

$P = \sum_j (P_{i, i-1} A_i a_{i-1}^\dagger + P_{i, i+1} A_i a_{i+1}^\dagger)$ , where  $A_i$  is an annihilation operator for  ${}^4T_1$  excitation on ion  $i$  of sublattice  $A$ , and  $a_{i \pm 1}^\dagger$  creates a spin deviation on its first neighbor. The  $P$ 's are interaction constants similar to those defined in Ref. 2. The exciton operators can be expressed as Fourier sums of the corresponding momentum operators  $A_k$ , as well as for the usual magnon operators  $\alpha_k^\dagger, \beta_k$ .  $P$  is then given by  $\sum_k P_k$ , where the important terms  $P_k$  are  $P_k = P_{001} \exp(ik_z c) u_k A_k \alpha_k^\dagger + P_{00\bar{1}} \exp(-ik_z c) u_k A_k \alpha_k^\dagger$ , where  $u_k$  is the usual magnon sublattice weighting function. By considering the crystal symmetry, we obtain the components  $\xi(110)$  and  $\eta(1\bar{1}0)$  of the electric vector polarization which are  $P_k^\xi, \eta = 2iu_k P_{001}^\xi \sin(k_z c)$ , where the  $\xi$  and  $\eta$  components are distinct for a sublattice exciton.

<sup>8</sup>G. G. Low, A. Okazaki, K. C. Turberfield, and R. W. H. Stevenson, Phys. Letters **8**, 9 (1964).

<sup>9</sup>R. L. Green, D. D. Sell, R. S. Feigelson, G. F. Imbusch, and H. J. Guggenheim, to be published.

<sup>10</sup>See Ref. 6, and also A. Missetich and R. E. Dietz, in Proceedings of the Conference on Localized Excitations in Solids, Irvine, California, 1967 (Plenum Press, Inc., New York, 1968), p. 379.

<sup>11</sup>L. F. Johnson, R. E. Dietz, and H. J. Guggenheim, Phys. Rev. Letters **17**, 13 (1966).

<sup>12</sup>We have found that the trapping probability increases with temperature, and can be reduced by stressing the crystals uniaxially along the 001 direction. Such a stress is also sufficient to render the trapping probability nearly independent of temperature between 1.3 and 4.2°K. Since the intrinsic exciton emission is nearly invisible at 4.2°K in an unstressed crystal, all data recorded in Figs. 2(a) and 2(b) were made under a stress of 25 kg/mm<sup>2</sup>.

<sup>13</sup>This is the low-temperature lifetime of the weakly perturbed traps, measured in Ref. 9, which have essentially the same wave function as do the intrinsic exciton states.

## ZEEMAN EFFECT AND SYMMETRY OF THE INTRINSIC SnO<sub>2</sub> EXCITON

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The Zeeman effect of the intrinsic SnO<sub>2</sub> exciton (direct forbidden) has been measured at 1.8°K, thus facilitating the identification as well as the interpretation of the anisotropic exciton spectra. The exciton symmetries and possible band symmetries are obtained on the basis of group theory and appear to be consistent with the valence band of O  $2p$  functions and the conduction band of Sn  $5s$  functions, both being crystal field split.

In our previous report<sup>1</sup> the anisotropic absorption spectrum of SnO<sub>2</sub> ( $D_{4h}$  symmetry) at very low temperatures was described. Exciton structure composed of a series of sharp lines having absorption coefficients less than 100 cm<sup>-1</sup> was found near the fundamental absorption edge (3.597 eV at 1.3°K) for light polarized perpendicular to the  $c$  axis. The crystals were transparent in this spectral region for light polarized parallel to the  $c$  axis. The photon energies of the exciton lines satisfy the relation for the hydrogenlike series beginning with the  $n = 2$  quantum state.

The situation where the  $n = 1$  state is totally inactive to light is expected to arise if the transitions between the Bloch states at either side of the direct gap are forbidden by selection rules, as in the case of Cu<sub>2</sub>O.<sup>2</sup> However, it is not self-evident that this situation is the case in SnO<sub>2</sub>, since the conduction and valence bands of this

material may be considered to be  $s$ -like and  $p$ -like, respectively.

In the present Letter, measurements of the Zeeman effect are briefly described. The results facilitate the identification as well as the interpretation of the anisotropic exciton spectra. The exciton symmetries and possible band symmetries are obtained on the basis of group theory. It is shown that the experimental facts are not inconsistent with the valence band of O  $2p$  functions and the conduction band of Sn  $5s$  functions.

The measurements were made spectrophotometrically using a Spex Model 1700-II grating spectrometer in the second order (reciprocal dispersion, 5.5 Å/mm) and an EMI 6256S photomultiplier. The crystals, prepared by the vapor reaction method,<sup>3</sup> were cut into platelets of 0.2- to 0.5-mm thickness with the  $c$  axis in the plane. The crystals were immersed in liquid helium at

1.8°K. An electromagnet which has a light-guiding hole through the center axis of the poles and which can produce fields up to 15.2 kG was used. Crystals showed remarkable differences in the sharpness of the lines; the spectra observed with a "good" crystal are reported here.

Absorption spectra observed with the magnetic field perpendicular to the  $c$  axis and parallel to the vector of the exciting photon  $\vec{q}$  are shown in Fig. 1. New absorption lines appear on the higher energy side of each zero-field line and their intensities increase with increasing magnetic field strength. Furthermore, all the lines undergo energy shifts. With the magnetic field parallel to the  $c$  axis no new lines were observed, but broadening and energy shifts of the zero-field lines were observed (the data are not presented here). These observations can be interpreted satisfactorily if the transitions are assumed to take place at the  $\Gamma$  point from a crystal ground state to the hydrogenic  $P$  states as will be shown in the following.

The symmetry of an exciton state is represented as  $\Gamma_c \times \Gamma_v \times \Gamma_e$  where  $\Gamma_c$ ,  $\Gamma_v$ , and  $\Gamma_e$  are the symmetries of the conduction band, the valence band, and the hydrogenic envelope function, re-

spectively.<sup>4</sup> Assuming the valence band to be  $p$ -like and the conduction band to be  $s$ -like in  $\text{SnO}_2$ , Ohta<sup>5</sup> concluded on the basis of group theory that at  $\vec{k}=0$  the conduction band will be split, because of crystal field effects, into two states  $\Gamma_1^+$  and  $\Gamma_4^+$ , and the valence band into nine states,  $\Gamma_1^+$ ,  $\Gamma_2^+$ ,  $\Gamma_3^+$ ,  $\Gamma_4^+$ ,  $\Gamma_5^+$ ,  $\Gamma_2^-$ ,  $\Gamma_3^-$ ,  $\Gamma_5^-$ , and  $\Gamma_5^-$ , where  $\Gamma_5^+$  and  $\Gamma_5^-$  are doubly degenerate states. This complexity in the energy bands of  $\text{SnO}_2$  arises from the fact that the unit cell of  $\text{SnO}_2$  contains two and four nonequivalent sites for tin and oxygen, respectively. One may assume that the lowest conduction band at  $\vec{k}=0$  would have  $\Gamma_1^+$  symmetry, since the  $\Gamma_1^+$  state is totally symmetric and is expected to lie below the  $\Gamma_4^+$  state. With this assumption one may deduce the symmetries of the possible exciton states in  $\text{SnO}_2$  at the band edge by reducing  $\Gamma_c \times \Gamma_v \times \Gamma_e$  for any combinations of  $\Gamma_e$  and nine possible  $\Gamma_v$  (two of which are equivalent). The results for  $S$ -,  $P_0$ -, and  $P_{\pm 1}$ -like envelope functions are presented in Table I.

In a crystal with  $D_{4h}$  symmetry a transition to a final state of  $\Gamma_2^-$  or  $\Gamma_5^-$  symmetry from a  $\Gamma_1^+$  ground state at  $\vec{k}=0$  is dipole allowed for light polarized parallel or perpendicular to the  $c$  axis.

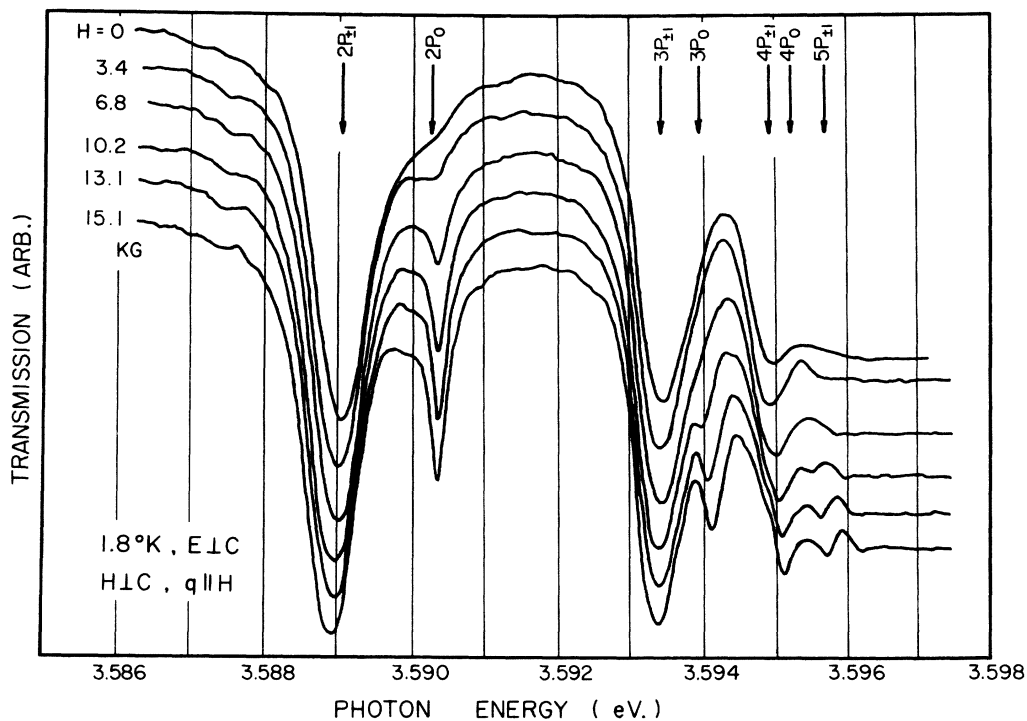


FIG. 1. The Zeeman effect of the intrinsic exciton states in  $\text{SnO}_2$ . Crystal No. 1732 (thickness, 0.40 mm) at 1.8°K for  $\vec{H} \perp c$  and  $\vec{q} \parallel \vec{H}$ . The arrows represent the zero-field energies of the exciton states calculated semiempirically using the anisotropic-exciton-mass formalism.

Table I. Symmetries of the exciton states possible in  $\text{SnO}_2$ , assuming that the lowest conduction band has  $\Gamma_1^+$  symmetry.

Valence states	Hydrogenic envelope functions		
	$nS(\Gamma_1^+)$	$nP_0(\Gamma_2^-)$	$nP_{\pm 1}(\Gamma_5^-)$
$\Gamma_1^+$	$\Gamma_1^+$	$\Gamma_2^-$	$\Gamma_5^-$
$\Gamma_2^+$	$\Gamma_2^+$	$\Gamma_1^-$	$\Gamma_5^-$
$\Gamma_3^+$	$\Gamma_3^+$	$\Gamma_4^-$	$\Gamma_5^-$
$\Gamma_4^+$	$\Gamma_4^+$	$\Gamma_3^-$	$\Gamma_5^-$
$\Gamma_5^+$	$\Gamma_5^+$	$\Gamma_5^-$	$\Gamma_1^- + \Gamma_2^- + \Gamma_3^- + \Gamma_4^-$
$\Gamma_2^-$	$\Gamma_2^-$	$\Gamma_1^+$	$\Gamma_5^+$
$\Gamma_3^-$	$\Gamma_3^-$	$\Gamma_4^+$	$\Gamma_5^+$
$\Gamma_5^-$	$\Gamma_5^-$	$\Gamma_5^+$	$\Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+$

One may understand from Table I that the observed anisotropic properties (active only for light with  $\vec{E} \perp c$ ) and absorption intensity ( $<100 \text{ cm}^{-1}$ ) of the exciton spectrum can be interpreted consistently if the top valence band is assumed to be one of three states,  $\Gamma_2^+$ ,  $\Gamma_3^+$ , or  $\Gamma_4^+$ . This assumption leads to the assignment of the zero-field lines as transitions from the crystal ground state to the hydrogenic  $nP_{\pm 1}$  states.

A magnetic field perpendicular to the  $c$  axis of the crystal represents a perturbation of symmetry  $\Gamma_5^+$ . This perturbation mixes any of the  $\Gamma_1^-$ ,  $\Gamma_4^-$ , and  $\Gamma_3^-$  states with the  $\Gamma_5^-$  state. It is expected that  $P_{\pm 1}$  and  $P_0$  states will be mixed by the field, and in accord with this,  $P_0$  increases in strength as the field is increased if the measurement is made in the geometry of  $\vec{H} \perp c$  and  $\vec{H} \parallel \vec{q}$ . As another result of the state mixing, the lower state (say  $P_{\pm 1}$ ) will be moved to lower energies, and the higher state (say  $P_0$ ) to higher energies. The results of the Zeeman effect are qualitatively in good agreement with this prediction. One may now assign the new lines as  $nP_0$ . Rather large energy shifts seen in the higher states ( $n=4, 5$ ) may be interpreted in terms of the diamagnetic Zeeman effect.

A magnetic field parallel to the  $c$  axis, on the other hand, represents a perturbation of symmetry  $\Gamma_2^+$ . This mixes  $\Gamma_5^-$  with itself. Hence one may expect that  $P_{\pm 1}$  is split into  $P_{+1}$  and  $P_{-1}$  states. The observation of the broadening of the lines in the geometry of  $\vec{H} \parallel c$  and  $\vec{q} \perp \vec{H}$  is not inconsistent with this prediction.

An anisotropic-exciton-mass formalism has been derived by Hopfield and Thomas,<sup>6</sup> and also by Wheeler and Dimmock,<sup>7</sup> by using the ellipsoidal effective-mass approximation. The formalism can be used to describe the experimental situation of a weakly bound exciton if the exciton-

mass anisotropy and dielectric anisotropy are small enough to be regarded as a perturbation of the Hamiltonian for a hydrogenic system.

The experimental fact that the exciton line series satisfies the relation for the hydrogenlike series<sup>1</sup> implies that the  $\text{SnO}_2$  exciton belongs to the category of "weakly bound" and "slightly anisotropic" excitons. The zero-field state energies of the  $\text{SnO}_2$  exciton are calculated semiempirically by using the expressions presented by Wheeler and Dimmock [see Eqs. (10)-(18) and Table I in Ref. 7]. The calculated energies of  $nP_{\pm 1}$  and  $nP_0$  states (where  $n=2, 3, 4$ , and 5) are shown by arrows in Fig. 1. Good agreement between calculation and experiment is seen when the experimental values are extrapolated to the limit of  $H=0$ . The analysis with the anisotropic-exciton-mass formalism leads to estimates of the anisotropy parameter  $\mu_x \epsilon_x / \mu_z \epsilon_z$  (where  $\mu$  and  $\epsilon$  are the reduced mass and dielectric constant, respectively) as 1.55 and the effective Rydberg constant as 0.0345 eV. The anisotropic parameter is rather large compared with those of CdS,<sup>6</sup> CdSe,<sup>7</sup> and ZnS,<sup>8</sup> but it is barely within the limit in which the first-order perturbation calculation of the effective-mass equation is allowed.

On the basis of the assumptions that the transitions occur at the  $\Gamma$  point and that the bottom conduction band has symmetry  $\Gamma_1^+$ , it has been shown that the anisotropic properties and the Zeeman effect of the intrinsic  $\text{SnO}_2$  exciton absorption can be interpreted satisfactorily. The interpretation has led us to the assignment of the top valence band as one of the three states  $\Gamma_2^+$ ,  $\Gamma_3^+$ , or  $\Gamma_4^+$ . The decision among these states can not be made only from the present investigation.

With the alternative assumption that the bottom conduction band has symmetry  $\Gamma_4^+$ , one can give essentially the same interpretation as that presented above. In this case, however, one may be led to the assignment of the top valence band as one of the three states  $\Gamma_1^+$ ,  $\Gamma_2^+$ , or  $\Gamma_4^+$ .

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## RAMAN SCATTERING FROM InSb SURFACES AT PHOTON ENERGIES NEAR THE $E_1$ ENERGY GAP\*

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We have observed surface electric-field-induced and resonance-enhanced Raman scattering by  $q \approx 0$  LO phonons in the spectra obtained from InSb surfaces. The data indicate that excitons are responsible for the resonance enhancement. The effects of temperature and externally applied electric fields are discussed. The results suggest the possibility of studying the surface electronic properties by Raman spectroscopy.

During a series of experiments performed to obtain the Raman scattering spectra of coupled LO-phonon-plasmon modes in  $n$ -type InSb using a He-Ne laser at 6328 Å and a backward scattering geometry, we found that the  $q \approx 0$  LO phonon appears at a frequency  $\omega_{\text{LO}} = 191 \text{ cm}^{-1}$  regardless of the concentration of carriers in the volume of the crystal. Further, the  $q \approx 0$  LO-phonon band is observed for scattering geometries in which, according to the polarization selection rules for the Raman scattering tensor (RST),<sup>1</sup> it should be forbidden. The strengths of the  $q \approx 0$  LO-phonon band in these scattering geometries were, however, observed to increase with increasing conduction-electron concentration. It is shown in this Letter that these effects are due to the depletion layer at InSb surfaces<sup>2</sup> whose thickness is comparable with or larger than the skin depth at 6328 Å. This accounts for the observed independence of the LO-phonon frequency on the carrier concentration in the volume of the crystal. The breakdown of the selection rules for the first-order RST and the increasing strength of the  $q \approx 0$  LO-phonon band with increasing carrier concentration in the volume of the crystal are attributed to an electric-field-induced Raman scattering by the electric field present in the depletion layer. In addition, the large observed scattering intensities and their temperature dependence indicate a resonance effect which, unlike previous observations of resonant Raman scattering at the fundamental energy gap,<sup>3</sup> occurs at the  $E_1$  energy gap (1.89 eV).<sup>4</sup>

The experiments were performed on undoped and Te-doped InSb crystals of  $n$  type with carrier concentrations in the range from  $1.5 \times 10^{15}$  to  $1.4$

$\times 10^{18} / \text{cm}^3$ .<sup>5</sup> (110) surfaces were obtained by cleavage in air and no further treatment was given to the surface. The spectra were excited with a 50-mW He-Ne laser operating at 6328 Å (1.96 eV). In order to identify the spectra, the (110) surface is described by the following Cartesian system of coordinates:  $y \equiv [110]$ , which is normal to the surface, and  $x' \equiv [1\bar{1}1]$  and  $z' \equiv [\bar{1}12]$ , which are contained in the surface.

The spectra of Fig. 1, showing the  $q \approx 0$  TO- and LO-phonon bands, correspond to the  $(x'x')$  component of the RST. The incident and scattered radiation (inside the crystal) as well as the scattering wave vector  $\vec{q} = \vec{k}_{\text{inc}} - \vec{k}_{\text{scatt}}$  were along  $y'$ . Similar spectra were obtained for the  $(z'z')$  component, while the spectra for the  $(z'x')$  component show only the band of the  $q \approx 0$  TO phonons. According to the selection rules for the first-order RST,<sup>1</sup> the  $q \approx 0$  LO-phonon band is forbidden for the scattering geometries and the polarizations of the incident and scattered radiation corresponding to the three types of spectra.

Due to the large absorption coefficient of InSb at 6328 Å, the observed scattered radiation originates only from the skin depth, which is about 500 Å. Since no changes are observed in the  $q \approx 0$  LO-phonon frequency, we have to assume that the concentration of carriers in this region is smaller than  $1 \times 10^{15} / \text{cm}^3$ .<sup>6</sup> This indicates the presence of a depletion layer with a width which is at least of the same order as the skin depth. It has been shown<sup>2</sup> that the Fermi level at InSb surfaces is pinned at a fixed position within the forbidden energy gap which is independent of the doping of the material and of temperature in the range between 300 and 77°K. Under these condi-