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Resolved Quadrupolar Transition in TiO_2

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We report an investigation of the direct forbidden absorption edge of TiO_2. For the first time we have resolved the weak quadrupolar 1*s* exciton and measured its binding energy. Taking into account polaron effects, we estimated the bare electron effective mass in the Γ_1 minimum of the conduction band and obtained a fairly reasonable value of $3m_0$.

The forbidden exciton series in semiconductors have long been a subject of interest. However, all experimental work was restricted to SnO_2 and Cu_2O. SnO_2 belongs to the $D_{4h}{}^{14}$ symmetry group. At low temperature, the absorption edge spectrum exhibits a sharp hydrogenlike series of exciton lines when the light is polarized perpendicularly with respect to the fourfold C axis ($E\perp C$). The quadrupolar character of the transition associated with the $n=1$ exciton state has been well established.[1] Cu_2O has a cubic symmetry (point group O_h) but a compression along any of the three equivalent fourfold axes (001) reduces its symmetry into a tetragonal one. The point group is again D_{4h}, with the C axis parallel to T. Experimental results[2] show that, under (001) uniaxial stress T, the forbidden yellow series disappears in the $E \parallel T$ configuration and is only observed in the $E\perp T$ configuration. In other words, the forbidden exciton series of Cu_2O reduces to the forbidden one of SnO_2, with the same selection rules, under tetragonal compression.

In this Letter we identify TiO_2 which belongs to the same $D_{4h}{}^{14}$ symmetry group as SnO_2, as being a new material with a direct forbidden absorption edge. This contrasts with recent reports which identifies TiO_2 as an indirect-band-gap semiconductor.[3-5] We resolve the weak quadrupolar 1*s* exciton state and determine the exciton binding energy. Taking into account the high values of the dielectric constant, and correcting for the associated polaron effects, we get the first estimate of the bare effective mass in the Γ_1 minimum of the conduction band.

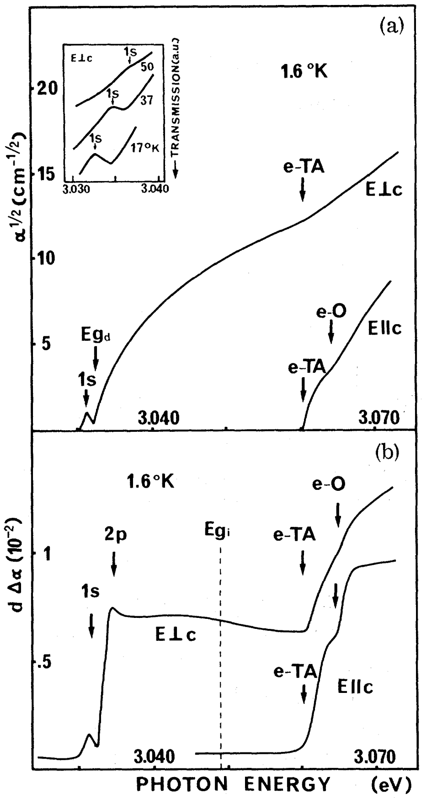

FIG. 1. (a) Absorption spectra of TiO_2 at 1.6°K with $E \parallel C$ and $E \perp C$ polarization. The 1*s* structure (3.031 eV) is the forbidden exciton. The O and TA components are phonon-assisted absorption edges associated with the indirect threshold found in both polarizations. Inset: experimental transmission spectra obtained at three different temperatures on a 1.8-mm-thick sample. The experimental resolution is 0.5 meV. (b) Wavelength modulation absorption spectra obtained at 1.6°K. Note the strong structure associated with the 2*p* exciton.

Our experimental results are shown in Fig. 1. With an $E \perp C$ polarization, we find at 1.6°K a sharp structure (1*s*) which appears at 3.031 eV and corresponds with a very small absorption strength ($\alpha \sim 2$ cm^{-1}) characteristic of forbidden transitions. It is an intrinsic feature of the crystals which is only resolved on our thickest samples and at very low temperature [see inset in Fig. 1(a)]. It is not found with an $E \parallel C$ polarization, and a detailed analysis of the absorption components[6] permits us to draw the following conclusions: (i) With an $E \perp C$ polarization, the fundamental absorption edge corresponds to a direct forbidden gap (the 1*s* exciton is at 3.031 eV) and the transition appears weakly through second-order interaction. From the disappearance of the structure at about 50°K, we estimate a binding energy $E_b \sim 4$ meV. (ii) In polarizing $E \parallel C$, the fundamental absorption edge is indirect ($E_{gi} = 3.049$ eV) and mainly assisted by two different phonons: a transverse acoustic mode ($E_{\mathrm{TA}} = 11$ meV) and an optical mode ($E_{\mathrm{O}} = 15$ meV). The corresponding replica appear above 20°K. The transition is allowed also in polarizing $E \perp C$. (iii) The difference between the thresholds of these two absorption processes results in the so-called dichroism (29 meV at 1.6°K), which is now explained as being an energy difference between two absorption processes and not a difference in two phonon energies associated with the same absorption edge, as was proposed in Ref. 1.

Figure 1(b) shows the fine structure of the forbidden components (wavelength derivative spectrum). The 1*s* and 2*p* components are now better resolved and their separation in energy is 30 meV. The 2*p* exciton is the most important one and this is well accounted for by group-theoretical arguments: The unit cell of rutile (TiO_2) contains two titanium and four oxygen atoms which are located at nonequivalent positions, and so the energy band structure is very complicated. However one knows from simple bonding arguments that in TiO_2 the 3*d* shell of titanium is empty and the 2*p* shell of oxygen is filled; so the conduction and valence bands are made of states from these two shells, respectively. The crystal field splits the valence band into states of symmetries Γ_1, Γ_2, Γ_3, Γ_4, Γ_5, Γ_2', Γ_3', and $2\Gamma_5'$, while the conduction band splits into $2\Gamma_1$, Γ_2, Γ_3, $2\Gamma_4$, and $2\Gamma_5$. The irreducible representations which describe the symmetry of the transition into the exciton states are contained within the direct product $\Gamma_v^* \times \Gamma_{\text{e-h}} \times \Gamma_c$, where Γ_v and Γ_c are the irreducible representations according to which the electronic wave function of the valence and conduction bands transforms, and $\Gamma_{\text{e-h}}$ describes the symmetry of the relative electron-hole motion.

We use the standard assumption[5,7] that the transition occurs at the Γ point of the Brillouin zone, between the fully symmetric Γ_1 minimum of the conduction band and the Γ_3 maximum of the valence band. This is in good agreement with the results of (i) simple tight-binding[5] and (ii) first-principles[7] band-structure calculations. This is also in good agreement with the Γ_3 symmetry predicted for the maximum of the valence band in VO_2, RuO_2, OsO_2, and IrO_2 which are all 3*d*, 4*d*, or 5*d* transition-metal oxides with the rutile structure.[8,9] This is also the experimental scheme in SnO_2.

In this case, all selection rules are given in Table I. The direct transition $\Gamma_{3v} \rightarrow \Gamma_{1c}$ is forbid-

TABLE I. Selection rules for the creation of direct excitons ($\Gamma_3 \rightarrow \Gamma_{1c}$) in TiO_2. E.D., electric dipole; E.Q., electric quadrupole. Please note that all processes are forbidden through magnetic dipole interaction.

$\Gamma_{3v} \times \Gamma_{e-h} \times \Gamma_{1c}$	Γ_3 (ns)	Γ_4' (np_z)	Γ_5' (np_{xy})
E.D.			
$(\Gamma_2')_{\parallel} + (\Gamma_5')_{\perp}$	0	0	$\perp$
E.Q.			
$(\Gamma_1 + \Gamma_5)_{\parallel} + (\Gamma_3 + \Gamma_5 + \Gamma_5)_{\perp}$	$\perp$	0	0

den through both electric-dipole and magnetic-dipole interaction for spherical-symmetry excitons, but is allowed through a weak electric quadrupole interaction with an $E \perp C$ polarization. It is strictly forbidden with $E \parallel C$. The creation of p_z-type excitons is also strictly forbidden, but the creation of p_{xy} excitons is allowed by electric dipole interaction with $E \perp C$. This is in good agreement with the experimental findings of Fig. 1 which show the $2p$ exciton to be much more important than the $1s$ one. This is the third example in solid state physics of a well-resolved quadrupolar excitonic line. Mainly because of their larger binding energy and stronger matrix elements, the dipole-allowed p-type excitons in Cu_2O and SnO_2 have been extensively investigated.

Concerning the binding energy of excitons in anisotropic crystals, an anisotropic-exciton-mass formalism has been developed by Gerlach and Pollman.[10] For weakly bound excitons, this formalism reduces to the perturbation results and the exciton energies are

$$E_{nlm} = -\frac{1}{n^2}\left[1 + \frac{\beta}{3}\left(1 + 2\,\frac{l(l+1) - 3m^2}{(2l+3)(2l-1)}\right)\right]R_{\mathrm{eff}}, \qquad (1)$$

where $R_{\mathrm{eff}} = e^4\mu_{\perp}/2\hbar^2\epsilon_{\parallel}\epsilon_{\perp}$ which represents the effective Rydberg constant, and β is the anisotropy parameter ($\beta = 1 - \epsilon_{\perp}\mu_{\perp}/\mu_{\parallel}\epsilon_{\parallel}$, with μ and ϵ the exciton reduced mass and low-frequency dielectric constant, respectively). From Fig. 1 we get an energy difference $E_{100} - E_{211} = 3$ meV which gives an effective Rydberg $R_{\mathrm{eff}} \sim 4$ meV. This is a surprisingly small value in view of the large effective masses expected for TiO_2 but not with respect to its very high dielectric constant. In order to ascertain this result, we have attempted a fit in the sense of the direct-forbidden-transitions theory given by Elliott[11]:

$$\alpha \sim C(\hbar\omega - E_g)^{3/2}\pi x(1 + x^2)e^{\pi x}/\sinh(\pi x), \qquad (2)$$

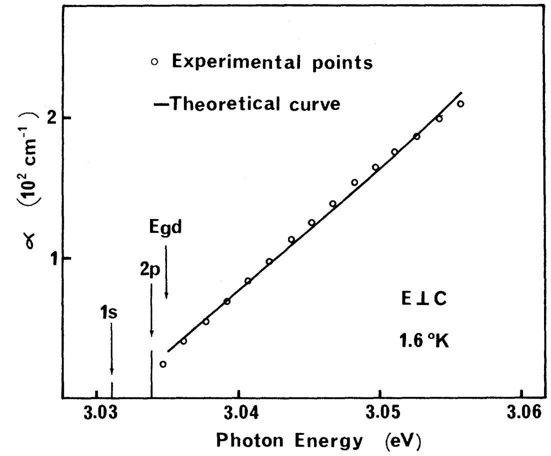

FIG. 2. Comparison of experimental data with the theoretical energy dependence expected from Eq. (2). $C \approx 0.7$ meV$^{-3/2}$ cm^{-1} and $R_{\mathrm{eff}} = 4$ meV.

where $x = [R_{\mathrm{eff}}/(\hbar\omega - E_{gd})]^{1/2}$ and C is a normalization constant. The results are shown in Fig. 2 and support the value $R_{\mathrm{eff}} = 4$ meV.

Now, since we know the values of the dielectric constant at low temperature $\epsilon_{\parallel} = 257$ and $\epsilon_{\perp} = 111$,[12] we deduce an isotropic reduced mass of the exciton $\mu = 8m_0$. This value is in fairly close agreement with (i) the electronic density-of-states effective mass deduced from transport experiments by Acket and Volger ($5m_0 < m_e < 8m_0$) and (ii) an independent optical determination from the field dependence of Franz-Keldysh oscillations in electroreflectance at liquid-nitrogen temperature[13] ($\mu = 6m_0$). If we neglect the hole contribution to the excitonic mass, we get a lower limit for the electronic effective mass of $m_e = 8m_0$.

Because of the strong ionicity of TiO_2, this result should be discussed in light of the polaron theory. In first approximation, all transport properties seem to be accuratly described by a large-polaron theory in which the "bare" electron (m^*) is dressed by a cloud of LO phonons (Γ_2' symmetry) of energy 831 cm^{-1} (103 meV). The strength of the coupling constant is measured by the dimensionless parameter

$$A = \frac{e^2}{\hbar}\left(\frac{m^*}{2\hbar\omega_p}\right)^{1/2}\left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right]. \qquad (3)$$

With $\epsilon_0 = 111$ and $\epsilon_\infty = 6$,[14] we get $A = 1.91\sqrt{m^*}$. With the polaron effective mass $8m_0$ and the bare effective mass m^* being connected by the relation ship $m_p^* = m^*/(1 - \frac{1}{6}A)$, we get $A \sim 3.6$ and $m^* \sim 3m_0$. For TiO_2 this simple model could be questionable because of the complexity of the primitive unit cell with three different polar modes.

A more refined calculation has been carried out by Eagles[14] which shows (i) that the simple model discussed before is a very good approximation and (ii) that the coupling constant including all polar modes of TiO_2 is $\langle A \rangle = 1.77\sqrt{m^*}$. This gives $\langle A \rangle = 3.4$ and $m^* \sim 3m_0$ in very good agreement with our first determination.

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Torsional Spectroscopy by NMR in the Rotating Frame

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Nuclear-spin Zeeman states prepared at a low temperature in the rotating frame were matched to the torsional ground-state splittings of NH_4 and CH_3 groups in solid lattices at a higher temperature. A resonant transfer of order was observed to occur instantaneously. Measurements yield a part of the torsional spectrum and the torsional relaxation time. From the torsional relaxation, the torsional lifetime broadening of a NH_4 ground state in ammonium iodide at 10 K was found to be ~ 1 Hz.

Because a nuclear-spin Zeeman system and a torsional system of atomic groups (such as CH_3 or NH_4) embodied in a solid lattice are coupled strongly[1-7] by the magnetic dipolar interaction which contains both spin and space operators, it is possible to induce a double resonance by adjusting the rf field H_1. In resonance, any experimentally prepared difference of population distributions between the two systems vanishes in a time which is orders of magnitudes shorter than either the spin-lattice or torsional-phonon relaxation time. For this reason the concept of a semiequilibrium of the Zeeman plus torsional system is applicable. In other words, it is possible to resonantly cool (or heat up) the torsional system by a cold (hot) Zeeman system without interference from the lattice. With this double resonance method it is possible to determine a part of the torsional spectrum and its specific heat. In addition, the torsional relaxation time, a quantity which has not been measured before, can be detected without any disturbance from the Zeeman system.

The experiment begins by establishing a nuclear Zeeman system in the rotating frame by the spin-locking pulse sequence. With this sequence the equilibrium nuclear magnetization $\vec{M}_0$ in high field is turned 90° off the high-field direction and an rf field $\vec{H}_1$ is established parallel to $\vec{M}_0$. After spin locking, the nuclear Zeeman levels population is characterized by a spin temperature of the order of 10^{-2} K while the lattice (and torsional) temperature is ~ 10 K. When Zeeman and torsional energies are brought in resonance (by varying H_1) the considerably different populations are equalized in a time which is shorter than the spin-spin lattice relaxation time T_2 and orders of magnitudes shorter than torsional (T_{1T}) or spin-lattice relaxation time. In other words, after the semiequilibrium in the rotating frame is established the resulting magnetization is considerably smaller than the high-field value M_0. This loss of spin polarization, which is the result of the resonant heating of nuclear spins by the torsional system, is maximum when the two systems are perfectly matched. Thus the loss of magnet-