

type-IIb semiconducting diamond which is known to be the purest natural diamond available (aluminum acceptors $\sim 3 \times 10^{16} \text{ cm}^{-3}$, nitrogen donors $\sim 3 \times 10^{15} \text{ cm}^{-3}$).¹⁹

Note added in manuscript. Hamakawa *et al.*⁴¹ have recently reported detailed measurements on electro-absorption near the direct edge in Ge. They show that their data cannot be fitted to the one-electron-band-

⁴¹ Y. Hamakawa, F. A. Germano, and P. Handler, *Phys. Rev.* **167**, 703 (1968).

theory calculations, and that the exciton is probably responsible for most of the observed behavior.

ACKNOWLEDGMENTS

We are grateful to W. F. Cotty of Industrial Distributors, London, and to Dr. F. A. Raal and Dr. L. du Preez of the Diamond Research Laboratory, Johannesburg for providing the diamonds used in these investigations. One of us (P.D.) is indebted to the Science Research Council for provision of a research studentship.

Ultraviolet Reflectivity Spectra of $\text{CdS}_{1-x}\text{Se}_x$ Single Crystals*

R. L. HENGHOLD AND C. R. FRAIME

Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio 45433

(Received 19 April 1968)

The fundamental reflectivity of single-crystal platelets of $\text{CdS}_{1-x}\text{Se}_x$ has been measured at 90°K with linearly polarized light of wavelength longer than 1100 \AA . Measurements were performed with the electric vector parallel and perpendicular to the c axis of the crystal. The transitions $E_1(A_1, A_2, B)$, E_0' , F_1 , E_2 , a shoulder on the low-energy side of E_2 , and E_1' were followed across the composition range. The structure in the reflectivity curves is interpreted in terms of existing knowledge of the band structure of wurtzite materials.

I. INTRODUCTION

IN recent years much study has been devoted to the determination of the electronic energy band structure of the II-VI semiconducting compounds. While much previous work, both experimental and theoretical, has been done, a complete energy-band picture of the II-VI compounds (especially the wurtzite structure) does not yet exist and many of the optical transitions at high symmetry points are not very well understood. The experimental data presently available consist of transmission, emission, and reflection measurements at the band edges (Γ points) and reflection measurements of the higher-energy transitions for the pure compounds.¹ The solid solutions formed from the pure compounds have been studied near the edge²⁻⁴; however, with the exception of one recent investigation,⁵ they have not been studied at energies above the edge. Data on solid solutions are very useful in theoretical band-structure studies, since they allow one to trace a

particular transition across the composition range and, in many cases, to match reflectivity peaks resulting from particular transitions in one of the pure compounds with the corresponding peaks in the other pure compound.

Two of the II-VI compounds which form a continuous range of solid solutions are CdS and CdSe, both of which crystallize in the wurtzite structure. The pure compounds of CdS and CdSe have previously been studied by Cardona^{1,6} who reported the energy of several direct interband transitions above the fundamental gap. The variation of band gap with increasing Se concentration in the $\text{CdS}_{1-x}\text{Se}_x$ solid solutions has been studied by Handelman and Kaiser.²

The present study is concerned with the variation which occurs in the higher-energy transitions of the $\text{CdS}_{1-x}\text{Se}_x$ system with increasing Se concentration. The data were obtained by measurement of the reflectivity spectra over the entire composition range of the $\text{CdS}_{1-x}\text{Se}_x$ solid-solution system for wavelengths between 1150 and 3150 \AA , i.e., for photon energies in the range of 4 to 11 eV . The incident light was plane polarized and the reflectivity was recorded for single-crystal platelets (in the as-grown condition) at 90°K with the electric vector both parallel and perpendicular to the crystal hexagonal axis.

* Work performed at the Aerospace Research Laboratories Wright-Patterson Air Force Base, Ohio.

¹ M. Cardona and G. Harbeke, *Phys. Rev.* **137**, A1467 (1965).

² E. T. Handelman and W. Kaiser, *J. Appl. Phys.* **35**, 3519 (1964).

³ F. L. Pedrotti and D. C. Reynolds, *Phys. Rev.* **127**, 1584 (1962).

⁴ E. A. Davis, R. E. Drews, and E. A. Lind, *Solid State Commun.* **5**, 573 (1967).

⁵ R. E. Drews, E. A. Davis, and A. G. Leiga, *Phys. Rev. Letters* **18**, 1194 (1967).

⁶ M. Cardona, *Solid State Commun.* **1**, 109 (1963).

II. EXPERIMENTAL ARRANGEMENT

The measurements were made using a 1-m Jarrel Ash vacuum ultraviolet monochromator fitted with a reflection chamber similar to that described by Cardona.¹ This chamber was isolated from the monochromator by a LiF window and was pumped out to approximately 10^{-7} Torr by a separate vacuum system which was well trapped, using both zeolite and liquid nitrogen. This precaution was taken in order to ensure that the crystal surfaces remained relatively free of adsorbed gas during the low-temperature measurements. The light source used in these experiments was a Tanaka-type capillary discharge lamp with 60-cps ac excitation and with hydrogen as a source gas. The hydrogen discharge emitted a continuous spectrum above 1650 Å and a line spectrum between 1100 and 1650 Å. In this latter range, reflectivity values were recorded only at the peak maxima of the source spectrum, providing approximately thirteen experimental points in the short-wavelength range. In the long-wavelength range (above 1650 Å) experimental values of reflectivity were recorded every 10 Å. The incident light was plane polarized by reflection at Brewster's angle from a lithium fluoride plate. The polarizer attachment followed the design of Cardona.¹ The detection of both the incident and reflected light was accomplished by use of the same photomultiplier tube which could be rotated in the reflection chamber.

The samples used were single-crystal platelets grown from the vapor phase at the Aerospace Research Laboratories. Previous work³ has shown that $\text{CdS}_{1-x}\text{Se}_x$ solid solutions grown by this method are very homogeneous. Crystal composition was determined, using the data of Shiozawa⁷ on the variation of the fundamental gap energy with composition at room temperature. In the present study, the fundamental gap of the crystal samples was measured at room temperature, using a Model 14R Cary Recording Spectrophotometer, and the composition was then determined from Shiozawa's data.

III. RESULTS

Representative samples of reflectivity spectra for incident light polarized with the electric vector parallel

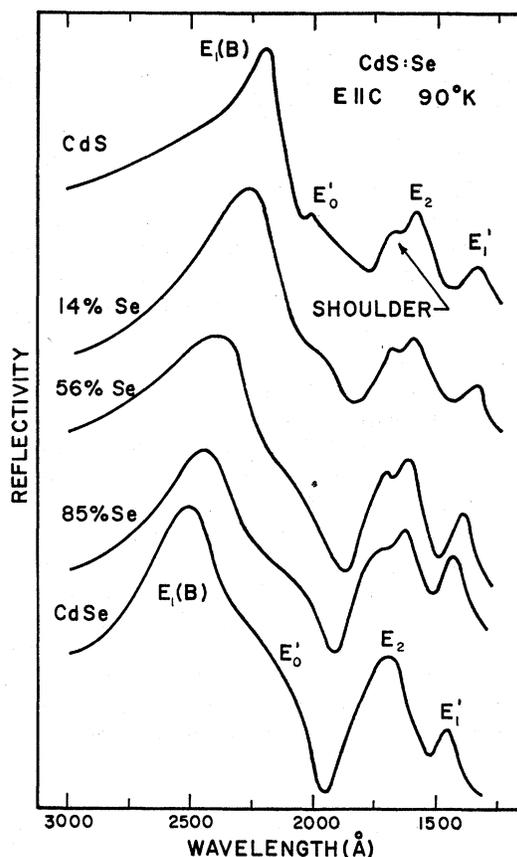


Fig. 1. Typical reflectance of several $\text{CdS}_{1-x}\text{Se}_x$ platelet crystals of different composition (mole %) measured at 90°K with $\mathbf{E}\parallel c$.

to the c axis of the crystal are shown in Fig. 1. Measurements were made on a total of twelve solid-solution compositions spaced across the composition range as well as the pure compounds. Each of the peaks in these curves is thought to correspond to a direct interband transition in the wurtzite lattice and the labels assigned to these peaks are those originated by Cardona.¹

The transitions followed across the composition range for parallel polarization are shown in Table I. The shoulder on the low-energy side of E_2 is rather difficult to find in many cases since it falls near a region of the

TABLE I. Energies (in eV) of the observed reflectance peaks of $\text{CdS}_{1-x}\text{Se}_x$ platelet crystals for several different compositions (mole %). These values represent data taken at 90°K for both $\mathbf{E}\perp c$ and $\mathbf{E}\parallel c$.

Peak	Composition $\mathbf{E}\parallel c$					Composition $\mathbf{E}\perp c$				
	CdS	14% Se	56% Se	84% Se	CdSe	CdS	14% Se	56% Se	84% Se	CdSe
$E_1(A_1)$	5.00	4.66	4.35	4.22	4.18
$E_1(A_2)$	5.00	4.84	4.58	4.44	4.50
$E_1(B)$	5.60	5.46	5.12	5.08	4.95	5.57	5.33	5.00	4.96	4.87
E_0'	6.15	6.36	6.05	5.90	5.98	6.18	5.98	5.70	5.61	5.60
F_1	7.12	6.89	6.62	6.47	6.40
E_2 (shoulder)	7.40	7.34	7.34	7.17	7.10	7.60	7.47	7.24	7.13	6.95
E_2	7.90	7.80	7.70	7.64	7.40	7.95	7.80	7.81	7.70	7.60
E_1'	9.30	9.32	8.98	8.79	8.65	9.20	9.02	8.94	8.75	8.70

⁷ L. R. Shiozawa, Aeronautical Research Laboratory Eight Quarterly Report (unpublished).

hydrogen spectrum where the continuum ends and the line spectrum begins. The variation of these transitions across the alloy range is shown in Fig. 2. Both the experimental points and a quadratic polynomial least-squares fit to these points are shown. This fit was made by weighting the two end points much more heavily than the intermediate points since the end-point values are the result of measurements made on many samples, whereas each intermediate value is a result of measurements made on, at most, two crystal samples. The energies of the transitions in the pure compounds and three representative solid-solution compositions are listed in Table I.

Representative samples of reflectivity spectra for incident light polarized with the electric vector perpendicular to the c axis of the crystal are shown in Fig. 3. As in the case of parallel polarization, measurements were made on a total of twelve different solid-solution compositions and the pure compounds. The labels assigned to the peaks (see Table I) are again those of Cardona. The variation of these transitions across the composition range is shown in Fig. 4. Again the experimental points and a quadratic polynomial least-squares fit to these points are shown. The energies of these transitions for the pure compounds and three representative solid-solution compositions are listed in Table I.

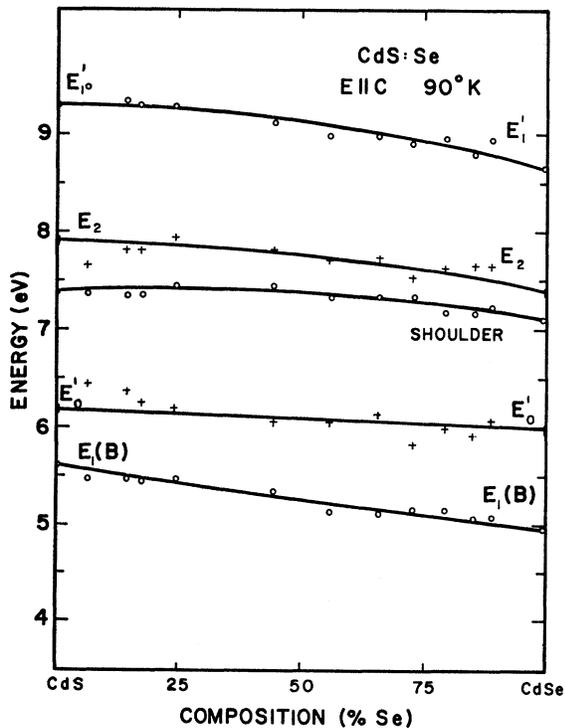


FIG. 2. Dependence of the energies of the reflectance peaks of $\text{CdS}_{1-x}\text{Se}_x$ platelet crystals on composition (mole %) for 90°K and $\mathbf{E}\parallel c$. The points represent the experimental data and the solid lines are the least-squares fit to the data points.

The plots of transition energy versus composition (Figs. 2 and 4) indicate considerably more scatter in experimental values for the higher-energy transitions: E_2 , E_2 (shoulder), and E_1' . This is due to the fact that only the line spectrum of hydrogen could be used in this region and thus small changes in the position of a reflectivity peak are difficult to determine for these transitions.

IV. DISCUSSION

The curves of transition energy versus solid-solution composition are observed to be slowly varying across

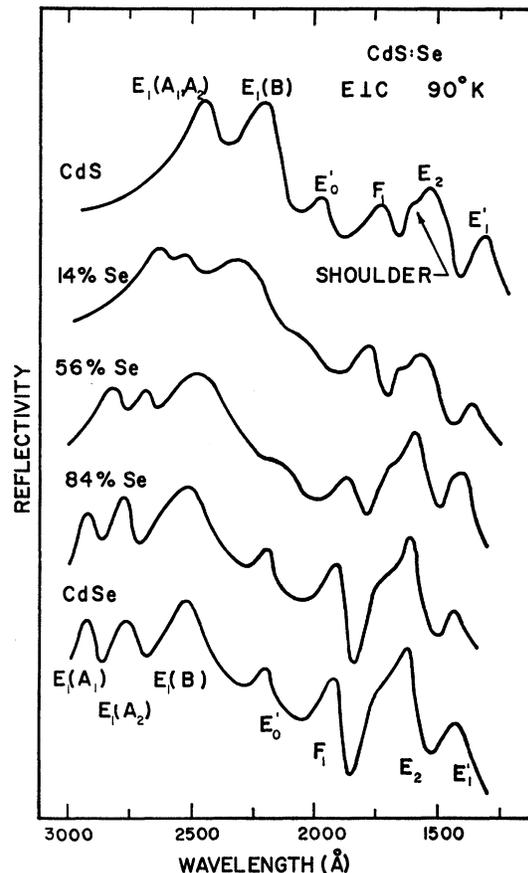


FIG. 3. Typical reflectance spectra of several $\text{CdS}_{1-x}\text{Se}_x$ platelet crystals of different composition (mole %) measured at 90°K for $\mathbf{E}\perp c$.

the composition range. This variation is very nearly linear; however, slight departures from linearity do appear. The curve of E_0 , the fundamental gap energy, versus alloy composition is sublinear,² i.e., it is described by a quadratic equation with a positive coefficient on the squared term. With this in mind one observes from Figs. 2 and 4 that, in general, the curvature changes from a sublinear curve for the lower-energy transitions, through a nearly linear variation, to, in some cases, a slightly superlinear curve for the higher-energy transi-

tions. It must be noted, however, that this nonlinear behavior at the higher energies is somewhat questionable. This can be seen from an examination of the coefficients of the second-order polynomial used in the least-squares fit. These coefficients, along with the total root-mean-square residue, are shown in Table II. From this table one observes that the coefficients of x^2 are indeed small and in fact that the effect of this term is of the same order of magnitude as the statistical error associated with the curves. Thus the behavior of these higher-energy transitions with composition may indeed be linear. To our knowledge, there is at present no quantitative theoretical explanation for a nonlinear variation of transition energy versus crystal composition. The only theoretical study of the $\text{CdS}_{1-x}\text{Se}_x$ solid-solution system is that of DeWitt, Euwema, and Collins⁸ who have performed a pseudopotential calculation and have found basically a linear behavior of energy with composition.

Since the variation of transition energy versus solid-solution composition is smooth across the entire range, there is a high probability that the same transition is responsible for a particular reflectivity peak across the entire composition range. By following the various transitions across the composition range we have been able to identify the $E_1(A_1)$, $E_1(A_2)$ splitting from pure CdSe to approximately 14% Se. For crystals with a Se content of less than 14%, this splitting is unresolved and has not been observed in pure CdS. This splitting has been associated with the spin-orbit interaction¹ and thus, if this interpretation is correct, should be much smaller for CdS than for CdSe. The present results appear to be in agreement with such an interpretation. It is worth noting, however, that the magnitude of this observed splitting does not decrease uniformly across the composition range but appears to decrease rather rapidly below the 20% Se composition. Furthermore, the F_1 peak in pure CdSe has also been positively identified as appearing at 6.40 eV as a result of following F_1 from pure CdS to pure CdSe. This peak at 6.40 eV does not appear in Cardona's reflectivity curve for

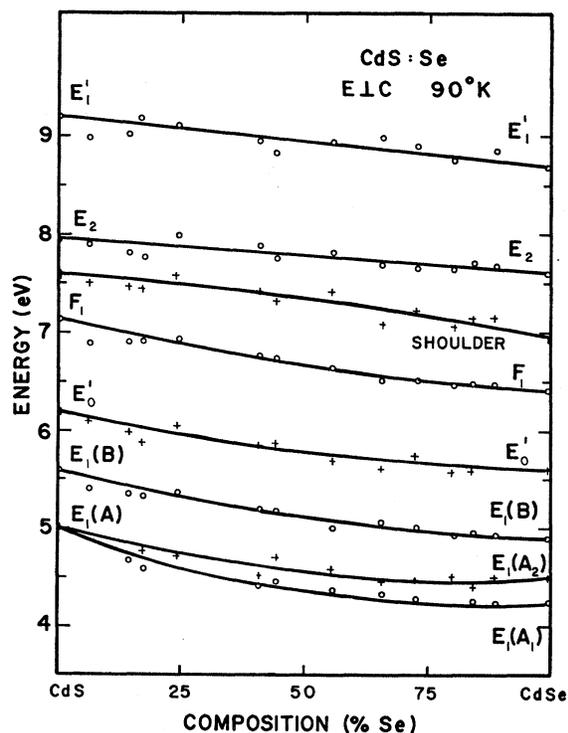


FIG. 4. Dependence of the energies of the reflectance peaks of $\text{CdS}_{1-x}\text{Se}_x$ platelet crystals on composition (mole %) for 90°K and $E \perp c$. The points represent the experimental data and the solid lines are the least-squares fit to the data points.

CdSe. Instead he has identified a shoulder at 6.80 eV with the F_1 peak.¹ This shoulder was also observed in the present work and could in fact be traced across the composition range. The F_1 peak and the shoulder on the low-energy side of E_2 are thus two separate peaks and must be associated with separate interband transitions.

Recent theoretical calculations of the band structure of the wurtzite lattice (particularly CdS and CdSe) have been performed by Bergstresser and Cohen⁹ and

TABLE II. Coefficients of least-squares fit of reflectivity data to a second-order polynomial ($E = ax^2 + bx + c$). The error given is the total root-mean-square residue of the data points for each curve.

Peak	Coefficients $E \perp c$				Coefficients $E \parallel c$			
	a	b	c	Error	a	b	c	Error
$E_1(A_1)$	1.05×10^{-5}	-1.81×10^{-2}	5.00	7.3×10^{-2}
$E_1(A_2)$	7.70×10^{-5}	-1.27×10^{-2}	5.00	5.4×10^{-2}
$E_1(B)$	5.00×10^{-5}	-1.19×10^{-2}	5.57	3.5×10^{-2}	9.62×10^{-6}	-7.45×10^{-3}	5.60	4.7×10^{-2}
E_0'	4.84×10^{-5}	-1.06×10^{-2}	6.18	6.2×10^{-2}	-1.13×10^{-5}	-6.35×10^{-4}	6.15	9.8×10^{-2}
F_1	4.00×10^{-5}	-1.12×10^{-2}	7.12	4.9×10^{-2}
E_2 (shoulder)	-3.20×10^{-5}	-2.75×10^{-3}	7.56	7.1×10^{-2}	-4.45×10^{-5}	1.55×10^{-3}	7.40	4.2×10^{-2}
E_2	-3.37×10^{-5}	-3.11×10^{-3}	7.95	5.9×10^{-2}	-4.13×10^{-5}	-8.54×10^{-4}	7.90	8.7×10^{-2}
E_1'	4.48×10^{-5}	-5.44×10^{-3}	9.20	1.1×10^{-1}	-5.83×10^{-5}	-6.55×10^{-4}	9.30	6.6×10^{-2}

⁸ J. S. DeWitt, R. N. Euwema, and T. C. Collins, in *II-VI Semiconducting Compounds: 1967 International Conference*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 611.

⁹ T. K. Bergstresser and M. L. Cohen, *Phys. Rev.* **164**, 1069 (1967).

TABLE III. Comparison of experimental energies with those suggested by Bergstresser and Cohen and those possible from the band model of Euwema *et al.* The experimental values are those measured at 90°K for $E \perp c$.

Peak	Experimental Energy (eV)	CdS			CdSe					
		Bergstresser and Cohen Trans.	Bergstresser and Cohen Energy (eV)	Euwema <i>et al.</i> Trans.	Euwema <i>et al.</i> Energy (eV)	Experimental Energy (eV)	Bergstresser and Cohen Trans.	Bergstresser and Cohen Energy (eV)	Euwema <i>et al.</i> Trans.	Euwema <i>et al.</i> Energy (eV)
$E_1(A)$	5.00	$\Gamma_6-\Gamma_3$	5.0	$\Gamma_6-\Gamma_3$	4.95	4.18 4.50	$\Gamma_6-\Gamma_3$	4.3	$\Gamma_6-\Gamma_3$	3.63
$E_1(B)$	5.57	U_4-U_3 U_3-U_3	5.7 5.6	U_4-U_3 U_3-U_3	5.64 5.80	4.87	U_4-U_3 U_3-U_3	5.0 5.0	U_4-U_3 U_3-U_3	4.57 4.68
E_0'	6.18	H_3-H_3	6.7	H_3-H_3	6.57	5.60	H_3-H_3	6.0	H_3-H_3	5.17
F_1	7.12	M_2-M_1	6.8	K_3-K_2	7.41	6.40	M_2-M_1	6.2	K_3-K_2	6.55
E_2 (shoulder)	7.60					6.95				
E_2	7.95	K_3-K_2 K_2-K_2	7.8 8.0	M_4-M_1	8.13	7.60	K_3-K_2 K_2-K_2	7.1 7.2	M_4-M_1	7.50
E_1'	9.20	$\Gamma_6-\Gamma_5$ $\Gamma_1-\Gamma_1$	8.5 8.4			8.70	$\Gamma_6-\Gamma_5$ $\Gamma_1-\Gamma_1$	7.9 7.7		

by Euwema, Collins, Shankland, and DeWitt.¹⁰ Bergstresser and Cohen have applied a semiempirical approach using a pseudopotential technique and have included a calculation of the real and imaginary parts of the dielectric constant. Euwema *et al.* have taken a first-principles approach using a self-consistent orthogonalized-plane-wave model and have not as yet completed the calculations of the dielectric constant.

Bergstresser and Cohen assign the $E_1(A)$ peak to a $\Gamma_6-\Gamma_3$ transition, $E_1(B)$ to a U_4-U_3 or U_3-U_3 transition, E_0' to an H_3-H_3 transition, F_1 to an M_2-M_1 transition, E_2 to a K_3-K_2 or a K_2-K_2 transition, and E_1' to a $\Gamma_6-\Gamma_5$ or $\Gamma_1-\Gamma_1$ transition. The labeling used here is that commonly used by most experimentalists, i.e., Slaters notation with the Γ_5 and Γ_6 irreducible representations reversed. An analysis of the band structure of Euwema *et al.* shows that the above assignments for $E_1(A)$, $E_1(B)$, and E_0' are possible ones on the basis of their band model; however, the assignments given to F_1 , E_2 , and E_1' above do not fit. If the assignments given by Bergstresser and Cohen to F_1 and E_2 were switched, i.e., if F_1 were assigned to a transition at the K point and E_2 to a transition at the M point, the band diagram of Euwema *et al.* would fit the experimentally observed values. No specific assignment has been made for the peak on the low-energy side of E_2 by Bergstresser and Cohen; however they do assign two possible transitions to E_2 . The one at K_3-K_2 is a lower-energy transition and that at K_2-K_2 is of higher energy. This lower-energy

¹⁰R. N. Euwema, T. C. Collins, D. G. Shankland, and J. S. DeWitt, Phys. Rev. 162, 710 (1967).

transition might explain the shoulder on E_2 for perpendicular polarization; however, it does not explain the shoulder in parallel polarization since the K_3-K_2 transition is forbidden in that polarization. The various experimental values along with the assignments of Bergstresser and Cohen and the possible assignments from the band structure of Euwema *et al.* are listed in Table III.

V. CONCLUSIONS

The reflectivity of the $\text{CdS}_{1-x}\text{Se}_x$ solid-solution system has been measured using light polarized both perpendicular and parallel to the c axis of the crystal. The crystal samples used were single-crystal platelets in the as-grown condition. Transitions in the range of 1150 to 3150 Å were followed across the alloy range and have been given the assignments: $E_1(A_1, A_2, B)$, E_0' , F_1 , E_2 , a shoulder on the low-energy side of E_2 , and E_1' . In all cases the change of transition energy versus solid-solution composition was found to be a smooth one which was sublinear for lower-energy transitions and was very slightly superlinear for some higher-energy transitions.

ACKNOWLEDGMENTS

The authors are indebted to F. L. Pedrotti, T. C. Collins, C. W. Litton, and J. S. DeWitt for several stimulating conversations concerning this work. We also express our appreciation to M. Cardona for his helpful comments on our results.