PHYSICAL REVIEW B VOLUME 52, NUMBER 11 15 SEPTEMBER 1995-I

Urbach tail of anatase TiO_2

H. Tang, F. Lévy, H. Berger, and P. E. Schmid
Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
(Received 17 January 1995; revised manuscript received 7 April 1995)

The fundamental absorption edge of the anatase phase of TiO_2 has been studied by performing polarized optical transmission measurements on single crystals at temperatures ranging from 4.2 to 300 K. An Urbach tail has been found that shows an exponential spectral dependence down to liquid-helium temperature. The optical gap of anatase has been estimated to be 3.420 eV in polarization $\mathbf{E}\perp\mathbf{c}$, and 3.460 eV in polarization $\mathbf{E}\parallel\mathbf{c}$. Our experimental results can be accounted for in terms of the theory of Toyozawa and co-workers, which ascribes the Urbach tail to the momentary localization of excitons due to phonon interaction. Comparing, in this case, the measured abosrption spectra of anatase and rutile, we conclude that the excitons in anatase are self-trapped while those in rutile are free. This opposite nature of exciton states in anatase and rutile is consistent with the results of previous photoluminescence studies.

I. INTRODUCTION

Compared with rutile, anatase is a less common form of TiO_2 that has received very little attention. Both polymorphs have a tetragonal unit cell. But rutile, which contains two TiO_2 molecules per unit cell, has lattice constants $a = 4.5937$ Å and $c = 2.9587$ Å. This is the most stable and dense phase of TiO_2 (density 4.250 g/cm^3). Anatase, which contains four molecules per unit cell, has lattice constants $a = 3.7842$ Å and $c = 9.5146$ Å. It is a metastable and less dense phase, with a density of only 3.894 g/cm^3.

Recently, anatase TiO_2 has attracted particular interest, owing to its extraordinary role in a recently developed electrochemical photovoltaic cell of promising efficiency.[1] The electrical, magnetic, and photoluminescence properties of anatase TiO_2 have then been investigated and found to be significantly different from those of rutile.[2-5] A striking contrast is the opposite nature of the exciton states in the two phases of TiO_2, i.e., self-trapped excitons in anatase against free excitons in rutile.[5-8]

In this paper, we present a detailed investigation of the fundamental absorption edge of anatase TiO_2 in the temperature range 4.2–300 K. The absorption edge of anatase is found to be of the Urbach type, and depends on photon energy and temperature according to the standard relation[9]

$$\alpha(E)=\alpha_0 \exp\left[-\sigma\frac{E_0-E}{kT}\right], \tag{1}$$

where $\alpha(E)$ is the absorption coefficient, E is the photon energy, E_0 is an estimate of the optical gap, α_0 is a constant, and σ is the steepness parameter which is temperature dependent according to the equation

$$\sigma(T)=\sigma_0\left[\frac{2kT}{\hbar\omega_p}\right]\tanh\left[\frac{\hbar\omega_p}{2kT}\right]. \tag{2}$$

σ_0 is a constant and $\hbar\omega_p$ is a phonon energy.

Two different models account for the Urbach rule observed in pure single crystals. One of them, developed by Dow and Redfield, ascribes the Urbach tail to the ionization of excitons by internal electric microfields produced by phonons, charged impurities, lattice disorder, etc.[10] The other one, developed by Toyozawa and co-workers, ascribes the Urbach tail to the influence of phonon fields on the center-of-mass motion of excitons, i.e., the momentary self-trapping of excitons.[11-14] According to many reports in the literature, the first model applies well to III-V and II-VI compounds where the exciton-phonon coupling is relatively weak and the excitons are mostly free. The second model applies more to highly ionic crystals such as alkali halides and oxides, where the exciton-phonon coupling is large.[15-18] In this case, the steepness parameter σ_0 is inversely proportional to the exciton-phonon-coupling constant g:

$$\sigma_0=\frac{s}{g}, \tag{3}$$

where s is the steepness index. This index has been determined by Schreiber and Toyozawa to be 1.50 ± 0.06 for direct absorption edges and 0.85 ± 0.05 for indirect ones.[13] Therefore, the exciton-phonon-coupling constant can be deduced from the experimental values of σ_0. The self-trapping of excitons occurs when g is larger than a critical value[13]

$$g_c=1-(2\nu)^{-1}, \tag{4}$$

where ν is the number of nearest-neighboring sites for exciton intersite transfer.

II. RESULTS AND DISCUSSION

The growth of anatase single crystal by chemical transport reactions has already been reported.[19] As-grown anatase crystals are lightly blue, because they were reduced in the presence of hydrogen during the growth. After annealing in oxygen at 873 K for 48 h, all anatase crystals become colorless.

After being x ray oriented all crystals were ground to thin slabs with $\{100\}$ faces, and polished to achieve good optical quality. The measured samples included (i) two slabs of annealed (colorless) anatase crystal with thicknesses of 0.52 and 0.115 mm, and (ii) two slabs of colorless rutile crystal with thicknesses of 0.55 and 0.12 mm.

Polarized optical-absorption measurements have been done using a direct sample in and sample out technique. All samples were placed in a cryostat, cooled by a continuous flow of liquid helium. The temperature was controlled in the range 4.2–300 K and stabilized within ±0.2 K. A 150-W xenon-arc lamp was used as the light source. The spectral recording system included a Spex 1870 spectrometer, an S-20 type photomultiplier, and a lock-in amplifier (model SR510).

The absorption coefficients were derived from the apparent transmittance $(T=I/I_0)$ after properly correcting for the reflection loss (R). The corresponding experimental values of the reflectivity have already been reported.[20] It was slightly adjusted in order to find $\alpha\approx 0$ in the transparent region.

Figure 1 shows semilogarithmic plots of the polarized absorption spectra of anatase and rutile for a series of temperatures ranging from 4.2 to 300 K. The absorption edge of anatase clearly demonstrates an exponential energy dependence, in both $\mathbf{E}\perp\mathbf{c}$ and $\mathbf{E}\parallel\mathbf{c}$ polarizations, at all temperatures ranging from 4.2 to 300 K. Except for $\mathbf{E}\parallel\mathbf{c}$ at $T\leq 100$ K, this exponential dependence covers more than two orders of magnitude. The slope of the curves decreases with increasing temperature, and extrapolations of the exponential part of the spectra lead to a focal point (E_0,α_0) which gives an estimate of the optical gap. This is the typical Urbach behavior described by Eq. (1). As the temperature is lowered below 100 K, the absorption spectrum of anatase becomes independent of temperature, and both the position and slope remain constant. As compared in Fig. 1, the absorption edge of rutile behaves differently. Above 250 K, rutile also shows an exponential absorption edge. However, at low temperatures (<200 K) the steepness of the absorption edge sharply increases and phonon structures start to resolve. Particularly in the $\mathbf{E}\parallel\mathbf{c}$ spectrum, the phonon sidebands rise in intensity with increasing temperature between 10 and 100 K, and are smoothed out at $T\geq 200$ K.

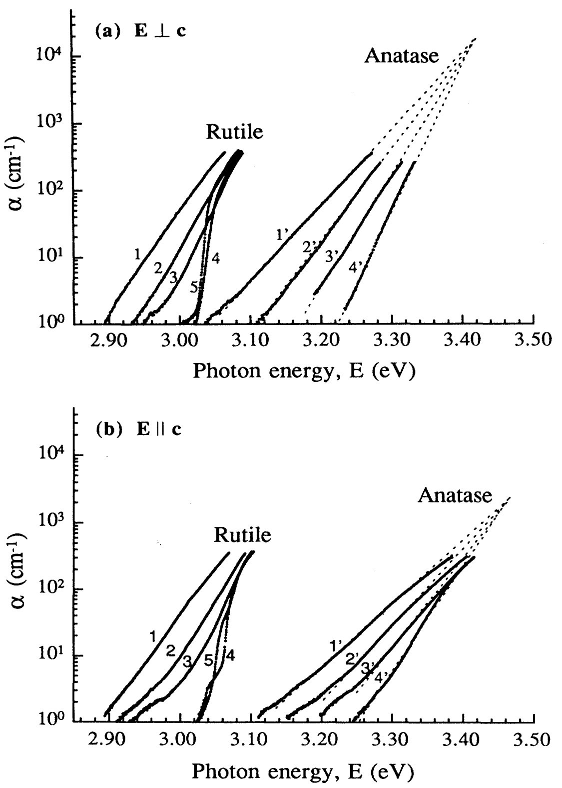

FIG. 1. Absorption spectra of anatase and rutile TiO_2 measured at different temperatures for (a) $\mathbf{E}\perp\mathbf{c}$ and (b) $\mathbf{E}\parallel\mathbf{c}$ polarizations. The temperatures have been indicated as follows: 1-1′: 300 K; 2-2′: 250 K; 3-3′: 200 K; 4: 100 K; 4′: ≤100 K; and 5: 10 K.

In order to compare with the results of the literature, the low-temperature absorption data of anatase and rutile have been plotted as $\alpha^{1/2}$ versus photon energy in Fig. 2. Phonon structures are hardly observable in anatase, in both polarizations, while the threshold of phonon-assisted transitions resolve clearly in rutile. This confirms the data of Pascual, Camassel, and Mathieu.[7] Rutile has a direct band gap strictly forbidden in polarization $\mathbf{E}\parallel\mathbf{c}$ and an indirect allowed transition slightly higher in energy. Based on the assignments of phonon structures and the phonon energies given in Ref. 7 $(TA=11$ meV and $O_1=15$ meV), from Fig. 2 we find the direct gap E_{gd} at 3.035 eV and the indirect gap E_{gi} at 3.051 eV at $T=10$ K. These are exactly the values given by Pascual, Camassel, and Mathieu.[7]

Figure 3 shows isoabsorption curves at 50 cm^{-1} for anatase and rutile. They give an estimate of the optical dichroism at the fundamental absorption edge. We find that anatase has a larger dichroism than rutile (at 50 cm^{-1}). For both crystals, the $\mathbf{E}\perp\mathbf{c}$ edge is at a lower energy than the $\mathbf{E}\parallel\mathbf{c}$ edge. In anatase, the dichroism increases with increasing temperature. In rutile, it decreases with increasing temperature and disappears at room temperature.

The Urbach tail parameters of anatase have been deduced from the experimental spectra according to Eqs. (1) and (2). In Fig. 4, we show the steepness parameter σ as a function of temperature. The experimental data fit Eq. (2) with $\sigma_0=0.733\pm0.016$, $\hbar\omega_p=24.8\pm1.5$ meV, for $\mathbf{E}\perp\mathbf{c}$; and $\sigma_0=0.621\pm0.008$, $\hbar\omega_p=30.6\pm1.0$ meV, for $\mathbf{E}\parallel\mathbf{c}$. Clearly, at high temperature σ is very close to σ_0, while at low temperature it decreases and gives a finite and constant slope (σ/kT) from 100 K down to liquid-helium temperature. This is a manifestation of the so-called self-trapping of excitons in anatase.

Two other Urbach parameters of anatase (α_0 and E_0) have been obtained from the linear extrapolations of $\log_{10}(\alpha)$ versus E plotted in Fig. 1. We find $\alpha_0=2\times10^4$ cm^{-1} and $E_0=3.420$ eV for $\mathbf{E}\perp\mathbf{c}$, and $\alpha_0=3\times10^3$ cm^{-1} and $E_0=3.460$ eV for $\mathbf{E}\parallel\mathbf{c}$. E_0 is indicative of the energy value of the absorption edge below which the Urbach tail extends. Therefore, similar to the situation encountered in rutile, the fundamental absorption edge in anatase appears located at higher energy in polarization **E**||**c** than in polarization **E**⊥**c**. Concerning the oscillator strength of the two transitions, we find $\alpha_0(\mathbf{E}\perp\mathbf{c})$ nearly one order of magnitude larger than $\alpha_0(\mathbf{E}\|\mathbf{c})$.

While the Urbach behavior of the absorption edges prevents an unambiguous determination of the nature of the transitions, the **E**⊥**c** and **E**||**c** absorption edges of anatase can be tentatively assigned to be direct and indirect transitions, respectively. In this case, some difference between a direct edge and an indirect one can be traced. The theoretical modeling by Sumi and Toyozawa points out that the absorption tail associated with an indirect transition follows the exponential spectral dependence less accurately and over a smaller range of absorption coefficient than that associated with a direct one.[11] This is indeed what we find if we compare the **E**||**c** spectra in Fig. 1(b) to the **E**⊥**c** spectra in Fig. 1(a).

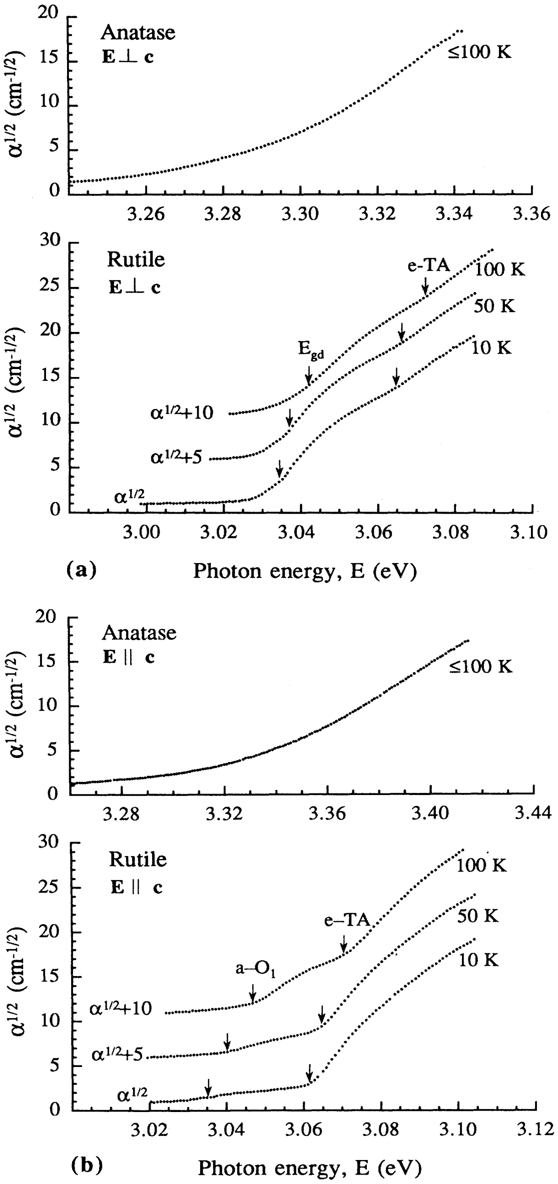

FIG. 2. Absorption spectra of anatase and rutile TiO_2 at low temperatures, plotted as $\alpha^{1/2}$ vs photon energy, for (a) **E**⊥**c** and (b) **E**||**c** polarizations. Assignments of the thresholds for rutile are based on the work of Ref. 7.

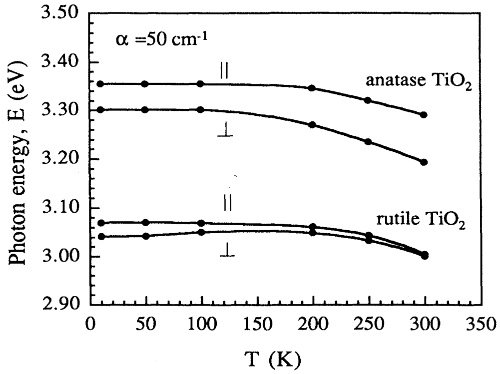

FIG. 3. Isoabsorption curves of anatase and rutile forms of TiO_2 at $\alpha=50\ \mathrm{cm}^{-1}$.

Exciton-phonon-coupling constant in anatase can be deduced from the experimental steepness parameters using Eq. (3). We find $g=s/\sigma_0=(1.50\pm0.06)/0.733=2.05\pm0.08$ for the direct edge in **E**⊥**c** polarization, and $g=(0.85\pm0.05)/0.621=1.37\pm0.08$ for the indirect edge in **E**||**c** polarization. Both values exceed the critical limit required for self-trapping of excitons $[g_c=1-(2\times8)^{-1}=0.937]$.[5] Therefore the critical condition of self-trapping of excitons $(g>g_c)$ appears well satisfied in anatase. One may argue that our tentative assignment of the **E**⊥**c** edge to a direct one is not correct. In this case, one should use the smaller value 0.85 instead of the larger one 1.50 for the index s in order to deduce the constant g. Even in this case, we have $g=(0.85\pm0.05)/0.733=1.16\pm0.07$. This is still larger than g_c. Therefore, independently of the uncertainty of our assignment, it can be concluded that self-trapping of excitons indeed occurs in anatase TiO_2.

In contrast, the absorption edge of rutile shows ex-

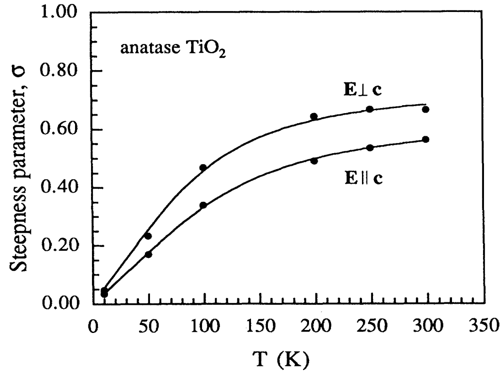

FIG. 4 Steepness parameter σ vs temperature, based on the experimental data in Fig. 1. The solid curves represent a fit from Eq. (2).

ponential spectral dependence only at high temperature (≥ 250 K; see Fig. 1). At this high temperature, as indicated in Fig. 3, the dichroism in rutile vanishes and the spectra measured in both polarizations become identical. Since the direct edge of rutile is strictly forbidden in $\mathbf{E}\|\mathbf{c}$ polarization and only weakly allowed in $\mathbf{E}\perp\mathbf{c}$ polarization, the exponential absorption tail of rutile at high temperature is determined by the indirect allowed transition. From the measured steepness parameter $\sigma(300\ \mathrm{K})=0.90$, we have $g=(0.85\pm0.05)/0.9=0.94\pm0.05$. For rutile,[5] $g_c=1-(2\times10)^{-1}=0.95$. Therefore the critical condition for self-trapping of excitons ($g>g_c$) is not satisfied. In agreement with the low-temperature behavior of the absorption edge, it is concluded that excitons in rutile are basically free.

III. CONCLUSION

We have shown that the two anatase and rutile forms of titanium dioxide display essentially different behaviors at the fundamental absorption edges. This is because of the opposite types of exciton states. The absorption edge of rutile is characterized by phonon sidebands extending near the fundamental transition thresholds at low temperature. In contrast, the spectral dependence of the absorption edge in anatase follows the Urbach rule at all temperatures down to liquid-helium temperature. According to the exciton-phonon interaction model of Toyozawa and co-workers, the exciton-phonon-coupling constants in anatase can be evaluated from the slope of the Urbach tails. We find 2.05 for $\mathbf{E}\perp\mathbf{c}$ and 1.37 for $\mathbf{E}\|\mathbf{c}$. These coupling constants largely surpass the critical value, predicting that excitons are self-trapped in anatase. The opposite nature of exciton states in anatase and rutile correlates with their structural differences. Both polymorphs of TiO_2 are built on a network of coordinated TiO_6 octahedra. Excitons in such structures are called charge-transfer excitons. They result from iteration between conduction-band electrons located on Ti 3*d* states and holes formed essentially by the O 2*p* states.[5,21] The anatase and rutile structures differ significantly in the coordination of the TiO_6 octahedra. In rutile, each TiO_6 octahedron is connected to ten neighboring ones on sharing a corner or an edge. In anatase, the coordination of the TiO_6 octahedra is less compact, and each octahedron is coordinated only with eight neighboring ones. In consequence, in the anatase structure, the intersite transfer of excitons is weaker and the localization of excitons through coupling to phonons is favored.

---

[1] M. Graetzel, Comments Inorg. Chem. **12**, 93 (1991).

[2] L. Forro, O. Chauvet, D. Emin, L. Zuppiroli, H. Berger, and F. Lévy, J. Appl. Phys. **75**, 633 (1994).

[3] H. Tang, K. Prasad, R. Sanjinès, P. E. Schmid, and F. Lévy, J. Appl. Phys. **75**, 2042 (1994).

[4] O. Chauvet, L. Forro, I. Kos, and M. Miljak, Solid State Commun. **93**, 667 (1995).

[5] H. Tang, H. Berger, P. E. Schmid, F. Lévy, and G. Burri, Solid State Commun. **87**, 847 (1993).

[6] A. Amtout and R. Leonelli, Solid State Commun. **84**, 349 (1992).

[7] J. Pascual, J. Camassel, and H. Mathieu, Phys. Rev. B **18**, 5606 (1978).

[8] H. Mathieu, J. Pascual, and J. Camassel, Phys. Rev. B **18**, 6920 (1978).

[9] K. S. Song and R. T. Williams, *Self-Trapped Excitons* (Springer-Verlag, Berlin, 1993), p. 24.

[10] J. D. Dow and D. Redfield, Phys. Rev. B **5**, 594 (1972).

[11] H. Sumi and Y. Toyozawa, J. Phys. Soc. Jpn. **31**, 342 (1971).

[12] K. Cho and Y. Toyozawa, J. Phys. Soc. Jpn. **30**, 1555 (1971).

[13] M. Schrieber and Y. Toyozawa, J. Phys. Soc. Jpn. **51**, 1528 (1982).

[14] Y. Toyozawa, J. Lumin. **12/13**, 13 (1976).

[15] C. Bosio and W. Czaja, Philos. Mag. B **63**, 7 (1991).

[16] M. Neumann-Spallart, E. Galun, G. Hodes, C. Lévy-Clément, Y. Marfaing, E. Muranevich, and R. Tenne, J. Appl. Phys. **73**, 7753 (1993).

[17] L. Samuel, Y. Brada, and R. Beserman, Phys. Rev. B **37**, 4671 (1988).

[18] J. Liebler and H. Haug, Europhys. Lett. **14**, 71 (1991).

[19] H. Berger, H. Tang, and F. Lévy, J. Cryst. Growth **130**, 108 (1993).

[20] H. Tang, H. Berger, P. E. Schmid, and F. Lévy, Solid State Commun. **92**, 267 (1994).

[21] L. G. J. De Haart, A. J. De Vries, and G. Blasse, J. Solid State Chem. **59**, 291 (1985).