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Thermoabsorption in SnO_2[†*]

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The thermoabsorption spectra of SnO_2 crystals have been measured near the fundamental absorption edge at 25, 80, and 115 °K with polarized light. New fine structure above the exciton continuum is observed with light polarized $\vec{E}\perp\vec{c}$ which appears to be associated with exciton-phonon quasi-bound-states. For $\vec{E}\,||\,\vec{c}$ the onset of a direct-allowed transition is indicated at about 4.0 eV.

I. INTRODUCTION

We have studied the thermally modulated optical transmission of SnO_2 (stannic oxide) near the fundamental absorption edge, using polarized light, at temperatures of 25, 80 and 115 °K. For the incident light polarized perpendicular to the crystal axis, $\vec{E}\perp\vec{c}$, fine structure is observed which may well be associated with the exciton-phonon quasi-bound-state (EPQBS) of Toyozawa.[1] The experimental data do not necessarily mandate the presumption of EPQBS, but an evaluation of the existence-criteria parameters given by Toyozawa indicates that the EPQBS likely exist; stannic oxide is partially ionic, with intermediate electron-LO-phonon coupling. The results for $\vec{E}\,||\,\vec{c}$ indicate the onset of a direct-allowed transition for that polarization around 0.4 eV higher than the $\vec{E}\perp\vec{c}$ absorption edge.

II. SnO_2 BACKGROUND

Crystallizing in the tetragonal "rutile" structure (two molecules per unit cell, point group D_{4h}), stannic oxide, SnO_2, is electrically and optically uniaxial.

For incident light polarized $\vec{E}\perp\vec{c}$, as Nagasawa and Shionoya[2-4] first reported, a shallow direct-forbidden exciton is observed in the absorption spectrum at low temperatures with a series limit at 1.2 °K of 3.5971 eV. Their excellent work and that of Agekyan[5,6] have established the bottom conduction-band and top valence-band extrema symmetries as Γ_1^+ and Γ_3^+, respectively (direct gap at $k=0$). Above 100 °K the exciton series is overspread by an exponential "Urbach" tail attributed to transitions from a Γ_5^- valence band (direct-allowed for $\vec{E}\perp\vec{c}$) about 0.15 eV below the top Γ_3^+ valence band.

For $\vec{E}\,||\,\vec{c}$ the absorption edge is relatively broad and featureless (no exciton series is seen), having a shape relatively independent of temperature. The gradual onset of the $\vec{E}\,||\,\vec{c}$ edge is attributed to the fact that the $\Gamma_3^+ \rightarrow \Gamma_1^+$ transition is triply forbidden for $\vec{E}\,||\,\vec{c}$. It has been suggested[7] that the lowest-energy direct-allowed transitions to the conduction band for $\vec{E}\,||\,\vec{c}$ occur from a Γ_2^+ valence band several tenths of an electron volt below the Γ_3^+ and Γ_5^- bands.

III. EXPERIMENTAL

The SnO_2 crystals used are of high quality,[8,9] which is significant since, as hypothesized by Agekyan[5], early observations of apparent indirect absorption tails in SnO_2 may have been due to lack of crystal line perfection. Two samples were cut as flat plates with "*a*" (100) faces, and polished. The samples, designated A and B, were 0.32 and 0.48 mm thick, respectively. Their carrier concentrations were in the mid-10^{16}-cm^{-3} range.

Temperature modulation was accomplished by passing a pulsed heating current through the samples, through ohmic contacts on the ends. The average dc temperature rise while the current was applied was usually (5–10) °K, and the modulation depth was less than 1 °K. The frequency of modulation was typically about 6 Hz. A high-pressure xenon lamp was used in conjunction with a Perkin-Elmer fore-prism/grating monochromator (model 160-98G) as a source of monochromatic light. The monochromatic output was chopped at 210 Hz and focused into the sample through a calcite Glan-Thompson polarizer. The sample was mounted in a Dewar on a heat sink, which in turn was in contact with liquid nitrogen or liquid helium. The transmitted signal was detected by a photo-multiplier whose output was fed to two phase-sensitive synthronous amplifiers used in parallel to detect the 6-Hz signal, which was proportional to the change in transmitted intensity ΔI, and the 210-Hz signal, which is proportional to the transmitted intensity I. The ratio $\Delta I/I$ was then recorded directly using an analog divider.

IV. RESULTS

Figures 1–3 show ΔI/I for $\vec{E}\perp\vec{c}$ at 25, 80, and 115 °K, respectively (the temperatures quoted refer to the cold-block temperatures before the application of the modulation). Figures 4 and 5 show $\Delta I/I$ for $\vec{E}\parallel\vec{c}$ at 25 and 80 °K, respectively. The vertical $\Delta I/I$ scale in each of these figures is given in artitrary units which would be of order 10^{-5}.

V. DISCUSSION, $\vec{E}\perp\vec{c}$

Neglecting reflection and thermal expansion, the measured quantity $\Delta I/I$ is proportional to the derivative of the absorption coefficient α with respect to temperature T, that is to $d\alpha/dT$. In the present work the principal effect of the temperature modulation is to shift the band gap. The quantity measured is consequently also proportional to $d\alpha/d(\hbar\omega)$ or the wavelength derivative of the spectrum. Considering this point in more detail, modulating the temperature[10] can modulate the band gap, the phonon population, and/or the breadth of structure. The effect of a temperature change in the present case is most easily appreciated by comparing the data taken at different temperatures (Figs. 1–3). The primary change is clearly the change in band gap evident as a shift of the entire structure to lower energy as the temperature is increased. The effect of the change in phonon population is not important because as will be argued below, the observed structure is not due to a phonon absorption process. Broadening of the exciton structure does occur but examination of the line shapes associated with the exciton structure at 25 °K (see the lines marked $n=2$, 3, and 4 in Fig. 1) shows that, while present, it is a small effect. (The positions marked on the horizontal axis were placed using the line spacings determined at 1.3 °K by Nagasawa and Shionoya.)

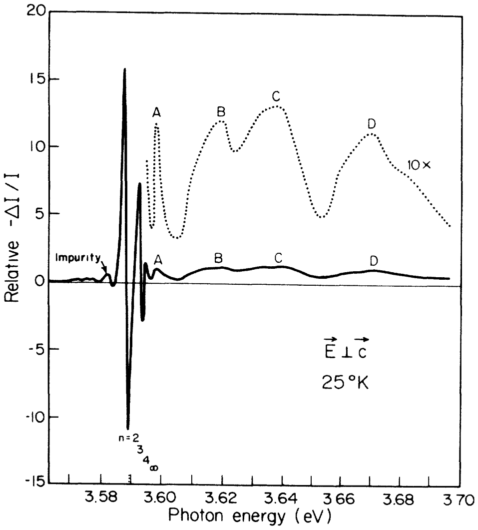

FIG. 1. Thermoabsorption, $\Delta I/I$, at 25 °K in stannic oxide for light polarized $\vec{E}\perp\vec{c}$. The temperature quoted here and for the data in Figs. 2–5 refers to the sample temperature before application of the modulating signal. The vertical scale here and in Figs. 2–5 is in arbitrary units; $\Delta I/I$ was typically of order 10^{-5}–10^{-4}.

The $n=2$ exciton line at 25 °K is very similar in shape to a simple derivative with respect to energy or wavelength of an exciton absorption line. The $n=3$ and 4 lines are more asymmetrical with respect to the horizontal axis, with no negative-going portion of the $n=4$ line being seen. This asymmetry can be a result of some line broadening as an accompanying effect of the modulation[11] or may simply be due to the fact that the negative-going peak of one line is influenced by the positive-going peak of an adjacent line, or vice versa. Probably both phenomena contribute to some extent.

At 80 °K the $n=2$ line is still distinct but has broadened and is merging into the $n=3$ line, although a shoulder due to the latter is still discernible. Figure 3, showing fragmentary data at 115 °K, shows that all the structure is shifted and further broadened, and only the $n=2$ exciton line is distinct. The advantage of the derivative technique is apparent here; the exciton has not previously been observed above 80 °K.

At the temperature employed there was no observation of the weak $n=1$ line observed by others at $T<5$ °K,[2,5] nor was there any other fine structure below the band-to-band threshold except the $n\geq 2$ exciton lines and a presumed impurity structure to be discussed next.

For $\vec{E}\perp\vec{c}$ at 25 °K a structure was observed in

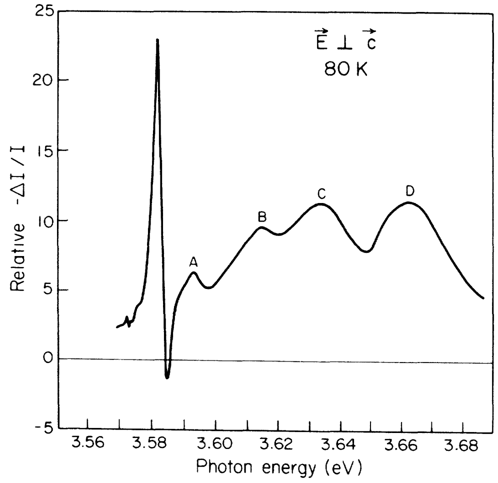

FIG. 2. Thermoabsorption, $\Delta I/I$, in stannic oxide at 80 °K for light polarized $\vec{E}\perp\vec{c}$.

sample A between 3.575 and 3.585 eV, with an estimated position (taken as the zero crossing on the graph on Fig. 1) 13 meV below the band-to-band threshold. This feature has no proper place in the exciton scheme, nor is it near any possible positions of LO-phonon replicas of exciton levels. Thus the structure is interpreted as being due to an unidentified impurity present in sample A; it was not observed in sample B.

The structures A, B, C, and D above the $\vec{E}\perp\vec{c}$ absorption edge (about 3.598 eV at 25 °K) have not, to our knowledge, been reported previously. They are not seen for the incident-light-polarized $\vec{E}\parallel\vec{c}$. The peak A at 3.598 eV at 25 °K probably cannot be attributed to the threshold of band-to-band transitions since the derivative trace suggests an almost steplike behavior in α. According to Elliott's theory,[12] the absorption coefficient in the exciton quasicontinuum of bound states joins smoothly to the ionization limit of the exciton series and consequently would not contribute a peak in the derivative spectrum. Peak A may in fact be a manifestation of the exciton-phonon quasi-bound-state (EPQBS) and will be discussed further below.

On going from 25 to 80 °K the peaks B, C, and D maintain a fairly constant height relationship among themselves, while at the same time the exciton structure weakens with respect to them all. Lacking precise knowledge of the modulation depth and other parameters, we cannot say what happens to the absolute heights of these structures on going from 25 to 80 °K. It is probable, however, that they do not change appreciably, while the exciton lines follow the usual pattern of weakening (in the derivative) at the higher temperature. Peak A weakens with respect to peaks B and C on going from 25 to 80 to 115 °K, but not to as great an extent as does the exciton structure.

The weak temperature dependence of the relative heights of A, B, C, and D implies that they are not associated with phonon-absorption-assisted transitions (e.g., from the second Γ_5^- valence band), processes in which the temperature dependences of the phonon populations would be important. In other words, peak D would have to be associated with a lower-energy LO phonon than peak C, and should have increased significantly with respect to the latter at low temperature, because of the kT in the denominator of the exponential expression for phonon populations. Similar considerations apply as well to the remaining structures.

Modulation of phonon populations N_p (average number of phonons per mode) would not be observed through its influence on transitions involving phonon creation, since N_p typically enters these effects through a term $(N_p + 1)$ and $N_p \ll 1$ for LO phonons in SnO_2 at the temperatures used. We therefore attempt to explain the observed structures A, B, C, D because of their energy position with respect to the $\Gamma_3^+ \rightarrow \Gamma_1^+$ edge, in terms of phonon-creation-assisted electronic transitions, but assuming that band-gap shift is the dominant observed effect in $\Delta I/I$.

The complexity of the SnO_2 lattice-vibration spectrum (six atoms per unit cell in a noncubic structure) demands a pragmatic restriction of attention to the longitudinal-optical (LO) phonons. At $k = 0$ in SnO_2 there are[13,14] four LO-phonon en-

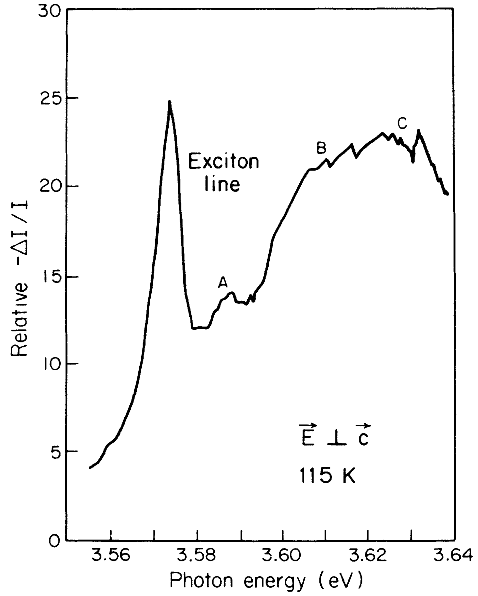

FIG. 3. Thermoabsorption, $\Delta I/I$, in stannic oxide at 115 °K for light polarized $\vec{E}\perp\vec{c}$.

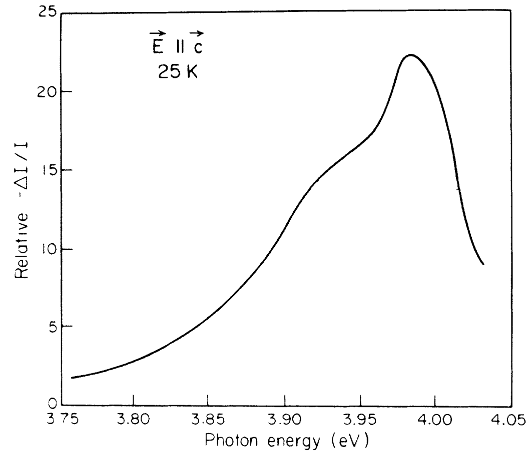

FIG. 4. Thermoabsorption, $\Delta I/I$, in stannic oxide at 25 °K for light polarized $\vec{E}\parallel\vec{c}$.

ergies: 34, 46, and 95 meV belonging to phonons of the Γ_5^- representation and involving atomic motions perpendicular to the crystal axis, and 87 meV for atomic motions parallel to the c axis (Γ_2^- representation).

Group-theoretical calculations reduce the number of possibilities to consider for phonon-assisted transitions to exciton states. Restricting our considerations to $k=0$, we follow the method used by Elliott.[15] Starting from the crystal ground state, the Γ_5^- representation for light-polarized $\vec{E}\perp\vec{c}$ implies a Γ_5^- intermediate "virtual" state; we then inquire which phonons can connect this intermediate state to the particular final state in question. The results are shown in Table I.

We see that the nS exciton states, which are dipole forbidden for first-order absorption with $\vec{E}\perp\vec{c}$, may be excited with phonon assistance. In Fig. 6 we have indicated the threshold positions (photon energies) for which there may occur transitions to exciton states accompanied by creation of a free LO phonon. On each horizontal line the possible threshold positions are marked by "x" for phonon-emission-assisted transitions to the exciton level at the low-frequency (left) end of the line. This is done for the $n=1$ and $n=2$ exciton levels and for the continuum, or band gap. For simplicity, the contributions of $n \geq 3$ levels are not shown. Pursuant to the group-theoretical results, we note that the contributions for $n=2$ involve indirect transitions to $2s$ states of the exciton, not to $2p$ levels.

On particular interest to the interpretation of the data are the recent observations and discussions of the exciton-phonon bound state (EPBS) and quasi-bound-state (EPQBS) in other materials.[16–19] These states are most relevant to partially-ionic materials having intermediate electron–LO-phonon coupling strength (Frohlich coupling constant $\alpha \sim 1$; in such cases the classic second-order perturbation treatment for free-phonon emission accompanying electronic transitions may not be valid, in particular for the examples of compound semiconductors in which the exciton binding energy ϵ_B is less than, or not much greater than, the LO-phonon energy $\hbar\omega_{\text{LO}}$. Experimental observations so far in which the EPBS and EPQBS have been observed have dealt with direct-gap materials in which the exciton line(s) are visible in the transmission spectrum.

As pointed out in the references noted,[15–18] if the second-order perturbation treatment is valid, the contribution to the optical absorption coefficient α resulting from transitions to an exciton state at an energy E_{ex} above the electronic ground state accompanied by the emission of free LO phonons (energy $\hbar\omega_{\text{LO}}$) begins gradually at a threshold photon energy $\hbar\omega = E_{\text{ex}} + \hbar\omega_{\text{LO}}$ and peaks at an energy slightly higher (higher by $m\hbar\omega_{\text{LO}}$, $m \sim 1$). The EPBS and EPQBS occur when the energy of the exciton-phonon complex is lowered by their mutual interaction so that the observed structure is shifted to lower energy, possibly enough so that the peak may even lie below the threshold for free phonon emission. The EPQBS, as distinguished from EPBS, occurs when the threshold lies above the exciton series limit.

Of course, in the present experiment, the quantity plotted is not the absorption coefficient α itself, but its derivative with respect to photon energy $\hbar\omega_0$. Thus the peak in α would be located by the zero crossing in a positive-negative sequence in the derivative, assuming no additional background contributions were present. As shown by Elliott,[12] for phonon energies above a direct-forbidden edge at E_g, α should go as $(\hbar\omega - E_g)^{3/2}$, beginning a little above the edge. This is, of course, the most important observed contribution to the absorption, and is seen in the present work as the derivative $\alpha(\hbar\omega - E_g)^{1/2}$. Thus all fine structure observed here is superimposed on this positive background contribution, and the "zero crossings" are dis-

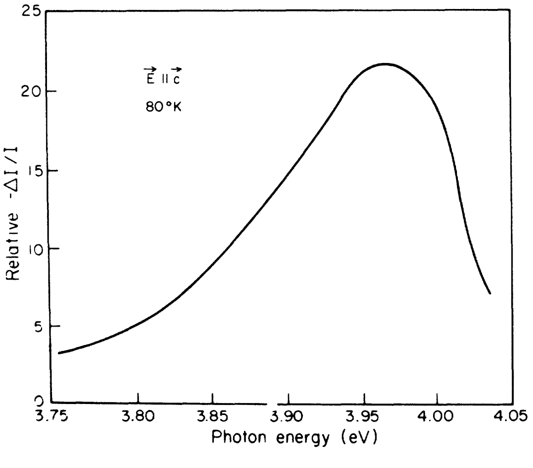

FIG. 5. Thermoabsorption, $\Delta I/I$, in stannic oxide at 80 °K for light polarized, $\vec{E}\parallel\vec{c}$.

TABLE I. Selection rules for phonon-assisted transitions in SnO_2 at the Γ point, $\vec{E}\perp\vec{c}$.

Final electronic state	Representation	Possible LO phonons
nS	Γ_3^+	Γ_5^- (34, 46, 95 meV)
nP_z	Γ_4^-	none
$nP_{x,y}$	Γ_5^-	none

placed above the horizontal axis to positions where they are harder to locate precisely.

The existence of the EPQBS depends[18] on three material-dependent parameters: $\xi = \epsilon_B/\hbar\omega_{LO}$; $\eta = 4\mu/M$, where $M = m_e + m_h$, and $\mu = m_e m_h/M$, where m_e and m_h are the electron and hole band masses, respectively; and $\gamma = K'(1/K_\infty - 1/K_s)$ where K' is the effective dielectric constant for the exciton, K_∞ is the high-frequency dielectric constant, and K_s is the static dielectric constant.

Use of these parameters directly is difficult, so we have proceeded by analogy with the case of CdTe, in which the EPQBS has been observed.[19] In the appendix we show that the parameter values in SnO_2 are, in fact, more favorable for EPQBS existence with the 46- or 95-meV LO phonons than they are in the case of CdTe. The EPQBS is not likely to exist in SnO_2 involving the 34-meV LO phonons.

While we have not considered the EPQBS oscillator strength in SnO_2, and an extension of the theory to the direct-forbidden case is needed, a large oscillator strength would not be required for our observations.

It is now possible to propose some tentative hypotheses connecting the structures noted experimentally with the EPBS/EPQBS theory. The assignments have been formulated in view of the facts that (a) the EPQBS-related peak in α may be shifted to a slightly lower energy than the corresponding threshold position as marked in Fig. 6, and (b) the observation is of $d\alpha/d(\hbar\omega)$, which includes the background contribution noted earlier.

Peak C may be associated with the EPQBS formed by the 1*s* exciton level and the 95-meV LO phonon. Peak A may be similarly associated with the 1*s* exciton and 46-meV LO phonon. If it is assumed that the EPQBS can be formed by $n > 1$ exciton states as well, peak B can be associated with the 2*s* exciton level and the 46-meV LO phonon. A possible difficulty with this assignment is that, from the data, the binding energy (i.e., displacement of the hard-to-identify zero crossing below the indicated threshold) would appear to be larger than in the case for peak A, which is not forecast by Toyozawa's indication of a weaker interaction for smaller ξ. Finally, peak D may also involve the $n > 1$ exciton states with the 95-meV LO phonon, with little EPQBS binding energy indicated.

The linewidth behavior can also be correlated with the EPQBS model. The EPQBS linewidth is not particularly sensitive to temperature—hence the small change in the shapes of B, C, and D on going from 25 to 80 °K. (Of course, this feature would not be unique to EPQBS.) Relative to the others, however, peak A does weaken and broaden on going from 25 through 80 to 115 °K. We suggest that peak A is possibly attributable to a step in α produced by truncation of the EPQBS Lorentzian line shape at the band edge.[18] Since this step would occur over an energy interval of width kT, we have a qualitative reason for the decline in its derivative with increasing temperature, as well as for the general narrowness of peak A.

It is also possible to interpret the data by invoking the EPQBS for peak A only. Another set of assignments for peaks B, C, and D is possible, for example, based on the occurrence of free-phonon emission. In this interpretation peak B may involve the 1*s* exciton, plus emission of 46-meV LO phonons. For peak C we could have $n > 1$ excitons plus 46-meV LO-phonon creation, while peak D could be due to formation of the 1*s* exciton accompanied by creation of the 95-meV LO phonons. The effects of $n > 1$ excitons associated with 95-meV LO phonons would be assumed to occur somewhere beyond peak D. While this interpretation is less satisfactory than the first analysis presented, it is the only other reasonable interpretation of which the authors are aware that can explain all of the structure.

VI. DISCUSSION, $\vec{E} \parallel \vec{c}$

In considering the $\vec{E} \parallel \vec{c}$ results we first note that, since the shape of this absorption edge is nearly independent of temperature,[20] thermal modulation causes predominantly a shifting of this edge also.

The experimental results, Figs. 4 and 5, for $\vec{E} \parallel \vec{c}$ show a trace that rises gradually from near the noise level at 3.75 eV, attaining a single peak

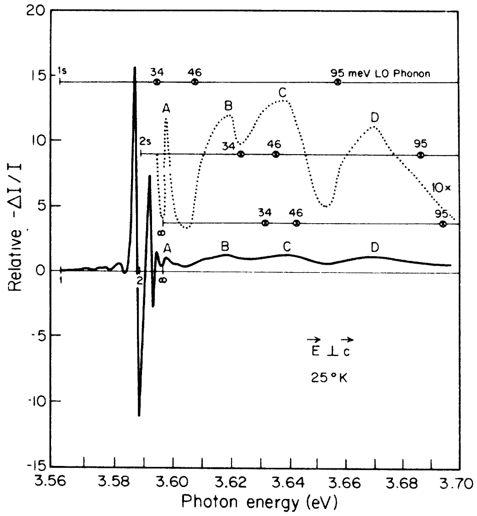

FIG. 6. Data of Fig. 1 are repeated here with the addition of the phonon energies measured from the $n = 1$, $n = 2$, and continuum of the exciton series (see the text).

near 3.97–4.01 eV at 25 °K, or 3.95–4.0 eV at 80 °K. The peak is narrower at 25 °K, but otherwise little fine structure is indicated. A shoulder does seem to appear between 3.92 and 3.96 eV at 25 °K, but in view of the experimental uncertainties its existence must be regarded as uncertain.

It has been suggested,[7] based on photocurrent observations, that a Γ_2^- valence band underlies the top two valence bands 3.6–3.8 eV below the conduction-band minimum at room temperature. Taking into account the 0.2-eV shift in the absorption-edge position that occurs on cooling to 80 °K,[20] the direct-allowed $\vec{E} \| \vec{c}$ transition would be at 3.8–4.0 eV, which is in approximate agreement with the structure observed in thermoabsorption (see Figs. 4 and 5). The peak position in $d\alpha/d(\hbar\omega)$ should correspond to the onset of the direct-allowed absorption; therefore these observations support the hypothesis in (7) and offer an estimate of the direct-allowed gap for $\vec{E} \| \vec{c}$ at about 4.0 eV, placing the Γ_2^- valence band about 0.4 eV below the top valence band.

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APPENDIX: EPQBS EXISTENCE-CRITERIA PARAMETER EVALUATION

Here we evaluate the existence-criteria parameters for EPQBS in CdTe and SnO_2, and show with reference to the theory of Toyozawa[1] that in some cases the parameters in SnO_2 are even more favorable than in CdTe, in which EPQBS have apparently been observed. Calculations for the additional examples of CdS, CdSe, and ZnO are not shown here but generally lend additional support to the view that SnO_2 belongs in this class of materials. The parameters used below are defined in the text.

For SnO_2 we must evaluate the contributions to $1/K_\infty - 1/K_s$ ($\vec{E} \perp \vec{c}$ values) by each of the three Γ_5^- LO-phonon modes, which we number 1 (34 meV), 2 (46 meV), and 3 (95 meV). From Refs. 14 and 21 we take $K_\infty = 3.785$; $K_s = 13.5$. For the rutile structure, Eagles[22] has been shown how to apportion $1/K_\infty - 1/K_s$ among the modes, by computing dimensionless quantities f_α^2 such that the effective contribution from mode α, $(1/K_\infty - 1/K_s)_{\text{eff}\,\alpha}$, is given by

$$\left(\frac{1}{K_\infty} - \frac{1}{K_s}\right)_{\text{eff},\alpha} = f_\alpha^2\left(\frac{1}{K_\infty} - \frac{1}{K_s}\right).$$

For SnO_2, following their transport measurements, these were determined by Fonstad and Rediker[9]: $f_1^2 = 0.017$; $f_2^2 = 0.392$; $f_3^2\, 0.541$, yielding

$$(1/K_\infty - 1/K_s)_{\text{eff},1} = 0.00323, \quad \alpha = 1$$
$$(1/K_\infty - 1/K_s)_{\text{eff},2} = 0.0745, \quad \alpha = 2$$
$$(1/K_\infty - 1/K_s)_{\text{eff},3} = 0.112 \quad \alpha = 3.$$

For the band mass m_e we use 0.24 times the free-electron mass m_0, noting that the density-of-states effective mass[23] is $0.275 m_0$ (the anisotropy is slight) and that the Frohlich coupling constant is about 0.9.[9] The hole-band mass m_h in SnO_2 is not known but probably is considerably greater than m_e; for parametric values we use $1.0 m_0$ and $4.0 m_0$.

For the effective dielectric constant we use $K' = \mu(R_H/\epsilon_B)$, where $R_H = 13.6$ eV.

In Table II we summarize the results of the calculations for SnO_2.

Similarly using material constants of CdTe from Refs. 19, 24, and 25 we find $\eta = 0.71$, $\xi = 0.45$, and $\gamma = 0.41$. Noting that from the theory of Ref. 19 the existence of EPQBS is favored by decreasing η, increasing γ, and increasing ξ up to $\xi \sim 1$, we conclude that, since EPQBS have apparently been observed in CdTe, their existence in SnO_2 is likely for cases involving the 1s exciton level and 46-or 95-meV LO phonons.

TABLE II. EPQBS existence parameters for SnO_2.

		$m_h = 1.0$ [a]	$m_h = 4.0$
		$\eta = 0.62$	$\eta = 0.21$
34-meV LO phonon	$\xi = 1.025$	$\gamma = 0.28$	$\gamma = 0.0304$
46-meV LO phonon	$\xi = 0.765$	$\gamma = 0.65$	$\gamma = 0.70$
95-meV LO phonon	$\xi = 0.369$	$\gamma = 0.97$	$\gamma = 1.05$

[a] Masses are expressed in units of the free-electron mass m_0.

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[1] Y. Toyozawa, in *Proceedings of the Third International*

Conference on Photoconductivity, edited by E. M. Pell (Pergamon, Oxford, 1971), p. 151.

[2] M. Nagasawa and S. Shionoya, Phys. Rev. Lett. 24, 409 (1966).

[3] M. Nagasawa and S. Shionoya, Phys. Rev. Lett. 21, 1070 (1968).

[4] M. Nagasawa and S. Shionoya, J. Phys. Soc. Japan 30, 158 (1971).

[5] V. T. Agekyan, Opt. Spect. 29, 395 (1970).

[6] V. T. Agekyan, Opt. Spect. 29, 487 (1970).

[7] M. Nagasawa and S. Shionoya, Japan J. Appl. Phys. 10, 727 (1971). Also C. Rieck, Ph.D. thesis (MIT, 1972) (unpublished); J. L. Jacquemin, C. Alibert, and M. DeMurica, Phys. Status Solidi 51, K75 (1972).

[8] C. G. Fonstad, A. Linz, and R. H. Rediker, J. Electrochem. Soc. 116, 1269 (1969).

[9] C. G. Fonstad and R. H. Rediker, J. Appl. Phys. 42, 2911 (1971).

[10] See, for example, M. Cardona, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Suppl. 11.

[11] B. Batz, in *Semiconductors and Semimetals*, Vol. 9, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1972), p. 316ff.

[12] R. J. Elliott, Phys. Rev. Lett. 108, 1385 (1957).

[13] R. S. Katiyar, P. Dawson, M. M. Hargreave, and G. R. Wilkinson, J. Phys. C 4, 2421 (1971).

[14] R. Summitt, J. Appl. Phys. 39, 3762 (1968).

[15] R. J. Elliott, Phys. Rev. 124, 340 (1961). We carry out these calculations using a second-order perturbation-theoretic model for the transition as a "two-step" process involving a virtual intermediate state, but do not restrict application of the results to the details of a particular interaction. Indeed, the exciton-phonon interaction that we will later consider vanishes exactly at $k = 0$ because of the exciton's electrical neutrality but we wish to learn which transitions would be forbidden *a priori* to this fact, because of crystal symmetry.

[16] E. I. Rashba and Y. B. Levinson, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors*, edited by M. Miasek (Polish Scientific Publishers, Warsaw, 1972), Vol. 2, p. 1197.

[17] Y. Toyozawa, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors*, edited by S. P. Keller, J. C. Hensel, and F. Stern (National Technical Information Service, Springfield, Va., 1970), p. 5.

[18] J. C. Hermanson, Phys. Rev. B 2, 5043 (1970).

[19] J. Dillinger, C. Konak, V. Prosser, J. Sak, and M. Zvara, Phys. Status Solidi 29, 707 (1968).

[20] M. Nagasawa and S. Shionoya, J. Phys. Soc. Japan 30, 1118 (1971).

[21] H. J. Van Daal, J. Appl. Phys. 39, 4467 (1968).

[22] D. M. Eagles, J. Phys. Chem. Solids 25, 1243 (1964).

[23] K. J. Button, C. G. Fonstad, and W. Dreybrodt, Phys. Rev. B 4, 4539 (1971).

[24] E. Kartheuser, in *Polarons in Ionic Crystals and Polar Semiconductors*, edited by Jozef T. Kevreese (North-Holland, Amsterdam, 1972), p. 515ff.

[25] B. Ray, *II-IV Compounds* (Pergamon, Oxford, 1969).