Raman-scattering spectra of $YBa_2Cu_3O_{6.5}$ superconductor with ordered oxygen vacancies

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The ordering of oxygen vacancies has been achieved in a $YBa_2Cu_3O_{6.5}$ system. This ordering leads to the formation of a new crystal phase (the ortho-II phase, $T_c = 53$ K). The Raman-scattering spectra of the ortho-II phase have been measured at 300 K. These spectra contain the bands at 229, 593, 553, and 630 cm^{-1}, in addition to the Raman spectra of the disordered ortho-I phase. The assignment of the new bands is discussed on the basis of the symmetrized nuclear oscillations which were calculated for the $2a \times b \times c$ unit cell.

The lattice structure and the superconducting properties of $YBa_2Cu_3O_{7-x}$ crystals change with changing oxygen concentration.[1] The orthorhombic phase (space group D_{2h}^1), with the superconducting transition temperature near 93 K, corresponds to seven oxygen atoms in the unit cell ($x = 0$). The tetragonal phase ($x = 1$, space group D_{4h}^{17}) corresponds to a loss of oxygen atoms in the O(4) sites, destroying the copper-oxygen chains...O(4)–Cu(1)–O(4)...and hence the superconducting properties. It was assumed that the oxygen vacancies become partially ordered in the *ab* planes because of the observation of yet another superconducting phase with the superconducting transition temperature near 60 K (Ref. 2). Electron-diffraction studies revealed a complex partial ordering of vacancies[3]: doubling of the unit cell along the *a* axis, with $x = 0.5$, and the presence of a superlattice of size $2\sqrt{2a} \times 2\sqrt{2b} \times c$, with $x = 0.125$. Takabatake *et al.*[4] have reported a high degree of ordering of the vacancies with the formation of a new phase: the ortho-II phase with a unit cell $2a \times b \times c$ (Fig. 1) and with a superconducting transition temperature of 53 K.

We have achieved an ordering of oxygen vacancies in $YBa_2Cu_3O_{6.5}$ polycrystals corresponding to an ortho-II phase, whose Raman-scattering spectra we have measured at 300 K. The new bands observed by us are explained in terms of the calculated symmetrized nuclear displacements in the expanded unit cell $2a \times b \times c$.

The $YBa_2Cu_3O_{6.5}$ samples with ordered oxygen vacancies were synthesized in several stages from pure powders of Y_2O_3, $BaCO_3$, and CuO, using the procedure described in Ref. 4. After heating the original mixture in air at 850–910 °C for 24 h, it was pressed into pellets. The pellets were held in flowing oxygen at 900–950 °C for 24 h and then were slowly cooled in a furnace. The samples obtained in this manner were again heated at 660–690 °C in flowing oxygen for 24 h and then quickly cooled to liquid-nitrogen temperature. This set gave us samples with an oxygen concentration corresponding to $x = 0.5$. To achieve order in the oxygen vacancies, we annealed the pellets in an evacuated cell at 500–550 °C for 120 h.

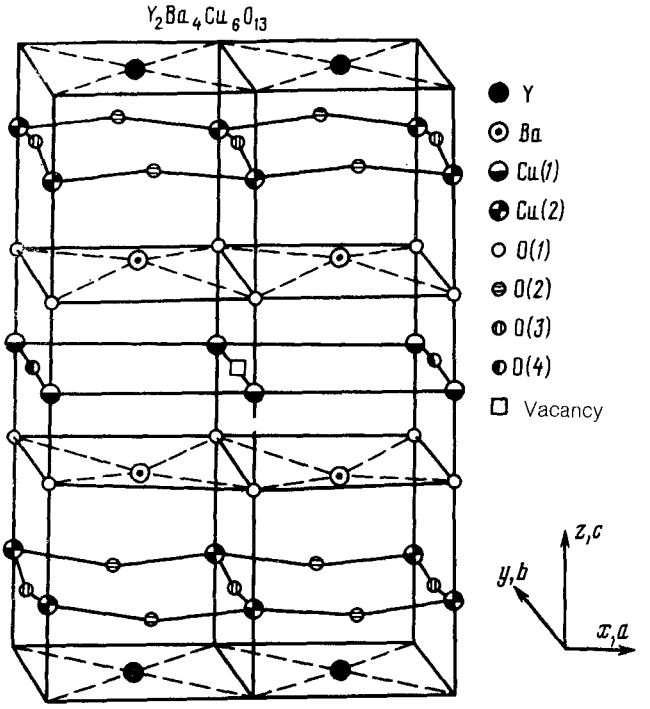

FIG. 1. Unit cell of the ortho-II phase of an $YBa_2Cu_3O_{6.5}$ crystal with ordered oxygen vacancies.

The pellets fabricated by a procedure described above were used to measure the temperature dependence of the electrical resistance (Fig. 2). The measurements were carried out using a four-probe method at a current of 5 mA. We found that at $T_c \approx 53$ K the resistance decreases sharply, that it vanishes at 51 K, and that it exhibits a smooth, metallic behavior as the temperature is lowered from 300 K to 70 K. Such behavior of the resistance is in good agreement with that reported by Takabatake *et al.*[4] in samples with a high degree of ordering of the oxygen vacancies in the *ab* planes.

The Raman-scattering spectra were excited by the 5145 Å line from an Ar^+ laser. The 50-mW beam from this laser was focused at a spot 50 μm in diameter. The Raman-scattering spectra were recorded at 300 K in a backscattering geometry, using a OMARS-89 Raman spectrometer with an optical-rule detection.

The Raman-scattering spectra of the pellets with ordered vacancies are shown in Fig. 3, a and b. In addition to the bands which characterize the Raman-scattering spectrum of samples in which the vacancies are not ordered, we see a series of new bands. In the parallel-polarization spectrum the 336- and 487-cm^{-1} bands are in good agreement with those reported in Refs. 5 and 6. In the spectrum we also see an intense 593-cm^{-1} band and less intense bands at 630, 553, and 236 cm^{-1}, which we attribute to the enlargement of the unit cell as a result of ordering of the oxygen vacancies. The 236- and 593-cm^{-1} bands are more intense in the case of parallel polarization, whereas

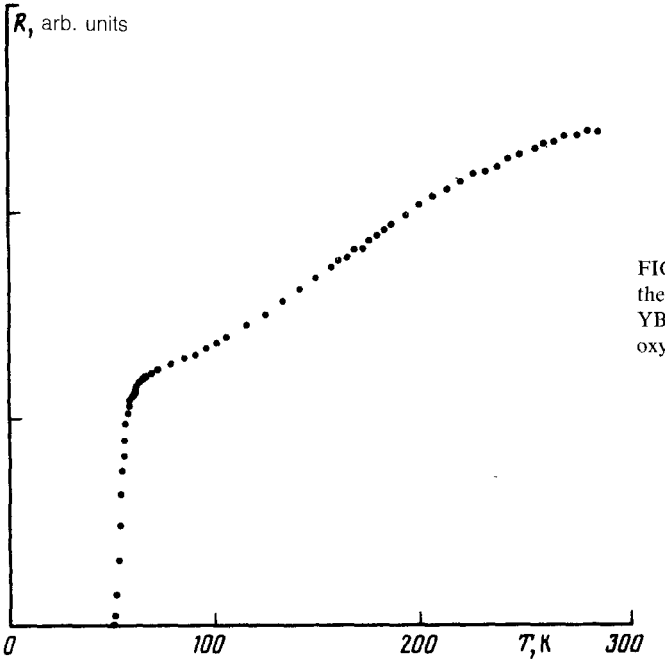

FIG. 2. Temperature dependence of the electrical resistance of an $YBa_2Cu_3O_{6.5}$ sample with ordered oxygen vacancies.

the 553- and 630-cm^{-1} bands become more intense in the case of perpendicular polarization, suggesting that they belong to the vibrations that are not totally symmetric.

We have calculated the symmetrized displacements of the $2a \times b \times c$ unit cell which characterizes the ortho-II phase with ordered vacancies (see also Ref. 7). At

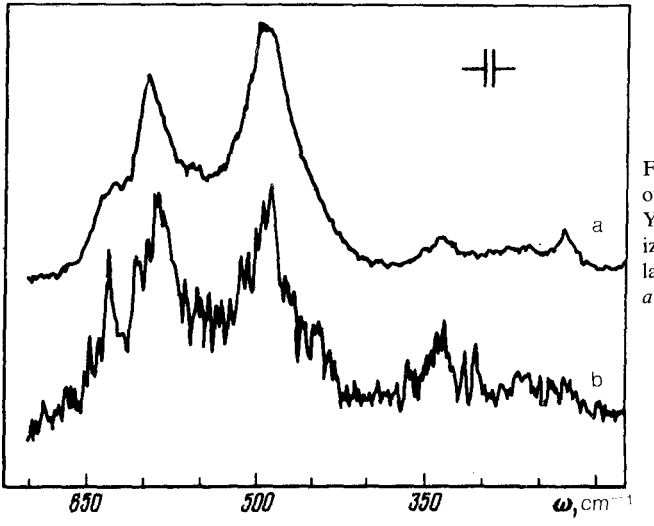

FIG. 3. Raman-scattering spectra of the ortho-II phase of $YBa_2Cu_3O_{6.5}$ with a parallel polarization (a) and perpendicular polarization (b). The scale ratio of the *a* and *b* spectra is 3:1.

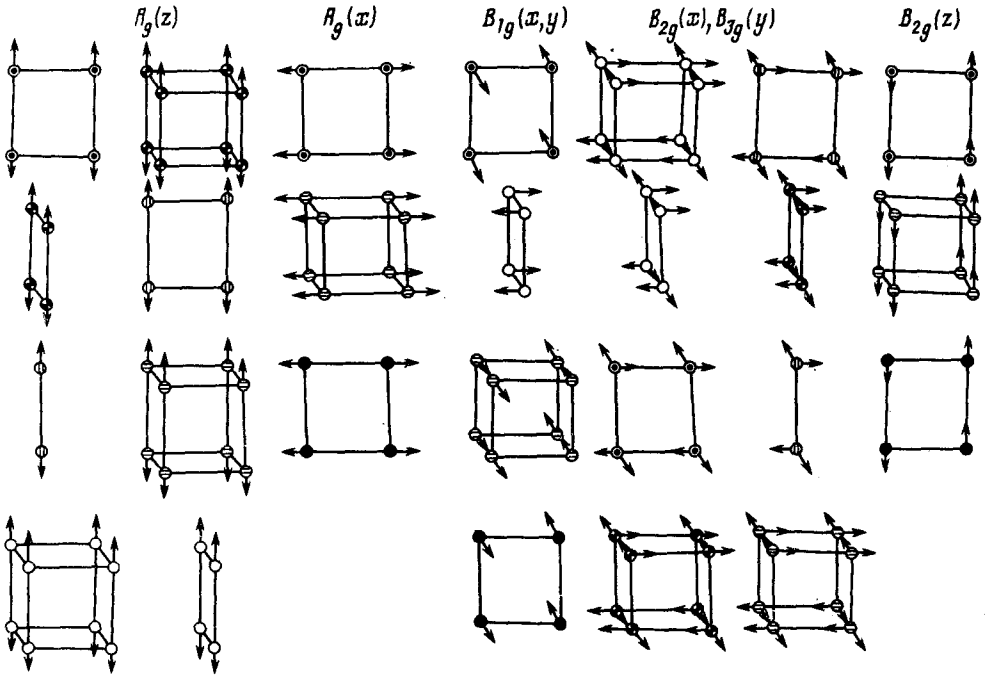

FIG. 4. Symmetrized even displacements of the unit-cell nuclei of the ortho-II phase, which contribute to point Γ of the Brillouin zone (see Fig. 1 for the notation used for the nuclei).

point Γ of the Brillouin zone there are 75 vibrational degrees of freedom which transform in accordance with the irreducible representations of the point group D_{2h} as follows:

$$11A_g + 4B_{1g} + 11B_{2g} + 8B_{3g} + 2A_u + 14B_{1u} + 12B_{2u} + 13B_{3u}.$$

All of the symmetrized displacements affecting the modulation of the electric polarizability are shown in Fig. 4. The doubling of the lattice along the x direction led to the appearance of new nonequivalent groups of atoms, compared with those of a simple lattice, and also to the transfer of the point X at the boundary of the Brillouin zone of a simple lattice to the center of the new zone. This procedure led to new symmetrized displacements. In a simple lattice, for example, there are $5A_g$ displacments, all of which are directed along the c axis (the z displacements). In the expanded cell three more totally symmetric z displacements and three x displacements, which were previously absent, are added. Also can be seen are the displacements of the B_{1g} symmetry, which are absent in disordered vacancies. The scattering tensor for the B_{1g} modes has nondiagonal components, α_{xy}, and contributes to the scattering of perpendicular polarization from the ab crystal plane. The expansion of the cell adds six vibrational degrees of freedom of the B_{2g} symmetry and three vibrational degrees of freedom of the B_{3g} symmetry.

In accordance with the analysis of the vibrations of the expanded unit cell, the

Raman-scattering spectra of polycrystalline samples in the ortho-II phase contain new vibrational bands. Of these bands the 593- and 230-cm^{-1} modes, which appear preferentially in the parallel polarization, can naturally be attributed to the A_g vibations (see Fig. 4). The low-frequency mode may stem from the x displacements of the Y nuclei, since the other new mode, which stems from the displacements of the Cu(2) nuclei, should have a frequency of 100 cm^{-1} (Ref. 6). The frequency of the second mode is close to the vibrational frequencies of the oxygen nuclei. It can be tentatively attributed to the x displacements of the O(2) nuclei, although it may also contain the displacements of the O(1) and O(3) nuclei.

To clearly identify the vibrational modes of the ortho-II phase, it is necessary to measure the polarized Raman-scattering spectra of the single-crystal samples with a high degree of vacancy ordering.

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