# Experimental study of the effect of carrier concentration on the vibrational spectrum of $YBa_2Cu_3O_{7-y}$

A. V. Chumachenko, M. G. Zemlyanov, O. E. Parfionov, P. P. Parshin, and A. A. Shikov

*Kurchatov Institute, 123182 Moscow, Russia*

A. V. Muzychka

*JINR, 141980, Dubna, Moscow Region, Russia*

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Deformations of the phonon spectrum of a 1-2-3 YBaCuO compound due to variations in the free carrier concentration caused by both Ca doping and changes in the oxygen content have been studied using inelastic neutron scattering. We have found that the cutoff energy of the phonon spectrum rises as the number of free carriers decreases. There is satisfactory agreement between the experimental phonon spectrum cutoff energy and a calculation using a simple model that takes into account screening of the interaction among ions by free carriers.
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## 1. INTRODUCTION

By now, properties of cuprate high-$T_c$ superconductors have been studied extensively in numerous experimental and theoretical works. Nonetheless, there is no universal approach to the mechanism of superconductivity in these materials. Specifically, there are no fundamental constraints on vibrations of the crystal lattice taking part in coupling among free carriers,[1] and the BCS theory, which was developed for "common" superconductors. It is not surprising, therefore, that attention is focused on properties of the electron and phonon subsystems and on the effects on the electron–phonon interaction in high-$T_c$ superconductors. A feasible line of research in this field is to study the correlation between the spectrum of lattice vibrations and electronic properties of the system, e.g., when they vary with the free carrier concentration.

The concentration of free carriers in $YBa_2Cu_3O_{7-y}$ and other cuprate HTSC can be changed both by doping with atoms of a different valence and by varying the content of oxygen, since the carrier concentration drops with $y$, and at $y>0.5$ the material is a dielectric.[2,3]

The effect of doping on the phonon spectrum of LaCuO and YBaCuO has been studied experimentally, e.g., via the effect of Sr, Ca, and Ba doping on the phonon spectrum of LaCuO[4] and of Zn and Ag doping on the YBaCuO spectrum.[5–7] In addition, the effect of the metal–dielectric transition due to low oxygen concentration on the spectrum of thermal excitations in the crystal lattice of YBaCuO has also been investigated.[4,8] In all cases both the substitutional doping and variation in the oxygen concentration changed the spectral distribution of phonon modes, primarily its cutoff energy.

In all cuprate high-$T_c$ superconductors, the curve of $T_c$ versus concentration of free carriers has a maximum.[9] Moreover, on the left slope of this curve there is a correlation among three parameters, namely, the critical temperature $T_c$ drops with concentration, and the phonon spectrum cutoff energy increases. A question arises about how the phonon spectrum will be affected by doping that yields more free carriers, so that their concentration corresponds to the maximum, or even the descending slope of this curve, i.e., the system is overdoped.

In a 1-2-3 compound this can be done by doping with Ca, since the substitution of Ca for Y at constant oxygen content leads to a higher carrier concentration, hence a lower $T_c$.[10]

In the present work, we have used inelastic neutron scattering to study the effect of free carrier concentration on the YBaCuO phonon spectrum by both doping the material with calcium and varying the oxygen content over a wide range.

## 2. EXPERIMENT

Polycrystalline $YBa_2Cu_3O_{7-y}$ and $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.92}$ samples were manufactured from oxides of yttrium, barium, and copper by the conventional solid-state synthesis technique,[10] which yields reproducible single-phase samples with a predetermined composition.

A dedicated effort was undertaken to maximize the oxygen content in Ca doped samples. To this end they were annealed at low temperature in an oxygen atmosphere. The oxygen content was derived from measurements of the lattice parameters using published data on their variations due to changes in the oxygen concentration. In case of oxygen deficiency, samples were additionally annealed in an oxygen atmosphere. We found using the thermogravimetric technique that a Ca doped sample could be saturated with oxygen to $7-y=6.92$. Thus the oxygen content could be made equal in both Ca-doped and undoped samples.

The technique of varying the oxygen content in samples was described in detail by Parfionov and Konovalov,[3] who studied electronic properties of YBaCuO samples with oxygen deficiency synthesized in the same way as our samples.

The oxygen content was ultimately determined using the thermogravimetric technique with an uncertainty $\Delta y=0.01$. According to x-ray diffraction data, all the samples were

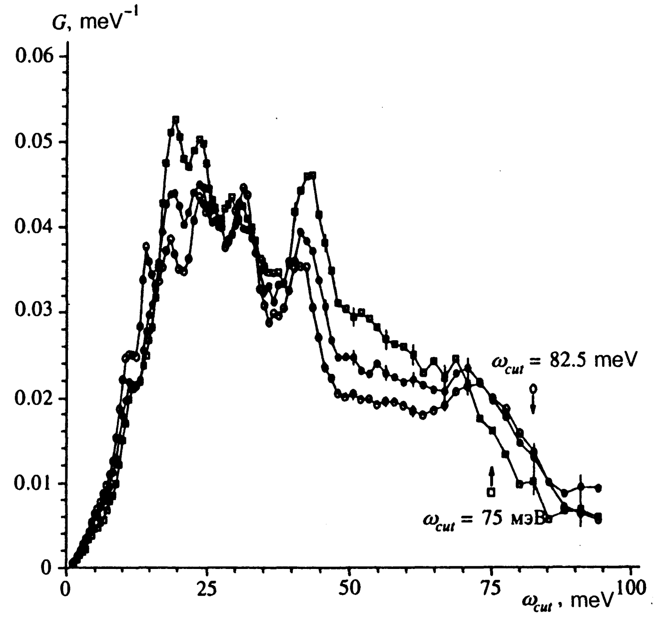


FIG. 1. Phonon density of states in $YBa_2Cu_3O_{7-y}$: measurements at $y=0.08$ (□); $y=0.28$ (●); $y=0.93$ (○).

essentially single-phase, and their lattice parameters were in a good agreement with published data on materials of similar composition.

The superconducting transition temperature in a Ca-doped sample, $T_c=80\pm1$ K, was determined independently by three techniques, namely from measurements of the resistance and magnetic susceptibility versus temperature, and of the jump in specific heat. The critical temperatures obtained by the three methods agreed to within the experimental uncertainty.

Inelastic neutron scattering experiments were conducted at room temperature on samples of $YBa_2Cu_3O_{7-y}$ ($y=0.93$, 0.55, 0.42, 0.28, and 0.08) using a time-of-flight spectrometer with a cold neutron source,[11] and on $YBa_2Cu_3O_{6.92}$ and $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.92}$ samples using a KDSOG-M backscattering spectrometer[12] with the beam from an IBR-2 pulsed reactor. Experimental data recorded at various scattering angles were processed in the noncoherent approximation to obtain a generalized (neutron-weighted) phonon density of states, $G(\omega)$[4] (Figs. 1 and 2).

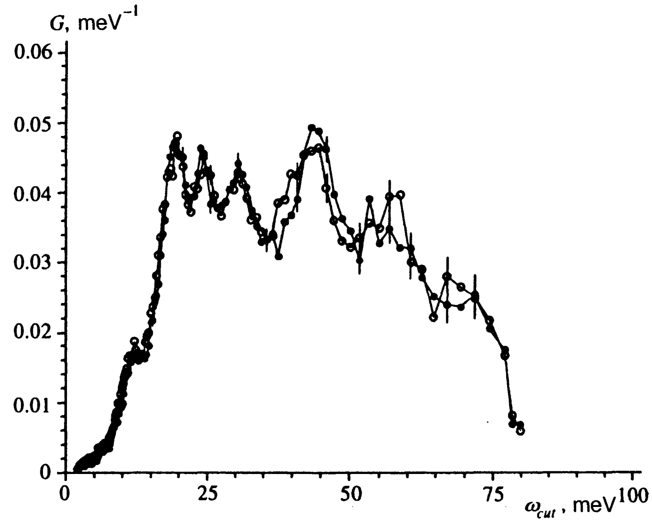


FIG. 2. Phonon density of states in $Y_{1-x}Ca_xBa_2Cu_3O_{6.92}$: measurements at $x=0$ (●); $x=0.2$ (○).

## 3. DISCUSSION

The basic features of phonon spectra of materials with different oxygen concentrations studied in our work fully coincide with those reported in other publications.[8,13,14] Figure 1 shows spectra of compounds with $y=0.08$, 0.28, 0.93.

Variations in the oxygen concentration (Fig. 1) lead to a redistribution of intensity among the 23, 27, and 33-meV peaks. The phonon density of states in the 40–60 meV range decreases with decreasing oxygen concentration, and a new feature emerges in the form of a peak at 15 meV, which is most prominent at the minimum concentration ($y=0.93$). Given partial phonon spectra of copper atoms in $YBa_2Cu_3O_{7-y}$ [14] and model calculations,[15] we assume that the peak is due to oscillations of copper atoms at Cu1 sites. One can see that the high-frequency edge of the phonon spectrum shifts to higher energies[16] as the oxygen concentration decreases. Figure 3(a) shows the cutoff energy of the phonon spectrum plotted as a function of $7-y$ in the range studied in this work.

Variations in the intermediate frequency range of the phonon spectrum of $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.92}$ can be seen in Fig. 2. In the 40–50 meV energy range, the phonon density of

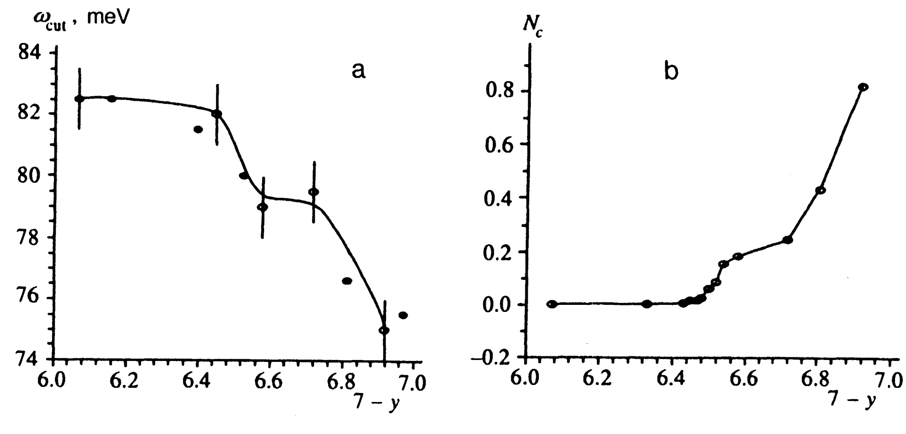


FIG. 3. a) Cutoff frequency of the phonon spectrum in $YBa_2Cu_3O_{7-y}$ versus oxygen concentration: measurements of this work (○); Ref. 8 (●); b) concentration of free carriers in $YBa_2Cu_3O_{7-y}$ versus oxygen content (Ref. 3).

states decreases with Ca doping and new modes emerge at 58 and 67 meV, whereas the cutoff energy remains unchanged.

According to calculations by Chaplot,[15] the phonon spectrum of YBaCuO is highly anisotropic, and high-energy phonons around 80 meV are due to oscillations of oxygen atoms and polarized in the $CuO_2$ plane. On the other hand, it is well known that charge transfer takes place in layered cuprate superconductors predominantly along $CuO_2$ planes. Therefore one should expect that carrier concentration effects are more pronounced around the cutoff energy.

Since carrier concentration drops with oxygen content, variations in the cutoff energy of the phonon spectrum (Fig. 3(a)) might be linked to the screening effect of free carriers on the interaction among ions. In the dielectric phase $(y>0.5)$, the ion–ion interaction is not screened, and the phonon frequencies are constant with oxygen concentration.

The data plotted in Fig. 3(b) are taken from Ref. 3, which reported on the room-temperature carrier concentration derived from Hall measurements at various oxygen contents. An important point is that the interpretation of the Hall measurements without accurate data on the electron spectrum near the Fermi level is not quite correct. On the other hand, some experimental studies[17,18] indicate that, except for the heaviest doping, the Hall measurements yield accurate estimates of the free hole concentration in YBaCuO. Moreover, measurements of the number of holes in the $CuO_2$ plane versus the oxygen concentration in single crystals obtained by x-ray absorption spectroscopy (Ref. 19, Fig. 10) and spin-dependent neutron scattering (Ref. 20, Fig. 15) agree over the range $0.15 \leqslant y \leqslant 0.5$ with the curve in Fig. 3(b) to within the experimental uncertainty.

Comparing the curves in Figs. 3(a) and 3(b), one can see that changes in the cutoff energy reflect changes in the carrier concentration. This correlation indicates that our assumption about the effect of energy renormalization on the highest-energy mode is quite legitimate.

The dependence of the cutoff energy $\omega_{\rm cut}$ on the carrier concentration $N_c$ can be estimated using the model described by Pines,[21] in which the screening action of free carriers on the ion interaction is treated in terms of the static dielectric function $\varepsilon(q,0)$ of the electron gas:

$$\omega_{\rm cut}^2 = \omega_{\rm cut}^2(0) - \Omega_a^2[\varepsilon(\mathbf{q},0)-1]/\varepsilon(\mathbf{q},0), \tag{1}$$

where $\omega_{\rm cut}(0)$ is the frequency of the high-energy mode in the dielectric phase, $\omega_{\rm cut}$ is the modified phonon frequency, and $\Omega_a^2$ describes the electron–ion interaction potential.

The free-electron model is in good agreement with experimental data on the electron density of states at the Fermi level for a wide range of high-$T_c$ superconductors.[22] If the Fermi surface is isotropic, the $\mathbf{q}$-dependent static dielectric function is described by the formula[21]

$$\varepsilon^{3D}(N_c) = 1 + \frac{4(3\pi^2 N_c)^{1/3}}{\pi a_0 q^2}\chi(q,k_F), \tag{2}$$

where $a_0$ is the Bohr radius, $\chi(q,k_F)$ is the Hartree function, and $k_F=(3\pi^2 N_c)^{1/3}$.

Therefore the cutoff frequency can be expressed in terms of the free carrier concentration:

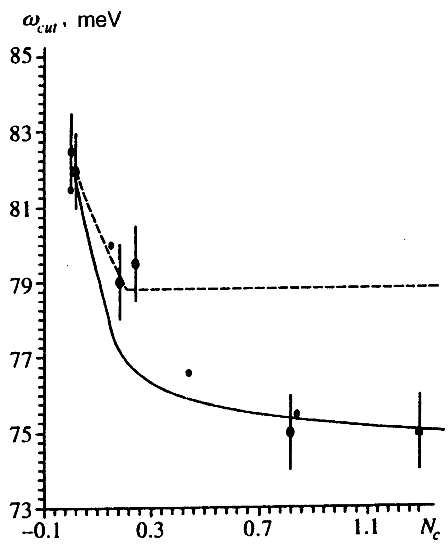


FIG. 4. Cutoff energy of the phonon spectrum versus carrier concentration: measurements of this work in $YBa_2Cu_3O_{7-y}$ (○); in $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.92}$ (□); measurements in $YBa_2Cu_3O_{7-y}$ from Ref. 8 (●); three-dimensional calculations are given by the solid curve; two-dimensional calculations are given by the dashed curve.

$$\omega_{\rm cut}^2(N_c) = \omega_{\rm cut}^2(0) - \Omega_a^2[\varepsilon(N_c)-1]/\varepsilon(N_c). \tag{3}$$

The experimental curve of $\omega_{\rm cut}(N_c)$ was approximated by the function in Eq. (3). The wave vector $\mathbf{q}$ in Eq. (2) was selected with due account of the $YBa_2Cu_3O_{7-y}$ phonon spectra,[23] which indicate that the highest-energy mode has a wave vector aligned with the $[\zeta\zeta 0]$ axis at the Brillouin zone boundary. The only fitting parameter $\Omega_a$ in Eq. (3) has a clear physical meaning: it follows from Eqs. (2) and (3) that in the long-wavelength limit, $q \to 0$ and $\varepsilon \to \infty$, we have $\omega_{\rm cut}^2(N_c) = \omega_{\rm cut}^2(0) - \Omega_a^2$.

Taking into account that the screening free carriers form a quasi-two-dimensional system,[24] we have calculated the static dielectric function in the approximation of a cylindrical Fermi surface. In this case the function $\varepsilon(N_c)$ has the form[25]

$$\varepsilon^{2D}(N_c) = 1 + \frac{2}{\pi a_0 q^2} k_z \mathrm{Re}[1-(1-4k_{xy}^2/q^2)^{0.5}],$$

where

$$k_z = 2\pi/c, \quad c = 11.6\ \text{Å}, \quad k_{xy} = (2\pi c N_c)^{0.5}.$$

Two- and three-dimensional calculations are shown in Fig. 4. A sharp knee in $\omega^{2D}(N_c)$ corresponds to $2k_F = q$. The fitting parameters in the two- and three-dimensional cases are $\Omega_a^{2D} = 32$ meV and $\Omega_a^{3D} = 37$ meV. In the long-wavelength limit, the phonon energies derived from these parameters are 73 and 76 meV, which are close to the experimental value of 72 meV.[23]

At low carrier concentration, the curve calculated with the two-dimensional model is in better agreement with the experimental data. On the other hand, at large $N_c$, the curve derived from the three-dimensional model better conforms to the experimental data. This may be due to the system of current carriers gradually acquiring three-dimensional features as the carrier concentration increases.

The satisfactory agreement between the experimental curve of $\omega_{\mathrm{cut}}(N_c)$ and calculations with Eq. (3) (Fig. 4) provides further evidence that the shift in cutoff energy is most probably due a renormalization of phonon mode energies by the free-carrier screening of the interaction among ions in the lattice.

As noted above, the Ca doping of YBaCuO does not lead to a clear shift in the phonon spectrum cutoff energy (Fig. 2). Estimates using Hall measurements indicate that the number of free carriers per elementary cell in $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.92}$ is $N_c = 1.3 \pm 0.2$, which is notably higher than in undoped YBaCuO, $N_c = 0.8 \pm 0.1$.[3] On the other hand, the critical temperature $T_c$ in Ca-doped samples is 80 K, whereas in undoped samples it is 90 K. Thus at 20% doping with Ca, the superconductor is overdoped, which corresponds to the descending slope of the $T_c$ curve plotted versus carrier concentration.[9] The graph in Fig. 4 indicates that the drop in the cutoff energy expected at this carrier concentration is within the statistical measurement uncertainty. Therefore we interpret the equality between the cutoff energies of YBaCuO phonon spectra in Ca-doped and undoped samples in terms of the saturation of screening at high carrier density. This is consistent with data on the electron density of states at the Fermi level derived from low-temperature measurements of the specific heat. These data lead to the conclusion that 20% Ca doping has little effect on the electron density of states at the Fermi level. As regards the correlation between changes in the cutoff energy and $T_c$ mentioned above, it is probable that in an overdoped system, some mechanism decoupling free carriers becomes more important.

To sum up, we have shown that

1) 20% Ca doping of $YBa_2Cu_3O_{7-y}$ does not change the phonon spectrum cutoff energy; the cutoff energy drops with oxygen concentration in the range $y < 0.5$, and at $y > 0.5$ the cutoff energy is constant;

2) the experimental cutoff energy versus free-carrier concentration is in satisfactory agreement with a simple model that includes the effect of free-carrier screening of interaction among ions;

3) no correlation between changes in the cutoff energy and $T_c$ has been detected in Ca-doped YBaCuO.

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