The spectrum of the argon-treated specimen differs from the others showing a double peaked structure around the maximum intensity. The raw data were evaluated by subtracting the background measured on the empty sample holder and taking into account the thermal occupation of the phonons and the detector efficiency. The generalized phonon DOS[13] $G(\omega)$ obtained this way is plotted in Fig. 3 for the pristine- and argon-treated samples. The vertical scale is normalized to the intensity of the elastic scattering. For the pristine sample phonon, DOS peaks are visible at 11 and 17 meV, the argon-treated sample shows peaks at 10, 17, and 22 meV, and some spectral weight is moved from the higher energies to the lower ones. A shoulder-type DOS enhancement appears around 5 meV for both the pristine- and argon-treated specimens. Analysis of the low-energy part of the spectra serves no indication for soft modes around or below 1 meV.

In the framework of the BCS theory, high critical temperatures may be due to high phonon frequencies $\langle\omega\rangle$, or strong electron-phonon coupling λ^*. Soft phonons may be coupled to the electrons particularly strongly; in fact, it was McMillan[12] who noted first that for a given class of materials the softer lattice leads to stronger coupling, $\lambda^* \approx 1/\langle\omega^2\rangle$. Contrary to the predictions of Jorgensen *et al.*, Barisic *et al.*, and Yu *et al.*[10] our results do not show any evidence for a Peierls-type soft mode as the driving mechanism of the high-T_c superconductivity.

In the energy range investigated the phonon DOS is mainly due to the acoustic modes but low-energy optical phonons may also contribute to the spectral weight. Because of the relatively large scattering cross section of the oxygen nuclei, the measurement is more sensitive to phonon modes involving oxygen motion. The difference around 19 meV between the phonon DOS of pristine and argon-treated samples may be related to the change in the superconducting properties. More detailed phonon calculations are necessary to clarify this point, especially because the change of the phonon spectrum may be a simple consequence of the change in the crystal structure, as illustrated in Table I. We note that in a study of the La_2CuO_4-based superconductors Renker *et al.*[13] obtained low-energy phonon DOS quite similar to ours and Ramirez *et al.*[14] also observed a phonon mode centered at 11 meV in $La_{1.85}Sr_{0.15}CuO_4$.

If the superconductivity is due to a direct electron-electron coupling, as suggested by Anderson, Fukuyama and Yosida, and Varma, Schmitt-Rink, and Abrahams *et al.*[11] and others, then the critical temperature may be different in spite of the similar phonon spectra. Our experiments are entirely compatible with this interpretation.

In conclusion, we compared the electric properties, structure, and generalized phonon density of states in two superconducting compounds. The two materials were identical except for the oxygen contents. The material with lower oxygen content has a structure closer to tetragonal. No evidence was discovered for soft-phonon-mode-driven superconductivity and the minor differences in the phonon spectra are not likely to explain the drastic change in the critical temperature.

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