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Superconductivity of TiO$_2$ grains by plasmon resonances

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Abstract

The understanding of phonon-induced charge transport in nanostructured TiO$_2$ is crucial for new generation solar cells, photocatalytic and H$_2$ producing devices. We present results of phonon modes in rutile derived as surface plasmon resonances in the crystalline planes. We find a compound state of two phonon modes centered at 24 THz in the bulk, which can exhibit enhanced polaronic state in the nanostructured system. We discuss the possible appearance of high T_c superconductivity.
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1. Introduction

Titanium dioxide (TiO$_2$) is a wide-band-gap semiconductor of importance for new photocatalysts and solar energy converters [1,2]. In these devices, photogenerated carriers induce a chemical reaction or develop an electric potential, depending critically on the transport properties. For TiO$_2$-based dye-sensitized solar cells, the efficiency is typically limited by electron transport through TiO$_2$ nanostructures [1,2]. TiO$_2$ is an ionic transition-metal oxide, exhibiting strong electron–phonon coupling which determines low room temperature electron mobilities [3–5]. The discrepant values of mobility [3–5] and efficiency of electron transport remain unresolved, although it is clear that they are determined by electron–phonon interactions that give rise to polaron formation and scattering events. Rutile is the most common and stable TiO$_2$ polymorph with a tetragonal structure with $a\nabla$ 4.6 Å and $c\nabla$ 2.9 Å. While anatase-type TiO$_2$ is more commonly used in solar cell devices [1] rutile has been shown to behave very similarly in such devices.

In this paper we investigate electron–phonon interactions in single crystal and nanostructured rutile, with phonon modes obtained as resonance modes on crystalline planes by the DDSCAT method [6,7]. We find a mode at 24 THz, composed of two modes with short and long lifetimes. The former is attributed to the polaron coupling dominating in the single crystal, the latter may become the dominant one in nanostructured crystal, where it can induce high conductivity and the possible appearance of superconductivity.

2. Lattice modes

We consider vibrations of ions in a crystal plane of the ionic material. They can be studied by analyzing the generated electric field. In the dipole approximation, in which the dimension of oscillators is much smaller than the wavelength, the total field satisfies the DDSCAT equation deduced for polarizable point dipoles [6,7]. If the plane is composed of a sufficiently large number of dipoles, the equations can then be transformed into a scalar form

$$E(\vec{r}_j) = E_o e^{i\vec{k}\cdot Rj} + V_o \sum_i \frac{e^{ik|\vec{r}_j - \vec{r}_i|}}{|\vec{r}_j - \vec{r}_i|} E(0) \tag{1}$$

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where the index i runs over the sites of the planes. Here, $E(\vec{r}_i)$ represents a field component and $V_o = 2k^2\alpha/3$ [8]. We consider an optical mode in which the radiation is incident perpendicularly, i.e. the wavevector $\vec{k}$ is orthogonal to its surface, close to the center of the Brillouin zone, i.e. $k < 2\pi/a$, a being the lattice constant. The solution of this system turns out [8] to be composed of two terms, one is the transmitted + reflected wave by each plane, the other is a wave decaying with either side distance from the plane with a characteristic length of the order of the lattice constant. A 3D single crystal can be described by adding the contributions of all the lattice planes. For points on a given plane the evanescent waves from successively planes can be neglected since they decay with distance $|z|$ from the planes as $\exp(-2\pi|z|/a)$. The reflected waves from the planes from the right side of the given plane and the transmitted waves from the left planes contribute each a term $\exp(ikma)$, with m an integer which interfere destructively in a diatomic lattice where the periodicity is $2a$ [9]. Therefore in the limit of a very large system we can consider only one plane as a model to describe optical vibrations in the system in the dipole approximation.

The t-matrix $E(0)$ of this problem is a complex quantity depending on the complex polarizability α and the cut-off representing the smallest distance of lattice lines on the plane, having a pole structure at resonances [8]. The polarizability $\alpha = \alpha' + i\alpha''$ is deduced from the Clausius–Mossotti relation $4\pi\rho\alpha/3 = (\varepsilon - 1)/(\varepsilon + 2)$ [9]. Here, ρ is the bulk crystal density, and ε the dielectric function, this being related to the complex refraction index $N + iK = \varepsilon^{1/2}$ whose values can be assumed known for a given system in the suitable wavelength range.

3. Results

Detailed analysis has been carried out for TiO$_2$ rutile single crystals, by using experimentally reported values of the complex refraction index [10] for frequencies ranging from the ultraviolet (0.4 μm) to the infrared (36.4 μm). Missing data at certain wavelengths have been reproduced by a linear interpolation of neighboring data. In the range 3.0–0.11 eV the K values are quite small (smaller than 10^{-2}) so they have been put equal to zero in the evaluation. This range corresponds to a transmission without absorption below the band gap, which is $\cong 3.0$ eV.

In the following we show results for the quantity $\beta = |E(0)|^2$ and the lifetime τ of resonances on varying the parameter d.

Big peaks of $\beta \approx 10^3$ at the scale $d \cong (10^{-13}–10^{-14})$ cm are obtained within the visible part of the spectrum, which correspond to plasmon resonances of electronic origin (Fig. 1). On decreasing d, a secondary maximum ≈ 1 appears in the infrared at $\cong 15$ μm. With a further decrease of d, progressively the large maximum shifts to the right and decreases in intensity while the secondary maximum grows. At $d = 7.5 \times 10^{-16}$ the two maxima of β become equal and we observe that the center of mass of the two res-
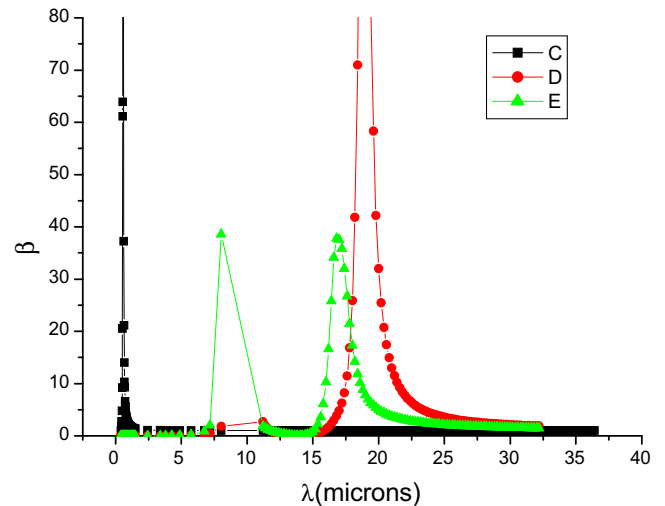

Fig. 1. The β values as a function of wavelength at decreasing values of: $d = 2.8 \cdot 10^{-13}$ cm (C), $d = 5 \cdot 10^{-16}$ cm (D) $d = 7.5 \cdot 10^{-16}$ cm (E). Two maxima of equal weight occur around 24 THz in the case (E).

onant states coincides with 24 THz (Fig. 1), the LO phonon frequency reported in the literature and obtained from reflectivity data in single crystal rutile [11,12].

The two maxima never merge and their shift in wavelength is about 5 μm. On decreasing d further the intensity of the left maximum decreases, while the right maximum increases on shifting simultaneously towards the far infrared.

This maximum can reach β values comparable to the left maxima obtained in the visible ($\beta \cong 170$ in the case of Fig. 1). The shift of the maxima (left and right) is accompanied by a change of the width, which corresponds to the change of the lifetime (Fig. 2). The order of magnitude of lifetimes of the right states is in agreement with those reported [11], up to room temperature. However, the lifetime of the left state is much longer, of order 10^{-11} s.
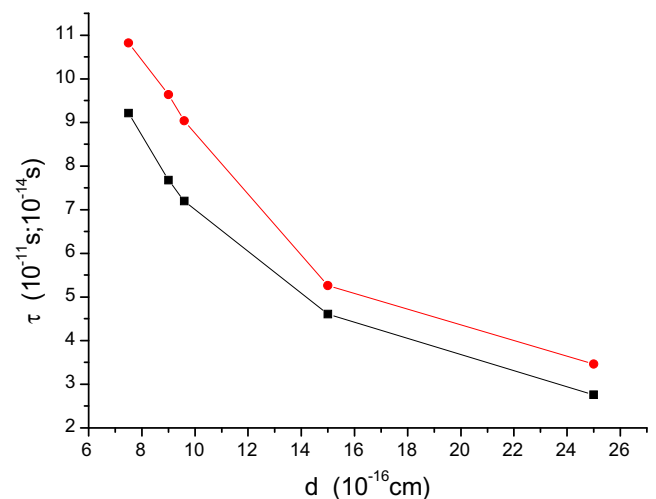

Fig. 2. Lifetime of left (upper curve, units 10^{-11} s) and right (lower curve, units 10^{-14} s) states for low d.