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Electron Energy-Loss Spectra of CdS, CdSe, and CdTe

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A study has been made of the electron energy-loss spectra of the three II*B*-VI*A* compounds, CdS, CdSe, and CdTe. These spectra have been obtained by both electron reflection and electron transmission. The electron-reflection measurements were made over an energy-loss range of 0 to 50 eV on single crystals cleaved in an ultrahigh vacuum atmosphere. Changes in these spectra were then observed as the surface was slowly contaminated. The electron-transmission measurements were made using as-grown platelets or thin films. The spectra of these compounds consist of a series of low-lying peaks between 0 and 9 eV associated with interband transitions from the valence band and a peak between 12 and 15 eV associated with an interband transition from the *d* band. There also exists a peak between 9 and 12 eV and another between 15 and 19 eV. The former has been tentatively identified as a surface-plasmon peak, the latter as a bulk plasmon. These results are compared with optical reflectivity measurements and induced-electron-emission measurements.

I. INTRODUCTION

During the past decade several experimental studies have been reported on the higher-energy band structure of the II*B*-VI*A* compounds, CdS, CdSe, and CdTe. These studies have involved several different techniques, among them ultraviolet reflectivity, transmission electron spectroscopy, and photoemission. Ultraviolet reflectivity studies have been reported by Cardona and Harbeke,[1] Balkanski and Petroff,[2] and Walker and Osantowski[3] for CdS; by Cardona and Harbeke[1] and Balkanski and Petroff[2] for CdSe; and Cardona and Greenaway[4] for CdTe. Transmission electron energy-loss (TEEL) measurements have been reported by Pradal and Gout[5] and by Tomoda and Mannami[6] for CdS and CdSe, and by Gauthé[7] and Pradal and Gout[5] for CdTe. Photoemission measurements on CdS have been made by Kindig and Spicer[8] and on CdSe and CdTe by Shay and Spicer.[9] Finally electron spectroscopy for chemical analysis (ESCA) results have been reported for all three compounds by Vesely and Langer.[10] There is general agreement between the reflectivity measurements; however one finds considerable disagreement between the transmission electron energy-loss measurements of Tomoda and Mannami and those of Pradal and Gout and Gauthé.

The results reported in this present study were obtained from electron spectroscopy measurements, both reflection and transmission. Reflection electron energy-loss (REEL) measurements were made on CdS, CdSe, and CdTe bulk single crystals. TEEL measurements have been made on thin platelets of CdS and thin films of CdTe. Previous energy-loss measurements on these compounds are TEEL measurements on thin films. Furthermore no measurements on CdTe are reported by Tomoda and Mannami. TEEL measurements are useful in that the energy-loss curve obtained in this way is proportional to $\mathrm{Im}(1/\epsilon)$. Thus such measurements can readily be compared to optical reflectivity values. REEL measurements on the other hand can be made on cleaved single-crystal surfaces and thus should be representative of the bulk semiconductor. Furthermore by making measurements in ultrahigh vacuum both before and after contamination by controlled leaks, the effect of surface condition can be ascertained and surface properties studied.

II. EXPERIMENTAL

The electron reflectivity apparatus is shown schematically in Fig. 1. It consists of an electron gun, sample mount and cleaver assembly, energy analyzer, and electron multiplier. These components are housed in an ultrahigh-vacuum chamber employing ion pumping. This chamber is sealed by metal gaskets and can be baked. After bakeout at 250 °C, pressures in the low 10^{-10} Torr range are possible. Immediately inside the vacuum chanber is a pillbox made of conetic foil which was used to shield the electron system from stray magnetic fields.

The electron gun is a standard, commercially available gun utilizing electrostatic focusing and deflection. This gun was used to produce a monoenergetic electron beam of energy 200 to 1500 eV.

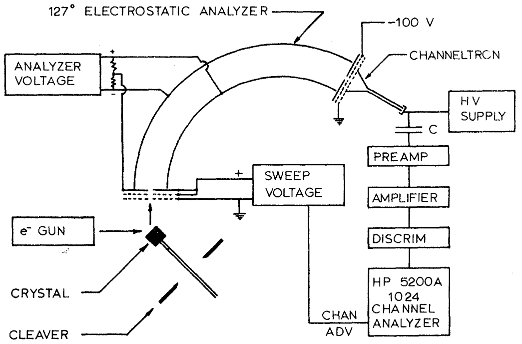

FIG. 1. Schematic of the apparatus used for the REEL measurements.

Measurements were ordinarily made at 200, 500, and 1000 eV. The energy analyzer is an electrostatic 127° type described by Hughes and Rojansky.[11] The particular analyzer used here had a mean radius of 1.65 in., a plate separation of 0.375 in., and a plate width of 1.5 in. The slit widths used were slightly over 0.002 in. which should produce a theoretical resolution $(\Delta E/E)$ of 0.0015. The experimentally recorded resolution was 0.0025. The detector used was a Bendix Channeltron Multiplier which was shielded against collection of stray electrons. The crystals were mounted in a pressure-type holder which could be moved from outside the vacuum chamber by a bellows-sealed manipulator. This manipulator allowed for motion in the x, y, and z planes. The z motion was used to retract the crystal for cleaving and the x and y motions for positioning the cleaved face in the electron beam. The cleaver consisted of two razor blades, one of which could be moved by a linear-motion feed through from outside the chamber.

Electrons leaving the gun at energy E_0 were scattered from the crystal surface at an angle of 90° with respect to the incident beam direction. Before entering the energy analyzer they were accelerated in a plane-parallel field in order to restore any energy lost in interaction with the sample. The energy analyzer could thus be set to pass electrons of energy E_0 and energy distributions were recorded by sweeping the acceleration voltage. In this way any nonlinearity in the energy analyzer could be avoided. Upon leaving the analyzer the electrons were detected by the electron multiplier. The output pulses were amplified, shaped, and recorded using a Hewlett-Packard model No. 5200A multichannel analyzer in the multiscalar mode.

Electron-energy distributions were obtained by sweeping the accelerator plates using the channel advance voltage from the multichannel analyzer. This voltage was amplified using a Kepco model No. ABC 200 programmable power supply. Three sweep ranges have been used in this study: 0–25.6, 0–51.2, and 0–102.4 eV. The choice of these sweep ranges provides the x axis of the multichannel display with 0.025, 0.05 and 0.1 eV/channel, respectively. Sweep speeds corresponding to approximately 50 msec/channel were used in this study. Data acquisition was continued until sufficient data were collected to provide a good statistical representation. Run times vary from 10 min to several hours depending on beam current, rate of surface changes, etc.

The experimental apparatus used to make the TEEL measurements has been discussed in detail elsewhere.[12] These measurements were made using a 10-keV monoenergetic electron beam and an energy analyzer capable of resolving peaks separated by 0.75 eV. The scattered electrons were collected in a small solid angle about the beam direction.

The samples used in these measurements were as follows. The TEEL measurements on CdS were made using as-grown platelets. The platelets chosen were very thin ($<0.2\ \mu$) and were mounted so that the c axis and the plane of the platelet were perpendicular to the beam direction. The TEEL measurements on CdTe were made using thin films prepared by flash evaporation. The films were less than 500 Å thick and were mounted at 90° to the direction of the beam. The samples used for the REEL measurements were all oriented single crystals. They were cleaved in an ultrahigh vacuum chamber (5×10^{-10} Torr) immediately prior to the measurements. The cleavage plane used in the case of CdS and CdSe was the $(10\bar{1}0)$ plane and in the case of CdTe the (011) plane.

Since the initial surface studied was obtained by cleaving in the mid 10^{-10} Torr range, it was assumed to be a "clean" surface. Characterization of this surface by other techniques such as low-energy electron diffraction (LEED) was not possible in this case. The surface was successfully contaminated by allowing ambient room air into the chamber through a desiccant and a leak valve. No attempt was made to selectively contaminate with specific gases.

III. RESULTS

The energy-loss spectra obtained from the REEL measurements on CdS, CdSe, and CdTe are shown in Fig. 2. These are three representative spectra of the many which were recorded. Certain details are clearer on some spectra taken on a particular sample as compared to others. One observes from these curves the similarity in the spectra of the three compounds. Each has a series of low-lying peaks between 0 and 10 eV, a

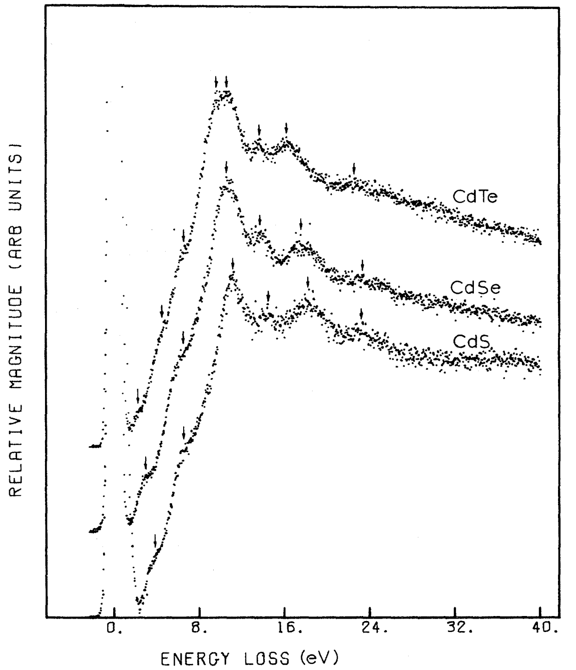

FIG. 2. A comparison of the REEL spectra obtained from CdS, CdSe, and CdTe. All were measured using a clean sample surface and 500-eV electrons.

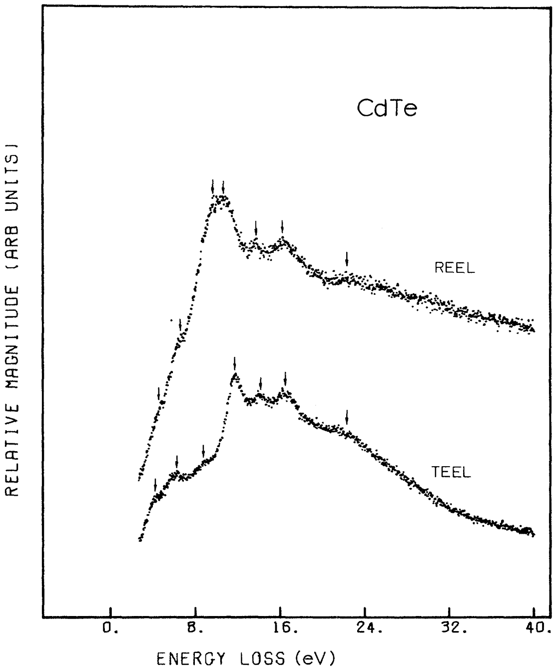

FIG. 4. Comparison of the REEL and TEEL spectra of CdTe.

sharp dominant peak around 11 eV, and peaks near 14, 17, and 22 eV. Some spectra also show a rather broad weak peak in the region of 34 to 36 eV. Comparisons between the REEL and TEEL measurements on CdS and CdTe are shown in Figs. 3 and 4, respectively. There is general agreement between the REEL and TEEL results and in fact considerable similarity between the TEEL spectra themselves. One clear distinction between these two however is the sharp TEEL peak in CdTe at 11.8 eV.

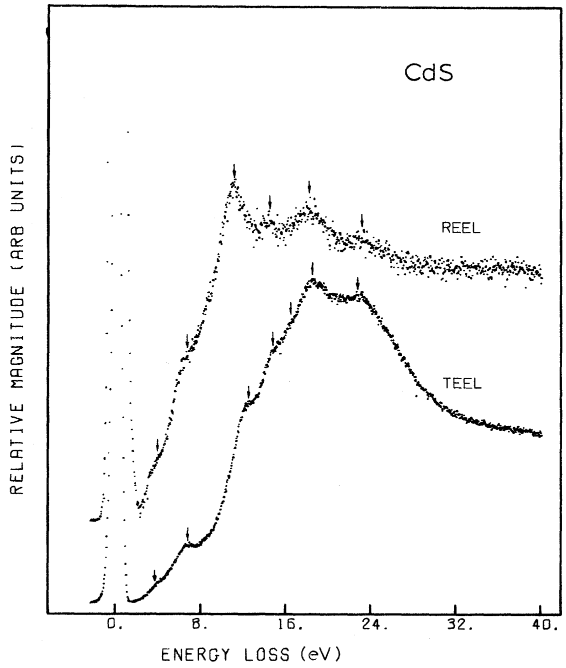

FIG. 3. Comparison of the REEL and TEEL spectra of CdS.

The variation of the REEL spectra of CdS, CdSe, and CdTe with various stages of surface contamination is shown in Figs. 5–7, respectively. The curves in these figures were taken using 500-eV electrons. The A curve of Figs. 5 and 7 was taken immediately after cleavage at 5×10^{-10} Torr; the B curve after a 1-h exposure at a pressure of 1×10^{-7} Torr of dry ambient air. The C curve of Fig. 5 was taken after exposure at a pressure of 1×10^{-4} Torr; that of Fig. 7 after exposure at a pressure of 1×10^{-6} Torr. The A curve of Fig. 6 was taken immediately after cleaving at 5×10^{-10} Torr; curves B and C were taken at a pressure of 1×10^{-9} Torr at one day intervals after cleavage. Curves D and E were recorded after an exposure to dry ambient air at a pressure of 1×10^{-4} Torr. One notes that, in general, the peak near 11 eV in each spectrum decreases in height with respect to the 17-eV peak. Eventually the 11-eV peak nearly disappears and the 17-eV peak dominates. Spectra were also taken with different incident beam energies. The variation in REEL spectra with beam energy from

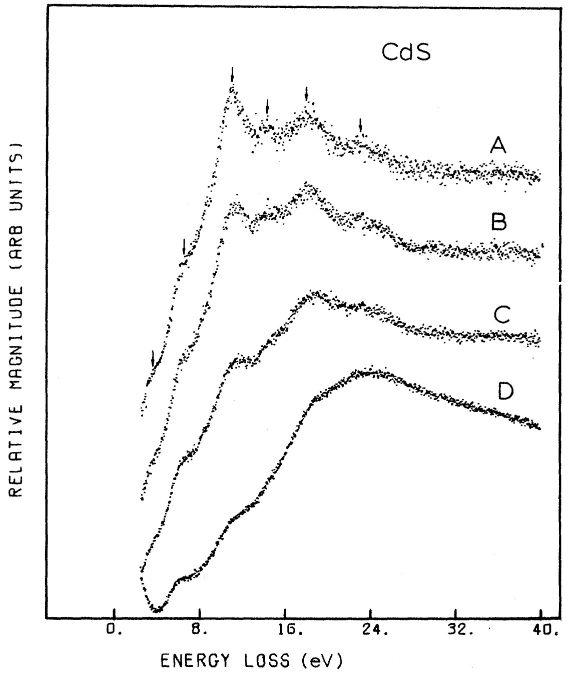

FIG. 5. Variation in the REEL spectrum of CdS as the surface becomes contaminated. Curve A was taken immediately after cleaving of 5×10^{-10} Torr; curve B was taken after a pressure rise to 1×10^{-7} Torr; curve C after a 12-h exposure to a pressure of 1×10^{-4} Torr and curve D after 48-h exposure to 1×10^{-4} Torr.

a clean CdTe surface is shown in Fig. 8. One notes here that the 200-eV spectra indicate a 9.6-eV peak which is higher than the 10.7-eV peak. As the beam energy is increased and the bulk material is probed more deeply, the 9.6-eV peak drops in height and the 10.7-eV peak dominates. As can be seen from Fig. 7, this same peak, i.e., 9.6 eV, decreases as the surface contaminates.

IV. DISCUSSION

The various energy-loss values obtained in this study have been recorded along with previous measurements in Table I. In discussing these results we shall consider the low-lying peaks at energies less than 9 eV, the peak at 14 eV, the peak around 11 eV, and then the 17-eV peak.

The low-lying peaks in CdS occur at 4.0 and 6.8 eV in the REEL spectra and at 3.9 and 6.9 eV in the TEEL spectra. These peaks agree quite well with those obtained by Tomoda and Mannami[6] on CdS films. In order to compare these with ultraviolet reflectivity values a Kramers–Kronig analysis must be performed on the reflectivity data and the energy-loss function calculated. Such a calculation has been performed on CdS by Balkanski and Petroff[2] who finds peaks in $\mathrm{Im}(1/\epsilon)$ near 6.2 and 9.0 eV. Since this is a region of large interband absorption the above peaks can be associated with interband transitions from the valence band. The low-lying peaks in CdSe occur at 3.0 and 6.4 eV for the REEL measurements. These are in agreement with the TEEL measurements of Tomoda and Mannami. The only $\mathrm{Im}(1/\epsilon)$ values available are those given in the paper by Tomoda and Mannami. Their curve indicates a peak in $\mathrm{Im}(1/\epsilon)$ at 6.5 eV; the lower 3-eV peak cannot be checked since their curve does not extend below 4 eV. These two peaks in CdSe are also ascribed to interband transitions from the valence band. The low-lying peaks in CdTe appear at 2.2, 4.5, and 6.5 eV in the REEL spectra and at 2.4, 4.2, and 6.1 eV in the TEEL spectrum. This compound was not investigated by Tomoda and Mannami and no $\mathrm{Im}(1/\epsilon)$ curve exists. Examination of the reflectivity spectra however indicates strong absorption in this range and thus these peaks are probably interband transitions associated with the valence band. There is also a peak at 10.7 eV in the REEL spectrum and a peak at 11.8 eV in the TEEL spectrum. The TEEL peak is a very dominant one. We suggest that these two peaks result from the same source,

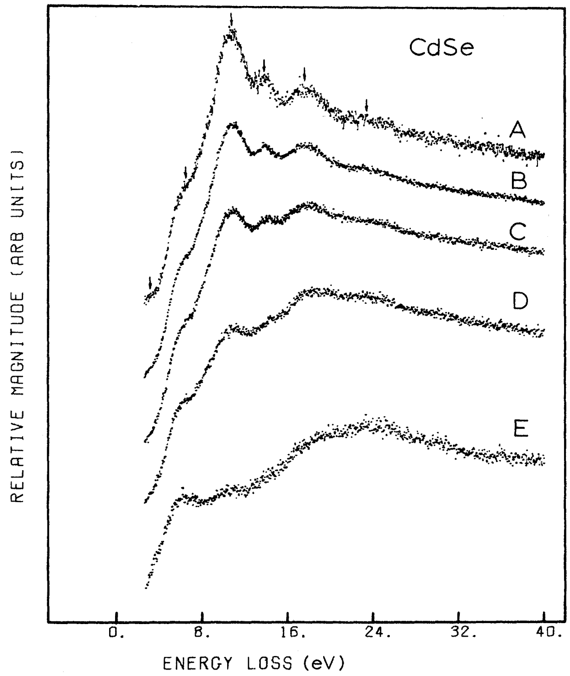

FIG. 6. Variation in the REEL spectrum of CdSe as the surface becomes contaminated. Curve A was taken immediately after cleaving at 5×10^{-10} Torr; curve B, 1 day later at 1×10^{-9} Torr; curve C, 2 days later at 1×10^{-9} Torr; curve D after a 12-h exposure to a pressure of 1×10^{-4} Torr; and curve E after 48-h exposure to 1×10^{-4} Torr.

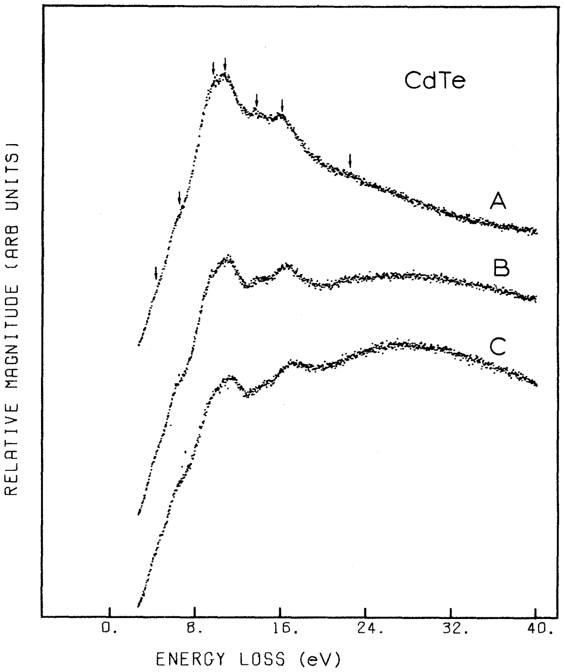

FIG. 7. Variation in the REEL spectrum of CdTe as the surface becomes contaminated. Curve A was taken immediately after cleaving at 5×10^{-10} Torr; curve B after a 1-h exposure to a pressure of 10^{-7} Torr; and curve C after a 12-h exposure to a pressure of 10^{-6} Torr.

the REEL peak being shifted to lower energies as a result of the 9.6-eV peak present in that spectrum. This peak is also believed to be due to an interband transition from the valence band.

The peaks seen at 14.4, 13.8, and 13.6 eV in the REEL spectra of CdS, CdSe, and CdTe, respectively, are believed due to the transition from the Cd *d* band. This assignment is based upon the ESCA measurements made by Vesely and Langer.[10] They place the *d* bands of CdS, CdSe, and CdTe at 11.4, 11.5, and 11.1 eV, respectively, below the Fermi level. Assuming that the final state for the *d*-band transition is the *L* point in the conduction band, these values would correspond to transition energies of 14.8, 14.3, and 13.5 eV.

The peaks at 11.2, 10.7, and 9.6 eV in the three compounds CdS, CdSe, and CdTe, respectively, are seen to be surface dependent. This is evident from the rate of change in the spectra with surface contamination as shown in Figs. 5–7 and the variation of peak height with beam energy shown in Fig. 8. Furthermore these peaks are seen to be very small shoulders in the TEEL spectra where no attempt was made to maintain clean surface conditions. These observations would indicate that this peak in each of the spectra of the three compounds is associated with a surface phenomenon such as the excitation of a surface plasmon at a vacuum-semiconductor interface.

As a test of this one can use the information available from a Kramers–Kronig analysis of optical reflectivity data. Such an analysis yields the dielectric constants ϵ_1 and ϵ_2. Ritchie[13] has shown that near a surface-plasmon resonance the real part of the dielectric constant ϵ_1 equals -1. Balkanski and Petroff[2] have calculated the dielectric constants for CdS and find that ϵ_1 is near a value of -1 only in the region of 10 eV. Almassy and Hengehold[14] performed a Kramers–Kronig analysis of optical data from CdS and also found this to be true. Thus, on the basis of the surface dependence of this peak and the behavior of ϵ_1, the above assignment is reasonable in the case of CdS. Even though the behavior of ϵ_1 is not available for CdSe and CdTe this same assignment appears reasonable due to the marked similarity in the shape and behavior of the REEL spectra.

The remaining large peak in the REEL spectra occurs at 18.2 eV in CdS, 17.6 eV in CdSe, and 16.1 eV in CdTe. The corresponding peak in the TEEL spectra is at 18.6 eV in CdS and 16.4 eV in CdTe. The peak is not highly surface dependent and is rather dominant in both the REEL and TEEL spectra. This is particularly true when the sample surface has been sufficiently contaminated

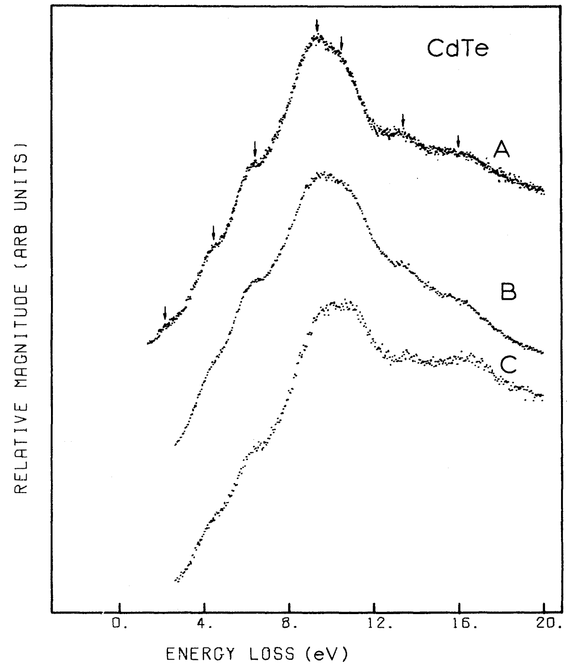

FIG. 8. Variation in the REEL spectrum of CdTe with incident electron energy. Curve A was recorded using 200-eV electrons; curve B using 500-eV electrons; and curve C using 1000-eV electrons.

so that the initially large surface-plasmon peak is reduced in size. Balkanski and Petroff[2] calculated the Im$(1/\epsilon)$ function from their optical reflectivity data and found that this function has a large peak at 18.6 eV for CdS and at 20.7 eV for CdSe. This peak occurs at an energy where the optical constants ϵ_1 and ϵ_2 are positive but near zero. The values given by Balkanski and Petroff are in close agreement with the electron energy-loss values in the case of CdS, but differ somewhat in the case of CdSe. This difference may result from the inaccuracies of the Kramers–Kronig inversion calculation. On the basis of these facts we have tentatively assigned this peak in the three compounds to a bulk plasma oscillation.

The band structure of these compounds indicates a valence band containing the two cation "*s*" electrons and the four anion "*p*" electrons. Below this band exists the "*d*" band containing the cation "*d*" electrons and a band containing the anion "*s*" electrons. It is presently believed that the anion "*s*" band lies below the "*d*" band although no firm experimental evidence for this exists. Below these bands lies the inner ionic core. Raether[15] considers the plasma-oscillation condition for a solid with three bands, i.e., in this case the conduction band, valence band, and *d* band. He gives the following expression for the experimentally observed plasma frequency ω_p:

$$\omega_p^2 = \frac{\omega_{p0}^2 + (e^2/m\epsilon_0)\sum f_{cd}}{1 - \delta\epsilon_1^b} .$$

Here ω_{p0} is the free-electron plasma frequency of the valence-band electrons, ϵ_0 is the permittivity of free space, f_{cd} is the oscillator-strength coupling of the *d* electrons to the valence band and $\delta\epsilon_1^b$ is the contribution of the *d* electrons to the static dielectric constant. Thus, if there is a *d*-band to valence-band coupling, one expects the observed plasma frequency to be enhanced over the free-electron value. The term $\delta\epsilon_1^b$, representing the screening contribution of the *d* electrons to ϵ_1 can be either positive or negative depending on whether the applied frequency ω is greater than or less than the *d*-band transition frequency. If $\delta\epsilon_1^b$ is positive, the $(1-\delta\epsilon_1^b)$ term in the denominator of ω_p^2 would cause a further enhancement over the free-electron plasma frequency of the valence electrons. Thus, as a result of these two terms, one could expect the plasma frequency to be shifted to values considerably larger than the free-electron value.

In the present compounds the valence band consists of two cation *s* electrons and four anion *p* electrons yielding free-electron plasma energies of 12.9 eV for CdS, 12.3 eV for CdSe, and 11.3 eV for CdTe. As these values are clearly below the experimentally observed values it appears as

TABLE I. A comparison of the experimental values obtained by various investigators using REEL, TEEL, optical reflectivity, and ESCA. All values are given in eV and are identified at the top of the columns as follows: *I* is the interband transition, *D* is the *d*-band transition, *S* is the surface plasmon, *P* is the bulk plasmon, and 2*P* is the double bulk plasmon. The reference from which the values were taken is shown in parentheses; the REEL and TEEL values not followed by a reference are from the present study.

	I	*I*	*I*	*S*	*I*	*D*	*I*	*P*	*P*+*I*	2*P*
					CdS					
REEL	4.0	6.8		11.2		14.4		18.2	23.2	36.0
TEEL	3.9	6.9		12.6		14.9	16.7	18.6	22.6	
TEEL (6)	3.1	6.2	8.4					17.7	22.8	
TEEL (5)		5.5						20.5		
Im $(1/\epsilon)$ (2)		6.2	9.0	11.6				18.6		
ESCA (10)						14.8				
					CdSe					
REEL	3.0	6.4		10.7		13.8		17.6	23.2	36.5
TEEL (6)	2.6	5.7		11.9		14.2		17.2	23.3	
TEEL (5)		5.5						20.5		
Im $(1/\epsilon)$ (2)		6.5		11.1				20.7		
ESCA (10)						14.3				
					CdTe					
REEL	2.2	4.5	6.5	9.6	10.7	13.6		16.1	22.5	
TEEL	2.4	4.2	6.1	8.8	11.8	14.1		16.4	22.4	
TEEL (7)				5.8				16.9		
TEEL (5)			6.5						23.5	
ESCA (10)						13.5				

if a strong d-band contribution exists. Furthermore, since ω_p is greater than the d-band transition frequency, $\delta\epsilon_1^b$ is positive and the screening effect of the d electrons results in a further shift to higher energies.

As has been stated earlier the peaks at 11.2 eV in CdS, 10.7 eV in CdSe, and 9.6 eV in CdTe are surface dependent and have been assigned to a surface plasmon associated with the vacuum-semiconductor interface. The theoretical values to be expected for these surface-plasmon energies cannot be easily determined since nearby interband transitions must be taken into account in the case of a semiconductor. For a free-electron gas the surface-plasmon energy is $\hbar\omega_p/(1+\epsilon_s)^{1/2}$, where $\hbar\omega_p$ is the bulk-plasmon energy and ϵ_s is the dielectric constant of the region bounding the surface. For a vacuum-plasma interface $\epsilon_s = 1$ and the application of this relation to the present data yields 12.9 eV for CdS, 12.4 eV for CdSe, and 11.4 eV for CdTe. If consideration is made for shifts in these energies as a result of structure in ϵ_1 and ϵ_2, the assignment made above appears reasonable.

In addition to these peaks there is an indication of a broad peak in the region of 36 eV. This is probably due to a double-plasmon event. There is also a peak in all spectra, both REEL and TEEL, in the region of 22 to 24 eV. This peak is also present in the TEEL measurements of Tomoda and Mannami. The peak is possibly a combination of a bulk plasmon and an interband transition. Each of these materials has a strong interband transition near 6 eV as can be seen from the reflectivity. The combination of this peak plus the bulk-plasmon peak yields 25.0, 24.0, and 22.6 eV in CdS, CdSe, and CdTe compared to measured values of 23.2, 23.2, and 22.5 eV.

The values obtained in this study are in good agreement with those reported by Tomoda and Mannami[6] although the present interpretation differs from theirs. The present values do however differ considerably from those reported by Pradal and Gout.[5] Comparison of their curve shapes with those presented in Figs. 5 and 6 of this paper indicate a similarity between their curves and the surface contaminated curves D and E of Figs. 5 and 6, respectively. Such contamination might account for the observed differences.

V. CONCLUSION

A comparison has been made of the data obtained by electron reflection, electron transmission, and optical measurements in order to better identify the peaks observed in the energy-loss spectra. The result of this comparison indicates that the spectra are quite similar in structure and consist of a region below 9 eV containing interband-transition peaks, a region between 9 and 12 eV containing a highly surface-dependent peak identified as being due to a surface plasmon, a peak between 12 and 15 eV identified as a d-band transition and a dominant peak between 15 and 20 eV assigned to a bulk plasmon. The distinction between the surface-plasmon and bulk-plasmon peaks is based primarily upon the behavior of these peaks under different surface conditions.

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