changes in the exchange potential should also affect the results for Mo and we have seen (Ref. 8) that this is not necessary to get agreement with experiment. This, coupled with the fact that Mo and W differ in several experiments, leads us to attribute these differences mainly to relativistic effects.

ACKNOWLEDGMENTS

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Exciton Spectrum of ZnO

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The absorption and reflection spectra of ZnO crystals have been studied in the region of intrinsic absorption, and the data have been interpreted in terms of the wurtzite model given by Birman. Three intrinsic exciton transitions have been observed, one associated with each of the three valence bands. Several bound-exciton transitions have also been observed. The data have been analyzed, and a number of exciton parameters in ZnO are reported which are somewhat modified from those previously reported.

I. INTRODUCTION

The fundamental exciton spectra of ZnO crystals was first investigated by Thomas.[1] He made a detailed study of the optical properties near the onset of intrinsic absorption and interpreted the data in terms of the wurtzite band structure derived by Birman.[2] The details of the band model are shown in Fig. 1. The conduction band is *s*-like, having Γ_7 symmetry. The valence band is *p*-like, splitting into three doubly degenerate bands due to spin-orbit and crystalline-field interactions. The top valence band has Γ_9 symmetry while the two lower valence bands have Γ_7 symmetry. The selection rules allow a $\Gamma_7 \rightarrow \Gamma_9$ transition for light polarized in the orientation $E \perp C$; $\Gamma_7 \rightarrow \Gamma_7$ transitions are allowed for both modes of polarization ($E \perp C$ and $E \| C$).

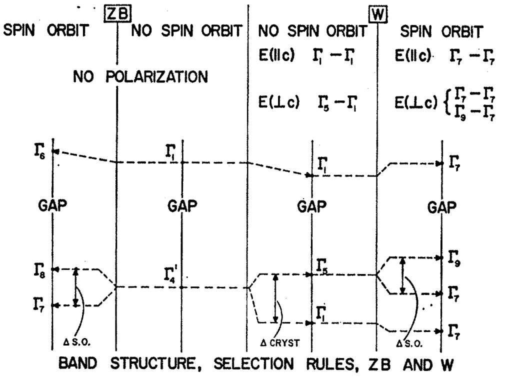

FIG. 1. Band structure and selection rules for zinc blende and wurtzite structures at the Γ symmetry point ($\mathbf{k}=0$). Crystal-field and spin-orbit splittings are indicated schematically. Transitions which are allowed for various polarizations of photon electric vector with respect to the crystalline "*C*" axis are indicated, i.e., $E \perp C$ or $E \| C$ (after Birman).

From reflection spectra Thomas identified three exciton series, one associated with each of the three valence bands. The two top valence bands (*A* and *B* bands) are split by approximately 0.006 eV, and the third valence band (*C* band) is separated from the *B* band by 0.038 eV. In reflection, the excitons formed from the *A* and *B* bands were active for light polarized with the *E* vector perpendicular to the crystal *C* axis ($E \perp C$). Excitons formed from the *C* band were active for light polarized with the *E* vector parallel to the crystal *C* axis ($E \| C$). Thomas also observed from absorption experiments that transitions from the top valence band were at least partially polarized in the mode $E \| C$. Based on these polarization experiments, he concluded that the states from the first and third valence bands were mixed and that the symmetries of two top valence bands were reversed in ZnO. This behavior is quite different from what has been observed from similar experiments in other II–VI compounds. For example, in a detailed study of the optical properties of CdS crystals near the absorption edge, Thomas and Hopfield[3,4] developed a theory from Birman's model that successfully explained their intrinsic exciton data. The intrinsic exciton structure of CdSe was similarly explained by Wheeler and Dimmock,[5] and more recently

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[1] D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).

[2] J. L. Birman, Phys. Rev. Letters **2**, 157 (1959).

[3] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[4] D. G. Thomas and J. J. Hopfield, Phys. Rev. **122**, 35 (1962).

[5] R. G. Wheeler and J. O. Dimmock, Phys. Rev. **125**, 1805 (1962).

the exciton structure of ZnS was explained by Wheeler and Miklosz.[6]

It is the purpose of this paper to report some experimental results that point to the extrinsic nature of the 3669.66-Å line. From these results we are proposing an alternative band assignment in ZnO. Based on the energy and polarization of the fine structure in the optical spectra of ZnO in the fundamental absorption region, the exciton spectrum is successfully explained on the basis of Birman's model of the wurtzite structure.

II. EXPERIMENTAL

Crystals from four different sources were used in this investigation; (1) large bulk crystals grown by the hydrothermal technique at Airtron (a division of Litton Industries); (2) large bulk crystals grown from the vapor phase and supplied by the Minneapolis Mining and Manufacturing Company; (3) a slab of ZnO grown from a flux and supplied by the Aerospace Corporation; (4) platelets [varying in thickness from a few microns (3–5) up to about 50 μ] and small bulk crystals grown from the vapor phase in our laboratory. In all of the reflection and absorption experiments, the crystals were immersed in the refrigerant (liquid He). Temperatures below 4.2°K were obtained by pumping on the liquid, and temperatures were measured by vapor-pressure thermometry, using an oil manometer. Both the transmission and reflection spectra were recorded on photographic plates using a Bausch and Lomb 2-m grating spectrograph. In the reflection measurements, the incident beam made an angle of less than 10° with respect to the normal from the crystal surface. The beam was polarized by passing through a Glan-Thomson prism.

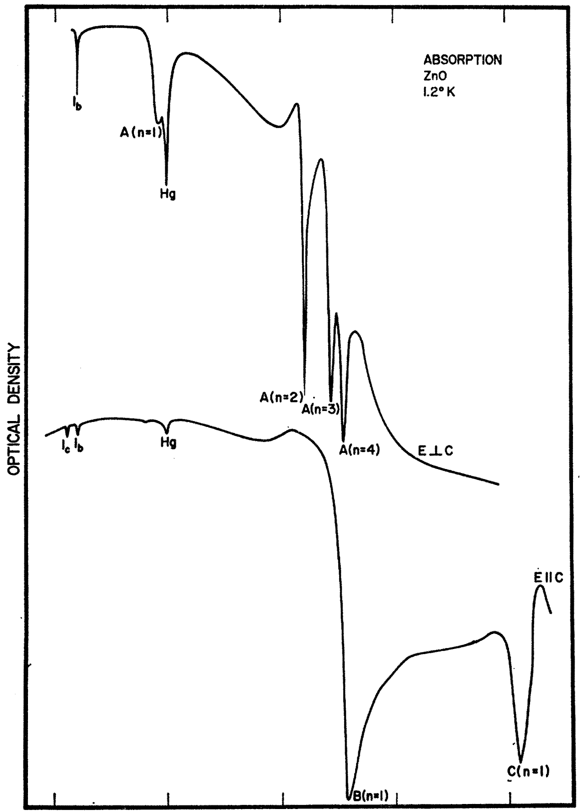

FIG. 2. Absorption spectra of a vapor-grown ZnO platelet at 1.2°K in polarized light. These absorption lines were observed as the self-absorption of a continuum emission from the crystals when excited by the ultraviolet light from a high-pressure mercury lamp. Hg refers to the mercury emission lines.

III. RESULTS

A. Absorption

A large number of absorption lines (both intrinsic and extrinsic) have been observed in ZnO. The most significant of these lines are shown in Table I. Many of these lines were observed as the self-absorption of a continuum emission from the crystals when excited by the ultraviolet light from a high-pressure mercury lamp. This technique is particularly useful for the high-energy intrinsic absorptions which would require crystals appreciably thinner than the thinnest we were able to obtain, in order to observe these absorptions by conventional transmission techniques. The extrinsic lines as well as the intrinsic absorptions at energies as high as the B-band excitons were observed by conventional transmission measurements.

The spectra shown in Fig. 2 comprises all of the intrinsic lines that have been seen in absorption. The intrinsic lines reported by Thomas[1] were determined by a Kramers-Kronig (K-K) inversion analysis of the reflection peaks.

The line at 3653.42 Å ($A, n=1$) and the $A, n=2, 3, 4$ states of exciton A are seen only in $E\perp C$. The A, $n=4$ state and the B, $n=1$ state are very close together

TABLE I. A summary of the absorption lines observed in polarized light in ZnO at 1.2°K.

Line	Polarization	Position (Å)	(eV)
I_{dB}	$E\perp C$	3638.44	3.4071
I_a	$E\parallel C$	3666.31	3.3812
I_b	$E\perp C$	3669.66	3.3781
I_c	$E\parallel C$	3671.99	3.3760
I_d	$E\perp C$	3682.61	3.3662
I_e	$E\perp C$	3683.33	3.3655
I_f	$E\perp C$	3684.07	3.3649
I_g	$E\perp C$	3690.22	3.3593
I_h	$E\perp C$	3694.93	3.3550
$A, n=1$	$E\perp C$	3653.42	3.3931
$A, n=2$	$E\perp C$	3620.11	3.4243
$A, n=3$	$E\perp C$	3614.59	3.4296
$A, n=4$	$E\perp C$	3611.82	3.4322
$B, n=1$	$E\perp C$, $E\parallel C$	3610.81	3.4331
$C, n=1$	$E\perp C$, $E\parallel C$	3572.86	3.4696

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[6] R. G. Wheeler and J. C. Miklosz, in *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 873.

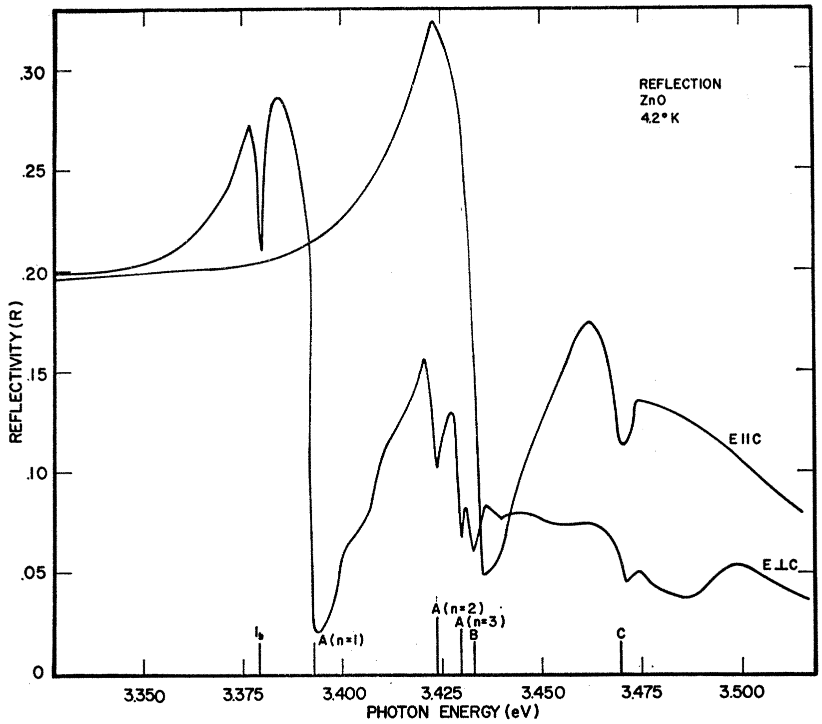

FIG. 3. Reflection spectra of a vapor-grown ZnO platelet at 4.2°K in polarized light. Indicated are also the positions of the absorption peaks at 1.2°K. Sharp reflection anomalies are seen corresponding with the position of each absorption line.

and are not resolved. The lines at 3610.81 Å (B, $n=1$) and 3572.86 Å (C, $n=1$) appear strong for light polarized with $E\|C$. The absorption of the C exciton for light polarized with $E\perp C$ is weak.

The impurity line at 3669.66 Å (I_b) is preferentially polarized for $E\perp C$ and the line at 3671.99 Å (I_c) is active for $E\|C$. The line I_b (labeled A_L by Thomas) and the line I_c (labeled A_m by Thomas[7]) are identified as the lines arising from the Γ_5 and Γ_6 states of an ionized donor complex.[8]

In addition to the above two extrinsic lines, several other extrinsic lines are observed as listed in Table I. The character and origin of several of these lines are discussed elsewhere.[8] A strong absorption is observed for the line 3682.61 Å (I_d) in the polarization $E\perp C$. This impurity line is approximately 0.027 eV below the (A, $n=1$) line. Another strong absorption line is observed at 3638.44 Å which is approximately 0.026 eV below the (B, $n=1$) line. It is likely that this line results from the impurity giving rise to the line I_d but associated with the B band.

The line I_a (3666.31 Å) has been observed in some crystals. This line was reported by Thomas and labeled B_F.[7] This is a very sharp line and splits in a magnetic field with a large g value (3.86). The line, when seen, is very weak and is polarized with $E\|C$.

B. Reflection

The reflection spectra from a vapor-grown platelet at 4.2°K are shown in Fig. 3. A densitometer trace of the reflection spectra from a vapor-grown platelet and from a flux-grown bulk crystal as well as a hydrothermally grown bulk crystal are shown in Figs. 4(a), 4(b), and 4(c), respectively. The absolute reflectivities were obtained by normalizing to a reflectivity value calculated from the index of refraction of 2.0 in a spectral region (around 6100 Å) where the crystal is transparent. The values of the reflectivities were taken from a calibrated photographic plate. These reflection spectra are qualitatively very similar to those reported by Thomas.

The positions of the absorption peaks at 1.2°K are indicated in Fig. 3. Sharp reflection anomalies are seen corresponding with the position of each absorption line. The A ($n=1$, 2, 3, 4) states are active for the polarization $E\perp C$. The $A(n=4)$ and $B(n=1)$ states are not resolved in the $E\perp C$ polarization. The B ($n=1$) and C ($n=1$) states appear strong in the $E\|C$ polarization. The C ($n=1$) state is appreciably weaker in the $E\perp C$ polarization than in the $E\|C$ polarization as is also the case for CdS.[3]

The reflection minima corresponding with the position of the bound-exciton line I_b (Thomas A_L) appears strong for $E\perp C$. The observation of bound-exciton lines in the reflection spectra has never been reported for II–VI compounds; however, in CdSe[9] as well as in CdS,[10]

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[7] In the recent paper by J. J. Hopfield and D. G. Thomas, Phys. Rev. Letters **15**, 22 (1965), the line A_m was labeled A_{12} and the line B_F as B_6.

[8] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **140**, A1726 (1965).

[9] C. W. Litton, T. C. Collins, and D. C. Reynolds (to be published).

[10] Two of us (Y. S. P. and D. C. R) have observed bound exciton lines in the reflection spectra of CdS.

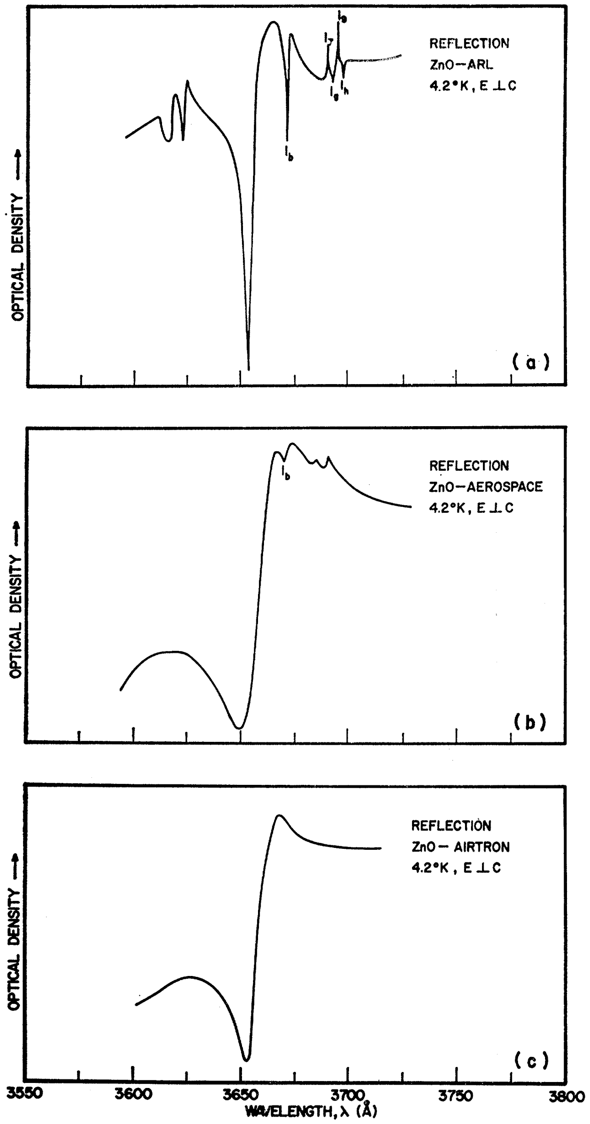

FIG. 4. A densitometer trace of the reflection spectra from (a) a vapor-grown platelet, (b) a flux-grown bulk crystal, and (c) a hydrothermally grown bulk crystal of ZnO at 4.2°K for $E \perp C$. The variation of the strength of I_b (labeled A_L by Thomas) in different crystals of ZnO is to be noted. In (a) the I_b line is most pronounced, in (b) the strength of I_b is considerably reduced, and in (c) it is completely absent. Note also in (a) the reflection anomalies due to the bound-exciton lines I_g(3690.22 Å) and I_h(3694.93 Å). Similar anomalies due to the bound-exciton lines were also observed in the reflection spectra of CdSe and CdS crystals.

anomalies due to bound excitons have been observed in the reflection spectra. In ZnO, bound-exciton lines other than I_b are also observed. In Fig. 4(a), the line I_g (3690.22 Å) is a bound exciton arising from an ionized donor complex, and the line I_h (3694.93 Å) is a bound exciton arising from a neutral donor or acceptor complex. Both of these lines appear as reflection anomalies. Figure 5 shows other bound-exciton lines I_d (3682.61 Å) and I_5 (3687.54 Å) observed in the reflection spectra of another crystal.

The resonant frequencies associated with the reflection anomalies were determined from a Kramers-Kronig analysis. Figure 6 shows a plot of the imaginary part of the dielectric constant ϵ_2 for both modes of polarization at 4.2°K. For many of the lines, the resonant frequencies obtained by K-K analysis and the positions of the absorption peaks coincide. The resonant frequencies for the $A(n=1)$ and $B(n=1)$ lines obtained from K-K analysis do not correspond with the absorption lines. Here the deviation is as much as 0.01 eV. This discrepancy is believed due to shallow bound excitons influencing the K-K analysis for the ground-state A exciton and the excited states of the A exciton influencing the K-K analysis for the ground-state B exciton. The applicability of K-K analysis to reflection oscillators that are closely spaced in energy is questionable.[11]

In Fig. 7 is plotted the intensity of the reflection anomaly for the 3669.66-Å line with respect to the 3653.42-Å line as a function of temperature. In this plot, the intensity of the 3653.42-Å line is normalized to a constant intensity at each temperature and the intensity of the 3669.66-Å line is plotted relative to it. It is noted that at 180°K the 3669.66-Å line has dissappeared. If these two lines were due to the A and B intrinsic exciton

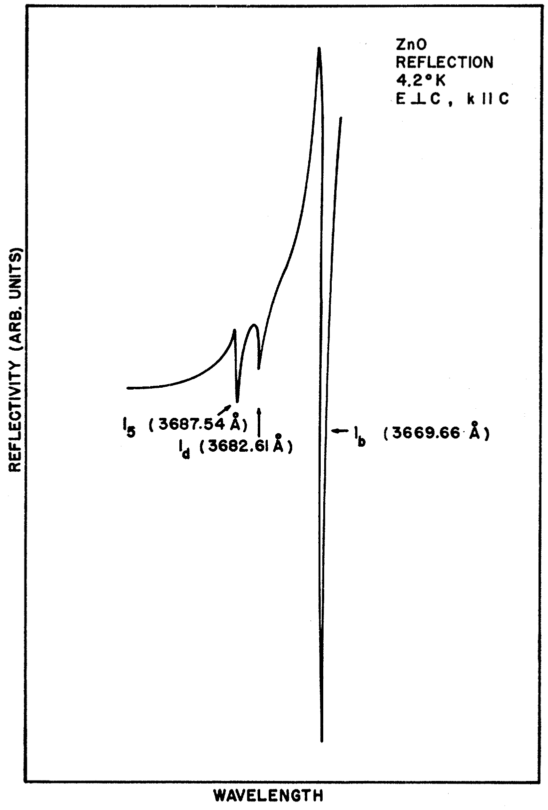

FIG. 5. The observation of more bound-exciton lines other than those in Fig. 4(a) in the reflection spectra of a prism-type ZnO at 4.2°K. This spectra was taken for wave vector of the incident beam in the z direction, i.e., $\mathbf{K} \| C$.

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[11] J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963).

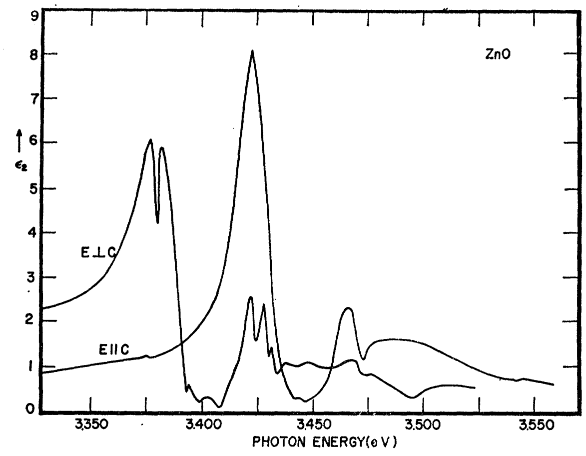

FIG. 6. A plot of the imaginary part of the dielectric constant ϵ_2 of ZnO at 4.2°K for both modes of polarization as derived from a Kramers-Kronig analysis of the reflectivity data of Fig. 3. Note that the resonant frequencies for the $A(n=1)$ and $B(n=1)$ lines obtained from K-K analysis do not correspond with the absorption lines. This deviation is as much as 0.01 eV.

transitions in ZnO, it would be reasonable to assume that they would both show a very similar temperature dependence. This would be a consequence of them both having approximately the same binding energy. A very different temperature dependence would result if the 3669.66-Å line were due to a bound-exciton complex. In this same figure an emission line is observed on the low-energy side of the 3669.66-Å line. This line is due to a bound-exciton complex and disappears when the temperature reaches 77°K. In an effort to determine the origin of the line I_b, experiments were performed analogous to the work of Woodbury[12] in CdS; that is, the ZnO crystals were baked in a Zn vapor at 600°C for periods of 16 h and 48 h. The results of the experiments are shown in Fig. 8. The reflection spectrum of the crystal before being baked is shown in Fig. 8(a). In this figure, the line I_b is typical for crystals grown in our laboratory. After being baked for 16 h at 600°C in Zn vapor, the intensity of the line I_b is appreciably reduced, as shown in Fig. 8(b). After baking the crystal for an additional 48 h at 600°C in Zn vapor, the line I_b has almost disappeared, as is seen in Fig. 8(c).

Zeeman splitting of the line I_b has shown that it could be explained as an exciton bound to an ionized donor complex.[8] One possible explanation of the baking experiments is that the crystals as grown contain zinc vacancies. These vacancies are compensated by donor impurities resulting in ionized donors to which excitons are bound resulting in line I_b. Baking in zinc removes the zinc vacancies thus changing the ionized donors to neutral donors with a corresponding reduction in the intensity of the line I_b. Another explanation might be that the centers resulting in the line I_b are chemical impurities and that these are removed by baking in zinc, similar to the mechanism by which chemical impurities are removed from CdS by baking in cadmium.[13]

IV. DISCUSSION

The essential features of the reflection and absorption spectra of ZnO described above are: (1) the existence

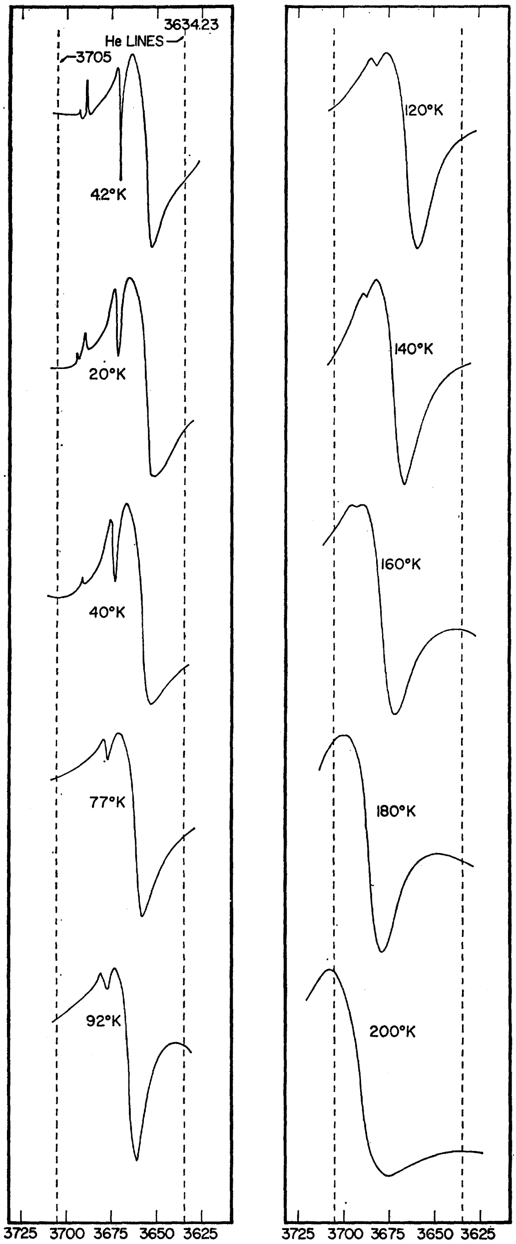

FIG. 7. The intensity of the reflection anomaly for the 3669.66-Å (I_b) line with respect to the 3653.42-Å ($A, n=1$) line as a function of temperature. Significant is the fact that at 180°K the I_b line disappears while the ($A, n=1$) line still persists. Note also that some emission lines due to bound-exciton complexes observed on the low-energy side of the I_b line disappear in the neighborhood of 77°K.

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[12] H. H. Woodbury, Phys. Rev. 134, A492 (1964).

[13] M. Aven and H. H. Woodbury, Appl. Phys. Letters 1, 53 (1962).

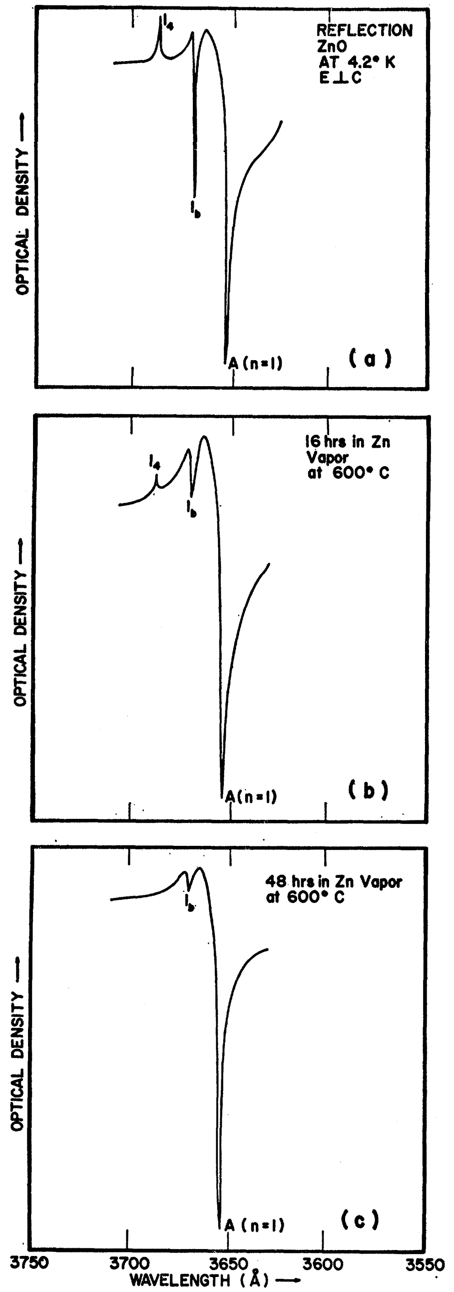

FIG. 8. Reflection spectra of a vapor-grown ZnO crystal at 4.2°K for $E \perp C$ before and after baking the crystals in a Zn vapor. (a) Before baking, (b) after baking at 600°C for a period of 16 h, and (c) for a period of 48 h.

of three intrinsic exciton bands (the A, B, and C bands) with the associated excited states ($n=2$, 3, 4) observed for the A band, (2) a number of bound exciton lines, some of which were observed in both absorption and reflection spectra, and (3) the consistency of the intrinsic excitons in all of the ZnO crystals studied and the great variability of the extrinsic excitons with the different ZnO specimens. The ground-state A exciton as well as its excited states are active only in $E \perp C$. This polarization indicates that the excited states are either S or P_0 states. The $P_{\pm 1}$ states should be observed in both modes of polarization. This is further verified by magnetic field studies. The excited states were not observed to split in fields up to 45 000 G. The S and P_0 states split as the difference of the electron and hole g values, whereas the $P_{\pm 1}$ states split as the sum of the electron and hole g values. This would indicate that the electron and hole g values are nearly the same, thus accounting for the fact that the excited states were not observed to split. The excited states did, however, show a diamagnetic shift. The excitons associated with the B and C bands are active in both modes of polarization. Thus, the intrinsic exciton spectrum in ZnO is satisfactorily explained by Birman's[1] model and is very similar to that observed in other II-VI compounds, namely, CdS, ZnS, and CdSe.

The essential difference between the work reported here and that of Thomas[1] is in line assignments. Thomas interprets the line I_b (labeled A_L by Thomas) as the ground-state A-exciton transition. We, in turn, interpret this line as a bound-exciton line resulting from an ionized donor complex. The strength and reproducibility of the line in many crystals is such that one is likely to interpret the line as being of an intrinsic nature. We cite in the following some of the experimental evidence that points to the extrinsic nature of the line:

(a) The intensity of the line I_b is always less than that of the 3653.42-Å (A, $n=1$) line. The ground-state A exciton would be expected to be the most intense transition.

(b) The line I_b splits in a magnetic field, as would be expected for a charged donor complex arising from a $\Gamma_7 \rightarrow \Gamma_9$ transition.[8]

(c) The variation of the strength of I_b in different crystals of ZnO. In the reflection spectra of some crystals, the line I_b is not always present as illustrated in Fig. 4. In the vapor-grown platelets the I_b line is most pronounced. In the flux-grown crystal the strength of I_b is considerably reduced, and in the hydrothermally grown crystal it is completely absent. In all of these crystals the strength of the 3653.42-Å line is essentially comparable.

(d) The very different temperature dependence of the line I_b from that of the ground-state exciton. One would not expect the temperature dependence of the ground-state A exciton to be appreciably different from that of the ground-state B exciton since they have approximately the same binding energy.

(e) The fact that the line I_b disappears when the crystal is baked in Zn vapor demonstrates the extrinsic nature of the line.

(f) Assuming the exciton series has a hydrogen-like set of energy levels, one can calculate the binding energy of the exciton from the ground-state energy and the excited-state energies. The results of the calculations are as follows:

Energy levels $(A, n=\alpha, \beta)$	Binding energy E_B (eV)
$(A, n=1, 2)$	0.042
$(A, n=1, 3)$	0.041
$(A, n=2, 3)$	0.038

Thus the excited-state energies establish that the ground-state exciton energy is the 3653.42-Å $(A, n=1)$ line rather than the I_b line.

Since a bound exciton complex is made up from an impurity atom (or lattice defect) to which is bound an intrinsic (free) exciton and since the intrinsic exciton is a property of the crystalline host lattice, a question naturally arises concerning the relative intensities of absorption lines that derive from these two types of excitons. This is especially so when the bound-exciton lines are observed to be nearly as intense as the intrinsic-exciton lines, a frequent observation in both the absorption and reflection spectra of the II–VI compounds. A case in point is shown in the ZnO reflection anomaly of Fig. 4(a), where, from a comparison of reflectivity minima, one observes an "impurity"-exciton line intensity comparable to that of the intrinsic exciton. In fact, the intensity of the line I_b is observed to be within an order of magnitude of the intrinsic-exciton intensity in a large number of ZnO crystals. Still another example of strong "impurity" exciton lines has been observed in the reflection spectra of CdSe and CdS platelets,[9,10] where bound-exciton peaks have been observed with intensities comparable to those of the intrinsic exciton reflection anomalies. In support of the experimental observations, and, in spite of our instinctive notions regarding line intensities, recent work has rather strikingly shown, on purely theoretical grounds, that it is reasonable to expect bound-exciton line intensities comparable to those of the intrinsic excitons in spectra of semiconducting solids.

The theory of "impurity" or defect absorption intensities in semiconductors has been studied by Rashba.[14] By use of the Fredholm method,[15] he finds that, if the absorption transition occurs at $k=0$ and if the discrete level associated with the impurity approaches the conduction band, the intensity of the absorption line increases. The explanation offered for this intensity behavior is that the optical excitation is not localized in the impurity but encompasses a number of neighboring lattice points of the host crystal. Hence, in the absorption process, light is absorbed by the entire region of the crystal consisting of the impurity and its surroundings.

In an attack on the particular problem of excitons which are weakly bound to localized "impurities," Rashba and Gurgenishvili[16] derived the following relation between the oscillator strength of the bound exciton F_d and the oscillator strength of the intrinsic excitons f_{ex}, using the effective-mass approximation

$$F_d = (E_0/|E|)^{3/2} f_{\mathrm{ex}}\,, \tag{1}$$

where $E_0 = (2h^2/m)(\pi/\Omega_0)^{2/3}$, E is the binding energy of the exciton to the impurity, m is the effective mass of the intrinsic exciton, and Ω_0 is the volume of the unit cell. If we now substitute the ZnO parameters for the line I_b (3669.66 Å) into Eq. (1), we find that F_d exceeds f_{ex} by more than four orders of magnitude $(F_d/f_{\mathrm{ex}} \gtrsim 10^4)$. Now let us assume an impurity concentration of $N_d \sim 10^{17}$ cm^3 (a plausible assumption for our platelet samples); let us also make the usually valid assumption of $N_{\mathrm{ex}} \approx 10^{22}$ for the intrinsic exciton concentration. From these assumptions, and the further assumption that the line intensities are equal to a simple product of density and oscillator strength $(I_d \approx N_d F_d)$, it is easy to see how "impurity" or bound exciton intensities which are within an order of magnitude of those of the intrinsic exciton lines can be realized [compare the I_b line strength with that of the intrinsic exciton, Fig. 4(a)]. An inspection of Eq. (1) reveals that, as the intrinsic exciton becomes more tightly bound to the associated center, the oscillator strength, and hence the intensity of the exciton complex line, should decrease as $(1/|E|)^{3/2}$, a fact which is nicely illustrated in a comparison of the I_h and I_g line intensities with that of I_b [see Fig. 4(a) or the I_d and I_5 lines of Fig. 5]. Note that the lines I_h and I_g, whose line strengths (as measured from reflectivity) are much less than that of I_b, appear to arise from exciton complexes in which the intrinsic exciton is much more energetically bound than is the exciton in the complex which gives rise to the line I_b; in particular, note that the lines I_h and I_g lie about 0.035 eV below the energy of exciton A (3653.42 Å), while the line I_b lies only 0.015 eV below the intrinsic exciton energy.

From the intrinsic exciton energies, a number of relevant parameters directly related to the band structure can be determined. Using the ground-state exciton energy $(A,\ n=1)$ and the first-excited-state energy $(A,\ n=2)$, and assuming the exciton has a hydrogen-like set of energy levels, the exciton binding energy can be calculated as follows:

$$h\nu_n = E_{\mathrm{gap}} - E_B/n^2\,,$$

where E_B is the exciton binding energy;

$$\therefore \quad E_B = \tfrac{4}{3} \times 0.0312 = 0.042 \text{ eV}\,.$$

At 1.2°K the energy gap is

$$E_{\mathrm{gap}} = 3.435 \text{ eV}\,.$$

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[14] E. I. Rashba, Opt. i Spektroskopiya 2, 508 (1957).

[15] W. V. Lovitt, *Linear Integral Equations* (Dover Publications, Inc., New York, 1950), 1st ed.

[16] E. I. Rashba and G. E. Gurgenishvili, Fiz. Tverd. Tela 4, 1029 (1962) [English transl.: Soviet Phys—Solid State 4, 759 (1962)].

The reduced exciton spherical mass can be estimated from the relation

$$E_B = e^4\mu/2\hbar^2\epsilon^2 = 13.6\mu/\epsilon^2 \text{ (eV)},$$

where ϵ is the low-frequency dielectric constant. The dielectric constants of ZnO are as follows[17]:

$$\epsilon_x = 8.47, \quad \epsilon_z = 8.84.$$

Therefore the reduced effective mass of the exciton is

$$\mu_x = 0.20 m_0,$$

where m_0 is the free-electron mass.

We have observed the diamagnetic shift of the $A(n=2)$ line to be approximately 3×10^{-4} eV at a field strength of 45 000 G for $H \| C$ and $E \perp C$. Assuming this to be the $2S$ state of the A exciton, the reduced exciton effective mass can be determined from the quadratic magnetic-field term calculated on the basis of the ellipsoidal model.[5]

$$14\sigma H_z^2 = 3\times10^{-4} \text{ eV},$$

where

$$\sigma = \tfrac{1}{4}(e^2/m_0c^2)\, a_0^2(1/\mu_x^3)\epsilon_x^2\eta .$$

Hence μ_x is found to be

$$\mu_x = 0.19 m_0,$$

in good agreement with that determined from the hydrogenic formula.

The effective Bohr radius is given by

$$a_0^1 = a_0(\epsilon_x/\mu_x)\eta^{1/2} = 22 \text{ Å}.$$

The spin-orbit interaction energy has been calculated by Herman *et al.*[18] for a number of the Group IV, III-V, and II-VI compounds, with fairly good agreement to experimental values. In the case of ZnO, one finds a value of +0.035 eV for the spin-orbit energy calculated from this method. However, if one tries to obtain the spin-orbit interaction energy from the quasicubic model,[19–21] which is given by the formula

$$\delta = \tfrac{1}{2}(2E_1+E_2) + \tfrac{1}{2}\left[E_2^2 - 2E_1(E_1+E_2)\right]^{1/2},$$

where E_1 is the energy difference between excitons A and B and E_2 is the energy difference between excitons B and C, a difficulty arises. In fact, one finds that δ is a complex number upon substitution of these energy differences into the above equation. Even if the line assignments of Ref. 1 are used, the spin-orbit interaction has a negative sign which is different from all the other II-VI compounds, and further has only a magnitude of 0.0087 eV. This leads one to investigate the origin of the quasi-cubic model. In this model it was assumed that only one term of the spherical harmonic expansion was important, thus only one parameter was needed. However, it should be pointed out that in ZnO the c/a ratio deviates appreciably from the ideal (1.60 compared to 1.63), which possibly would make more than one crystal field parameter necessary in order to describe the variation from the cubic field. If this be the case, the present quasicubic model is not applicable.

V. CONCLUSIONS

From the present line assignments and polarization properties, it is concluded that the band symmetries and valence-band ordering in ZnO are the same as in other II-VI compounds. The spin-orbit splitting is positive; however, the magnitude of the spin-orbit splitting can only be approximated. A comparison of the exciton parameters obtained from the present work with those previously obtained by Thomas is given in Table II.

TABLE II. Some parameters of exciton and energy band of ZnO.

	Present work	Thomas[a]
E gap	3.435 eV	3.436 eV
A exciton		
Ground-state energy	3.3931 eV	3.3768 eV
Exciton binding energy	0.042 eV	0.059 eV
E_{AB}, $\Gamma_9-\Gamma_7$	0.040 eV	0.006 eV
E_{BC}, $\Gamma_7-\Gamma_7$	0.037 eV	0.038 eV
Exciton effective mass, Mex*	0.20 M_0	0.31 M_0
Exciton Bohr radius, a'_0	22 Å	14 Å
LO phonon energy	0.072[b], 0.073[c]	
TO phonon energy	0.054[b], 0.051[c]	
Dielectric constant	$\epsilon_x=8.47$, $\epsilon_z=8.84$[d]	
Refractive index	$n=2.0$[e]	

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