The above magnetic band-structure parameters were also used to fit experimental measurements of dI/dH versus H. Typical results are shown in Fig. 6 for reverse bias voltages of 150 and 170 mV.

An attempt was made to observe oscillations of dI/dH in the high-bias region, for which $(V-V_k)>\xi_v$. A low-current diode was used in order to obtain high reverse bias voltages at acceptable power dissipation levels. The results for dI/dH versus V are shown in Fig. 7. According to the discussion in Sec. I in connection with Fig. 1, the period of the oscillations should increase abruptly as the transition is made from the low-bias case [process (1)] to the high-bias case [process (3)]. That no such discontinuous change in period is observed implies either that the high-bias region was never actually attained or that the amplitude of the expected oscillations is below the sensitivity of the instrumentation.

ACKNOWLEDGMENTS

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Contribution of Excitons to the Edge Luminescence in Zinc Oxide

R. L. WEIHER AND W. C. TAIT
Central Research Laboratories, 3M Company, Saint Paul, Minnesota

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The photoluminescence of "pure" ZnO at 77°K has been investigated. Multiple-emission maxima, both "intrinsic" and "extrinsic," have been observed in the near ultraviolet. Narrow emission bands (half-widths ≤ 3 Å) near 3690 Å are ascribed to the annihilation of bound (impurity) excitons. A broad asymmetrical band (half-width ≈ 22 Å) near 3747 Å is shown to be closely characterized by theory of the annihilation of free (intrinsic) excitons with the simultaneous emission of longitudinal optical phonons. Multiphonon emission bands, separated by approximately the energy of the longitudinal optical phonon, are observed at longer wavelengths. An emission band near 3677 Å is suggested to originate from the "direct" annihilation of free (intrinsic) excitons.

I. INTRODUCTION

THE luminescence of zinc oxide (ZnO) has been the subject of numerous papers.[1–6] The excellent review article on ZnO by Heiland, Mollwo, and Stockmann[1] in 1959 includes a comprehensive summary of the luminescence of ZnO to that data. More recently, several investigations[2–5] have reported on extensive studies of single crystals which have added much to our knowledge on this subject.

The photoluminescence and cathodoluminescence of ZnO near room temperature can be generally characterized by two broad bands, one in the near ultraviolet (uv) and one in the "green" portion of the spectrum. At lower temperatures, both of these broad bands exhibit structure in the form of series of nearly overlapping maxima. The energy separation between adjacent maxima has frequently led investigators to propose that the emission results from the recombination of electron-hole pairs, possibly through exciton states, accompanied by the emission of transverse and/or longitudinal phonons.[1,3] The exact assignment of these maxima, however, has not yet been made. In addition, numerous narrow (line half-widths ≤ 0.1 Å) absorption and emission lines in the near uv have been observed at near liquid-helium temperature.[4,5] These narrow lines have been shown by Reynolds, Litton, and Collins[5] to originate from bound-exciton complexes.

Andress[3] has thoroughly investigated the cathodoluminescence of ZnO crystals near liquid-nitrogen temperature. We refer the reader to that article,[3] or elsewhere,[1,6] for a discussion of the broad-band "green" emission. It was shown by Andress[3] that the near-uv emission at 90°K is nearly plane-polarized with the electric vector perpendicular to the c axis of the wurtzite crystal structure of ZnO. The ratio of intensities for emission polarized parallel and perpendicular to c axis was found experimentally to be

$$I_{||}/I_{\perp}=\exp(-0.035/kT) \tag{1}$$

near 90°K. This observation is consistent with theoret-

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[1] G. Heiland, E. Mollwo, and F. Stockmann, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 8.

[2] B. Andress and E. Mollwo, Naturwiss. **46**, 623 (1959).

[3] B. Andress, Z. Physik **170**, 1 (1962).

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

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

[6] P. S. Litvinowa, Zh. Eksperim. i Teor. Fiz. **27**, 636 (1949).

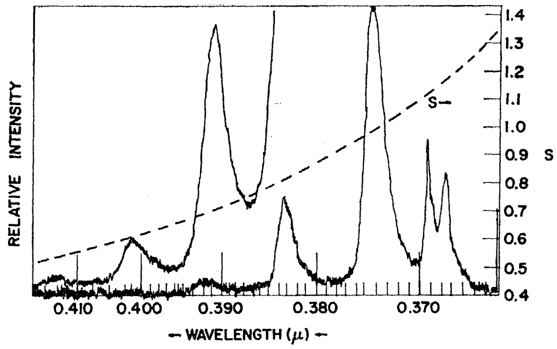

FIG. 1. Photoluminescence spectra of a typical "pure" ZnO crystal at 77°K. Note the nonlinear wavelength scale. The relative peak intensities are not corrected for the spectral sensitivity of the analyzing apparatus. The S factor, discussed in the text, is shown by the dashed line.

ical predictions by Hopfield[7] that the emission from wurtzite-type crystals should consist of two series of lines separated in energy by the valence-band splittings with appropriate polarizations, and with an intensity ratio of the form of Eq. (1). Optical studies[4,8] of the exciton structure of ZnO have placed the minimum of the conduction band and the maximum of the valence band near $k=0$ and have shown that the valence-band splittings are consistent with the model of Hopfield[7] and Birman.[9]

Because we will be frequently discussing the results of Andress,[3] a brief summary of his data on undoped crystals at 90°K will be given here. For $\mathbf{E}\perp c$, the primary (most intense) maximum was observed at 3.363 eV (3685 Å) with a small shoulder near 3.403 eV (3642 Å). Secondary (less intense) maxima were observed to commence at approximately 3.321 eV (3732 Å) and continue to lower photon energies. The energy spacings of the secondary maxima were approximately 0.074 eV (average), and the relative peak intensities decreased with each successive maximum going to lower photon energies. The positions of these maxima were shown to be dependent upon crystal doping and temperature. We should point out that the above observations are not unique to the work of Andress[3] and that similar results have been observed by others.

The purpose of this paper is to report on an investigation of the near-uv photoluminescence of relatively pure ZnO crystals grown in our laboratory. Data are presented which show maxima in the same wavelength range as that discussed above, but with less overlap of the maxima, narrower bandwidths, asymmetrical band shapes, and variations in relative peak intensities not previously reported. The origins of the various near-uv maxima are identified in terms of the "indirect" annihilation of free (intrinsic) excitons with the simultaneous emission of one or more longitudinal optical (LO) phonons, annihilation of bound (impurity) exciton complexes, and possibly the "direct" annihilation of free excitons.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

All the data presented here were obtained from single crystals of ZnO at 77°K. The crystals were immersed directly in liquid nitrogen to maintain a constant and uniform temperature. A common silvered quartz Dewar was used with flat unsilvered windows on the bottom, on which the crystals rested, to facilitate excitation by short-wavelength ultraviolet. The excitation source was a high-pressure xenon lamp appropriately filtered to produce a broad band of uv excitation in the wavelength range 2500 to 3500 Å.

The photoluminescence was collected with a lens at an angle of about 30° to the direction of excitation and analyzed with a Perkin-Elmer recording spectrophotometer (Model 350) operating in a single-beam mode and modified for external readout. The spectral sensitivity of the complete analysis system (lenses, monochromator, detector, etc.) was calibrated by replacing the luminescent sample with a small tungsten source of known temperature and spectral emissivity and scanning the wavelength range of interest. A wavelength-dependent factor S, defined as the ratio of the spectral intensity of the known source to the relative detector signal, was then calculated. Most of the data included herein have been corrected to relative spectral intensities by taking the product of the S values and measured signals. Uncorrected data are so noted in the text. The wavelength of the analyzing system was periodically calibrated with a hydrogen source to maintain a wavelength uncertainty of less than 1 Å. The spectral resolution of the monochromator was varied from sample to sample, depending upon the intensity of the photoluminescence; it was, in general, so narrow in comparison to the emission band as to have no influence on the observed shape. The resolution for strong photoluminescent samples was typically 1 Å or less. Estimates of the photoluminescence energy efficiencies were obtained by a method similar to that for obtaining the spectral sensitivity S, but included other factors such as amplifier gain, resolution (monochromator slit width), excitation intensity, etc.

All of the data were obtained from natural-grown crystal faces. The crystals were grown in this laboratory from the vapor phase with various growth conditions (carrier gas, temperature, etc.). The impurity content of the crystals used, as determined from emission spectroscopy, was on the order of 1 to 10 ppm. However, a fair correlation was obtained between purity and emission intensity, such that the most intense crystals contained only about 1-ppm impurities.

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[7] J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

[8] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Phys. Rev. **143**, 512 (1966).

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

Because some of the samples used were thin crystal plates, a significant contribution to the emission was observed from reflections off the back surfaces. This is especially notable because the contribution from the back-surface reflections is a strong function of wavelength because of the varying opacity of the crystals with wavelength in the region of the absorption edge and to the crystal thickness. It was shown that the contribution can markedly alter the observed shape of the emission bands and relative peak intensities in the vicinity of the absorption edge. This contribution was nearly eliminated by blackening the back sides of the crystals to reduce these reflections. Reabsorption of emission was considered negligible at wavelengths greater than 3700 Å because of the relatively weak absorption in this region and because the excitation radiation is absorbed in a very thin layer. However, reabsorption and a varying reflectivity from the front surface of the crystals undoubtably alter the emission bands in the region of high absorption at shorter wavelengths (3700 Å and shorter). The relative magnitudes of the shortest-wavelength bands, included herein, must be considered in doubt.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The photoluminescence of many crystals was measured, and it was soon obvious that not only the magnitude of the emission varied dramatically from crystal to crystal, but that the relative intensities of the various maxima in the near uv varied also. A typical emission spectrum of an as-grown crystal is shown in Fig. 1. Although the photon energies of equivalent maxima varied slightly from crystal to crystal, they generally occurred near 3677, 3690, 3747, 3834, 3917, 4010, and 4102 Å. These values are in close agreement with those of other investigators[1,3] in view of the reported dependence upon temperature and impurity content.[3]

The power-conversion efficiency of the integrated bands in the near uv was estimated to be approximately 1–2% for so-called "good" crystals. Estimates of values lower than 0.001% were obtained for other so-called "weak" crystals. The corresponding "green" emission for "good" crystals was very weak—the peak intensity in the near uv was greater than 50 times the peak intensity in the "green." Although not always true, the "weak" crystals generally emitted strongly in the "green" or visible. Similar observations were noted by Reynolds, Litton, and Collins,[5] although these observations are not consistent with data on doped crystals by Andress.[3]

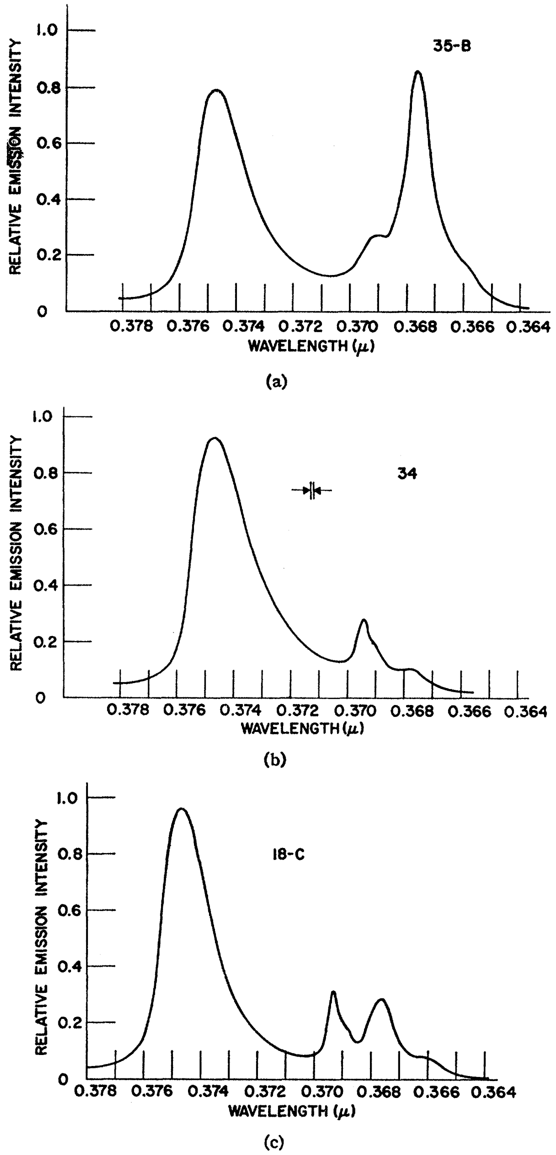

FIG. 2. Photoluminescence spectra of ZnO crystals demonstrating the "apparent extrinsic" nature of some of the bands in the near uv. (a) Spectrum showing an intense 3676 Å band and a nearly unobservable band near 3690 Å. (b) Spectrum showing a relatively weak band near 3695 Å and a nearly unobservable 3677 Å band. (c) Spectrum showing both bands with similar, but weak, intensity.

The emission spectra shown in Fig. 1 exhibit several subtle features not observed with "weak" crystals. The individual maxima are well defined with very little overlap of adjacent maxima. Some of the overlap in "weak" crystals is undoubtably due to poor resolution as a consequence of the lower intensity. However, even in certain "good" crystals, considerable overlap was observed with a resolution small compared to the emission bandwidth. Strains and other crystal imperfections may well account for some of the band broadening. It is also noted in Fig. 1 that some of the emission bands exhibit a definite asymmetry. In fact, the band near 3747 Å and all the additional bands at longer wavelengths show a definite asymmetry, being skewed towards shorter wavelengths. These bands, we feel, are associated with the "indirect" annihilation of free (intrinsic) excitons with simultaneous emission of one

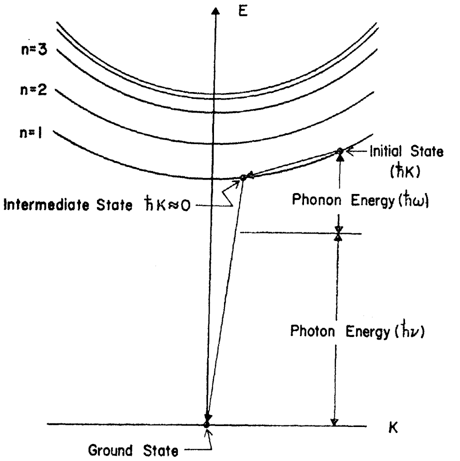

FIG. 3. E_K diagram for excitons depicting the process of "indirect" annihilation of free excitons. The arrows depict the annihilation of an exciton with energy E_K and the momentum $\hbar K$ by the emission of a photon of energy $h\nu$ and a LO phonon of energy $\hbar\omega$ to the "ground state" represented as a point.

or more LO phonons and will be more fully discussed later in this section.

It was noted in Sec. I that the most intense emission band (primary) of undoped ZnO observed by Andress[3] occurred near 3685 Å. Although similar emission spectra were observed on several crystals, these were not typical of the crystals investigated. In most of the crystals investigated, the emission band near 3747 Å was by far the most intense, as can be seen with reference again to Fig. 1. The peak intensities of the shorter-wavelength bands near 3677 and 3690 Å, relative to the 3747 Å band, varied over a wide range from crystal to crystal. For example, these bands were nearly unobservable in some crystals, as seen in Figs. 2(a)–2(c). In Fig. 2, (a) depicts a relatively intense 3676 Å band and a nearly unobservable band near 3690 Å; (b) shows a relatively weak band near 3695 Å and a nearly unobservable 3677 Å band; and (c) shows both bands with similar intensity but weak. It is to be noted in (b) and (c) that the band near 3695 Å may consist of several narrower bands. Although the shape and relative intensities of the fine structure near 3695 Å again vary from crystal to crystal, at least two narrow discrete bands have been observed with half-widths of approximately 3 Å.[10] We conclude that the discrete bands near 3695 Å are clearly indicative of bound (impurity) excitons because of the narrow half-widths, apparent extrinsic behavior, and because there are no known intrinsic states in ZnO with this energy separation. Although it may be coincidental, bound-exciton absorption and emission near liquid-helium temperature have been previously observed in the vicinity of 3690 Å.[4,5] The observed intensity variations of the band near 3677 Å also point towards an "extrinsic" origin, although reabsorption of the emission and condition of the surface of the crystal may be very significant at this wavelength. Additional comments on the nature of this band are made later in this paper.

It was seen earlier that both the emission band near 3747 Å and the bands at longer wavelengths exhibit appreciable asymmetrical skewing towards shorter wavelengths. We attribute the 3747 Å band to the indirect annihilation of intrinsic excitons with the simultaneous emission of one LO phonon. We attribute the longer-wavelength maxima to higher-order phonon processes because they exhibit similar band asymmetry and are spaced in energy approximately one LO phonon part. The maximum near 3834 Å should then result from a process similar to the above, but involving the simultaneous emission of two LO phonons. Continued to longer wavelengths, the order of the phonon process should increase by 1 with each successive maximum.

A schematic of this process involving one LO phonon is depicted in Fig. 3. The inverse process, namely, the simultaneous absorption of a photon and LO phonon, was calculated from second-order perturbation theory by Dietz, Hopfield, and Thomas[11] and was successfully applied by the same authors to account for the long-wavelength absorption edge in ZnO. Segall[12] has recently pointed out the importance of including the higher excited states ($n=2$, 3, 4, etc., in Fig. 3) as intermediate and initial states in explaining the long-wavelength absorption edge in CdTe. If the momentum of the photon is small compared to the momentum of the exciton ($\hbar K$) and is neglected, it can be shown that the emission probability ω_e per unit time per unit volume is given by

$$\omega_e = A(\nu) N_K [N_P(K)+1](n_\nu+1)\,, \tag{2}$$

where N_K denotes the number of excitons per state with momentum $\hbar K$, $N_P(K)$ denotes the number of phonons per state with momentum also equal to $\hbar K$, and n_ν is the number of photons per mode. The product of $A(\nu)N_P(K)(\sqrt{\epsilon})c^{-1}$ is the absorption coefficient for the inverse process and has been previously given by Dietz *et al.*[11] and Segall.[12] For the relatively low excitation rates used here, the quantity n_ν should be small compared to unity. Also, because of the relatively large LO phonon energy of ZnO ($\simeq 0.072$ eV) and low temperature of the measurements, $N_P(K)$ is small compared to unity.

A simple form of the relative emission as a function of photon energy can be obtained from Eq. (2), Ref. 11, and Ref. 12, if the initial and intermediate states are restricted to the lowest-lying exciton band.[13] Assuming a Boltzmann distribution of excitons in this band, one obtains

$$I(\mathrm{rel}) = u_1{}^2 (E_{x1} - h\nu)^{-2} (E_K - E_{x1})^{-1/2} \exp(-E_K/kT)\,, \tag{3}$$

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[10] The measured half-widths of these lines is probably resolution-limited, so that they may be even more narrow than 3 Å.

[11] R. E. Dietz, J. J. Hopfield, and D. G. Thomas, J. Appl. Phys. Suppl. **32**, 2282 (1961).

[12] B. Segall, Phys. Rev. **150**, 734 (1966).

[13] This restriction is not of major consequence in this case, as will be seen later in the discussion.

where $h\nu$ is the emitted photon energy, E_{x1} is the energy of the lowest-lying exciton near $K=0$, and E_K is equal to the sum of the photon and LO phonon energy $(h\nu+\hbar\omega)$. The term u_l is given by

$$u_l=\left[1+\frac{a_0^2\epsilon_s^2Mm_0^2(E_K-E_{x1})}{2h^2m_h^2}\right]^{-2}-\left[1+\frac{a_0^2\epsilon_s^2Mm_0^2(E_K-E_{x1})}{2h^2m_e^2}\right]^{-2},\qquad(4)$$

where a_0 is the first Bohr radius of the hydrogen atom, ϵ_s is the appropriate low-frequency dielectric constant, M is the mass of the exciton $(M=m_e+m_h)$, m_0 is the rest mass of an electron, h is Planck's constant $(h=2\pi\hbar)$, and m_e and m_h are the effective masses of the electrons and holes, respectively. The analysis of data can be further simplified by letting $E_K-E_{x1}=\Delta E$ in Eqs. (3) and (4). Equation (3) is then reduced to the form

$$I'(\mathrm{rel})=u_l^2(\hbar\omega-\Delta E)^{-2}\Delta E^{-1/2}\exp(-\Delta E/kT).\qquad(5)$$

One can readily calculate the relative emission as a function of ΔE, with the only parameter yet to be determined being the energy of the lowest-lying exciton E_{x1}.

The values of the other constants are not known exactly; the least certain are the electron and hole effective masses. We chose the values of $m_e=0.3m_0$ and $m_h=0.6m_0$ as best estimates.[14,15] The energy of the LO phonon is known with more certainty to be $\hbar\omega=0.072$ eV.[16] The square of the static-dielectric constant was calculated from the product of the anisotropic values[16] to be 65.9. These values alone govern the relative shape of the emission band, but its position is arbitrary on the photon-energy abscissa. Comparison with experiment was obtained by placing the calculated curve [from Eq. (5)] at a position on the photon-energy abscissa which gave the most reasonable fit.

Comparison of experimental curves with that calculated, as discussed above, is shown in Fig. 4. The solid line depicts the theoretical curve, and the symbols depict data from three different crystals. It is seen that the theoretical curve quite accurately describes the general shape of the observed emission band. The consequence of restricting the initial and intermediate states to only the lowest-lying exciton band is not serious in this case. Although the emission is somewhat changed by including the higher excited states, the renormalization and arbitrary photon-energy–abscissa method used tend to minimize this change, and the resulting calculated curves are not much different from those shown in Fig. 4. Theoretical curves were calculated which included the higher states as intermediate states, using the procedures outlined by Segall.[12] These calculated emission curves, after normalization, differed from Fig. 4 only in that the photon energy of the peak emission shifted slightly to higher energy (by approximately 0.001 eV), and the half-width of the band was increased by approximately 10%.

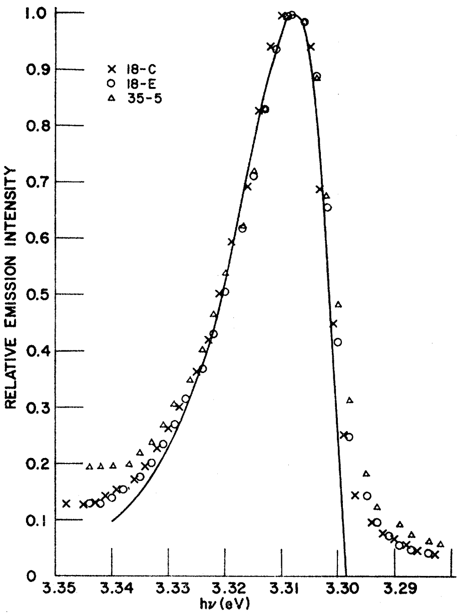

FIG. 4. A plot of the relative emission intensity for the band near 3747 Å as a function of photon energy showing the comparison between experiment and theory for the "indirect" annihilation of free excitons. The marks represent normalized data from three different ZnO crystals, and the solid line is the theoretical curve calculated from Eq. (5). The theoretical curve has been placed at a position on the photon-energy abscissa to obtain the best fit.

The photon energy at which the theoretical curve goes to zero is, by definition, $h\nu=E_{x1}-\hbar\omega$, from which one can calculate the energy of the lowest-lying exciton E_{x1} near $K=0$. The value we calculate is 3.3705 eV, which is in excellent agreement with the value of 3.3708 eV for the lowest-lying exciton (A) band reported by Thomas.[4] Park *et al.*[8] have recently proposed a modification of the line assignments given by Thomas.[4] They propose that the line near 3.3708 eV is a bound (impurity) exciton labeled I_b and that the lowest-lying free exciton is the band labeled B by Thomas.[4] Our work supports the line assignments given by Thomas.[4]

The possibility that the 3747 Å originates from the indirect annihilation of bound excitons near 3677 Å with the emission of LO phonons is precluded from the band shape of the 3747 Å band. Bound excitons are discrete states having essentially no kinetic energy, so that the emission occurs in very narrow bands. Haynes[17] has shown that the phonon-assisted annihilation of bound excitons results in essentially a replica of the direct annihilation of the bound excitons broadened only slightly by the dispersion of the phonons

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[14] M. Cardona, J. Phys. Chem. Solids **24**, 1543 (1963).

[15] R. L. Weiher, Phys. Rev. **152**, 736 (1966).

[16] E. C. Heltemes and H. L. Swinney, J. Appl. Phys. **38**, 2387 (1967).

[17] J. R. Haynes, Phys. Rev. Letters **4**, 361 (1960).

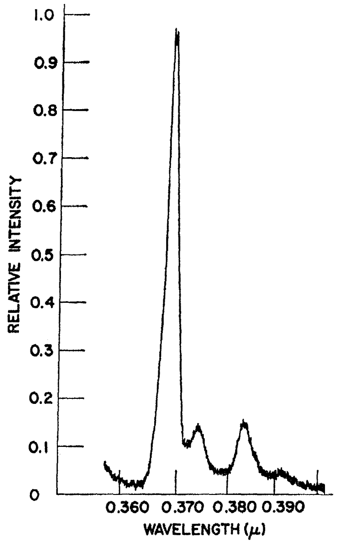

FIG. 5. An extreme example showing the dependence of the emission band near 3690 Å on the ratio of intensities of the two-phonon band (near 3830 Å) to the one-phonon band (near 3740 Å).

involved. It is clearly seen that the 3747 Å band is not a replica of the 3677 Å band.

One could also postulate that the emission band near 3747 Å results from the recombination of free holes (electrons) and trapped electrons (holes). However, Hopfield[7] has shown that the spectral shape of the emission band for this model is $E^{1/2}\exp(-E/kT)$ because of the Boltzmann distribution of the free carriers. The fact that the experimental data closely fit Eq. (3), which can be approximated by $E^{3/2}\exp(-E/kT)$, clearly supports the proposed exciton model over the trapped-carrier model.

It is to be noted that the previously discussed maximum near 3677 Å occurs very near the calculated value of E_{x1} obtained in the preceding analysis. This observation strongly suggests that this maximum originates from the direct annihilation of free (intrinsic) excitons. The intensity variation of this band may well result from strong reabsorption of emission, imperfections, and surface conditions. Similar variations can be observed in the emission due to the decay of free (intrinsic) excitons in CdS; this has been briefly discussed by Thomas and Hopfield.[18]

Attempts to determine the relative peak intensities of the phonon-assisted bands were only partially successful because they varied greatly from crystal to crystal. The relative intensities of these bands appeared to be dependent upon the existence and strengths of the shorter-wavelength bands. In the near absence of these shorter-wavelength bands, the ratio of the peak intensities of the two-phonon (3834 Å) band to the one-phonon (3747 Å) band was observed quite consistently to be between 0.25 and 0.30. However, even in these crystals, the relative intensities of the higher-order phonon-assisted bands were not at fixed ratios. An extreme example of the effect of the shorter-wavelength bands on the phonon-assisted bands was observed in a particular crystal which exhibited an intense band near 3690 Å and is shown in Fig. 5. It is seen in this extreme example that the peak intensity of the two-phonon (3834 Å) band appears to be actually greater than that of the one-phonon (3747 Å) band. This observation is not expected in the proposed model and requires further study. However, if our assignments of the various emission bands are correct, this observation indicates some sort of coupling between the intrinsic and extrinsic processes not understood at this time.

In conclusion, we have presented experimental data on the near-uv luminescence of "pure" ZnO. We have assigned the various emission bands to mechanisms pertaining to the annihilation of excitons. It was seen that the theory of "indirect" annihilation of free excitons quite adequately describes the broad emission band near 3747 Å. Because of the nature and position of the narrow emission bands near 3690 Å, we have ascribed them to the annihilation of bound (impurity) excitons. The assignment of the 3677 Å band to the "direct" annihilation of free (intrinsic) excitons is consistent with the energy-band model of Thomas[4] and with the analysis of the "indirect" annihilation of free excitons proposed for the 3747 Å emission band.

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