Date: 25 January 1974

Project Title: "Optical Interactions in Solids Relating to Solid State Detectors and Corrosion Control"

Project No: C-41-632 Continuation of C-41-606

Principal Investigator: Dr. James R. Stevenson

Sponsor: Air Force Office of Scientific Research

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RA-3 (6-71)
RESEARCH PROJECT TERMINATION

Date: December 10, 1974

Project Title: Optical Interactions in Solids Relating to Solid State Detectors and Corrosion Control

Project No: G-41-632

Principal Investigator: Dr. J. R. Stevenson


Effective Termination Date: 9-30-74 (Grant Expiration)

Clearance of Accounting Charges: 9-30-74

Grant Closeout Actions Remaining:
- Final Fiscal Report
- Final Patent Report

NOTE: Companion account is G-41-506.

Assigned to School of Physics

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Other
Optical properties of the Cd$_3$As$_2$-Cd$_3$P$_2$ semiconductor alloy system*

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(Received 26 November 1973)

The near-normal-incidence, room-temperature reflectance spectra of the Cd$_3$As$_2$-Cd$_3$P$_2$ semiconductor alloy system have been measured for photon energies $0.083 < E < 21$ eV. Synchrotron radiation has been used to extend the measurements to 30 eV for Cd$_3$As$_2$. These spectra are similar to those of III–V compounds. Comparison of the primary, reflectance data with the results of others and with the band-structure calculations has been made. The reflectance has been analyzed via the Kramers-Kronig relations. We report curves for a, k, K$_1$, K$_2$, and n$_{eff}$ for all the alloys studied. Strong structure in the fundamental absorption scales approximately linearly with alloy composition. Structure at 11 eV is associated with Cd d-band excitation.

I. INTRODUCTION

Considerable attention has been given to the II–V compounds of Zn$_3$As$_2$, Zn$_3$P$_2$, Cd$_3$As$_2$, and Cd$_3$P$_2$ as a result of their interesting transport properties; for example, Cd$_3$As$_2$ is a degenerate n-type semiconductor with an exceptionally large mobility, low effective mass, and a small band gap, whereas Zn$_3$As$_2$ is a p-type semiconductor with very low mobility, a comparatively large effective mass, and a large band gap.\textsuperscript{1-10} The practical interest in these binary semiconductors has been extended to the alloy systems Zn$_3$As$_2$-Cd$_3$As$_2$,\textsuperscript{17,18} Cd$_3$As$_2$-Cd$_3$P$_2$,\textsuperscript{19-22} and Cd$_3$As$_2$-Zn$_3$P$_2$.\textsuperscript{23} Since Cd$_3$As$_2$ is an end member of each of these alloy systems, it has undergone much investigation. As found in the above references, some controversy has centered on the nature of the fundamental absorption edge in Cd$_3$As$_2$.

Numerous investigations of the band structure of groups IV, III–V, and II–VI binary compounds (and their alloys) have been conducted by means of the analysis of their reflectance spectra. The interpretation of the results is facilitated whenever tentative band-structure calculations have been available.\textsuperscript{24} Band-structure calculations\textsuperscript{25,26} have recently been performed for several II–V compounds. As little research has been performed on these alloys beyond the fundamental absorption edge,\textsuperscript{27-30} the interpretation of our results has been aided by comparison with the above band-structure calculations and with some of the work on III–V semiconductors.

We have measured the near-normal-incidence reflectance spectra of these II–V alloys over a very large range (0.08-30 eV) of photon energy. The high-energy limit of our measurements was extended by use of ultraviolet radiation from the electron storage ring at the University of Wisconsin Physical Sciences Laboratory.\textsuperscript{31} A Kramers-Kronig analysis was used to generate the optical constants, and we have compared results with the limited (spectrally speaking) results of others.\textsuperscript{8,10,27,29} An assignment of a number of interband transitions has been made, and these transitions have been located as a function of alloy composition. Qualitative agreement has been obtained with the available band-structure calculations.

A brief discussion of the chemical considerations and the current band-structure calculations is presented in Sec. II. The experimental techniques are presented in Sec. III and the primary results are given in Sec. IV. Also included in Sec. IV is a discussion of the reflectance structure above 0.7 eV. Section V presents the optical constants and our interpretation of the transitions which underlie the fundamental absorption edge.

II. THEORETICAL CONSIDERATIONS

The II–V compounds Cd$_3$As$_2$ and Cd$_3$P$_2$ belong to the tetragonal crystal system. The space group for Cd$_3$As$_2$ is $I4_1d$ and that for Cd$_3$P$_2$ is $P4_2/nmc$.\textsuperscript{5,34} The unit cell for Cd$_3$As$_2$ is composed of 32 formula units, and the unit cell for Cd$_3$P$_2$ is composed of eight formula units. On the basis of Masumoto's x-ray work\textsuperscript{2} and a discussion of the polymorphic transformation\textsuperscript{32} in the related Cd$_3$As$_2$-Zn$_3$As$_2$ alloy system, we find that two Cd$_3$P$_2$ unit cells\textsuperscript{33} can be inscribed within the Cd$_3$As$_2$ unit cell.\textsuperscript{34} (The basal vectors are related by a factor $\sqrt{2}$; the c axes by a factor 2.)

The coordination of ions is similar in this and in the Cd$_3$As$_2$-Zn$_3$As$_2$ alloy system. In Cd$_3$As$_2$, the large As ions are cubic close-packed, and three-fourths of the tetrahedral interstices are occupied by Cd ions (note that vacancies exist in the ideal crystal structure). Each As ion is surrounded by Cd ions at six of the eight corners of a cube. The relative disposition of these vacancies differen-
iates the unit cells of the arsenides from those of the phosphides. If one envisions a lattice of arrows connecting adjacent pairs of these vacant sites, then the repeat distance along the $c$ axis of the pattern of arrows differs for the arsenides and the phosphides.

Although Cd$_3$As$_2$ and Cd$_3$P$_2$ possess slightly different crystal structures, the more important features of their electronic structures seem related to their similar chemical composition. The Cd and Zn atoms have an outer filled $s$ shell, an empty $p$ shell, and a filled $d$ shell about 9 eV below the filled $s$ shell. The As and P atoms have a filled $s$ shell and three electrons in their outer $p$ shell. No other electrons lie at energies accessible to our measurements. Table I lists the ionization energies, referred to vacuum, of the neutral atomic components of the alloys investigated. The $4d$ level at 17.6 eV for Cd has been obtained from the multiplicity-weighted average of the $^2D_{3/2}$ and $^2D_{5/2}$ terms given by Harrison. A first approximation to the separation of the $d$ band and valence band in the solid is given by the difference between the $d$ shell in the group-II B atom and $p$ shell of the group-V atom.

The above approximation ignores the energy shift caused by a transfer of charge in the more ionic crystals. In the event of such a shift, one should more appropriately use the first ionization energies of the stripped atoms. Suchet has formulated an empirical, electronegativity theory from which the homopolar and heteropolar contributions to the fundamental energy gap, $\delta_f = \delta_s + \delta_p$, have been computed for a large number of semiconducting, binary compounds. We define the fraction $f_i$ of ionic character as $f_i = \delta_p/\delta_f$. For Cd$_3$As$_2$, $f_i$ is found to be on the order of 1.0 while a value of 0.8 is found for Cd$_3$P$_2$.

Lin-Chung has performed pseudopotential calculations for the energy-band structures of Cd$_3$As$_2$, Zn$_3$As$_2$, Cd$_3$P$_2$, and Zn$_3$P$_2$. The crystal structure has been simplified by filling all the vacancies. For example, in Cd$_3$As$_2$ the vacancies are filled with Cd ions. This hypothetical unit cell then transforms into 16 fluorite unit cells with As$^{3-}$ replacing the Ca$^{2+}$ and the Cd$^{2+}$ replacing P$^{-}$ in the calcium-fluoride structure. The Brillouin zone for this fluorite structure is much larger than that for either Cd$_3$As$_2$ or Cd$_3$P$_2$ and is identical to that of the fcc structure. The high symmetry points of this fluorite structure are also symmetry points of the real Brillouin zone. Figure 1 demonstrates these two Brillouin zones. The Brillouin zone for the fcc structure is 16 times larger than that for Cd$_3$As$_2$ and four times larger than that for Cd$_3$P$_2$ (this follows since the real unit cells of Cd$_3$As$_2$ and Cd$_3$P$_2$ have a direct volume ratio of four-to-one). An effective vacancy pseudopotential is incorporated into the Cd atomic pseudopotential to account for the presence of the vacancies.

There is a strong similarity between the overall calculated energy-band structures of Cd$_3$As$_2$ and Cd$_3$P$_2$, and both resemble those of the III-V compounds (InAs, GaSb, etc.). Some experimental justification is present for these structure approximations, since the optical spectra to be given later are similar to those of III-V compounds. Figure 2 gives the energy-band structures for Cd$_3$As$_2$ and Cd$_3$P$_2$ as calculated by Lin-Chung.

### Table I. Ionization energies of the neutral atomic components of the alloys investigated.

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cd</th>
<th>P</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>4s</td>
<td>9.38 eV</td>
<td>8.99 eV</td>
<td>9.79 eV</td>
<td>9.24 eV</td>
</tr>
<tr>
<td>3d</td>
<td>17.40 eV</td>
<td>17.60 eV</td>
<td>18.35 eV</td>
<td>17.67 eV</td>
</tr>
</tbody>
</table>

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**FIG. 1.** First Brillouin zone of (a) body-centered tetragonal structure and (b) fluorite structure.
lowest valence band is an anion s-like level; the second valence band is a Cd s-like level; and the third and fourth are s-like about Cd and p-like about the anion. The valence-band maximum for Cd$_2$As$_2$ is at $\Gamma$; that for Cd$_3$As$_2$, slightly (~12%) off-center of the Brillouin zone. The bottom of the conduction band at $I'$ has an s-like representation.

The predicted energy gap for Cd$_3$As$_2$ is ~0.2 eV or smaller.

### III. Measurements

The energy range 0.083–30 eV required the use of four optical systems. The description of these systems has been reported in detail. The region $0.083 < E < 1.9$ eV (1.5–0.65 µm) was investigated by using a Perkin-Elmer Corporation "Optical Reflectance Attachment" and a Perkin-Elmer model 99 monochromator with a NaCl prism. Both a globar and tungsten-halogen lamp were used as sources, and a Reeder Corporation thermocouple was used with a synchronous-rectification detection scheme. The reflectance measurements were taken at room temperature and atmospheric pressure.

From 1.9 to 7.3 eV (6500–1700 Å) the sample chamber was constructed from an ultrahigh-vacuum (10–8 Torr) system of conventional design and was provided with an ion pump. A McPherson 0.3-m scanning monochromator with provisions for evacuation and easy interchange of gratings (1500–Å and 5000–Å blaze angles) served to span this range. A lithium-fluoride window flange was used to support the pressure differential between the reflectometer and monochromator. Both a tungsten-halogen lamp and a glow discharge in several Torr of hydrogen provided continuum sources in this range. A 13-stage photomultiplier (PM) tube and light pipe (phosphor coated above 3 eV) served as the base for simple dc detection.

The region from 7.3 to 21 eV (1700 to 600 Å) was investigated by means of a General Electric GEI-44854, 1-m normal-incidence monochromator, similar to that designed by Johnson. This monochromator was provided with an 800-Å blazed grating, and the sample chamber used by Hinson was employed. A 13-stage PM tube was used with a sodium-salicylate-coated light pipe and synchronous-rectification detection schemes. Below 13 eV, a glow-discharge lamp was operated in a dc mode to provide the many-lined hydrogen spectrum. A tuning-fork chopper interrupted the emergent beam from the monochromator and provided a reference signal. Above 13 eV, the glow-discharge lamp was operated in a repetitive, condensed discharge mode to provide the Hopfield continuum. The ac line to a McPherson 720 spark supply was interrupted to generate a 30-Hz fundamental in the radiation which reached the PM tube.

Synchrotron radiation from the 240-MeV electron storage ring at the University of Wisconsin’s Physical Sciences Laboratory provided an intense continuum which extended the high energy of our data to 30 eV. A simple reflectometer, employing a channel-electron multiplier in a current-integrated mode, was attached to the exit-slit housing of a 1-m, normal-incidence monochromator. Repeated scans were employed for the "sample-in" and "sample-out" configurations. The count rates were normalized to the electron-beam currents.

A total of eight samples were obtained from the Naval Research Laboratory (NRL) of Washington, D. C. All the members Cd$_x$(As$_{1-x}$P$_x$)$_2$, where $0 < x < 1$, were prepared by a modified Bridgman method. Our observations, as well as those of Wagner et al., were that the Cd$_x$(As$_{0.75}$P$_{0.25}$)$_2$ and the Cd$_x$(As$_{0.12}$P$_{0.88}$)$_2$ crystals are not mechanically strong. Radoff and Bishop have reported that for $x = 0.25$ the Bridgman-grown ingots show cracks associated with a solid-solid phase transition.

Mechanical polishing and etching techniques were
developed along lines suggested by the group at NRL.\textsuperscript{44} Polishing began with a mixture of 1-μm alumina powder (Union Carbide) and tap water, and was continued until no scratches were visible except those left by the powder. This was followed by polishing with a suspension of 0.05-μm diamond compound (Buehler AB Metadi) in a lapping oil (Buehler AB Automat). Final polishing was performed with a mixture of 0.05-μm (500-Å) alumina powder and distilled water. Only limited success was obtained with an etch consisting of a solution of bromine in methanol (5\%–0.08\% by volume). Little effort was expended toward orientation of the crystallographic axes. Although cracked, the crystalline regions of several of the samples were sizable.

IV. RESULTS AND TRENDS ABOVE 0.7 EV

The results of the near-normal-incidence reflectance measurements are presented in Fig. 3. These curves are zero shifted in relation to the percentage of the anion concentration. For several typical results, the nearly transparent or plasmon region is also shown in Fig. 4. The results of the extreme-uv measurements are presented in Fig. 5. Included in this latter figure are the results of measurements on the related compound Zn\textsubscript{3}As\textsubscript{2}.\textsuperscript{25} We note that the structure in the reflectance curves of the mid-members of this alloy system is as well defined as that for the end-members.

We defer treatment of the sharp structure below 0.7 eV in Fig. 3 and begin with a discussion of the structure in the range of 2 eV. Figure 3 suggests a linear scaling of the position of this peak versus the alloy composition. In accordance with the work of Sobolev \textit{et al.}\textsuperscript{29} on Cd\textsubscript{3}As\textsubscript{2}, we label this peak \( E_1 \). The more refined data of Sobolev has shown this peak to be split by \(-0.2\) eV (see Fig. 6). The center of gravity of our peak for Cd\textsubscript{3}As\textsubscript{2} agrees well with Lin-Chung’s band-structure (BS) calculation. The corresponding peak for Cd\textsubscript{3}P\textsubscript{2} agrees poorly with the respective BS calculation. See Table II for a comparison of these observed
peaks with the BS calculations. The probable assignments are made by analogy to the zinc-blende III–V compounds (e.g., GaAs).

The doublet character of this peak in Cd₃As₂ is presumably due to the spin–orbit splitting of the upper valence band (A₄) along the A direction. This upper valence band is p-like about the As atoms. A good estimate of the spin–orbit splitting of the upper valence band at the Γ point can be obtained from the spin–orbit splitting of the states of p character of the isolated anion atom (e.g., the terms ²P₁/₂ and ²P₃/₂ of AsIII). In going from the isolated anion atom to the solid, the splitting is enhanced by the factor ²⁻⁴⁻⁵⁻⁷. Using Moore’s tabulation of atomic terms, we thereby obtain 0.1 and 0.53 eV for the spin–orbit splitting at Γ in Cd₃P₂ and Cd₃As₂, respectively.

In analogy to the III–V compounds, the splitting observed in the reflectance structure is along the A direction. Along this direction the upper valence band is, presumably, further spin–orbit split. The degree of the latter splitting is ³/₄ of the splitting at the Γ point.

We therefore expect the observed splitting of the reflectance peak in the range of 2 eV to be 0.067 and 0.35 for Cd₃P₂ and Cd₃As₂, respectively. This estimate of 0.35 eV is in qualitative agreement with the 0.2-eV splitting observed by Sobolev. The resolution of our instrumentation in this region has prevented our observation of this splitting in Cd₃As₂. However, our estimated splitting of 0.067 eV for Cd₃P₂ would surely be obscured by lifetime broadening at room temperature. It is clear that the contribution to the “joint density of states” is large along a range of the line from Γ to L, since the bands A₁ and A₄ are nearly parallel in both Cd₃As₂ and Cd₃P₂ near the L point.

The peak in the range of 4 eV is labeled E₃.₄, since it corresponds to an average of the locations of the peaks E₃ and E₄ found by Sobolev in Cd₃As₂ (see Fig. 6). In both end-members of this alloy system we assume that the peak E₃ corresponds to the transition X₅’–X₃ and that E₄ corresponds to A₄–A₁. In Cd₃P₂, the nearby transition Γ₁₅–Γ₂₅ appears to be as likely an assignment as A₄–A₁ for peak E₄. The peak E₄ is not resolved in our data. We assume that peak E₃.₄ scales with the composition as shown in Fig. 3. If the peak E₃.₄ indeed scales as illustrated, then our results are in qualitative agreement with the BS calculations (see Table II).

The structure of this peak E₃.₄ represents a departure from the corresponding structure in the III–V compounds. In GaAs the similar peak, which is located around 5 eV, is associated with the transition X₅–X₃. A slightly higher-energy (~0.5 eV) satellite is identified with X₅–X₃ and

![FIG. 5. Reflectance spectra of Cd₃As₂ and Zn₃As₂.](image)

![FIG. 6. Relation of (A) the present results to (B) the 77 °K data and to (C) the 293 °K data of Ref. 29 (the upper curves are zero shifted).](image)
a lower-energy (−0.5 eV) energy shoulder is identified with \( \Gamma_{15} - \Gamma_{15} \) transitions. (The above representations belong to GaAs.\(^{48}\)) In contrast to this distribution of oscillator strengths in GaAs, we associate vanishingly small oscillator strength in the II–V alloys with the \( X'_1 - X' \) transition. The BS calculations predict \( X'_1 - X' \) to be at 3.4 eV and 2.7 eV in \( \text{Cd}_2 \text{P}_2 \) and \( \text{Cd}_2 \text{As}_2 \), respectively. The assignments \( \Lambda_3 - \Lambda_1 \) for a contribution to the peak \( E_{4,4} \) are nearly zone centered, and thus correspond to \( \Gamma_{15} - \Gamma_{15} \) in GaAs. However, in the \( \text{Cd}_2 \text{As}_2 - \text{Cd}_2 \text{P}_2 \) system, the transition \( \Lambda_3 - \Lambda_1 \) lies above \( X'_1 - X' \) (at least in \( \text{Cd}_2 \text{As}_2 \)), and in GaAs the transition \( \Gamma_{15} - \Gamma_{15} \) lies below \( X'_1 - X' \).

The decrease in reflectance between peak \( E_{3,4} \) and the rise at 11 eV is similar to that found in III–V compounds and corresponds to the near exhaustion of the \( f \)-sum rule for interband transitions.\(^{49}\) This over-all decrease in reflectance typically signals the onset of the plasmon region. Below, we shall find a broad peak in the characteristic-energy-loss function in the range of 9.5 eV for all members of this alloy system.

Figure 4 shows that all samples exhibit a sharp increase in the reflectance at −11 eV. Since the bonding in these alloys appears to have a large ionic character, it is reasonable to assume that the Cd 4d atomic levels generate a narrow band below the valence bands (in a tight-binding picture, charge transfer will lower these levels in the ionic solid). This consideration of the relative position of the d band is these alloys and the fact that this onset at 11 eV is independent of alloy composition lead us to the conjecture that this threshold corresponds to the onset of "real" d band-to-conduction-band transitions. The data obtained for \( \text{Cd}_2 \text{As}_2 \) and \( \text{Zn}_2 \text{As}_2 \) at the electron storage ring provide evidence that this structure at 11 eV is not due to an instrumental error (see Fig. 5).

In the ionic II–VI compounds \( \text{CdS}, \text{CdSe}, \) and \( \text{CdTe} \) Freeouf\(^{49}\) has identified a doublet at −13.5 eV with the spin-orbit-split transition from the Cd 4d level. In contrast, rudimentary measurements\(^{44}\) on elemental Cd have revealed no semblance of structure in this spectral region.

Since we have thus far chosen to interpret the reflectance structure directly and since there exists no values of the optical constants beyond the fundamental edge, we find it convenient to compare our reflectance values with the results of others at this stage of the exposition. A detailed account has been reported.\(^{40}\) We merely note here that the apparent tiny structure beyond the point labeled "MIN" in Fig. 4 is due to a systematic error.

Both Turner \textit{et al.}\(^{47}\) and Haidemenakis \textit{et al.}\(^{46}\) have reported infrared, plasma-edge, reflectance measurements for \( \text{Cd}_2 \text{As}_2 \). These measurements overlap our low-energy reflectance spectra and provide a check on our absolute values. We obtain better agreement with Ref. 3 and the percentage difference of the present results with respect to those of Turner \textit{et al.} is +8% at 0.25 eV. Since both Refs. 3 and 14 located the ir plasma edge at −0.05 eV, we shall subsequently define the optical dielectric constant to be that dielectric constant between the fundamental absorption edge and the Restrahlen bands or the ir plasma edge. We find that this definition is compatible with the optical properties of \( \text{Cd}_2 \text{As}_2 \), since the photon-energy interval between the plasma edge and the fundamental edge (−0.6 eV) is so large.

At higher photon energy we compare our reflectance values for the end member \( \text{Cd}_2 \text{As}_2 \) with those of Sobolev \textit{et al.}\(^{29}\) in Fig. 6. The curves labeled "B" and "C" are equally zero shifted as indicated to prevent overlap. The measurements of Sobolev have been performed on single, un-oriented crystals. His 293°K data are discontinuous not only in absolute magnitude, but also in shape. (Our data suffered background problems in the encircled region of this figure.) At 1.6 eV our data have an absolute error of +12% with respect to the data of Sobolev. In view of our error analysis,\(^{46}\) we believe the data of Sobolev are not well disposed to an absolute scale.

When the data of Fig. 6 are inspected more closely, it is seen that our structure is poorly defined relative to that of Sobolev. We can only assume that this lack of definition is due to the poor crystalline quality or that the damaged layer

<table>
<thead>
<tr>
<th>Reference No.</th>
<th>Peaks</th>
<th>( \text{Cd}_2 \text{As}_2 )</th>
<th>B.S. calculation</th>
<th>Probable location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference No.</td>
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<tr>
<td>Present results</td>
<td>Peaks</td>
<td>( \text{Cd}_2 \text{P}_2 )</td>
<td>B.S. calculation</td>
<td>Probable location</td>
</tr>
</tbody>
</table>
incurred during the mechanical polishing has not been removed by the etchant. Between 5 and 12 eV, Sobolev also obtained a series of peaks labeled $E_i - E_{0j}$.

Sobolev et al.\textsuperscript{37} has also performed rudimentary, reflectance measurements on Cd$_3$P$_2$. Figure 7 displays the present results for Cd$_3$P$_2$ and those of Sobolev, whose curve is given in arbitrary units. Their peak at ~4 eV is reasonable in view of our results. Note the strong similarity of this peak in our results for all members of this alloy system in Fig. 3. The fact that Sobolev has used a polycrystalline sample of Cd$_3$P$_2$ leads us to believe that the departure of our results from those (on single crystals) of Sobolev in Fig. 6 is attributable to a polycrystalline surface of our prepared samples. The remaining portion of their data on Cd$_3$P$_2$ does not seem reasonable.

V. OPTICAL CONSTANTS

Since the present results are representative of a polycrystalline surface, we have used the simple expressions

$$n = (1 - |\tilde{r}|^2)/(1 - 2|\tilde{r}|\cos \theta + |\tilde{r}|^2),$$

$$k = 2|\tilde{r}|\sin \theta/(1 - 2|\tilde{r}|\cos \theta + |\tilde{r}|^2),$$

for the real and imaginary components of the complex index of refraction

$$\tilde{N} = n + ik.$$  

The reflectivity is defined via

$$\tilde{r} = |\tilde{r}|e^{i\theta}, \quad 0 \leq \theta < \pi$$

so that the phase shift $\theta$ is that of the magnetic field.\textsuperscript{48,52} We have integrated the Kramers-Kronig integral

$$\varphi(E) = (-1/2\pi) \int_{0}^{\infty} \left( \ln \left| \frac{E'}{E - E'} \right| \right) \frac{dE'}{E'}$$

by choosing the upper-energy limit of the integral, so that the phase shift vanishes below the fundamental band gap.

Our assumed form for the reflectance ($R = |\tilde{r}|^2$) above 21 eV is not completely arbitrary. If indeed the absorption above 11 eV is due to the Cd 4$d$ levels, then the reflectance curve of Fig. 5 for Cd$_3$As$_2$ provides an "assumed" form for all members of this alloy system. That portion of the reflectance data below the adjusted upper limit has been numerically integrated by means of a computer program kindly furnished by Shay.\textsuperscript{53} The gap energies at which the phase shifts vanish are the room-temperature gaps reported by Wagner et al.\textsuperscript{20}

We present the results of the phase-shift analysis in the form of curves for the dual quantities $n$ and $k$. These curves are given in Fig. 8. The zero shifting for either family of curves is in the successive amount of one unit.

At 0.4 eV, we obtain the value of $n = 4.04$ for Cd$_3$As$_2$. In this same region, Haidemenakis et al.\textsuperscript{8} obtained the estimate $n = 4.3$ ($n_\infty = k_\infty$). Zdanowicz\textsuperscript{10} found $n = 5$ and $k = 0.04$ ($k = c\alpha/2\omega$) at 0.413 eV (3 $\mu$m). These latter values of $n$ and $k$ yield a normal-incidence reflectance of 0.44 [$\tilde{r} = (N - 1)/(N + 1)$], which is even 10% greater than our value. Recall that our reflectance was greater than that of both Refs. 3 and 8. Of greater significance is the fact that both these other results lead to an energy dependence of $n$ (and $R$) opposite ours in this low-energy region. The cause of the disagreement is not apparent.

Zdanowicz has found a sharp peak in $n$ at ~0.6 eV. This peak has been associated\textsuperscript{10,55} with the fundamental absorption edge in Cd$_3$As$_2$. The underlying transition is thought to be zone centered in the real crystal structure ($\Gamma_1s - \Gamma_{1u}$). Our Cd$_3$As$_2$ data exhibit only a weak shoulder in $n$ at ~0.6 eV.

Now use is made of the relations

$$\kappa_1 = n^2 - k^2$$

and

$$\kappa_2 = 2nk$$

which yield the real and imaginary components of the complex dielectric constant (relative permittivity)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{Relation of (A) the present results to (B) the 293 K data of Ref. 27 (the lower curve is given in arbitrary units).}
\end{figure}
The families of these quantities are given in Fig. 9. As usual, the structure in the $\kappa_2$ curve is seen to follow that in the reflectance.

We now turn our attention to the structure below 0.7 eV. The structure in this particular region is sufficiently well-defined as to be amenable to a description in terms of the joint density of states.

Several characteristic shapes in $\kappa_2$ resemble four basic forms ($M_0 - M_4$) of the joint density of states in the range of allowed transitions at critical points which are also symmetry points. Representative structure in $\kappa_1$ and $\kappa_2$, along with the reflectance $R$ is illustrated in Fig. 10. (True critical-point line shapes are rarely found in such spectra; however, they serve as a useful guide to line-shape analysis).

With the exception of Cd$_3$As$_2$, we have marked two discontinuities in the slopes of the $\kappa_2$ curves.

$$\tilde{\kappa} = \kappa_1 + i\kappa_2.$$  \hspace{1cm} (8)

The solid arrow locates what appears to be an $M_0$ critical point; the dotted arrow, an $M_4$ critical point. In the case of Cd$_3$As$_2$, the arrow appears to locate an $M_2$ critical point; however, we have encountered large relative error in this spectral region.

We have been aided in the determination of the location of the $M_0$ critical points by the room-temperature gaps of Wagner et al.$^{20}$ The underlying transition is $\Gamma_3 - \Gamma_1$, according to Lin-Chung's BS calculations. Figure 11 gives a plot of the location of this $M_0$ critical point as a function of alloy composition. Note the agreement with the transmission edges found by Ref. 20.

These critical-point identifications have been made in the following way. The sharp rise in the $\kappa_2$ curves at the point labeled by the solid arrow is characteristic of an $M_0$ critical point. Were this the only nearby contribution to the joint density of states, one would further expect $\kappa_1$ (and $R$, etc.) to rise sharply at this point.
since $k$ is small here) to peak at the same location. We observe that in all cases, except for Cd$_3$As$_2$, the $\kappa_1$ curve peaks above the location of the $M_0$ critical point. An explanation of this relative shift in structure is readily obtained if the change in slope of the $\kappa_2$ curves (located by the dotted lines) is due to an $M_1$ critical point. An $M_1$ critical point gives rise to peaking of the $\kappa_2$ curve slightly below the location of the $M_0$ critical point. Thus, we find that the interpretation of two nearby critical points, $M_0$ and $M_1$, contributing to a peaking of $\kappa_1$ and $R$ between the location of these critical points is consistent with the dielectric constants.

The location of the $M_1$ critical point is in qualitative agreement with Lin-Chung's BS calculations. The $X$ point and the $\Gamma$ point of the hypothetical structures are equivalent in the real crystal structure: the $X$ point becomes a $\Gamma$ point. We, therefore, envisage the direct transitions in the real structure giving rise to the $M_1$ critical point to be $\Gamma_1 - X_1$ in these alloys. We are unable to identify the exact type of critical point in Cd$_3$As$_2$, but we assume the same transition is involved. Lin-Chung has placed this transition $\Gamma_1 - X_1$ at 1.2 eV in Cd$_3$As$_2$, and believes that it corresponds to the direct gap $E_g$ found by Zdanowicz at -0.6 eV. In Cd$_3$P$_2$, she has placed the transition $\Gamma_1 - X_1$ at 1.875 eV. We find this transition at -0.63 eV in Cd$_3$P$_2$, and therefore have the same qualitative agreement with the BS calculations as did Zdanowicz for Cd$_3$As$_2$. Figure 11 also displays the composition dependence of this $M_1$ critical point and includes the low-temperature gaps given by Radoff and Bishop.

Error estimates for the dielectric constants have been discussed elsewhere. We report here that the optical dielectric constants have probable errors of $\pm 18\%$. In view of the above comparisons of our primary data with that of others, the optical constants at higher energy are only qualitatively correct.

The expression ("partial" sum rule)

$$n_{\text{eff}} = \left[2m/N(\hbar e)^2\right] \int_0^E E' \kappa(E') dE'$$

yields an effective number of free electrons contributing to the optical properties over a finite range $0 < E' < E$. $N$ is the atomic density of the solid. The successive values of $n_{\text{eff}}$ are displayed in Fig. 12. Since there are exactly 3.2 valence electrons per atom, we are somewhat surprised to find that these curves nearly saturate (before the rise at 12 eV) at a value of -2.2. In particular, since the Cd $d$-band transitions are expected to overlap nearly the tail of the fundamental absorption spectra in these alloys, we should look for an enhancement of $n_{\text{eff}}$ over the valence-electron contribution of 3.2. We attribute this disagreement to absolute reflectance values which are low above -6 eV. Sample $x = 0.12$ appears to represent a favorable counter example to the failure of $n_{\text{eff}}$. 

FIG. 10. Dielectric constants for typical samples.

FIG. 11. Location of the band-edge critical points as determined by the structure in $\kappa_2$. 

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to reach a higher level; however, the absolute reflectance data of this sample has been found to be inconsistent with our Kramers-Kronig extrapolation scheme.

The $f$-sum rule for interband transitions which involve the valence bands is nearly exhausted in the range of $9 \text{ eV}$. This remark is complimented by these curves of $n_{\text{eff}}$. It is also usually the case that these valence electrons, in conjunction with $d$-band contributions are able to participate in bulk plasmons. Figure 13 in fact shows a broad peak in the characteristic-energy-loss function $\text{Im}(1/\kappa)$. If the absolute values of our primary data indeed drop too fast in this photon-energy range, then these peaks provide a lower estimate of $\approx 9.5 \text{ eV}$ for the plasmon energy. For comparison, the free-electron plasmon energy, due to the valence electrons only is $13.13 \text{ eV}$ for Cd$_3$As$_2$. This latter number is given for crude comparison only. The $d$ bands not only enhance the effective number of electrons available to contribute to a plasmon, but also provide a measure of shielding.

...
of the Coulomb interactions. Furthermore, the dependence of the plasmon energy on the volume of the unit cell is weak ($E_p \propto V^{-1/2}$). Since the unit-cell volume change from Cd$_3$As$_2$ to Cd$_3$P$_2$ is small, we do not list the free-electron plasmon energies for the other alloys.

A partial summary of our results is presented in the form of a plot of the structure in $\kappa_2$ or $R$ versus the alloy composition. We present these findings in Fig. 14. The upper two curves have been obtained from the peaks in the reflectance data; the lower two curves, from the structure in $\kappa_2$.

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# Optical Interactions in Solids Relating to Solid State Detectors and Corrosion Control

The optical properties of cadmium arsenide, cadmium phosphide alloys are reported. The infrared characteristics of synchrotron radiation as a possible source for infrared spectroscopy and detector calibration have been studied. The relation of the extreme ultraviolet reflectance to the optical constants generated by a Kramers-Kronig analysis with applications to the cadmium-zinc-arsenide alloy are reported. The results of Auger electron spectroscopy and optical spectroscopy of magnesium-magnesium oxide surfaces are given with possible applications to...
corrosion studies and optical characterization of surfaces.
Final Scientific Report

Optical Interactions in Solids Relating to
Solid State Detectors and Corrosion Control

James R. Stevenson

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OBJECTIVES

The purpose of the research has been a study of optical interactions in solids and related physical properties of solid surfaces. Particular emphasis in the study was given to some complex tertiary semiconductor alloy systems. Although complex in nature, evidence exists for believing the semiconductor alloys will have important device applications in the future e.g. the variation in band gap with alloy composition. The research concentrated on the determination and analysis of data related to surface characterization such as that obtained from optical reflectivity and auger spectroscopy. The techniques and data are directly related to factors contributing to an understanding of surface stability and corrosion control in semiconductor devices. Synchrotron radiation from the electron storage ring at the Physical Sciences Laboratory of the University of Wisconsin was utilized to provide a continuum source in a compatible high vacuum environment. In addition the infrared characteristics of existing and proposed synchrotron radiation sources were investigated as possible infrared sources for application to infrared solid state spectroscopy.

ACHIEVEMENTS

1. An exhaustive study of the optical properties of the Cd₃As₂-Cd₃P₂ alloy system has been completed in the form of a PhD thesis by Dr. Maury Zivitz. The work has recently been published in Physical Review. The thesis is available as a report of the School of Physics of Georgia Institute of Technology. As this effort is part of the available scientific literature no further comments will be included on this phase of the work.

2. The infrared characteristics of synchrotron radiation were investigated as a possible radiation source for infrared spectroscopy and detector calibra-
tion. The results of this research has resulted in considerable interest within the scientific community. Details of the research were published in Applied Optics and a supplement to the paper is available as a report of the School of Physics, "Computer Calculations and Numerical Tabulations of Some MacDonald Functions". Tabulations of these functions are not available in the current literature.

3. An experimental system including a sample chamber for investigating a surface in ultra high vacuum using optical reflectivity and electron Auger spectroscopy has been developed. The system can be used without a window when the light is from an ultra high vacuum source such as an electron storage ring or with a window when the radiation source is at a higher pressure than desirable for Auger spectroscopy. The details of this system are included in the PhD thesis of Dr. Harry Ellis.

4. A study was completed on the relation of the extreme ultraviolet reflectance to the optical constants generated by a Kramers-Kronig analysis with application to samples of the alloy Cd$_x$Zn$_{3-x}$As$_2$. This research shows the need for measurements of the optical reflectance in the vacuum ultraviolet even though the interesting structure may be in the near infrared and visible. Dr. Ellis has used a classical model to investigate the effect of high energy extrapolations of reflectivity data. The convergence sum rules and the effects on peak height in the structure of optical constants have been investigated. A complete description of the results is available as the thesis of Dr. Harry Ellis. A talk on the results will be presented to the American Physical Society and a paper will be prepared for publication.

5. Our interest in surface electronic states, passive surface layers, and corrosion led to a preliminary investigation of studying the growth of surface layers via optical reflectivity and electron Auger spectroscopy.
Dr. John Carden, a physical chemist, and two graduate students Mr. Bill Wall and Mr. James Larsen were particularly helpful in the initiation of the research. Using magnesium metal and the formation of the oxide on the surface as the system of interest, we have demonstrated that ultraviolet spectroscopy of the surface will result in an ability to follow the destruction of a passive layer and the growth of a deeper oxide characteristic of corrosion. The possibility of extending these controlled studies into the infrared may result in a systematic selection of wavelengths for non-destructive characterization of oxide depth on the surface. The dramatic change of the optical constants in different wavelength regions as the surface oxide increases in depth may have significant applications not only to corrosion but also in the area of communications. The results of the preliminary investigations have been reported in a talk at the IV International Conference on Vacuum-Ultraviolet Radiation Physics in July, 1974 and will appear in the Proceedings of the Conference.

PROFESSIONAL PERSONNEL

The following individuals have participated in the research described above.

1. Dr. James R. Stevenson - Principal Investigator
2. Dr. Roger Bartlett - Postdoctoral Research Associate
3. Mr. Maury Zivitz - Graduate Research Assistant
4. Mr. Harry Ellis - Graduate Research Assistant
5. Mr. Abdol Gholamnezhad - Graduate Research Assistant
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8. Dr. L. N. Tharp - Auger Spectroscopy Consultant
9. Mr. James House - Electronics Technician
10. Dr. John Carden - Auger Spectroscopy Consultant and Research Scientist
11. Mr. Bill Wall - Graduate Research Assistant
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13. Mr. Samuel Formby - Graduate Research Assistant
14. Mr. Frank Ferrandino - Graduate Research Assistant
PAPERS PRESENTED


5. "Reflectivity of \( \text{Cd}_x \text{Zn}_{3-x} \text{As}_2 \) Semiconductor Alloy Systems," Conference Digest - 3rd. International Conference on Vacuum Ultraviolet Physics, Tokyo, Japan (1971).


7. "Optical Properties of \( \text{Cd}_x \text{Zn}_{3-x} \text{As}_2 \)," Seminar - Group F41 - DESY, Hamburg, W. Germany, August 10, 1972.


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PAPERS TO BE SUBMITTED OR PUBLISHED


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1. M. Zivitz, "The Optical Properties of the Cd$_3$As$_x$P$_{2-x}$ Alloy System", (1973.)

2. H. Ellis, "Relation of the Extreme Vacuum Ultraviolet Reflectance to the Optical Constants Generated by a Kramers-Kronig Analysis with Application to Samples of the Alloy Cd$_x$Zn$_{3-x}$As$_2$".

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9. T. F. Connally, Research Material Information Center, Oak Ridge National Laboratory.