

Room Temperature Oxygen Diffusion in the Presence of a Potential Gradient at a $\text{YBa}_2\text{Cu}_3\text{O}_6$ - $\text{YBa}_2\text{Cu}_3\text{O}_7$ Interface

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We have studied oxygen diffusion and ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals by monitoring oxygen concentration and disorder sensitive features in Raman spectra. We have found that oxygen diffuses from the bulk $\text{YBa}_2\text{Cu}_3\text{O}_7$ into the oxygen depleted $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ surface, probably via hopping along the O(1) and O(5) vacancies.

We performed the measurements in two steps. First samples were locally heated with a strong laser light. As a consequence oxygen was ejected out of the excited volume which is roughly determined by the laser penetration depth (approx. 60 nm) times the laser spot area (approx. $2000 \mu\text{m}^2$). Different laser powers were used for excitation. We have observed that the oxygen out-diffusion threshold depends on the oxygen partial pressure outside the sample (fig.2). After excitation was terminated oxygen concentration as a function of time was measured. We did it by taking Raman spectra after a certain time delay with the same setup as used for excitation but with a much lower laser power. Spectra were taken after 0, 5, 10 and 30 minutes delay. For the reference we took Raman spectrum before and during excitation too (fig.1). From the Raman spectra oxygen concentration can be determined by measuring the frequency of the O(4) z-axis vibration. The frequency ranges between 470 and 500 cm^{-1} dependent on δ ^[1]. We have observed time dependent frequency shift in delayed spectra which clearly indicates that oxygen in-diffusion is taking place. The oxygen in-diffusion time constant has been estimated to be approx. 10 min. It is important to notice that oxygen was diffusing back into depleted region when the sample was in air as well as in vacuum. It follows that oxygen mobility is quite high even at room temperatures.

Beside the 500 cm^{-1} Raman peak we have found another broad line at 580 cm^{-1} which normally does not appear in Raman spectra since it is symmetry forbidden. The intensity of this line dropped instantly (ms) after the laser power was turned down. A further smaller drop has been observed after 10 min which is the same time scale as for the oxygen in-diffusion. We contribute the appearance of this line to the break of the

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local symmetry due to oxygen disorder in O(1) and O(5) chain sites. This is consistent with the observation that the final intensity is higher at the oxygen concentration $\delta \approx 0.6$ than at $\delta \approx 1$. For $\delta = 1$ no oxygen is present in chain sites and there can be no disorder. The very similar time dependence of the 500 cm^{-1} peak shift and 580 cm^{-1} peak intensity suggests that the oxygen diffusion proceeds by hopping via the O(1) and O(5) chain sites.

In order to establish the origin of the fast decay at $t=0$ we made a similar experiment on ms time scale using chopped laser. We have found that the time dependence of the 580 cm^{-1} peak intensity closely follows the calculated temperature^[2] of the excited volume. The simplest explanation for this phenomenon is an anharmonic coupling of 580 cm^{-1} IR mode to other modes.

References:

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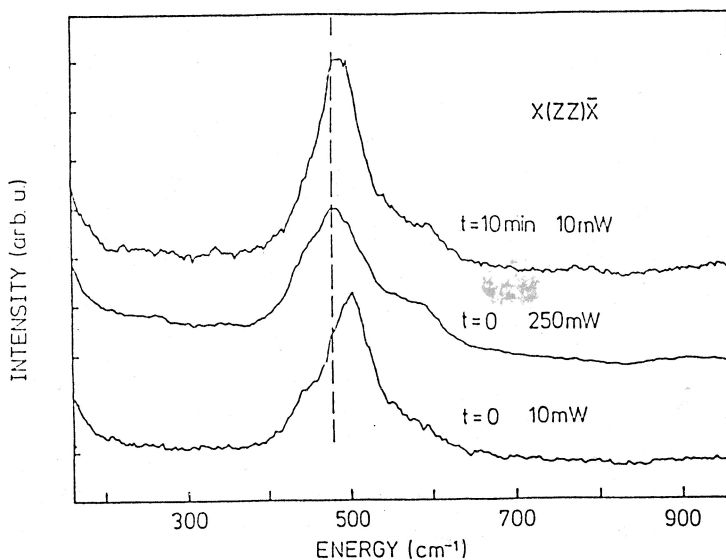


Figure 1. Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with different laser intensities and time intervals. The delayed spectrum (top) shows a visible shift towards higher frequency as a result of oxygen diffusion back into the surface.

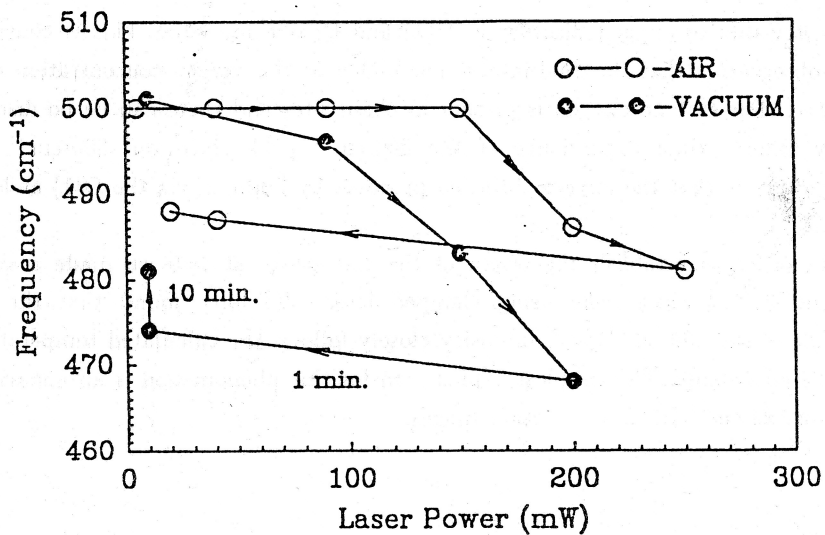


Figure 2. Frequency of the 500 cm^{-1} O(4) z-axis vibration as a function of laser intensity for the sample in air and in vacuum. All data except the last point of the vacuum cycle were taken within approx. 1 minute of each other.