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Photoinduced IR absorption in WO$_3$: determination of the polaron binding energy

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Abstract. Photoinduced IR absorption measurements are reported on WO$_3$. A photoinduced midinfrared small polaron peak centered at 4800 cm^{-1} (0.59 eV) was observed. The data were analyzed in the framework of the photon-assisted small-polaron hopping theory and briefly compared to previously published infrared absorption measurements in WO$_3$ and photoinduced IR absorption measurements in high T_c cuprates.

PACS. 71.38.-k Polarons and electron-phonon interactions – 78.30.Hv Other nonmetallic inorganics – 78.30.-j Infrared and Raman spectra

Recent indications of possible surface superconductivity at 91 K in sodium tungsten bronze Na$_x$WO$_3$ [1,2] has enhanced experimental interest in the idea of high-temperature bipolaronic superconductivity, which had led to the discovery of cuprate high temperature superconductors [3]. Measurements of polaron properties in this material may therefore be important for reaching a deeper understanding of the phenomenon.

Polarons and bipolarons in tungsten bronzes were studied in past with electron spin resonance and optical spectroscopy [4–6]. An optical absorption peak found at 0.71 eV in tungsten trioxide WO$_3$ was attributed to the photon-assisted hopping of small polarons [4]. It was also shown that bipolarons present in oxygen deficient WO$_3$ appear to dissociate under light illumination forming single polarons [5].

In cuprates [7–11] and manganites [12] measurements of the photoinduced (PI) infrared absorption have been shown to be a useful tool for investigating polaronic carriers, especially in the range of weak doping where PI absorption spectra are interpreted in terms of the photon-assisted hopping of small polarons [12,13]. It is therefore natural to extend measurements of the PI absorption also to WO$_3$ especially because the superconducting T_c is the largest at low carrier doping [1], much closer to carrier densities achieved by photoexcitation than in cuprates.

A ventron 99.7%-WO$_{3-x}$ powder sample (of unspecified oxygen deficiency x), greenish in appearance, was ground and mixed with KBr powder in 0.1–0.2 wt.% ratio and pressed into 12 mm diameter pellets. The pellets were mounted in a He-flow cryostat equipped with optical windows. Special care was taken that the KBr pellet was in a good thermal contact with the sample holder. PI spectra were measured at 25 K using an Ar$^+$-ion-laser photoexcitation at 514.5 nm ($h\nu = 2.41$ eV) with an optical fluence of ~500 mW/cm^2. To minimize heating effects due to laser light absorption in the sample and instrumental drift, the PI spectra were taken by alternating one sample scan (with the excitation laser on) and one reference scan (laser off) approximately every two seconds. At the same temperature a thermal-difference (TD) transmittance change was also measured without laser excitation by first measuring a reference spectrum and then increasing the sample holder temperature by 2 K and measuring a sample spectrum. To remove the effects of any instrumental drift, the same procedure was then inverted to measure the sample spectrum 2K above the given temperature first. The thermal difference (TD) transmittance change was then obtained by averaging both spectra.

The room temperature IR transmittance spectrum shown in Figure 1 is typical for an insulating material. There are two major phonon absorption peaks at 371 cm^{-1} and 839 cm^{-1}. The high frequency peak has a narrow shoulder at 779 cm^{-1}. The transmittance monotonically decreases towards higher frequencies mainly due to the increasing scattering in the KBr pellet at shorter wavelengths.

A PI transmittance spectrum at 25 K is shown in Figure 2b. Comparison of the PI spectrum with the TD spectrum in Figure 2a clearly shows that the PI spectrum is not caused by laser heating of the pellet. The PI spectrum is characterized by a relatively narrow structure in the phonon-frequency region and a broad absorption centered at 4800 cm^{-1} (0.59 eV). The structure in the phonon part shown in the inset in Figure 2 consists of a bleaching

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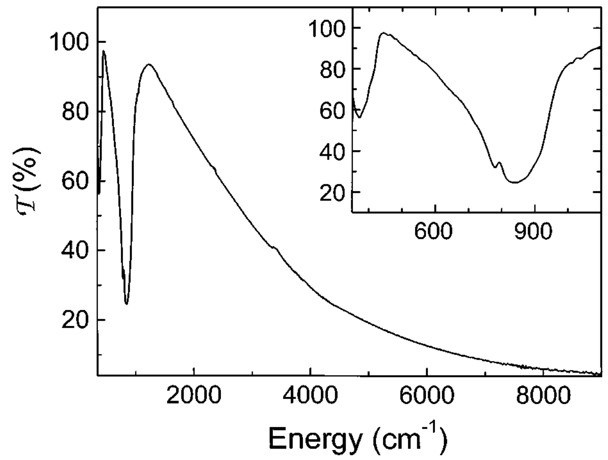

Fig. 1. Infrared transmittance of WO_{3-x} powder dispersed in a KBr pellet relative to a pure KBr pellet at room temperature. The inset shows infrared transmittance in the phonon-frequency region.

peak at 840 cm^{-1} and a weaker PI absorption peak at 929 cm^{-1}.

As previously in high T_c superconductors [13] and manganites [12] we fit the PI transmittance spectrum using the theoretical expression for optical absorption due to the small polaron hopping in the Holstein model [14–17], given in a compact form by Emin [17]. Assuming that $-\Delta\mathcal{T}_{\rm PI}/\mathcal{T}$ is proportional to the absorption coefficient [7], the PI transmittance is given by:

$$-\frac{\Delta\mathcal{T}_{\rm PI}}{\mathcal{T}} \propto \alpha \propto \frac{1}{\hbar\omega}\exp\left(-\frac{(2E_{\rm pol}-\hbar\omega)^2}{4E_{\rm pol}\hbar\omega_{\rm ph}}\right) \qquad (1)$$

where α is the absorption coefficient, $E_{\rm pol}$ is the polaron binding energy, ω the incoming photon frequency and $\omega_{\rm ph}$ the polaron phonon frequency. It can be seen from Figure 2b that the theoretical prediction fits well to the data in spite of simplicity of the Holstein model. The small-polaron binding energy and the polaron phonon frequency obtained from the fit are $E_{\rm pol} = 345 \pm 20$ meV and $\omega_{\rm ph} = 580 \pm 110$ cm^{-1} respectively. The polaron phonon frequency is in the range of oxygen vibrations as expected. However, when considering the polaron phonon frequency one must take into account that the width of the peak in equation (1), from where $\omega_{\rm ph}$ is determined, includes the prefactor which depends on details of the phonon cloud in the small polaron (and is 4 only in the 1D Holstein model).

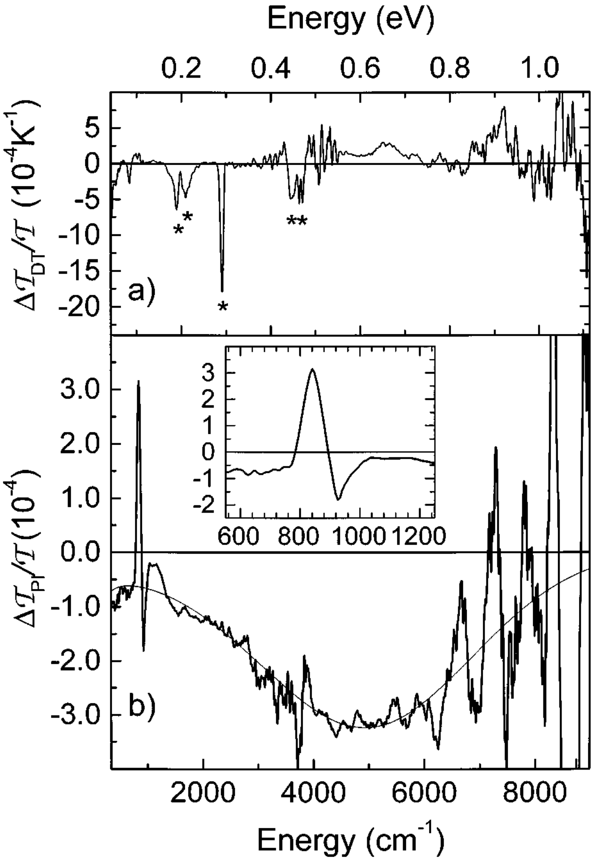

Fig. 2. (a) The thermal difference spectrum at 25 K and (b) the photoinduced transmittance spectrum at 25 K. The thin line in (b) represents the theoretical fit discussed in the text. The inset shows the photoinduced transmittance spectrum in the region of phonon frequencies. Stars in (a) indicate artefact peaks due to water vapor and CO_2 present in the spectrometer atmosphere.

In the phonon region of frequencies there are two possible contributions to the observed PI spectrum. The first contribution comes from the direct changes in the phonon spectrum due to polaron formation. In cuprates these were observed as new IR-active photoinduced local modes at frequencies which could not be attributed to intrinsic IR-active modes [7,8]. The other contribution comes from additional phonon screening due to the photoexcited (PE) carriers conductivity. We numerically simulated changes in the phonon spectrum due to the PE carriers screening using a modified dielectric function taking into account the PE carriers. Although it was possible to qualitatively reproduce the experimentally observed PI phonon lineshape using the model dielectric function derived from equation (1), it is not possible to reliably attribute the observed phonon bleaching entirely to the effect of screening by the PE carriers, since equation (1) is strictly valid only for $\omega \gg \omega_{\rm ph}$.

Comparing the PI spectra with infrared absorption in WO_3 single crystals, the latter shows a double-peak structure at low temperatures [4]. The peaks are centered at an energy which is approximately 1000 cm^{-1} higher than we find in the PI absorption. Moreover, the IR absorption structure is slightly narrower with a steeper onset at the low frequency edge. Despite the difference in the peak position the value of the polaron binding energy reported in reference [4] is the same as in our analysis. The reason for this apparent discrepancy is that the polaron binding energy reported in reference [4] is simply given as half the peak position energy, while in our case it is a parameter in the formula (1) which is not half the peak position energy. Thus we attribute the differences in the peak positions (and consequently the polaron binding energies) to small differences of oxygen stoichiometry [18].

Comparing the PI data with slightly Na-doped tungstate we find that Ruzicka *et al.* [18] observe no well-defined polaron signature in the MIR at energies around 5000 cm^{-1} in the optical conductivity of $Na_{0.01}WO_3$. Instead, in the doped sample they observe an increase in absorption around 0.1 eV (800 cm^{-1}) which is not observed in undoped WO_3. We attribute the different behaviour to significantly different doping levels and to the fact that the effects of Na doping may differ from photoexcitation because in the latter case both the electron and hole are excited, whereas in the former case WO_3 is electron-doped.

Finally, in comparison with PI spectra of the parent insulating compounds of high T_c cuprates [7,10,13] the PI spectra in WO_{3-x} show a simpler structure without the low frequency PI absorption around 1000 cm^{-1} that is observed in the cuprates. Nevertheless, the high frequency part of the PI absorption of high T_c cuprates has similar peak energies, although the PI absorption features are broader in the cuprates [10,11]. A similar peak energy in WO_3 implies a similar polaron binding energy, but it is not clear at present whether similar polaron binding energies can be correlated with similar magnitudes of superconducting critical temperatures in both systems.

To summarize, a photoinduced midinfrared small polaron peak centered at 4800 cm^{-1} (0.59 eV) was observed in photoinduced IR transmittance spectra measured in WO_{3-x} powder. The position of the PI peak is similar to the peak position previously reported in IR absorption measurements of WO_{3-x} single crystals [4]. The shape of the PI spectrum in WO_{3-x} is consistent with the photon-assisted small-polaron hopping [14–17] and the polaron binding energy of $E_{\text{pol}} = 345 \pm 20$ meV is extracted from the theoretical fit [17]. The binding energy is similar to that extracted from analyses of photoinduced absorption measurements in different undoped high T_c cuprates [10,11], implying some common physics in these materials.

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