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Band-structure enhancement of the indirect forbidden transitions

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We present an experimental investigation of the resonant enhancement of the indirect forbidden transitions near a direct-indirect crossover. Near-resonance conditions have been achieved in TiO_2 by tuning the relative energy positions of a direct forbidden gap (3.031 eV) with respect to an indirect one (3.049 eV). We find a band-structure enhancement of the indirect absorption strength when crossing the direct-forbidden gap. The quantitative details of the experiment can be satisfactorily accounted for by a simple model which includes (i) the stress-induced breaking of the selection rules and (ii) the resonance effect. Uniaxial compressions up to 24 kbars in [100] direction have been found necessary to tune the band gaps.

We present results of an experimental investigation of the crossover between a direct-forbidden and an indirect-forbidden transition. We perform the experiments on TiO_2 which displays at 1.6 K, first a direct-forbidden gap at 3.031 eV and, second, an indirect one at 3.049 eV. Using large uniaxial compressions, we render both transitions nearly degenerate in energy so that the direct-forbidden gap appears like a new channel, stress allowed, which enhances the indirect excitation process. This is done with help of uniaxial compressions ranging up to 24 kbar applied in the [100] direction. We find a definite band-structure enhancement of the indirect absorption strength when crossing the direct-forbidden gap: its intensity increases by roughly two orders of magnitude. The quantitative details of the experiment can be satisfactorily accounted for by a simple model which includes (i) the stress-induced breaking of the selection rules and (ii) the resonance effect. Resonance[1,2] and crossover[3,4] effects had been already reported but they concerned only parity-allowed transitions. To the best of our knowledge, this is the first report to deal with parity-forbidden transitions.

TiO_2 leads a series of crystals which crystallize with the tetragonal rutile structure (D_{4h}^{14} space group). At liquid-helium temperature, its band structure has been well characterized, both from an experimental[5–7] and a theoretical[8,9] point of view. The results are schematically drawn in Fig. 1. In polarization $\vec{E}\perp\vec{c}$, the lowest absorption edge corresponds to a quadrupolar transition $\Gamma_3 \rightarrow \Gamma_1$ which is first-order forbidden.[5] It is found at 3.031 eV at 1.6 K and is associated with the 1*s* state of an exciton whose binding energy[5,6] is 4 meV. The direct creation of *p*-like excitons (p_{xy} states, symmetry Γ_5') is also allowed through second-order approximation. The creation of p_z-like excitons (symmetry Γ_4') is totally forbidden. In polarization $\vec{E}\parallel\vec{c}$, the lowest absorption edge is associated[7] with an indirect transition $\Delta_{2,4} \rightarrow \Gamma_1$. The corresponding energy separation is 3.049 eV at 1.6 K. The transition is first assisted by an 11-meV phonon (acoustical mode, symmetry Δ_2) and then by a 15-meV phonon (optical mode, symmetry Δ_4). These results qualitatively agree with the band-structure calculation of Ref. 8. The main discrepancy lies in the $\Delta_{2,4}$ assignment of the subsidiary max-

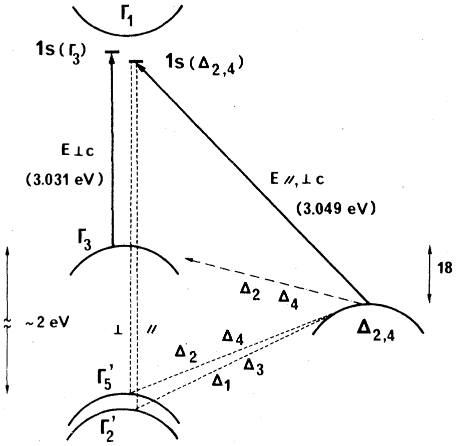

FIG. 1. Schematic band structure of TiO_2. The first-order forbidden transition $\Gamma_3 \rightarrow \Gamma_1$ (3.031 eV at 1.6 K) is weakly allowed in polarization $\vec{E}\perp\vec{c}$ by electric quadrupole interaction for *s*-like excitons (total symmetry Γ_3) and by electric dipole interaction for p_{xy}-like excitons (symmetry Γ_5'). The direct creation of p_z-like excitons (symmetry Γ_4') is completely forbidden in both polarizations. The binding energy of the exciton is 4 meV. The indirect transition $\Delta_{2,4} \rightarrow \Gamma_1$ appears in both polarizations (3.049 eV at 1.6 K) but should be assisted by different phonons. In fact the spin-orbit interaction which coulples the two intermediate levels Γ_2' and Γ_5' renders the transition allowed in both polarizations assisted by all Δ_i phonons. From symmetry considerations only, it has been found impossible to choose between a Δ_2 or Δ_4 assignment.

imum of the valence band which should have a Σ_4 symmetry according to the theoretical model. Very recently, this point was reinvestigated with help of a new band-structure calculations which includes the spin-orbit interaction.[9] In this case, the ordering of the two subminima is reversed and Δ_4 appears slightly higher than Σ_4. This is now in agreement with the experiment. Theoretical pressure coefficients have been also calculated, they are in satisfactorily agreement with the experimental findings.

We have investigated the stress-induced crossover of the direct and indirect transitions, using wavelength-modulated transmission measurements at liquid-helium temperature. All samples were cut from a single boule of TiO_2 single crystal[10] and were in the form of small parallelepipeds of approximate dimensions $1\times1\times10$ mm^3. They had their long dimension oriented in the [001] (crystal $\vec{c}$ axis) or [100] (crystal $\vec{a}$ axis) directions and all faces (including the small pressure faces) were optically flat and carefully polished. The calibrated uniaxial stress apparatus has been already described.[7]

A typical experimental spectrum, taken at zero stress with unpolarized light, is shown in Fig. 2. The first series of structures (around 3.030 eV) corresponds with the direct-forbidden gap and is associated with the perpendicular part of the incident light. The next series of structures (around 3.060 eV) corresponds with the indirect transition and is associated with the parallel component of the incident light. This point is worth noting. On very thin samples ($d\sim20$ μm), we could resolve the indirect transition in both polarizations.[6] The corresponding intermediate states, involved in the optical part of the excitation, were the deep valence-band extrema Γ'_5, ($\vec{E}\perp\vec{c}$), and Γ'_2 ($\vec{E}\parallel\vec{c}$). On thick samples ($d\sim1$ mm), this is no longer true. All of the perpendicular component of the incident light is first absorbed in the direct-forbidden process and the indirect gap appears only through the parallel component of the incident light (intermediate state Γ'_2).

Under [001] compression (stress directed along the crystal $\vec{c}$ axis) the tetragonal symmetry (D_{4h}^{14}) is fully conserved: the selection rules remain unchanged and all transitions shift without additional splitting. From the experimental spectra one finds that the threshold energies for the direct and the indirect transitions increase at a rate of 0.615 and 0.985 meV/kbar, respectively.[7] This shows that the energy difference $\Gamma_3-\Delta_{2,4}$ increases at a rate of 0.370 meV/kbar. Since the energy difference between $\Delta_{2,4}$ and the intermediate state Γ'_2 remains very large, the indirect transition should be nonresonant for this stress direction. In good agreement with a nonresonant behavior, we expect the strength of the differential signals associated with the indirect transition to be independent of the stress magnitude. This has been checked and the results obtained in the range $X=0$ to 20 kbars are

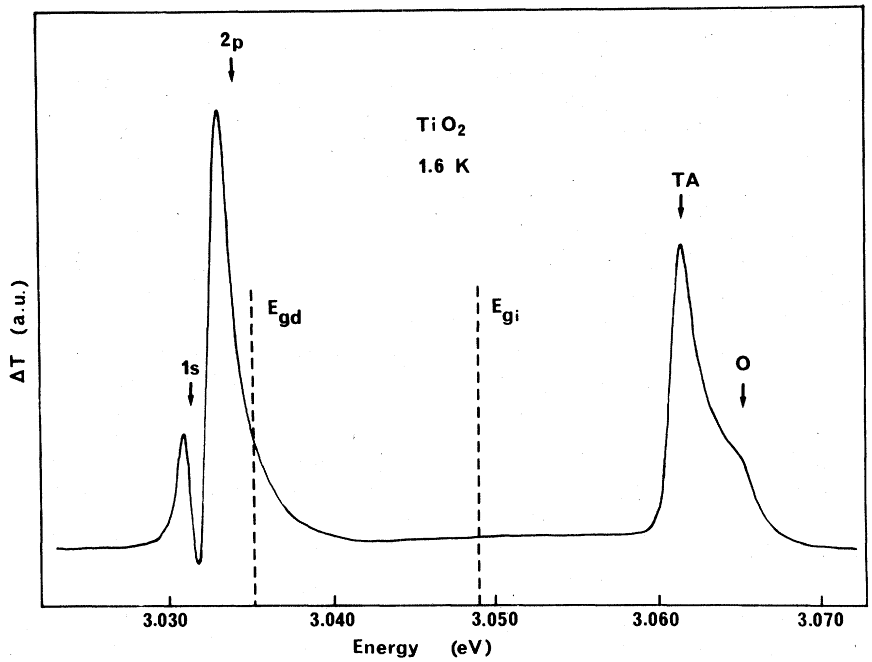

FIG. 2. Typical wavelength-modulated transmission spectrum obtained on a 1-mm-thick TiO_2 sample at pumped liquid-helium temperature (zero stress and unpolarized light). The direct-forbidden transition (E_{gd}) is associated with the perpendicular component of the incident light, the indirect-allowed phonon-assisted transition (E_{gi}) with the parallel component of the incident light.

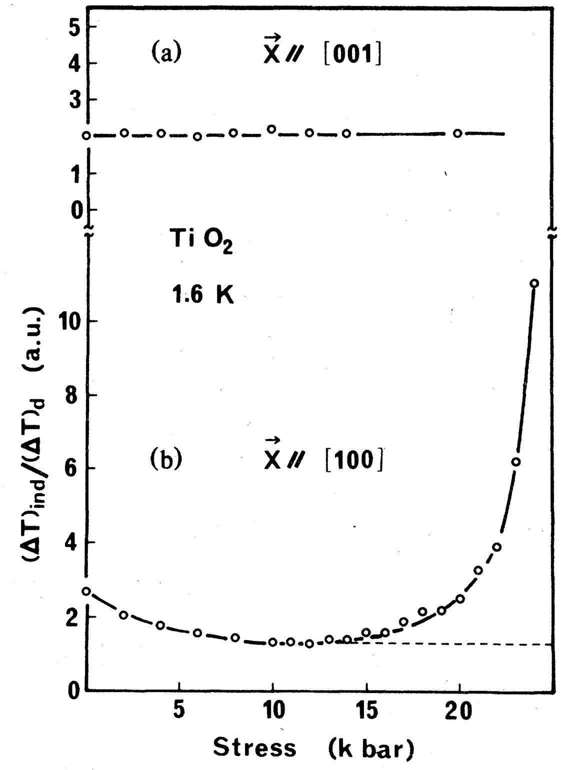

FIG. 3. Change in absorption strength as obtained for the indirect energy gap, under [001] and [100] uniaxial compressions. Note the fairly constant value achieved when the crystal structure is not changed (a). In opposite, when the crystal structure reduces to D_{2h} [see (b)], the valence band splits and the intensity starts to drop by a factor of 2. In the same time a new, nearly resonant, channel opens through the intermediate state Γ_3. This results in the sharp increase found around 24 kbar.

shown in Fig. 3(a). For clarity we normalize all data obtained from different runs to the 1s forbidden-exciton differential signal. Within experimental error, we find a constant value over the full experimental range.

Under [100] compression (stress directed along the crystal $\vec{a}$ axis) the tetragonal symmetry reduces to $D_{2h}(x)$. From the compatibility relations listed in Table I, we find that the direct-forbidden p_z-like exciton (unperturbed symmetry Γ_4') becomes stress allowed in polarization $\vec{E} \parallel \vec{c}$. In this case (and for this polarization) a new, nearly resonant, channel is opened for the indirect transition: the intermediate state is Γ_3. This transition is first-order forbidden and we can get the corresponding matrix element from a simple perturbation treatment. We consider simply the stress-induced coupling between the 1s direct exciton associated to the direct-allowed transition $\Gamma_2' \rightarrow \Gamma_1$ on the one hand, and the p_z-like forbidden exciton associated to the direct-forbidden transition $\Gamma_3 \rightarrow \Gamma_1$ on the other hand (see Fig. 1). These exciton states belong to Γ_2' and Γ_4' repesentations, respectively, and accordingly, they couple under application of a shear-strain component of Γ_3 symmetry, i.e., $(S_{11}-S_{12})X$. We can write

$$\begin{array}{cc} \Gamma_4' & \Gamma_2' \\ \left|\begin{matrix} 0 & E_{21}'(S_{11}-S_{12})X \\ E_{21}'(S_{11}-S_{12})X & -\Delta E \end{matrix}\right| \end{array} , \tag{1}$$

where ΔE is the energy separation between the two valence bands $\Delta E = \Gamma_3 - \Gamma_2' \sim 2$ eV, after Ref. 8. E_{21}' is the deformation potential constant which describes the coupling of the two excitonic states.

This gives in first-order perturbation an admixture coefficient

$$E_{21}'(S_{11}-S_{12})X/\Delta E \ . \tag{2}$$

The matrix element associated with the direct creation of Γ_4' excitons is then

$$P^2(\Gamma_4') = [E_{21}'(S_{11}-S_{12})X/\Delta E]^2 P^2(\Gamma_2') \ . \tag{3}$$

We are now in a position to write down an expression for the absorption coefficient. From standard theory of indirect transitions[11] we get at low temperature (phonon-emission only)

TABLE I. Compatibility relation between D_{4h} (unperturbed crystal symmetry) and D_{2h} ($\vec{X} \parallel \vec{a}$). At Γ point the dipolar transitions correspond to representation $(\Gamma_2')_\parallel + (\Gamma_5')_\perp$ and $(\Gamma_3')_\parallel + (\Gamma_2' + \Gamma_4')_\perp$, respectively.

D_{4h} ($X=0, \vec{X} \parallel \vec{c}$)	Γ_1 (Γ_1')	Γ_3 (Γ_3')	Γ_2 (Γ_2')	Γ_4 (Γ_4')	Γ_5 (Γ_5')	Δ_i ($i=1,2,3,4$)
D_{2h} ($\vec{X} \parallel \vec{a}$)	Γ_1 (Γ_1')		Γ_3 (Γ_3')		$\Gamma_2+\Gamma_4$ ($\Gamma_2'+\Gamma_4'$)	Δ_i ($i=1,2,3,4$)

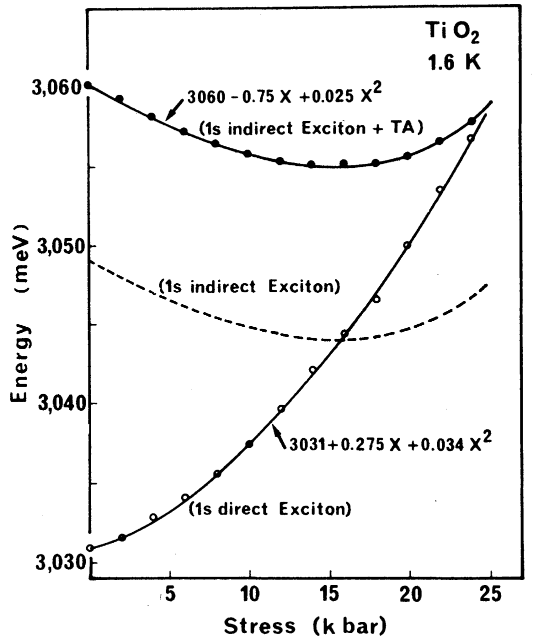

FIG. 4. Energy shift under [100] compression of the 1s direct-forbidden transition (excitonic gap $\Gamma_3 \rightarrow \Gamma_1$) and of the low-energy split component of the indirect transition (excitonic gap $\Delta_{2,4} \rightarrow \Gamma_1$). Note the close resonance, around 24 kbar, between the direct gap and the indirect gap assisted by a phonon emission. This almost completely cancels the energy denominator in Eq. (9).

$$\alpha_e^{(\mathrm{II})} = A \left[\sum_i \frac{1}{(\hbar\omega - E'_{gd})^2} + \left(\frac{E'_{21}(S_{11} - S_{12})X}{\Delta E} \right)^2 \times \frac{1}{(\hbar\omega - E_{gd})^2} \right] (\hbar\omega - E_{gi} - \hbar\Omega_{\Delta i})^{1/2} , \quad (4)$$

where $E'_{gd} = E_{\Gamma_1} - E_{\Gamma'_2}$ and $E_{gd} = E_{\Gamma_1} - E_{\Gamma_3}$. In this expression all electron-phonon matrix elements which connect $\Delta_{2,4}$ with Γ'_2 and Γ_3 have been taken identical and all unnecessary proportionality constants have been included in A. The first term corresponds to the nonresonant process (intermediate state Γ'_2) and gives the stress-independent contribution displayed in Fig. 3(a) for $\vec{X} \parallel \vec{c}$. The second comes from the stress-induced contribution (intermediate state Γ'_3). Because of the large energy separation ΔE which appears in Eqs. (2) and (3) we would not expect a strong effect if the energy denominator $(\hbar\omega - E_{gd})$ was large. In fact, this is not the case. At $X = 0$ the threshold energy corresponding to the strong acoustical process (TA-phonon emission) is

$$\hbar\omega = E_{gi} + \hbar\Omega_{\mathrm{TA}} = 3.060 \text{ eV} ,$$

which gives

$$\hbar\omega - E_{gd} = E_{gi} + \hbar\Omega_{\mathrm{TA}} - E_{gd} = 0.029 \text{ eV} .$$

The same energy difference would be 0.033 eV for the optical mode. Both values are two orders of magnitude smaller than the corresponding quantity for the nonresonant contribution $\hbar\omega - E'_{gd} \sim 2$ eV.

The stress dependence of E_{gi} and E_{gd} further cancels this energy difference. This is shown in Fig. 4 where we display the experimental data obtained for the 1s direct and indirect excitons.[7] Under [100] compression, the direct-forbidden gap increases with a rate

$$(E_{gd})_X - (E_{gd})_{X=0} = 0.275X + 0.034X^2 , \quad (5)$$

while the indirect one splits. One branch E^u_{gi} moves up with a rate

$$(E^u_{gi})_X - (E_{gi})_{X=0} = 1.0X + 0.025X^2 , \quad (6)$$

while the other one E^l_{gi} moves down

$$(E^l_{gi})_X - (E_{gi})_{X=0} = -0.75X + 0.025X^2 . \quad (7)$$

Both components remain associated with the emission of all Δ_i phonons. In Eqs. (6) and (7), the nonlinear contributions come from a stress-induced $\Gamma_1 - \Gamma_3$ interaction which has been already discussed.[7]

From Eqs. (5) and (7) we find a stress-induced crossover between the excitonic gaps E_{gd} and E_{gi} at about 16 kbar. This is shown in Fig. 4. The stress dependence of the vanishing energy denominator which appears in Eq. (4) is then

$$\begin{aligned}(\hbar\omega - E_{gd})_X &= (E_{gi} + \hbar\Omega_{\Delta i} - E_{gd})_X \\ &= E_{gi} - E_{gd} + \hbar\Omega_{\Delta i} - 1.025X \\ &\quad - 0.009X^2 \text{ meV} , \quad (8) \\ &= 18 + \hbar\Omega_{\Delta i} - 1.025X \\ &\quad - 0.009X^2 \text{ meV} .\end{aligned}$$

This gives for the magnitude of the low-energy, phonon-assisted absorption components

$$\alpha_e^{1(\mathrm{II})} = \frac{A}{2} \sum_i \left[\frac{1}{(\hbar\omega - E'_{gd})^2} + \left(\frac{E'_{21}(S_{11} - S_{12})X}{\Delta E} \right)^2 (18 + \hbar\Omega_{\Delta i} - 1.025X - 0.009X^2)^{-2} \right] \times (\hbar\omega - E_{gi} - \hbar\Omega_{\Delta i} + 0.75X - 0.025X^2)^{1/2} . \quad (9)$$

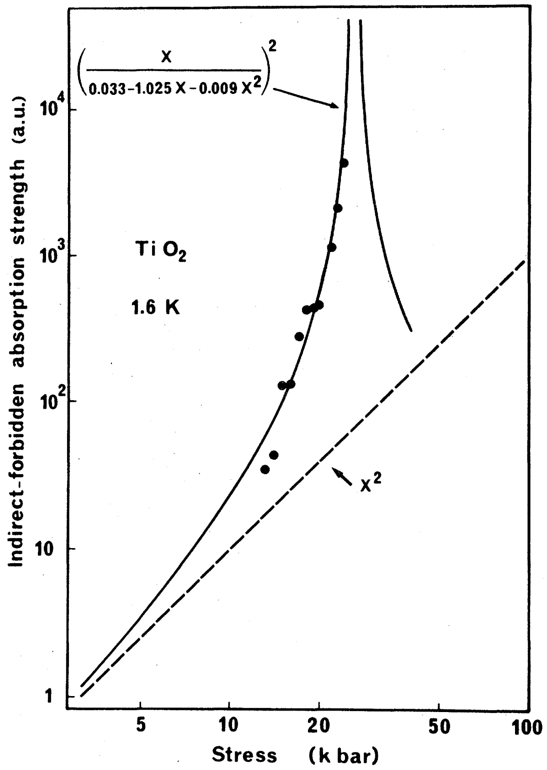

FIG. 5. Resonance enhancement of the indirect-forbidden transition associated with the intermediate state Γ_3 in polarization $\vec{E} \parallel \vec{c}$, (note the log-log scale). The stress dependence of the matrix element ($\sim X^2$) is given as a broken line and cannot explain the strong experimental change. The theoretical curve (full line) corresponds with the resonant par of Eq. (9) with a 15-meV phonon (Δ_4 symmetry).

The proportionality constant $\frac{1}{2}A$ comes from the stress-induced splitting and all stress dependences come from Eqs. (7) and (8). The larger the stress, the better the cancellation and the stronger the low-energy absorption component.

We plot in Fig. 3(b), the magnitude of the differential signal obtained for the low-energy absorption component normalized to the magnitude of the direct-forbidden exciton. In good agreement with a two channels picture, we find first, below 10 kbar, a decrease which corresponds with the nonresonant part of Eqs. (4) and (9) (intermediate state Γ_2'). The absorption strength just divides between the two split valence bands and tend toward an assymptotic limit ($A \rightarrow \frac{1}{2}A$). Above 10 kbar, the stress-induced interband matrix element associated with the Γ_3 channel together with the resonant cancellation starts to become important. We find a nonlinear increase, by roughly two orders of magnitude, of strength of the indirect transition. This is better displayed in Fig. 5 where we plot on a log-log scale the resonant contribution versus X. The best theoretical fit corresponds to the resonant part of Eq. (9) assuming a single-phonon energy $\Delta_i = 15$ meV (Γ_4 symmetry). In this case the enhancement predicted is in very good agreement with the experimental finding. We note that the simple stress dependence of the interband matrix element ($\sim X^2$) which is also plotted in Fig. 5 cannot explain the very large experimental increase. It is the resonant cancellation of the energy denominator which dominates of the effect.

Finally we come back to the selection rules. The phonon symmetry involved in the scattering process from Δ_2 or Δ_4 to Γ_3 depends on the peculiar symmetry of the subsidiary maximum of the valence band. A Δ_2 maximum requires a Δ_2 phonon (acoustical mode) and a Δ_4 maximum a Δ_4 phonon (optical mode). This explains our best fit in Fig. 5 which was obtained with a single-phonon mode. This is an optical mode (symmetry Δ_4) which accordingly, supports a Δ_4 assignment of the maximum of the valence band in $\vec{k}$ space.

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