

Raman study of the phonon anomaly in single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the presence of a magnetic field

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The frequency of the 340-cm^{-1} Raman-active O(II)-O(III) (z) out-of-phase mode in single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is measured as a function of magnetic field ($B \leq 12.7$ T) and temperature. We reproduce the well-established softening of this mode at T_c and confirm that this anomaly is connected with superconductivity since it reflects the usual $H_{c2}(T)$ relation. This provides additional evidence for the copper-oxygen planes being the crucial elements for superconductivity in this material. It also suggests strong coupling of this Raman phonon with electronic excitations in the superconductor.

Much experimental and theoretical effort has been devoted recently to the understanding of the new high- T_c superconductors. Raman scattering has contributed essential information on the vibrational structure of these materials allowing one to determine frequencies, eigenvectors, and optical selection rules of $\mathbf{k}=0$ phonons,^{1,2} to characterize isotopic substitution of oxygen,³⁻⁵ and to investigate effects related to the replacements of rare earths.^{6,7} With the advent of high-quality single-crystal samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ the anomalous temperature behavior of the 340-cm^{-1} O(II)-O(III) out-of-phase mode in the copper-oxygen planes^{7,8} became well established.⁹ The experiment presented here convincingly proves the relation between superconductivity and the anomalous softening of the 340-cm^{-1} phonon in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. In connection with recent calculations¹⁰ it also allows us to conclude that the corresponding electron-phonon interaction is of the strong-coupling variety. Such interaction should contribute, at least partially, to the high critical temperature.

Single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were grown as described elsewhere.⁹ Our sample had a surface of $200 \times 300 \mu\text{m}^2$ perpendicular to the c axis and was about $50 \mu\text{m}$ thick. The sample was twinned, a fact that was recognized by a pattern of narrow strips parallel to $[110]$ when it was illuminated with white light from different angles. Shielding measurements revealed a rather broad transition to superconductivity with $\Delta T \approx 15$ K at a T_c of 76 K (midpoint) (Fig. 1). From the position of the Cu-O bond stretching mode at 499.5 cm^{-1} we estimate an oxygen deficiency $\delta < 0.1$.¹¹

The sample was mounted in an exchange gas cryostat which allows measurement of backscattered radiation in the Faraday configuration with the c axis of the crystal parallel to the magnetic field. The temperature in the sample chamber was controlled by resistive heating against the flow of liquid helium. To measure and regulate the temperature we used an Allen-Bradley BB 110- Ω , $\frac{1}{8}$ -W carbon resistor which we calibrated against a Pt 100 platinum resistor at zero magnetic field. In our experimental temperature region (40–50 K) we found that the change in resistivity of the carbon resistor with magnetic

fields up to 12.7 T is $|\Delta R/R| < 0.3\%$, which is consistent with reports for similar temperatures.¹² The magnetic-field-induced spurious change of the temperature measured in the sample chamber is thus less than 0.5 K and can be neglected against the overall accuracy and reproducibility which was found to be ± 1.5 K.

The sample was illuminated with laser light from an Ar⁺-ion laser ($\lambda = 514.5$ nm) (25 mW) with a point focus of about $200 \mu\text{m}$ in diameter. This was a compromise with regard to the rather severe constraints imposed on the collection optics by the split-coil superconducting magnet (12.7 T).

A Spex 1404 double monochromator with a spectral bandpass of 7.5 cm^{-1} was used to disperse the scattered radiation. As a detector we used a GaAs photomultiplier tube which was cooled to -50°C by an alcohol refrigerator in order to obtain a low dark current. Thus, the detection threshold of the discriminator in the photon counting electronics could be held extremely low. This partially

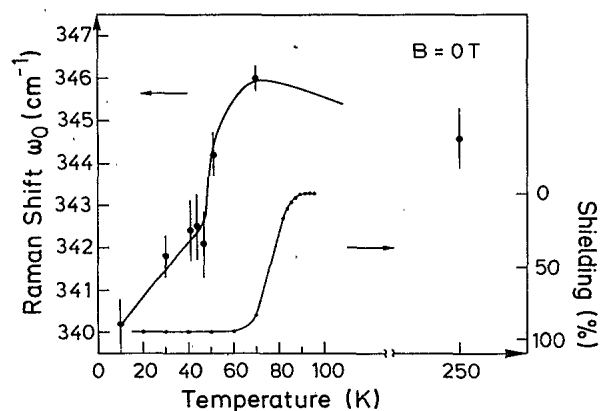


FIG. 1. Anomalous softening of the 340-cm^{-1} phonon in the copper-oxygen planes when single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is cooled below T_c at zero magnetic field. Also shown is the shielding-effect measurement of the same crystal. (The lines are drawn as guides to the eye.) Note that the temperature indicated in the figures is lower than the actual sample temperature due to laser heating (see text).

compensated for the unfavorable collection optics imposed by the magnet. The spectra were recorded as an average of two scans with an increment $\Delta E = 0.5 \text{ cm}^{-1}$ in the region from 320 to 360 cm^{-1} . A total accumulation time of 10 s per point was sufficient to obtain a comfortable signal-to-noise ratio.

The peak under investigation here has been shown to exhibit a Fano line shape^{9,13} reflecting the interaction between the O(II)-O(III) (z) out-of-phase phonon with the electronic continuum of the superconductor above the gap. Thus, we fitted the spectra with

$$I(\varepsilon) = I_0 \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} + \text{const},$$

where $\varepsilon = (\omega - \omega_0)/\Gamma$, to take the observed Fano asymmetry into account.^{14,15} The peak position, which we use in the following, is denoted by ω_0 , q is an asymmetry parameter, Γ is the half width at half maximum, I_0 a scaling factor, and the constant term is used to remove the electronic background and the dark counts. It is to be noted that the actual peak position does not coincide with ω_0 but is located at $\omega_0 + \Gamma/q$ which, for a typical linewidth of $\Gamma = 8.5 \text{ cm}^{-1}$ and $q = -4$, implies a shift of about 2 cm^{-1} in our spectra. The attainable resolution for ω_0 is $\pm 0.5 \text{ cm}^{-1}$.

The phonon under investigation has been shown to be an out-of-phase z -direction vibration of the oxygen atoms O(II) and O(III) in the copper-oxygen planes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.² Its anomalous temperature behavior was recognized quite early^{7,8} and experiments with single-crystal samples were able to show that an anomalous softening of about 4 cm^{-1} occurs in a rather narrow temperature region close to the superconducting transition temperature T_c .^{9,13} The phonon peak position ω_0 of the investigated sample is shown for different temperatures in Fig. 1. We detect a sudden change of about 2 cm^{-1} within a ΔT of 4 K at a temperature of 49 K. When the sample is cooled down further to 10 K the phonon frequency softens by another 2 cm^{-1} . For $T > T_c$, the phonon frequency peaks at an intermediate temperature before leveling off to a room-temperature value, about 4.5 cm^{-1} higher than that at 10 K. The difference of almost 30 K between the transition temperature found with the Raman measurements and T_c determined from shielding data is due to laser heating of the sample surface with a rather high intensity. When measuring a different sample at various reduced power densities we found that the onset of the anomaly moves up in temperature, extrapolating to $T_c (\pm 2 \text{ K})$ for zero-incident power. In view of the long measuring times involved we chose to perform the measurement at the higher powers. However, if the power density is too high, the phonon anomaly disappears irreversibly, a fact which can be traced to loss of oxygen at the surface (see Ref. 16).

To investigate the connection between this anomaly and the superconducting transition in a magnetic field we can cross the $H_{c2}(T)$ border in two directions: at constant temperature with variable magnetic field and at a constant magnetic field with variable temperature. While one might argue that due to the flux penetration there should be no sharp phonon softening observable when a magnetic

field is applied, the short coherence length of the extreme type-II superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ will only allow for a negligible normal conducting contribution to the scattering volume. Figure 2 shows the change in the peak position of the O(II)-O(III) (z) out-of-phase phonon with magnetic field for three different temperatures. At 41 K our maximum available magnetic field of 12.7 T is not enough to exceed H_{c2} and ω_0 stays at the "soft" value. At a temperature of 44 K we observe a shift of about 1 cm^{-1} and the data indicate a critical field H_{c2} of 10 T. The data for $T = 47 \text{ K}$ show a shift in ω_0 of about 1.5 cm^{-1} with a field of 4 T at the midpoint of change. In Fig. 3 we have plotted the change in ω_0 with temperature for zero field and a field of 10 T. The zero-field data show a midpoint of change of about 49 K, whereas the anomaly occurs at a temperature of 44 K when a field of 10 T is present.

These results prove that there is a connection between the anomalous phonon softening at T_c of the particular mode under investigation and superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. We obtain the value $H_{c2} = 10 \text{ T}$ at $T = 44 \text{ K}$ either by changing the magnetic field while keeping the temperature constant or vice versa. This reflects the reversibility of the superconducting phase transition. The values of $H_{c2}(T)$ which we obtain from these measurements are shown in Fig. 4. From these data we determine a value of $(dH_{c2}/dT)(T_c) = (2 \pm 1)(\text{T/K})$, which is compatible within the large error bars with results of other measurements.¹⁷

Since the O(II)-O(III) (z) out-of-phase phonon is the

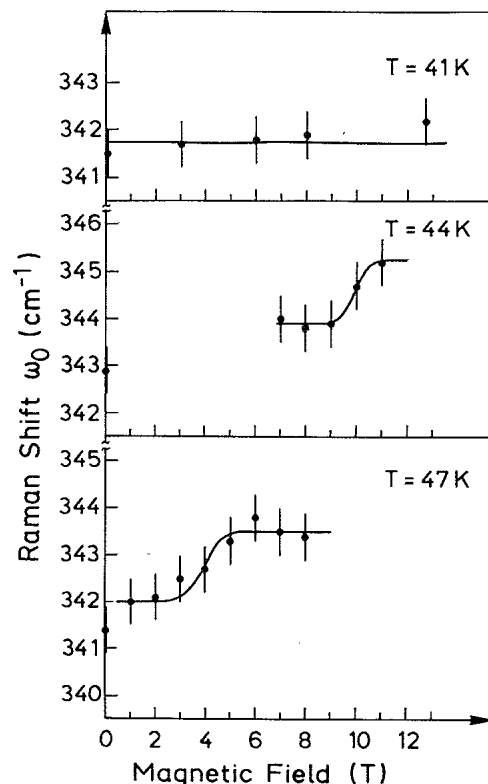


FIG. 2. Anomalous softening of the 340-cm^{-1} phonon with magnetic field for different temperatures. (The lines are drawn as a guide to the eye.)

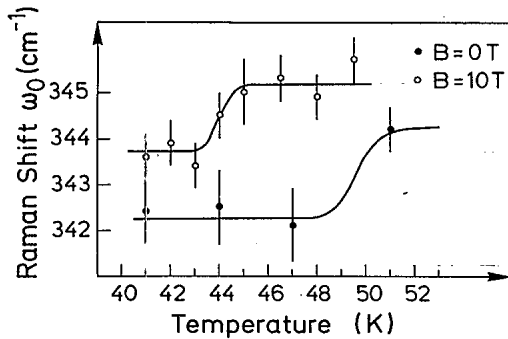


FIG. 3. Anomalous softening of the 340-cm^{-1} phonon with temperature for zero magnetic field and a field of 10 T. (The lines are drawn as a guide to the eye.)

only one of the five observed Raman-active modes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which exhibits this anomalous softening,^{2,10} and corresponds to vibrations of the copper-oxygen planes, our experiment supports the conjecture that the copper-oxygen planes are the crucial elements for superconductivity in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system. This is further supported by the fact that these planes are the common elements in all the classes of high- T_c superconductors which have been found so far.^{18,19} Similar anomalies should thus be observable in the bismuth and thallium compounds. The relation between the observed phonon anomaly and superconductivity indicates that there is strong interaction of the lattice vibrations with the electronic system. In fact, according to some recent calculations¹⁰ the phonon anomaly can be described within the strong-coupling limit of the BCS theory,²⁰ thus ruling out the conventional weak-coupling BCS theory. The latter would rather predict a phonon hardening when T de-

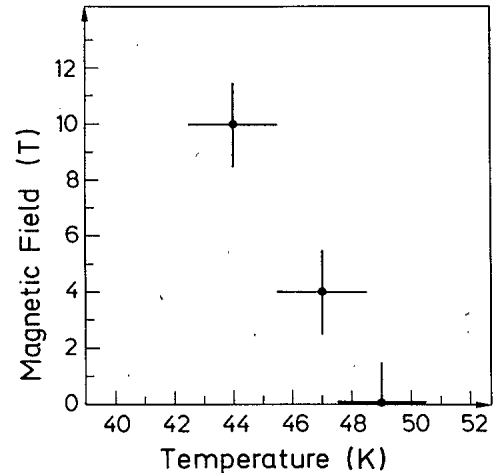


FIG. 4. Values of the upper critical field H_{c2}^{\perp} in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as obtained from Figs. 2 and 3 for different temperatures.

creases below T_c for phonons which have an energy above the BCS gap [$2\Delta = 226\text{ cm}^{-1}$ for a superconductor with a T_c of 93 K (Ref. 10)] like the O(II)-O(III) mode of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Under these circumstances it is to be expected that the electron-phonon interaction contributes at least partially to the high- T_c mechanism.

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