Excitonic effects in ZnTe at E_0 and E_1 gaps studied by wavelength-modulated reflectivity spectroscopy

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Wavelength-modulated reflectivity spectra of ZnTe have been studied in the energy range from 2.0 to 5.6 eV at 10 and 77 K and also above 77 up to 400 K to clarify the excitonic effects on the optical transitions at the E_0 and E_1 gaps. The derivative spectra of the real and imaginary parts of the dielectric constant were obtained by a Kramers-Kronig analysis of the measured spectrum. At 10 K, the spectrum of the E_1 gap with an M_1-critical-point symmetry can be explained by the Kane model. At high temperatures above some 250 K, the derivative spectrum of the E_0 gap can be reproduced by a line shape which is an admixture of the line shapes for the M_0 and M_1 critical points and that of the E_1 gap by the M_1 plus M_2 shapes. It means that the spectrum of ZnTe at the M_0 (or M_1) critical point can be interpreted by an M_0 (or M_1) plus exciton model. If we assume that the gap energy varies linearly with temperature, the temperature coefficient can be deduced to 5.6×10^{-4} and 6.5×10^{-4} eV/K for the E_0 and E_1 gaps, respectively.

I. INTRODUCTION

The Coulomb interaction between electron and hole affects significantly the reflectivity spectrum of semiconductors, in particular, of II-VI compounds with partially ionic chemical bonds. This excitonic effect is very drastic for the transition at the lowest gap, the E_0 gap, which is known, in general, to be at an M_0-type symmetry: Sharp exciton lines due to electron-hole bound states occur below the E_0-gap energy.[1] As to the next lowest gap, the E_1 gap, at the M_1 critical point, the so-called saddle point, there has been strong argument concerning the existence of an exciton bound state.[2,3] Its first complete theoretical calculation has been carried out by Kane,[4] using an adiabatic approximation. The Kane model was applied by Petroff and Balkanski[5] to ZnTe, ZnSe, CdTe, and HgTe by studying a spectrum of ϵ_2, the imaginary part of the complex dielectric constant $\epsilon=\epsilon_1+i\epsilon_2$, which was deduced from a reflectivity spectrum measured at 10 K, indicating the existence of the saddle-point exciton. More recently, optical-modulation techniques of various kinds have been proved to be a powerful tool both for the identification of a critical point and for the determination of its precise transition energy.[6] Wavelength-modulation spectroscopy gives the most straightforward interpretation than any other more widely used modulation spectroscopies such as electroreflectance and thermoreflectance spectroscopies.[7] And very recently, wavelength-modulation spectra have been reported on ZnSe and ZnS in visible and vacuum ultraviolet regions at temperatures from 19 to 300 K.[8,9] However, there have been no corresponding studies on ZnTe.

ZnTe is a p-type semiconductor with the widest forbidden gap among commonly used p-type semiconductors. Its chemical bond is partially ionic; it is a less ionic compound than ZnO and CdS, on which sharp excitonic line spectra have been reported to lie below the E_0 gap.[1] Optical properties of ZnTe have been studied mainly by reflectivity spectra,[4,10-13] and recently by modulation spectra including electroreflectance and thermoreflectance spectra,[14-17] at given temperatures. However, to our knowledge, there are no detailed studies of excitonic effects on the reflectivity spectrum over a wide temperature range in ZnTe.

This paper is concerned with wavelength-modulated reflectivity spectra of ZnTe in the energy range from 2 to 5.6 eV at 10 and 77 K and at various temperatures from 77 to 400 K. In order to compare the experiments with theoretical predictions, derivative spectra of the real part and the imaginary part of the complex dielectric constant were calculated by the Kramers-Kronig (KK) analysis. Changes in transition energy of the E_0 and E_1 gaps with temperature will be determined from the derivative spectrum.

II. EXPERIMENTAL

Single crystals of ZnTe were grown from the melt. The cleaved (110) face, with its opposite face ground to minimize back reflection, was used. The experimental setup for recording a modulation spectrum is shown in Fig. 1. The wavelength modulation was performed by vibrating the entrance slit of a Nihon-Kogaku P250 monochromator. An iodine-tungsten-filament lamp served as a light source in a wavelength region

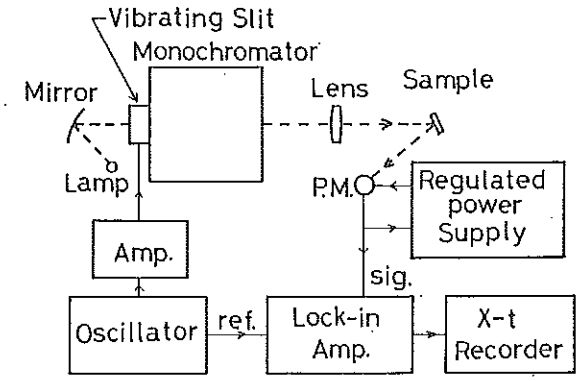


FIG. 1. Block diagram for measurements of the wavelength-modulated reflectivity spectrum.

above 390 or 360 nm, and a deuterium lamp in a short-wavelength region. A commonly used phase-sensitive detection system was utilized to measure the modulation spectrum. Reflected light from the sample surface was detected by an RCA 1P28 photomultiplier, where the supplied high voltage was so controlled that the dc signal remained unchanged with changes in wavelength. The ac signal was detected by a PAR HR-8 lock-in amplifier, and its output signal, which was proportional to the modulated reflectivity $\Delta R/R$, was recorded by an X-t recorder. In our system spurious signals due to structures in the spectrum of incident light or in the spectral response of the photomultiplier are superimposed on the true signal due to ZnTe. The spurious signals consisted of slowly changing backgrounds and strong structures in a region from 450 to 390 nm. In this region, no signals due to ZnTe are expected to be observed, as one can see in the reflectivity spectrum of ZnTe. To eliminate them, the spectrum of incident light was measured by the same setup and then subtracted from the measured spectrum. A reflectivity spectrum was determined as a ratio of incident light intensity to reflected light intensity, and both intensities were measured separately. Absolute reflectivities were obtained by the assumption that the reflectivity at the E_1 or E_2 peak was coincident with the previously reported value by Walter *et al.*[11] or by Freeouf.[12] Higher temperatures above 77 K were achieved by supplying power to a heater that was fixed to a sample holder. The temperature was carefully controlled within 1 K.

III. RESULTS

The wavelength-modulated reflectivity spectrum changes drastically in shape with changes in temperature. The spectra at 10, 77, 200, 300, and 400 K are presented in Fig. 2, together

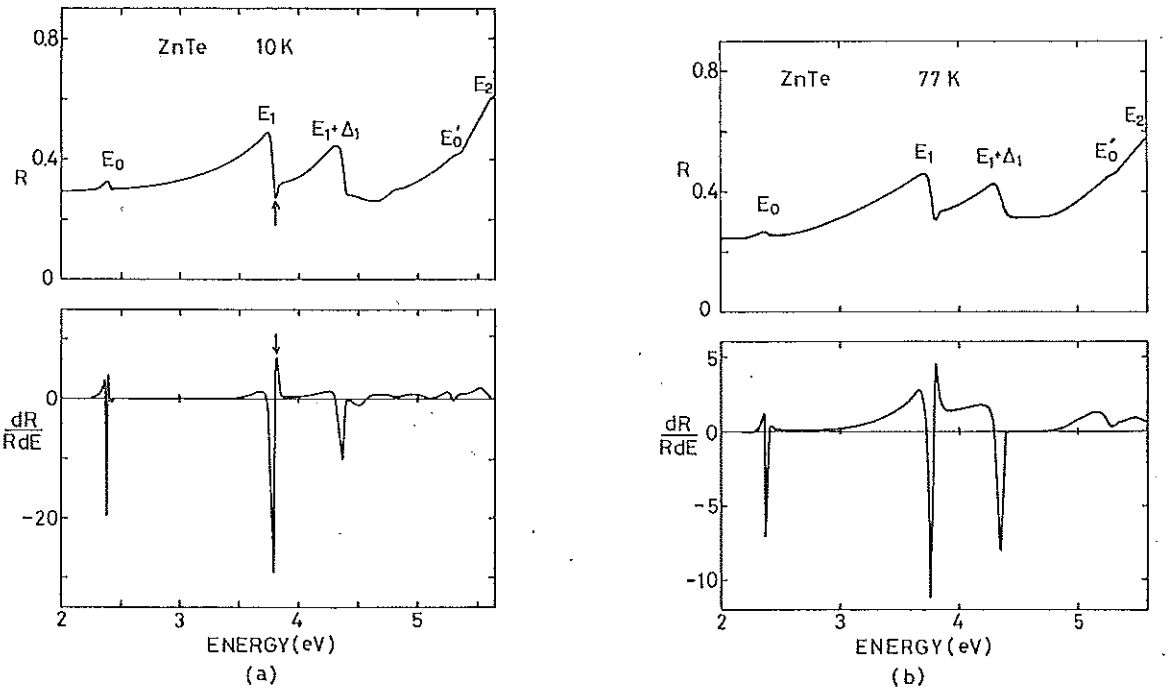


FIG. 2. (*Continued*)

FIG. 2. Reflectivity spectra and wavelength-modulated reflectivity spectra of ZnTe at (a) 10, (b) 77, (c) 200, (c) 300, and (e) 400 K.

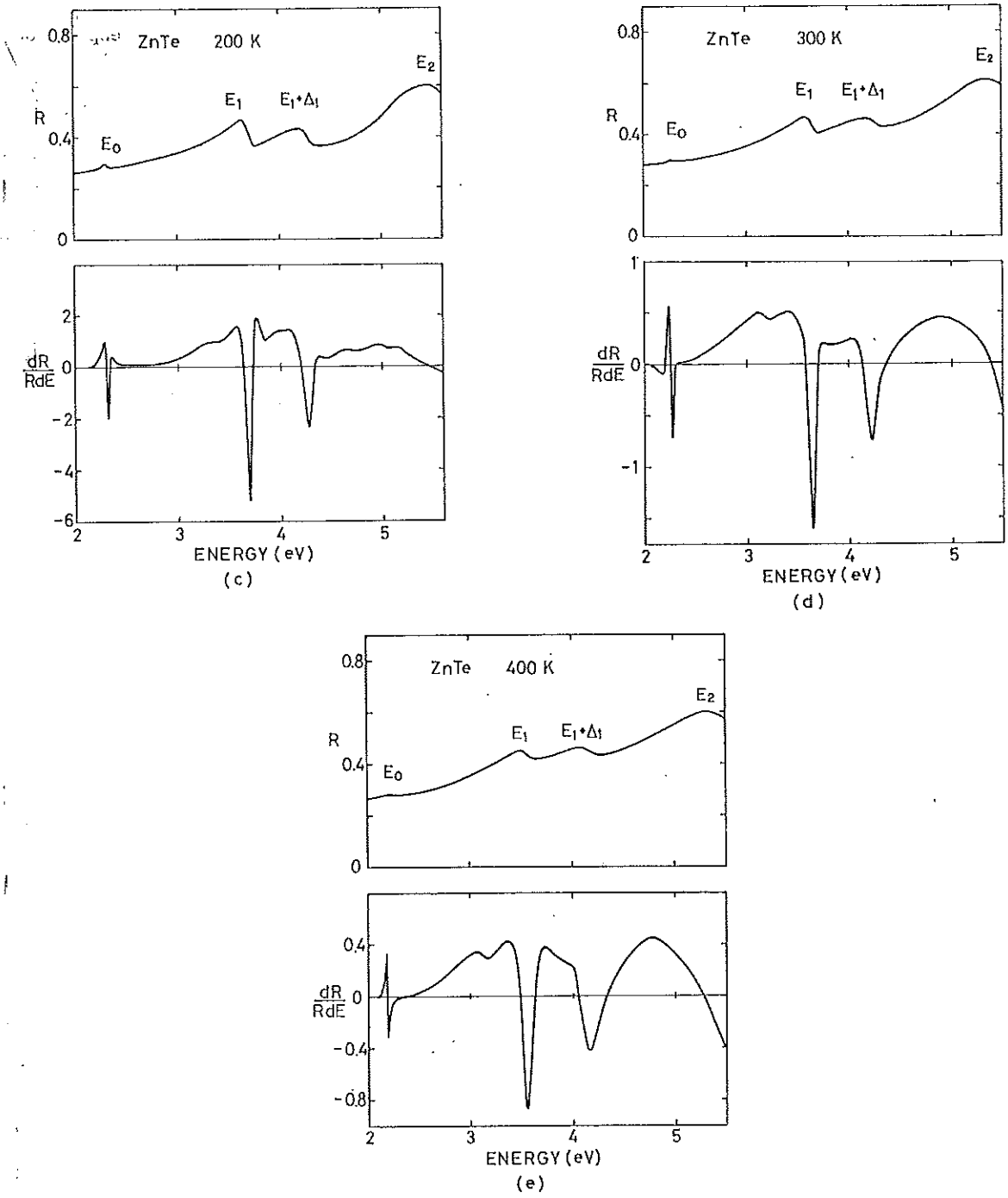


FIG. 2. (*Continued*)

with the corresponding reflectivity spectrum. Structures near 2.2, 3.7, 4.5, and 5.5 eV are called E_0, E_1, $E_1+\Delta_1$, and E_2, respectively, after the notations given by Cardona and Greenaway.[10] An additional weak structure was observed near 5.3 eV, at temperatures below 77 K, which was called E_0'. At lower temperatures, the modulation spectrum at the E_0 gap is approximately of an absorption type, while it becomes of a dispersion type at higher temperatures above some 250 K. The modulation spectrum at the E_1 gap and its spin-orbit-split-off gap is of an absorption type at above 300 K, but at lower temperatures it is asymmetric in shape due to the presence of a sharp peak on a higher-energy side, which is caused by the sharp dip in the reflectivity spec-

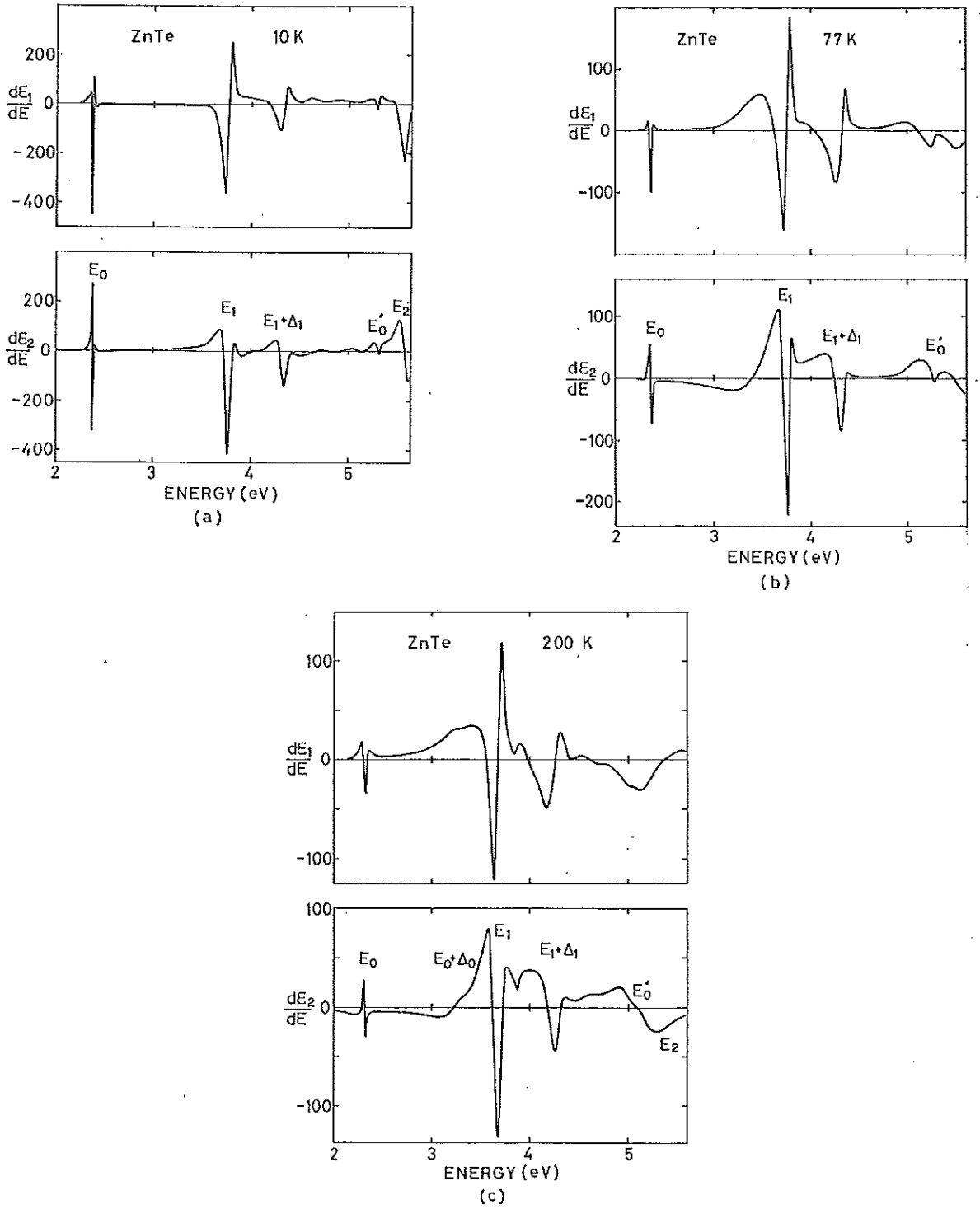
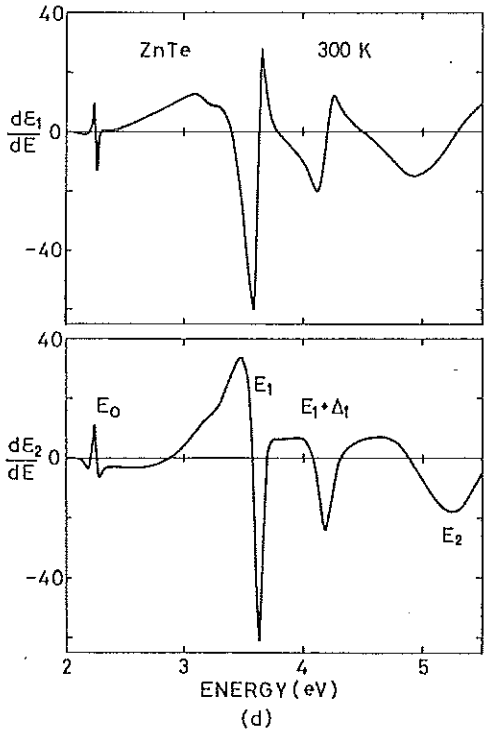


FIG. 3. Derivative spectra $d\epsilon_1/dE$ and $d\epsilon_2/dE$ of ZnTe at (a) 10, (b) 77, (c) 200, (d) 300, and (e) 400 K.

trum or the sharp drop in reflectivity at a higher-energy side.

Figure 3 shows the derivative spectra of $d\epsilon_1/dE$ and $d\epsilon_2/dE$ at 10, 77, 200, 300, and 400 K, calculated from the measured modulation spectrum in terms of the KK analysis. The structure at the E_0 gap is extremely sharp in shape at 10 K. Extended spectra for 10 K are presented in Fig. 4. A comparison of Fig. 2 with Figs. 3 and 4 reveals that the E_0 peak in the $d\epsilon_1/dE$ spectrum



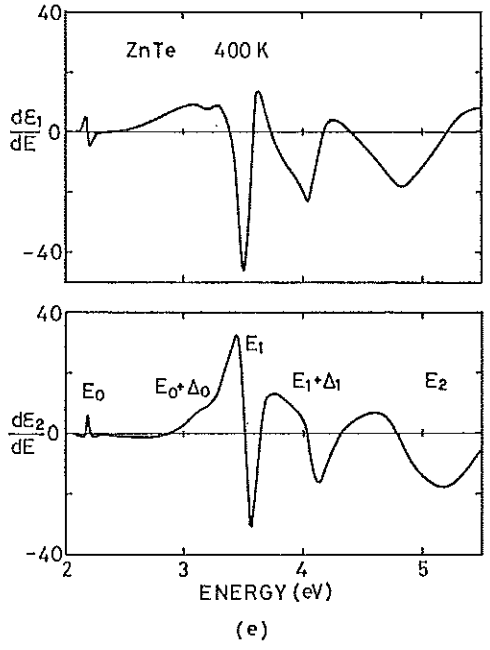


FIG. 3. (*Continued*)

is similar in shape to that in the reflectivity spectrum.

IV. DISCUSSION

The derivatives $d\epsilon_1/dE$ and $d\epsilon_2/dE$ were calculated from the modulation spectrum with an aid of a KK computer program developed by Kreiger *et al.*[18] For the KK transformation, reflectivities and their derivatives are required in the whole energy range. As to the reflectivity outside the photon energy range investigated in the present work, data of Freeouf[12] were used from 5.6 to 17.3 eV, and then it was extrapolated to zero at 25 eV, according to $R=CE^{-4}$ or CE^{-2}, where R is the reflectivity and E the photon energy.[19] Reflectivities in the region below 2.0 eV were calculated by using refractive indices reported previously[20] with an assumption of no absorption in this region. Figure 3 shows that the $d\epsilon_2/dE$ spectrum has nonpositive values in the region between the E_1- and E_2-gap energies. This nonpositive background may be partly caused by the incorrect absolute value of the reflectivity in the region investigated in the present work, and partly by the inadequate correction in the reflectivity and its derivative above 5.6 eV. The high-energy-extrapolation function might be responsible for the positive background, too. As one can see from Fig. 3, this background, however, does not at all alter the line shape of both the E_0 and E_1 structures. Therefore, we did

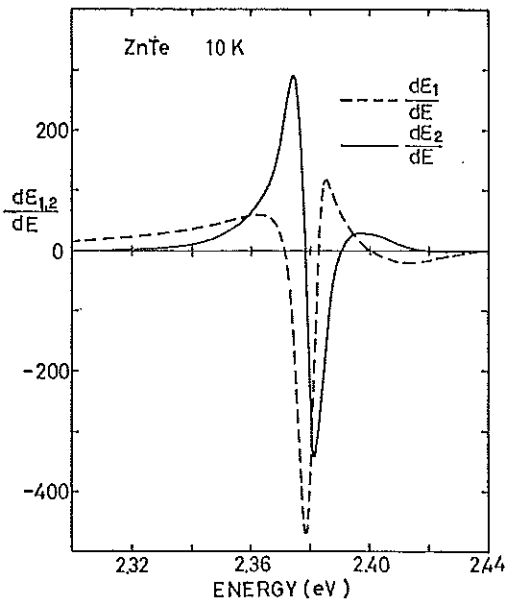


FIG. 4. Derivative spectra $d\epsilon_1/dE$ and $d\epsilon_2/dE$ of ZnTe at the E_0 gap.

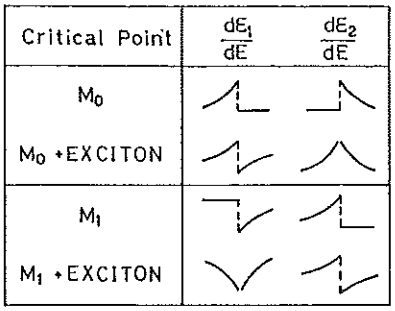


FIG. 5. Line shapes of the real and imaginary parts of the dielectric constant at the M_0 and M_1 critical points with and without exciton effects.

not make further efforts to correct it.

The spectrum of ZnTe changes in shape drastically with changes in temperature, which indicates that there are strong exciton effects on all structures investigated in this work. After theoretical treatments developed by Toyozawa *et al.*,[21] an exciton at an M_i critical point produces a line shape for ϵ_2 which is an admixture of the line shapes for M_i and M_{i+1} critical points ($M_4 \equiv M_0$). The derivative spectra $d\epsilon_1/dE$ and $d\epsilon_2/dE$ have been schematically summarized by Welkowsky and Braunstein.[22] For the readers' convenience, the spectra for the M_0 and M_1 critical points without and with exciton effects are presented in Fig. 5. The Kane model has yielded an ϵ_2 spectrum of ZnTe.[5] The spectrum and its numerical derivative are presented in Fig. 6, together with the $d\epsilon_2/dE$ spectrum measured at 10 K.

As is evident from Figs. 2–4 the modulation spectrum for the E_0 gap at 10 and 77 K is approximately of the Lorentzian type. This result may be quite reasonable, since it is well accepted that a sharp line in the E_0-gap region is due to a hydrogenlike bound exciton. Its line shape, however, deviates slightly from the ideal Lorentzian shape, and, furthermore, it has been reported that the line shape differed from one crystal to another.[13] Spatial dispersion may have effects on the shape of the exciton transition.[1,23] At present, the interpretation of the line shape has not established yet.

With a rise in temperature, the line shape of the structure at the E_0 gap changes gradually; $d\epsilon_1/dE$ becomes a dispersion type and $d\epsilon_2/dE$ a negative peak type. A comparison of the experimental spectra with those presented in Fig. 5 indicates that the observed line shape can be explained by the M_0+ exciton model at temperatures above about 250 K.

The structure at the E_1 gap at 10 K can be reproduced fairly well by the Kane model, as shown in Fig. 6. On the assumption that the low-energy zero cross provides an exciton transition energy, called E_{1ex}, and a high-energy zero cross, a band-to-band-transition energy, i.e., E_1, the energy of the E_1 gap is determined to be 3.8 eV and the binding energy of the E_1 exciton is deduced to be 0.13 eV at 10 K. On the other hand, at high temperatures, $d\epsilon_1/dE$ is of an absorption type and $d\epsilon_2/dE$ of a dispersion type; they are explained by the M_1 + exciton model. The same interpretation holds for the $E_1 + \Delta_1$ gap. The existence of the M_i exciton has identified also in the case of III–V compounds, for which Welkowsky and Braunstein[22] have verified that the spectrum of the E_1 gap can be interpreted by the M_1 + exciton model at 80 K.

The transition energies of the E_0 and E_1 gaps are determined from the $d\epsilon_2/dE$ spectrum as a function of temperature as presented in Fig. 7, where the energies of the maximum and the minimum, called P_1 and P_2, respectively, and the zero cross Z are plotted for the E_0 gap, and the low- and high-energy zero crosses, Z_1 and Z_2, respectively, and the minimum P are plotted for the E_1 gap. The M_i + exciton model demonstrates that the energy of the band-to-band

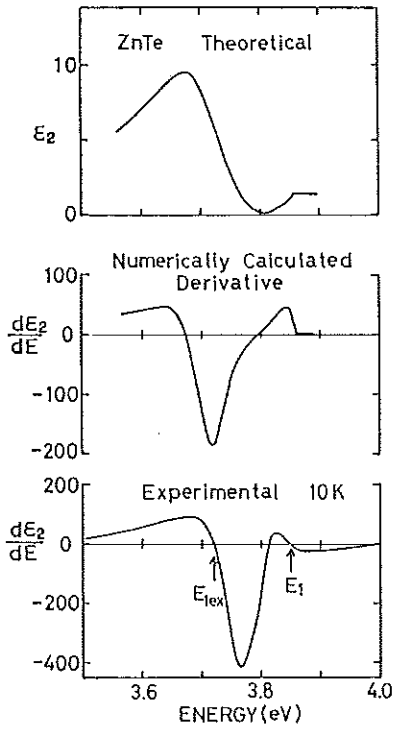
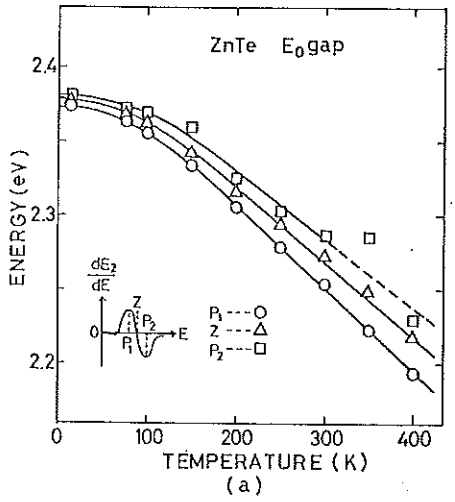


FIG. 6. ϵ_2 spectra of ZnTe at the E_1 gap calculated by Petroff and Balkansky (see Ref. 5) and its numerically calculated derivative spectrum and experimental derivative spectrum at 10 K.



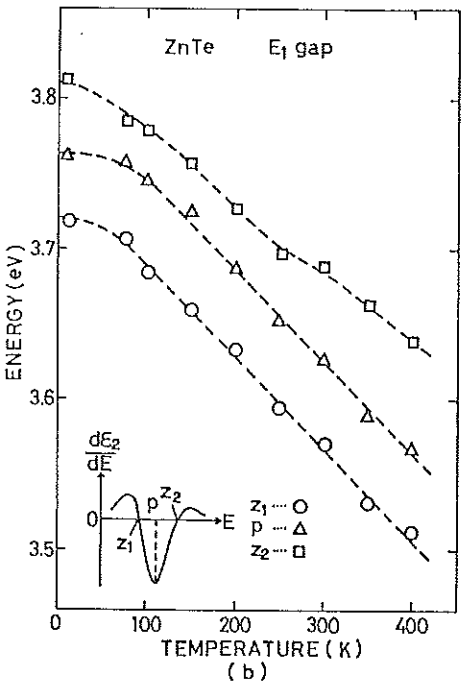


FIG. 7. The (a) E_0- and (b) E_1-gap energies of ZnTe as a function of temperatures.

transition is given by the energy of the maximum (P_1) for the E_0 gap and it is given by the energy of the zero cross (Z_1) for the E_1 gap. This model works well at high temperatures, but at low temperatures, a bound exciton state appears for both the E_0 and E_1 gaps, and the presence of the exciton creates changes in the line shape. Therefore, at present, we cannot determine which of the energies P_1, Z, and P_2 corresponds to the exact band-to-band-transition energy for the E_0 gap, although it can be said that at higher temperatures, probably above 300 K, P_1 may correspond to the E_0 gap. The temperature coefficient of the transition energy of the E_0 gap is 5.6×10^{-4} eV/K for P_1 and 5.1×10^{-4} eV/K for Z, whereas that of the E_1 gap is 6.5×10^{-4} eV/K for both Z_1 and P. The value for E_0 is in good agreement with the theoretically predicted value of 5.1×10^{-4} eV/K.[24] The spin-orbit splitting Δ_1 is estimated to be 0.57 eV, which is in good agreement with the reported values.[11,25]

For the E_2 gap, the $d\epsilon_1/dE$ spectrum is of a dispersion type and the $d\epsilon_2/dE$ spectrum is of an absorption type. The critical-point analysis suggests that the line shapes can be reproduced by the M_2 + exciton model. However, electronic structures calculated theoretically by Chelikowsky and Cohen[26] for zinc-blende-type III-V and II-VI compounds indicate that the largest peak E_2 in the reflectivity spectrum arises from a well-defined plateau region near the special point in the Brillouin zone for all compounds under study. Therefore, further studies should be carried out to identify the E_2 peak. It is noted that a numerically calculated $d\epsilon_2/dE$ spectrum by using the ϵ_2 spectrum by Walter *et al.*,[11] which was calculated in the one-electron frame free of exciton effects, cannot reproduce the observed line shape at all.

The reflectivity spectrum of Cardona and Greenaway[10] exhibits a weak structure, called E_0', lying at 4.82 eV at 77 K, whereas our observation shows that the structure lie at 5.3 eV, instead. The theoretical calculation of the reflectivity spectrum or the ϵ_2 spectrum for ZnTe suggests that a $K(8\text{-}9)$ transition with an M_0-type symmetry lies at 5.26 eV. This transition may be responsible for the 5.3-eV peak.

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