RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 4 1 AUGUST 1988

High-temperature Raman measurements of single-crystal $YBa_2Cu_3O_{7-x}$

K. F. McCarty and J. C. Hamilton
Sandia National Laboratories, Livermore, California 94550

R. N. Shelton
Department of Physics, University of California, Davis, California 95616

D. S. Ginley
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 14 April 1988; revised manuscript received 27 May 1988)

We report *in situ* Raman spectra from single-crystal $YBa_2Cu_3O_{7-x}$ in oxygen at temperatures from 20 to 770 °C and from $YBa_2Cu_3O_{6.2}$ in argon at temperatures from 20 to 545 °C. For $YBa_2Cu_3O_{7-x}$ in oxygen, a defect-induced phonon at ~ 570 cm^{-1} appears above ~ 500 °C and increases in intensity with increasing temperature and loss of oxygen. As $YBa_2Cu_3O_{6.2}$ is heated above ~ 100 °C, dramatic changes occur in the phonon bands, resulting from a three-dimensional reorganization (disordering) of the oxygen in the structure involving the formation of oxygen vacancies at the O(4) sites.

The electrical properties of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ depend critically upon the oxygen content and thermal history of the material. Raman spectra for orthorhombic (superconducting) phases and tetragonal phases at room temperature (RT) and below have established that the Raman-active phonon modes of $YBa_2Cu_3O_{7-x}$ are highly sensitive to oxygen content.[1-4] The Raman peaks observed are dominated by Cu-O vibrations and therefore probe the structure responsible for superconductivity.[5,6] Here we report Raman spectra from single-crystal $YBa_2Cu_3O_{7-x}$ at temperatures from 20 to 770 °C in oxygen and from $YBa_2Cu_3O_{6.2}$ at temperatures from 20 to 545 °C in argon. For $YBa_2Cu_3O_{6.2}$, we report the observation of a low-temperature (~ 100 °C) order-disorder transformation that involves a three-dimensional (3D) rearrangement of oxygen in the structure.

Copper has two distinct sites in $YBa_2Cu_3O_{7-x}$: planar sites, Cu(2), and linear-chain sites, Cu(1). The planar sites are actually distorted square pyramids with strong bonding to the planar oxygens [O(2) and O(3) sites] and weaker bonding to the out-of-plane oxygen [O(4) site].[7] The coordination of the other copper site Cu(1) depends upon whether the structure is orthorhombic or tetragonal. In the basal plane (i.e., $z=0$) of orthorhombic $YBa_2Cu_3O_{7.0}$, Cu(1) and O(1) form linear O-Cu-O chains along the *b* axis. Additional oxygen atoms, O(4), connect to the chains making Cu(1) planar and four-coordinate. In the tetragonal phase $YBa_2Cu_3O_{7-x}$ the O(1) and O(5) sites are either partially and equally occupied in a random manner ($\sim 0.6 < x < 1.0$) or are both totally vacant in the ordered phase $YBa_2Cu_3O_{6.0}$.[7-9]

The Raman measurements were made in a microprobe apparatus equipped with a hot stage through which gas could be flowed. A thin, platelet-shaped single crystal of $YBa_2Cu_3O_{7-x}$ was positioned in a notch cut in a hot-pressed slab of polycrystalline $YBa_2Cu_3O_{7-x}$ which itself was mounted in the hot stage. X-ray diffraction measurements of crystals from the same growth batch established that the large, flat surface of the crystal contained the *a-b* plane, consistent with the results of others[4] and with the polarization measurements from the present cyrstal. The crystal was oriented so that the **k** vectors of the incident and backscattered light beams were in the *a-b* plane. The crystal was not oriented with respect to rotation about the *c* axis. The 457.9-nm laser beam was focused to approximately 1 μm in diameter with 0.7 to 2.0 mW of incident power. Most measurements were made with incident and scattered light propagating perpendicular to the *c* axis of the crystal with either *zz* polarization (incident and scattered polarizations parallel to the *c* axis) or $xx=yy$ polarizaton (incident and scattered polarizatons perpendicular to the *c* axis). The temperature was calibrated by positioning a thermocouple in the notch normally occupied by the crystal and had an estimated error of ±20° at 750 °C.

Measurements consisted of heating the crystal from RT to 770 °C in pure oxygen and slowly cooling at a rate of 2 °C/min. The crystal was then heated in purified argon to 545 °C, held overnight at this temperature, and then cooled at 2 °C/min to RT. On the basis of various literature studies on the relationship between annealing temperature, oxygen content, and Raman shift,[1-3,10] we estimate a composition of $YBa_2Cu_3O_{6.2\pm0.1}$ for the results reported here for 545 °C anneal in argon. The uncertainty results largely from differing literature values and the temperature uncertainty in our measurements. We are presently conducting studies using a modified apparatus in which the absolute temperature is better characterized.

Figure 1 shows the Raman spectra (*zz* and $xx=yy$ polarizations) obtained during temperature holds of 5-10 min during cooling from 770 °C to RT in a flow of pure oxygen. While only cooling results are shown here, essentially the same spectra were obtained when heating the fully oxygenated crystal ($YBa_2Cu_3O_7$) from RT to 770 °C. Similar results have been obtained from polycrystalline samples. Between RT and 310 °C, only small

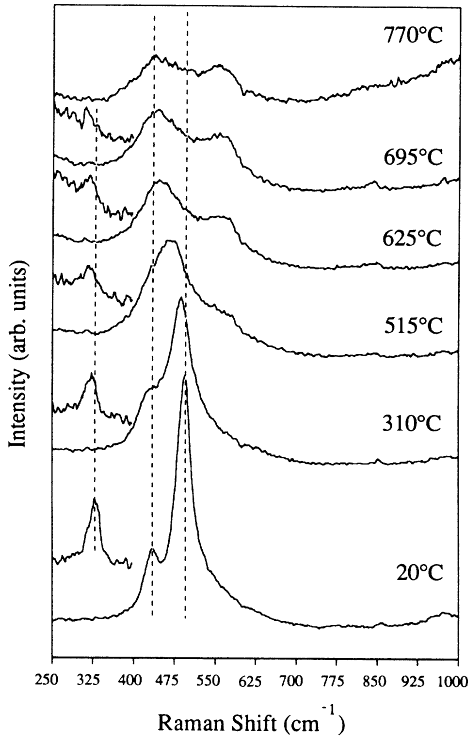

FIG. 1. Raman spectra of single-crystal $YBa_2Cu_3O_{7-x}$ during cooling from 770 °C to RT in O_2. The estimated oxygen content is ~6.5 at 770 °C and rises to ~7 at 450 °C. Below 450 °C, a constant oxygen content of ~7 exists. Spectra obtained with **k** vectors of incident and scattered light within the *a-b* plane and either zz polarization (full spectra) of $xx = yy$ polarization (insert spectra). Absolute scaling of spectra of the same polarization is the same, with linear offsets for clarity.

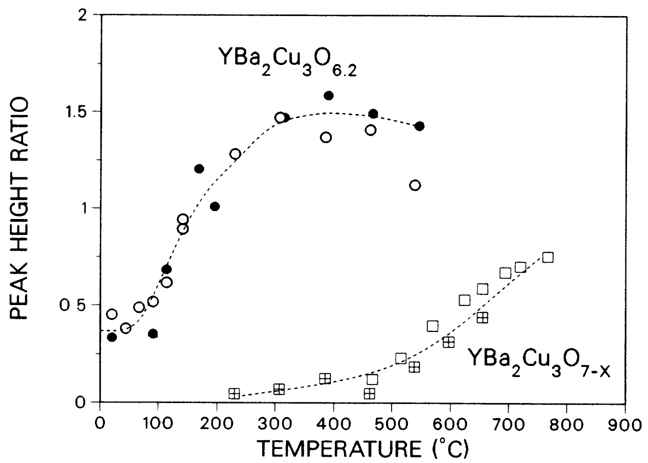

FIG. 2. Ratio of peak height of ~570 cm^{-1} peak to ~500-cm^{-1} peak: $YBa_2Cu_3O_{7-x}$ cooling in O_2 from 770 °C (hatched squares) and from 655 °C (open squares); $YBa_2Cu_3O_{6.2}$ cooling in Ar from 545 °C (open circles) and subsequent reheating in Ar (filled circles). Curves are to aid the eye.

changes occur in the intensity and position of the Raman peaks at 435 and 500 cm^{-1} (peak positions are the RT values). Above ~500 °C, the 500-cm^{-1} phonon band shifts sharply downward in frequency, a new broad peak develops at ~570 cm^{-1}, and the 435-cm^{-1} phonon band remains practically unchanged in intensity and frequency. At 770 °C, a single broad peak is observed centered around 440 cm^{-1} and it is no longer possible to distinguish between the peaks that were at 435 and 500 cm^{-1} at RT. The Raman features of $YBa_2Cu_3O_{7-x}$ heated in oxygen change in an apparently continuous fashion with temperature and there are no dramatic changes resulting from the orthorhombic-to-tetragonal phase transition at about 700 °C.[8] This result agrees with published low-temperature Raman data in which the peaks vary smoothly in position and intensity as a function of oxygen content.[1-3]

In an attempt to quantify the change occurring above 500 °C, the observed spectra were fit by two Lorentzian peaks superimposed on a quadratic background. The peak positions, their widths, and the quadratic background coefficients were optimized using a nonlinear least-squares fitting program. This procedure overlooks much of the complexity of the data, but provided a reproducible and tractable means of quantifying relevant peak heights. The square symbols of Fig. 2 represent the ratio of the peak heights of the ~570 cm^{-1} peak to the 500 cm^{-1} peak, illustrating that above ~500 °C, the intensity of the ~570 cm^{-1} peak increase dramatically relative to the 500 cm^{-1} peak. (While data were obtained below 230 °C, they are not plotted in Fig. 2 because the fitting procedure could not provide reliable fits to spectra with so little intensity at ~570 cm^{-1}.) *In situ* neutron diffraction measurements in oxygen environments have established that $YBa_2Cu_3O_{7-x}$ loses oxygen above ~450 °C by forming vacancies on the O(1) sites and that oxygen atoms then begin to occupy the O(5) sites at a slower rate.[8] A more careful analysis revealed that vacancies also occur at the O(4) sites at elevated temperatures.[9]

The growth of the ~570 cm^{-1} peak is clearly associated with increasing loss of oxygen and establishes that the peak results from oxygen vacancies, as previously suggested.[4,6] Based upon the observed ir spectrum and calculations of the lattice dynamics,[5,6] the ~570-cm^{-1} Raman peak can be assigned to the ir mode observed at ~575 cm^{-1} becoming Raman active through the loss of local inversion symmetry associated with the formation of oxygen vacancies (defects). The results presented here (**k** vectors of the incident and scattered light within the *a-b* plane) and preliminary measurements of $YBa_2Cu_3O_{6.2}$ at ~200 °C with the **k** vectors of the incident and scattered light normal to the *a-b* plane show that the α_{zz} component of the scattering tensor dominates the intensity of the ~570 cm^{-1} peak. Thus, the peak is assigned to be the B_{1u} mode which involves motion of O(4) and O(1) along the c axis, with a calculated frequency of 555 cm^{-1} [6] For heating at a fixed oxygen content, as reported here for $YBa_2Cu_3O_{6.2}$, and as will be reported elsewhere for other stoichiometries, the ~570 cm^{-1} peak is strongly temperature dependent and has little intensity at RT for slowly cooled materials. That is, even for tetragonal structures with their compete disorder of the occupancies of the O(1) and O(5) sites in the basal plane, there is little intensity at RT. Since vacancies at O(4) are known to be temperature dependent,[9] it is suggested that the intensity of the ~570 cm^{-1} Raman peak is largely determined by the vacancy concentration of the O(4) sites.

After equilibrating for 12 h in argon at 545 °C, $YBa_2Cu_3O_{6.2}$ was cooled to RT at fixed oxygen content in argon at 2 °C/min. Figure 3 shows the Raman spectra obtained after temperature holds of 5–30 min. The high-temperature spectra of $YBa_2Cu_3O_{6.2}$ have important differences from those of Fig. 1 (cooling in O_2). First, the peak at ~570 cm^{-1} is greater in intensity than the peak at 475 cm^{-1} (RT value of peak position), even at temperatures as low as 230 °C. Second, large changes occur between 230 °C and RT. Similar results have been obtained from polycrystalline samples with oxygen stoichiometries of ~6.0. Figure 4 shows the spectra obtained upon subsequently reheating the $YBa_2Cu_3O_{6.2}$ crystal from RT to 170 °C in argon in ~25 °C increments with temperature holds of 12 h before acquisition of the Raman spectra. Over a temperature range of ~50 °C (from 90 to 140 °C), the peak at 475 cm^{-1} decreases dramatically in intensity while the ~570 cm^{-1} peak increases in intensity. The peaks at 330 and 445 cm^{-1} are largely unchanged in intensity and frequency over this temperature range. After heating to 170 °C, the crystal was cooled to RT in ~25 °C increments with temperature holds of about 12 h, and was finally reheated in increments to 545 °C in argon over the course of 32 h. Figure 2 illustrates the peak-height ratios as a function of temperature obtained from the curve fitting for both heating and cooling. (The fitting procedure lumped together the 445- and 475-cm^{-1} peaks.) The peak-height ratios (and in fact the entire spectra) are virtually identical during slow cooling and heating. This indicates that near-equilibrium conditions are reversibly attained in the near-surface region probed by the laser even at these relatively low temperatures.

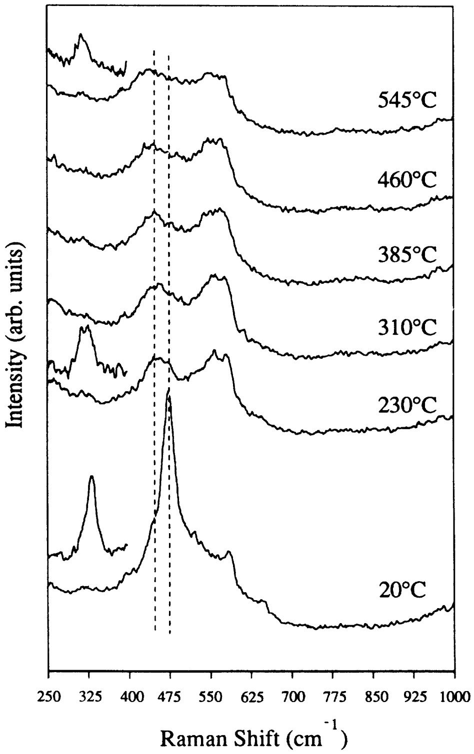

FIG. 3. Raman spectra of single crystal $YBa_2Cu_3O_{6.2}$ during cooling from 545 °C to RT in Ar. Same polarization geometries as Fig. 1.

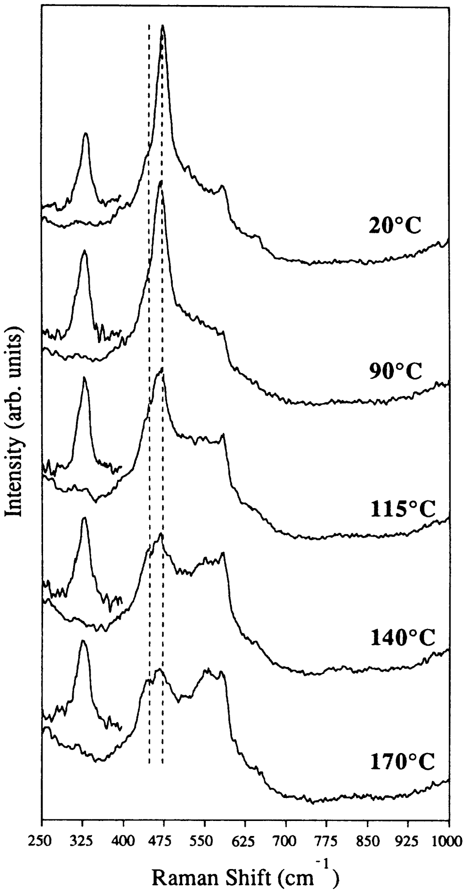

FIG. 4. Raman spectra of single crystal $YBa_2Cu_3O_{6.2}$ during heating from RT to 170 °C in Ar after cooling from 540 °C in Ar (refer to Fig. 3). Same polarization geometries as Fig. 1.

The 475 cm^{-1} mode (A_{1g} symmetry in the tetragonal phase) consists of the symmetric stretch of the O(4) oxygen atoms along the *c* axis about Cu(1). The 445 cm^{-1} mode (A_{1g}) consists of the in-phase bend of oxygen in the CuO_2 planes [O(2) and O(3)] along the *c* axis. The 330 cm^{-1} mode (B_{1g}) consists of the out-of-phase motion of O(2) and O(3) along the *c* axis.[5,6] The dramatic changes in the phonon structure of $YBa_2Cu_3O_{6.2}$ near 100 °C are interpreted as follows: With increasing temperature, a portion of the O(4) atoms move from their normal positions at the apex of the square pyramid into vacant sites at O(1) and O(5) positions on the Cu-O basal plane. The occupancy of the basal plane at the expense of the O(4) sites accounts for the loss of intensity of the 475-cm^{-1} peak and the increase in intensity of the normally forbidden peak at ~570 cm^{-1}. This rearrangement does not alter the geometry or occupancy of the CuO_2 planes. Therefore, the 330- and 445-cm^{-1} modes, involving only the motion of the oxygen atoms within the planes, are not affected. *In situ* neutron diffraction has recently established that vacancies at O(4) exist at elevated temperatures and can be maintained at RT by rapid quenching.[9] The O(4) vacancy concentration was found to be about 0.1 atoms per unit cell at 490 °C for a composition of approximately $YBa_2Cu_3O_{6.3}$. The present results suggest that the O(4) vacancy concentration is significantly greater for material with a larger oxygen deficiency and that the O(4) vacancies form at relatively low temperatures (~100 °C). The loss in intensity and large shift downward in frequency of the ~500 cm^{-1} phonon of $YBa_2Cu_3O_{7-x}$ in pure oxygen above ~500°C (Fig. 1) confirm that O(4) vacancies form at elevated temperatures even in materials with relatively high oxygen contents.[9]

On the basis of thermodynamic considerations and 2D models of the bonding interactions on the Cu-O basal plane, phase diagrams for $YBa_2Cu_3O_{7-x}$ have been predicted.[11,12] These studies show that at sufficiently low temperatures, disordered tetragonal structures should transform into a two-phase mixture of an ordered tetragonal and an ordered orthorhombic phase. Model calculations have only considered order/disorder transformations within the Cu-O basal plane.[11–13] As shown here, as $YBa_2Cu_3O_{6.2}$ is heated above ~100 °C, the structure disorders by breaking the Cu(2)-O(4) chains along the *c* axis. This is a 3D rearrangement of oxygen atoms, not just a 2D rearrangement of the oxygens in the basal plane. This study suggests that more attention be placed in investigating vacancies at the O(4) sites, particularly in oxygen deficient and quenched materials. These findings also are relevant to recent investigations of magnetic ordering in oxygen-deficient $YBa_2Cu_3O_{7-x}$. The Cu spins of $YBa_2Cu_3O_{6.15}$, for example, have 3D antiferromagnetic order below the Néel temperature of 127 °C (400 K).[14] The magnetic transition occurs at approximately the same temperature at which significant changes occur in the phonon spectrum in $YBa_2Cu_3O_{6.2}$. The relationship between the structural transition reported here and the magnetic transition is an issue worthy of further investigation.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Material Sciences, under Contract No. DEAC04-76DP00789. The authors thank R. E. Loehman of Sandia National Laboratories, Albuquerque for the hot-pressed sample.

---

[1] C. Thomsen, R. Liu, M. Bauer, A. Wittlin, L. Genzel, M. Cardona, E. Schönherr, W. Bauhofer, and W. König, Solid State Commun. **65**, 55 (1988).

[2] M. Hangyo, S. Nakashima, K. Mizoguchi, A. Fujii, and A. Mitsuishi, Solid State Commun. **65**, 835 (1988).

[3] R. M. Macfarlane, H. J. Rosen, E. M. Engler, R. D. Jacowitz, and V. Y. Lee, Phys. Rev. B **38**, 284 (1988).

[4] D. M. Krol, M. Stavola, W. Weber, L. F. Schneemeyer, J. V. Waszczak, S. M. Zahurak, and S. G. Kosinski, Phys. Rev. B **36**, 8325 (1987).

[5] F. E. Bates and J. E. Eldridge, Solid State Commun. **64**, 1435 (1987).

[6] R. Liu, C. Thomsen, W. Kress, M. Cardona, B. Gegenheimer, F. W. de Wette, J. Prade, A. D. Kulkarni, and U. Schröder, Phys. Rev. B **37**, 7971 (1988).

[7] T. Kajitani, K. Oh-Ishi, M. Kikuchi, Y. Syono, and M. Hirabayashi, Jpn. J. Appl. Phys. **26**, L1144 (1987).

[8] J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[9] J. D. Jorgensen, H. Shaked, D. G. Hinks, B. Dabrowski, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, W. K. Kwok, L. H. Nunez, and H. Claus, in *Proceedings of the International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, 1988* [Physica C (to be published)].

[10] K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L1228 (1987).

[11] A. G. Khachaturyan, S. V. Semenovskaya, and J. W. Morris, Phys. Rev. B **37**, 2243 (1988).

[12] L. T. Wille, A. Berera, and D. de Fontaine, Phys. Rev. Lett. **60**, 1065 (1988).

[13] M. Inoue, T. Takemori, and T. Sakudo, Jpn. J. Appl. Phys. **26**, L2015 (1987).

[14] J. M. Tranquada, D. E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston, Phys. Rev. Lett. **60**, 156 (1988).