High-frequency Raman scattering in tetragonal $GdBa_2Cu_3O_{6+x}$ single crystal

E. M. Fefer, G. É. Blumberg, Ya. O. Past, L. A. Rebane, and L. I. Leonyuk
Institute of Chemical and Biological Physics, Academy of Sciences of the Estonian SSR; M. V. Lomonosov Moscow State University

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It has been found that high-frequency bands at 590, 624, and 1240 cm^{-1} disappear from the Raman spectrum of a $GdBa_2Cu_3O_{6+x}$ ($x \sim 0.2$) crystal near the Néel temperature (~ 400 K).

Lyons *et al.*[1] and Krol *et al.*[2] have observed a Raman scattering by magnetic states of crystals of the $YBa_2Cu_3O_{6+x}$ type in the nonsuperconducting phase at 300 K. The wide band at 2600 cm^{-1}, of symmetry B_{1g}, is attributed to two-magnon scattering in CuO_2 planes, while the interpretation of the narrower band at 1200 cm^{-1} (of symmetry A_{1g}) is ambiguous. It corresponds to either a two-phonon scattering or a scattering by individual spin states near defects. The latter suggestion is based on the fact that this band is not found in the orthorhombic crystal, which does exhibit a superconducting transition.

In this letter we are reporting the first observation of the temperature dependence of the high-frequency Raman scattering of a $GdBa_2Cu_3O_{6+x}$ single crystal in the tetragonal phase with a low oxygen concentration. We have observed that the bands at 1240 cm^{-1} and near 600 cm^{-1} disappear near the Néel temperature, 400 K.

The $GdBa_2Cu_3O_{6+x}$ single crystals in the tetragonal phase have lattice constants[1] $a = 3.85$ Å and $c = 11.75$ Å. The crystals were grown in an alundum container and were cooled from 1150 °C at a rate of 1–5 deg/h. They contained an uncontrollable aluminum impurity.

The Raman scattering spectra were excited by the 5145-Å line of an Ar^+ laser. the laser beam was focused to a spot 50 μm in diameter; the beam power was 20 mW.

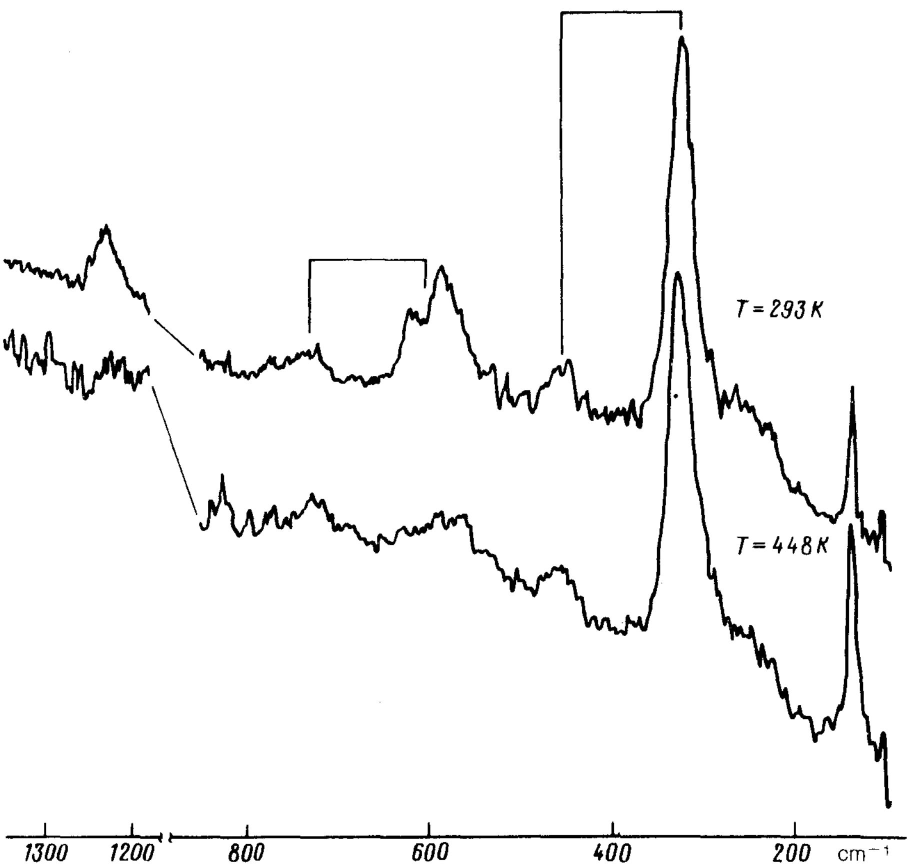

FIG. 1. Raman spectrum of the $GdBa_2Cu_3O_{6+x}$ ($x \sim 0.2$) single crystal in the $Z(XX)\bar{Z}$ polarization above and below the Néel temperature.

The spectra were measured in a backscattering geometry by an OMARS-89 Raman spectrometer with "optical-ruler" recording. The temperatures reported here correspond to the temperature of the crystal holder. The rise of the crystal temperature in the light spot was ~30 K.

The Raman spectrum of polarization $X(ZZ)X$ has an asymmetric band peaking at 483 cm^{-1} with a width of less than 30 cm^{-1}. Working from the dependence of the peak frequency of this band on the oxygen concentration, which is known[3,4] for $YBa_2Cu_3O_{6+x}$, and taking into account the 5-cm^{-1} high-frequency shift of this band when Y is replaced by Gd in oxygen-saturated crystals,[4] we estimate the oxygen concentration in our crystal to be $0\leqslant x\leqslant 0.4$.

Figure 1 shows the spectra of Raman scattering by the *ab* plane for the case in which the polarization of the incident light and also that of the scattered light are parallel to the crystal face. At 293 K the spectrum contains bands of limiting optical phonons at 140 and 330 cm^{-1}, along with some wider bands at 590, 624, and 1240 cm^{-1}. This spectrum contains a significant amount of quasicontinuous scattering, which intensifies toward higher frequencies. Against this background we see some wide satellite bands, shifted with respect to the 330-cm^{-1} band and the 590–624-cm^{-1} doublet band by ~140 cm^{-1}, i.e., by a frequency close to one of the phonon frequencies. The band at 580–590 cm^{-1} is usually attributed to a defect formed by the loss of bridge oxygen,[5,6] while the band at ~630 cm^{-1} is usually attributed to planar vibrations of a CuO_6 octahedron[5] or the presence of traces of a $BaCuO_2$ phase.[3] We observed that the bands at 590, 624, and 1240 cm^{-1} disappeared when the crystal was heated above ~400 K and then reappeared upon cooling. It can be seen from the high-temperature Raman spectrum in Fig. 1 that the phonon bands exhibit only a slight thermal broadening (~3 cm^{-1}) and a shift (2.5 cm^{-1}). The intensity of the quasicontinuous background increases slightly upon heating, while the three bands which we are discussing here become substantially fainter, nearly indistinguishable from the background.

The temperature at which these bands disappear (~400 K) is close to the Néel temperature of the $GdBa_2Cu_3O_{6+\delta}$ ($\delta<0.2$) crystal.[8]

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