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Rapid Research Note

Raman spectroscopy with UV excitation on untwinned single crystals of $YBa_2Cu_3O_{7-\delta}$

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Recent reflectance anisotropy studies on the material showed a photobleaching effect in the in-plane components of the dielectric function around 2.2 and 4.1 eV [1]. We present Raman spectra of oxygen deficient $YBa_2Cu_3O_{7-\delta}$ detwinned single crystals taken with laser excitation of 3.7 eV, close to the UV feature in the dielectric function, in search for a signal from the defect-induced Raman modes. While two groups of defect-induced mode at 230 cm^{-1} and 600 cm^{-1} behave very similar at the 2.2 eV resonance, we find clear differences for UV excitation. A peak at 600 cm^{-1} is identified as a copper-oxygen-chain related, defect-induced modes by its Raman selection rules. While this mode is enhanced beyond the strength of the Raman-allowed modes, the group at 230 cm^{-1} is absent. Low temperature experiments showed no change of the peak height under illumination, though the peaks are known to photobleach in the visible.

1 Introduction In a recent study of the reflectance anisotropy in the *a*–*b* plane of detwinned $YBa_2Cu_3O_{7-\delta}$ crystals we found illumination-induced changes around 2.2 eV and 4.1 eV (see arrows in inset of Fig. 1) [1]. The effect is similar to Raman photobleaching and persistent photoconductivity regarding the relatively large timescale (minutes to hours), the stability at low temperatures and the recovery at around room-temperature [2–6]. In particular, Raman experiments show chain-oxygen defect-related peaks around 230 cm^{-1} and 600 cm^{-1} losing intensity under illumination. These signals appear only in underdoped samples and are resonant at 2.2 eV excitation energy [4, 5]. According to their Raman selection rules, they appear for incoming and detected light with a polarization component along the copper-oxygen chains in the unit cell (notated as the *b*-direction). Their decreasing Raman signal is attributed to changes in the copper-oxygen chain fragments and the oxygen vacancy cites under illumination.

The Raman resonance profile around 2.2 eV matches the spectral feature observed in RAS and ellipsometry data in the chain direction of $YBa_2Cu_3O_{7-\delta}$. This connection prompted us to investigate the Raman spectra at higher, UV excitation energies, searching for another resonance of the defect-induced modes. Here we present a Raman study on two detwinned single crystals of $YBa_2Cu_3O_{7-\delta}$ with $\delta = 0.3$ and

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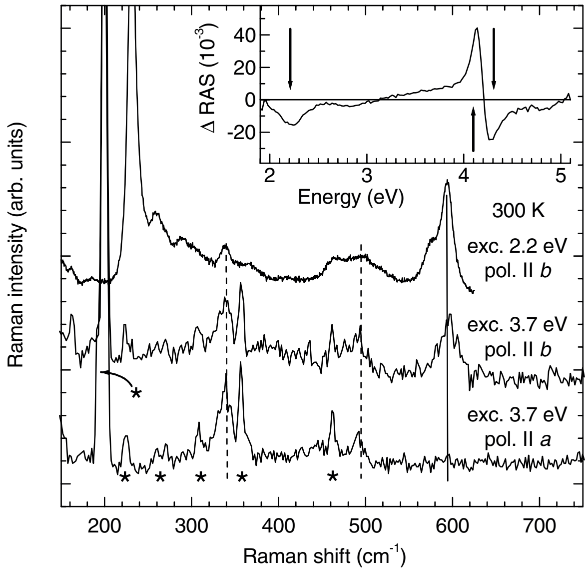

Fig. 1 Polarized Raman spectra of detwinned $YBa_2Cu_3O_{6.7}$ in $z(yy)z$ and $z(yy)z$ geometry taken at 300 K with 3.7 eV excitation energy. A peak at 600 cm^{-1} is exclusively present for incoming and detected polarization along the Cu–O-chain axis of the crystal. The upper spectrum, excited in the visible resonance (2.2 eV) with defect-induced peaks at 600 cm^{-1} and around 230 cm^{-1}, is shown for comparison. Dashed lines indicate Raman-allowed modes at 340 cm^{-1} and 495 cm^{-1}. The stars mark plasma lines. All spectra were offset for clarity. In the inset, a reflectance anisotropy spectrum after illumination has been subtracted from a spectrum taken prior to illumination. The dips and the peak at 2.2 eV, 4.1 eV and 4.3 eV (see arrows) mark the decrease, or increase respectively, in the reflectance anisotropy under illumination [1].

$\delta = 0.35$ at excitation energy 3.72 eV. The polarization dependence in the chain plane and various temperatures have been investigated.

2 Experimental The samples of crystalline $YBa_2Cu_3O_{7-\delta}$ were prepared using the flux-growth technique with yttria stabilized ZrO_2 trays. The method and proportions are the same as in Ref. [7] and the detwinning process under uniaxial stress is described in Ref. [8]. The oxygen content was reduced at 507 °C in an oxygen atmosphere of 14.5 mbar followed by a controlled cooling down process [9]. X-ray diffraction showed excellent crystal quality and detwinning.

A triple Dilor spectrometer equipped with UV mirror optic and gratings was used with a liquid-nitrogen cooled CCD detector. The 333.6 nm line of an Ar-ion laser was used for excitation. A power of 4 mW was focussed on a spot of 40 μm diameter. Spectra were accumulated for a total time between 15 min and two hours to make up for the weak Raman cross-section of the high-T_c materials. The full width at half maximum of the plasma lines is 5 cm^{-1} in the room temperature spectra and 7 cm^{-1} at low temperatures.

3 Results Figure 1 shows Raman spectra of a detwinned single crystal of $YBa_2Cu_3O_{6.7}$ taken in backscattering geometry on the *a–b* surface with parallel incident and detected polarization. The top trace is for resonant excitation in the visible (2.2 eV), whereas the two lower traces were excited in the UV (3.7 eV).

Two Raman allowed modes of $YBa_2Cu_3O_{7-\delta}$ are found at 340 cm^{-1} and 495 cm^{-1} in all three spectra in accordance with frequencies expected for room temperature and a reduced oxygen content [10, 11]. A third Raman allowed mode at 460 cm^{-1} overlaps with a plasma line in the UV. The focus of our interest is the peak at 600 cm^{-1}, which is comparable to the Raman allowed modes for polarization parallel to *b*, but absent for polarization parallel to *a*. The frequency as well as the selection rules match those of the photobleaching defect-induced mode observed at 595 cm^{-1} using resonant 2.2 eV excitation. This selection rule points to a strong coupling with the orthorhombic elements of the unit cell and is typical for the chain-related modes under visible excitation, thus showing the defect-related origin of the observed peak [10]. Contrary to the visible excitation spectra, no sign of the group of defect-induced peaks around 230 cm^{-1} is found. Note that the 230 cm^{-1} peaks dominates the visible spectrum; the peak is two orders of magnitude stronger than the Raman-allowed lines or the defect-induced mode at 600 cm^{-1}. This strong difference between the 230 and 600 cm^{-1} defect-induced groups under UV excitation is a remarkable feature, as they display a similar resonance profile and identical time dependence in photobleaching in

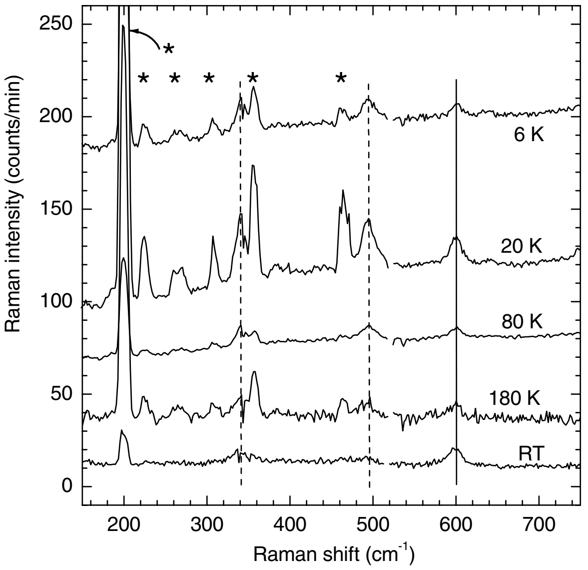

Fig. 2 UV-excited Raman spectra of $YBa_2Cu_3O_{7-\delta}$ at various temperatures. The room and the low temperature spectra were taken on two different crystals. Total accumulation times vary between 30 min and three hours. Dashed lines indicate Raman-allowed modes at 340 cm^{-1} and 495 cm^{-1}, the solid line the defect-induced mode at 600 cm^{-1}. The stars mark plasma lines. The spectra were offset for clarity, the one at 180 K had a linear background subtracted.

the visible range references. The discussion of origin of the Raman signal has concentrated on the more intense low frequency group in the literature. These are attributed to Cu–O-chain vibrations which are symmetry-forbidden in the ideal crystal, but become active when chains are refined to fragments with finite length. However, hardly any assignment of the higher energy mode has been attempted. Comparison to phonon frequency calculations points to a high-frequency vibration involving the bridging oxygen atom [10].

A possible reason for the absence of the low frequency modes is their photo-bleaching prior to sufficient accumulation, while some base signal of the 600 cm^{-1} mode remains. However, this explanation implies a much longer time scale for the bleaching of the 600 cm^{-1} group than for the 230 cm^{-1} peaks, which contradicts the findings using visible excitation. The absence of the 230 cm^{-1} peak is more likely due to a resonance effect. The resonance profile for this group of peaks could be much narrower than for the 600 cm^{-1} modes. Excitation-energy dependent measurements in the visible indeed found a slightly broader resonance window for the 600 cm^{-1} peaks [12]. It remains, nevertheless, surprising that the high-energy defect-induced Raman lines are stronger than the Raman-allowed phonons, while there is no trace of the 230 cm^{-1} peak. An absence of the 230 cm^{-1} mode resonance while the 600 cm^{-1} is present will greatly help in identifying the exact origin of the defect-induced phonons and the optical transition giving rise to the strong anisotropy in the RAS measurements. It would be promising to measure at higher excitation energy, i.e. at 4.1 eV, where all defect peaks are expected to be enhanced.

Figure 2 shows Raman spectra taken at various low temperatures, at which possible photobleaching slows down and should become easier to detect [13]. However, the low temperature spectra do not reveal a defect-induced signal at 230 cm^{-1} distinguishable from the plasma lines, and the spectra do not indicate a systematic change in intensity of the 600 cm^{-1} peak, which supports the resonance explanation of the missing 230 cm^{-1} peak. The spectra at 6, 80, 180 K display similar intensities, whereas the one at 20 K is somewhat enhanced. This magnitude of variation is typical for different spots on the sample surface, partly to some contamination on the sample surface in the cryostat. The room temperature spectrum was taken outside the cryostat on the second crystal, displaying a larger defect-induced peak compared to the Raman-allowed signal. This spectrum as well as the RT polarization dependent spectra of the first crystal were free of contamination traces.

We studied the accumulated spectra with respect to time, but did not observe a change in intensity. Due to the weak signal this could still come from the short decay times compared to the accumulation time (15 min minimum) of the spectra. Apart from this technical consideration, the absence of bleaching can be related to the UV excitation energy applied. The 4.1 eV resonance was attributed to intraionic excitations in copper atoms without chain-oxygen neighbors. It is possible that this kind of excitation does not interact with chain oxygen atoms and therefore does not alter the chains [1, 14, 15]. This can be tested in another UV-Raman experiment with additional illumination in the visible range. Lastly, the excitation of 3.72 eV used here is still far from the spectral feature at 4.1 eV. Outside the 4.1 to 4.3 eV range, the illumination-induced changes in RAS (see inset of Fig. 1) and therefore in Raman resonance conditions are small, even if the copper-oxygen chains are perturbed by light. Therefore, Raman spectroscopy might be little sensitive to altered copper-oxygen chains at excitation energy 3.7 eV.

4 Conclusion In conclusion, we report UV excited Raman spectra on detwinned crystals of $YBa_2Cu_3O_{7-\delta}$. Aside from the Raman-allowed modes at 340 cm^{-1} and 495 cm^{-1} we identify a feature at 600 cm^{-1} as an oxygen-defect-induced mode based on its selection rules and frequency, while the 230 cm^{-1} group known from visible excitation is missing. These modes are part of a group with very similar properties, including resonant behavior and photo-bleaching under visible excitation. Under UV excitation their resonance properties clearly differ, while selection rules of the observed mode are still the typical chain-related type. This provides a new and qualitatively different argument in the discussion about their origin. No photobleaching, nor a significant increase in intensity could be found at low temperatures. Considering the 4.1 eV resonance in the dielectric function that photobleaches in RAS experiments, further studies using that excitation energy appear promising.

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