

Effect of Pressure on the Absorption Edges of Some III-V, II-VI, and I-VII Compounds*

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The effect of pressure to 160 kilobars was measured on the absorption edges of the III-V compounds AlSb, GaSb, InP, and InAs, the II-VI compounds CdS, CdSe, and CdTe, and the I-VII compounds CuCl, CuBr, and CuI. It is possible to discuss the band structure of the III-V compounds with reasonable assurance relative to known group IV and III-V structures. For the II-VI and I-VII compounds, ionic and other effects must be important. A number of new phase transitions were noted at high pressure. For CuCl and CuBr the T - P curves of some of these transitions were established.

THE effect of pressure (in some cases as high as 160 kilobars) has been measured on the absorption edges of a number of III-V, II-VI, and I-VII compounds which have the zincblende or wurtzite structure at room temperature and atmospheric pressure. Previously^{1,2} results have been published on certain group IV, III-V, and II-VI compounds. In the case of CuCl and CuBr the temperature shift of the phase boundaries of several pressure-induced phase transitions was also obtained.

The experimental procedures have been previously described,^{3,4} except that the latest revised pressure calibration⁵ was used. In attempting quantitative interpretation of the results it must be kept in mind that the apparatus is not primarily suited to handling these very brittle substances, and to obtaining quantitative results in the pressure range below 20 kilobars.

A. III-V COMPOUNDS

The effects of pressure on the optical absorption spectra of the group III-V compounds AlSb, GaSb, InP, and InAs have been measured. In addition, an investigation has been made to help identify the source of an absorption band on the long-wavelength side of the absorption edge of GaSb at higher pressures.

AlSb was obtained from the Ohio Semiconductor Company, Columbus, Ohio, in the form of a section from a large polycrystalline ingot. Spectra were obtained for two samples, 11.3 and 12.4 mils in thickness. The DUR Spectrophotometer was used, with a tungsten lamp source and an RCA 7102 detector. A slit width of 2.0 mm was used on the monochromator. The resulting curves are nearly linear on a plot of $(\alpha x)^{\frac{1}{2}}$ vs wave number. In the pressure runs, the long-wavelength transmission and the reflection correction varied only

slightly between 10 and 50 kilobars, indicating that no crushing of the sample occurred. The shift of the absorption edge with pressure was measured from an initial value of 13 180 wave numbers at an absorption coefficient of 30 cm^{-1} , and is given in Fig. 1. The result is a monotonic red shift with increasing pressure, with a slope of -0.0016 eV/kilobar up to the highest pressure attained, 50 kilobars. The total shift at 50 kilobars is 660 wave numbers.

GaSb was provided by Dr. J. H. Racette, of the General Electric Research Laboratories, in the form of rectangular polished samples of three thicknesses, 4, 7, and 11 mils, having a carrier density of $3 \times 10^{17} \text{ cm}^{-3}$. All spectra were obtained on the infrared spectrometer, with a tungsten lamp source and a PbS detector, with a slit width of 2.0 mm on the monochromator. Spectra obtained for 11 and 4 mil samples at 1 atm located the absorption edge at 5500 cm^{-1} for an absorption coefficient of 30 cm^{-1} . The shift of the absorption edge with pressure was measured in three runs, and the results are given in Fig. 2. There is an initial blue shift having a slope of 0.0120 eV/kilobar. At 18 kilobars, there appears to be a change of slope, to about 0.0073 eV/kilobar, and between 32 to 50 kilobars the shift of the edge appears to be leveling off and beginning to go red, with a maximum blue shift of about 2750 cm^{-1} at about 45 kilobars.

In each run, a broad absorption band appeared on the long-wavelength tail of the absorption edge at higher pressures. This peak remained nearly constant

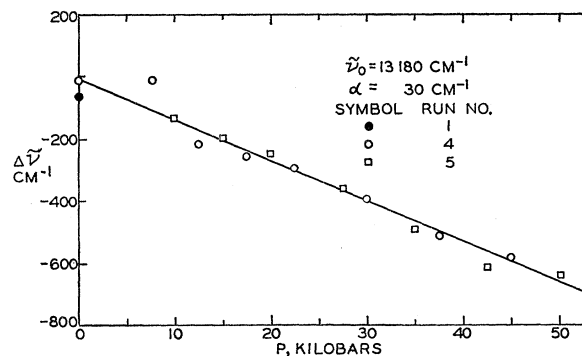


FIG. 1. Shift of AlSb absorption edge with pressure.

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¹ T. E. Slykhouse and H. G. Drickamer, *J. Phys. Chem. Solids* **7**, 210 (1958).

² A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, *J. Phys. Chem. Solids* **11**, 140 (1959).

³ R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, *J. Opt. Soc. Am.* **47**, 1015 (1957).

⁴ A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instr.* **31**, 511 (1960).

⁵ H. G. Drickamer, *Rev. Sci. Instr.* **32**, 212 (1961).

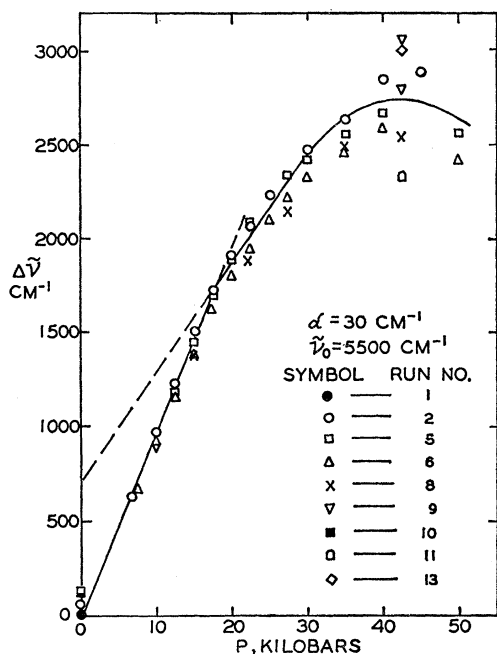


FIG. 2. Shift of GaSb absorption edge with pressure.

in intensity and location, as if the motion of the absorption edge itself were exposing it, allowing it to be observed. The spectra from a typical run are shown in Fig. 3. The peak in this case is centered at 6750 cm^{-1} and has an absorption coefficient of 12 cm^{-1} . In other runs, the absorption coefficient at this wave number varied from 6 to 35 cm^{-1} at a pressure of 42.5 kilobars. From 45 to 50 kilobars, in two runs, the intensity of the peak appeared to increase slightly, and remained more intense as the pressure was lowered.

To help identify the source of the absorption peak, samples were subjected to various treatments before loading and running in the $\frac{1}{8}$ -in. bomb. A 4 mil sample was heated in air for 40 hr at a temperature of 450°C , and cooled slowly. In the bomb at 42.5 kilobars, the absorption peak height was 32 cm^{-1} . The reflection correction was about normal, and the long-wavelength transmission of the sample decreased only slightly at the highest pressure. Another 4-mil sample was given the same heat treatment in an evacuated Vycor tube. In this case, the peak height was about 9 cm^{-1} , and was not affected by reducing the pressure from 42.5 kilobars to 1 atm, letting the bomb sit overnight and then increasing the pressure again to 42.5 kilobars. The long-wavelength transmission of the sample changed little under pressure, but the reflection correction had a slope about twice the normal value. In two separate experiments, 7 mil samples were bent to about 0.2% strain in the outer fibers, and spectra taken while bent, and after repeated flexing in opposite directions. The only apparent effect is an insignificant red shift on the edge, less than 100 wave numbers. One of these samples was then

subjected to pressure, and at 42.5 kilobars, the absorption peak height was 18 cm^{-1} . The reflection correction and long-wavelength transmission were normal. Finally, an 11 mil sample was cold-rolled by rolling a $\frac{5}{16}$ in. glass rod over it in one direction about 50 times with a downward force of 5 lb. A second sample mounted next to the first one crushed and broke up under this treatment. In the $\frac{1}{8}$ -in. bomb at 42.5 kilobars, the peak height was 7 cm^{-1} , and repeated cycling of the pressure between 42.5 kilobars and 1 atm had no effect on the peak. Also, a change in the intensity of the light passing through the sample, by a factor of 25, had no significant effect on the peak height.

Two x-ray powder diffraction patterns were obtained for crushed GaSb samples which had been placed under 100 kilobars pressure for five minutes. No extra lines were found in these patterns. The lattice spacings indicate a cube edge dimension of 6.10 angstrom units, and a Ga-Sb separation of 2.645 angstrom units.

InP was obtained in the form of small irregularly shaped pieces of single crystal material, from Dr. A. A. Giardini, of the U. S. Army Signal Research and Development Laboratory. Spectra were obtained on the infrared spectrometer, with a tungsten lamp source and a PbS detector, with a slit of 2.0 mm in the monochromator, for several unpolished samples in the $\frac{1}{8}$ -in. bomb and a polished sample in the $\frac{1}{2}$ -in. bomb. Several loadings were unsuccessful due to crushing of the samples, which appear to be extremely brittle. For the successful runs, the shift of the absorption edge with pressure was measured from an initial value of 11 100 wave numbers at an absorption coefficient of 30 cm^{-1} . The results are shown in Fig. 4. There is an initial blue shift with pressure up to about 40 kilobars, with a slope of $0.0046 \text{ ev/kilobar}$. Above 40 kilobars, a long tail develops on

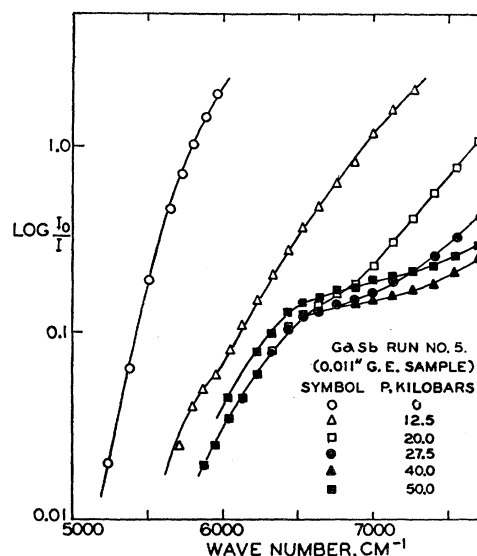


FIG. 3. GaSb absorption spectra at various pressures.

the long-wavelength side of the absorption edge, and the edge begins to shift red rapidly. Above 50 kilobars, the long-wavelength transmission dropped off rapidly, and the reflection correction increased rapidly in slope, indicating that the sample was being crushed. The maximum blue shift of the edge was 2500 wave numbers at about 45 kilobars.

InAs was obtained from the Ohio Semiconductor Company, in the form of a large polycrystalline section, labeled "type IN." Samples for the $\frac{1}{8}$ -in. bomb were polished to thicknesses from 6.7 to 7.8 mils thick. Spectra were obtained in the infrared spectrometer, using a globar source and a thermocouple detector, with a slit of 2.0 mm in the monochromator. The absorption curves at low pressures were very steep, increasing by two orders of magnitude within 300 wave numbers at 1 atm. At higher pressures, the absorption curves became less steep, and at 50 kilobars, the same increase required about 2000 wave numbers. The shift of the absorption edge with pressure was measured from an initial value of 2460 wave numbers at an absorption coefficient of 15 cm^{-1} , and the results are shown in Fig. 5. There is an initial blue shift up to 20 kilobars with a slope of $0.0048 \text{ ev/kilobar}$. At 20 kilobars, the shift with pressure appears to decrease, and from 20 to 50 kilobars, the slope of the shift is $0.0032 \text{ ev/kilobar}$. The maximum blue shift is about 1500 wave numbers at 50 kilobars.

It is apparent that the results obtained for AlSb, GaSb, InP, and InAs are closely related to the results previously reported for Si and Ge,¹ and for GaP, GaAs, and GaSb.² The similarities will be discussed below.

In the case of AlSb, the red shift with pressure indicates that the transition may be in the [100] direction, as is generally regarded to be the case also in Si. The slope of the shift for AlSb, $-0.0016 \text{ ev/kilobar}$, compares with a slope of $-0.0020 \text{ ev/kilobar}$ ¹ and $-0.0013 \text{ ev/kilobar}$ ⁶ reported for Si, and the slope of $-0.0017 \text{ ev/kilobar}$ ² reported for GaP, which is also interpreted as having a transition in the [100] direction. Thus,

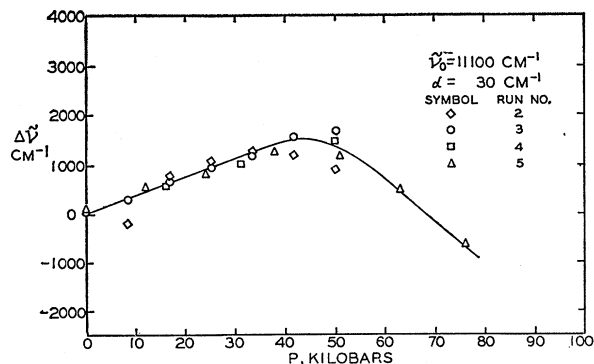


FIG. 4. Shift of InP absorption edge with pressure.

⁶ W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 102 (1958).

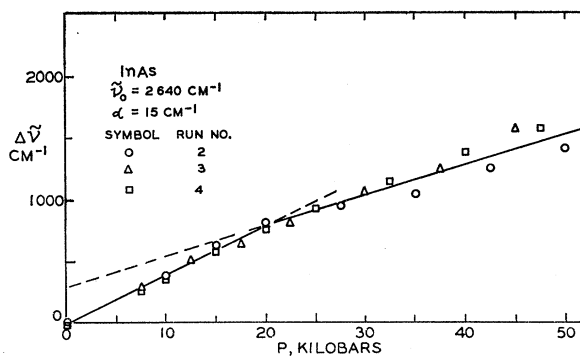


FIG. 5. Shift of InAs absorption edge with pressure.

although AlSb is isoelectronic with Ge, it may be more like Si in the relative order of the conduction band states.

The initial blue shift in GaSb agrees with the data previously reported by Edwards, Slykhouse, and Drickamer.² The slope of $0.0120 \text{ ev/kilobar}$ compares with the slope of $0.0123 \text{ ev/kilobar}$ previously obtained,² and the slope of $0.0157 \text{ ev/kilobar}$ reported by Taylor⁷ for the pressure range 0–2 kilobars. The change in the slope at 18 kilobars indicates a change in the transition direction, and the slope of $0.0073 \text{ ev/kilobar}$ is comparable with the slope of $0.0080 \text{ ev/kilobar}$ obtained for Ge, at about the same absorption coefficient for the indirect transition in the [111] direction. If the shift in GaSb between 18 and 32 kilobars is extrapolated back to 1 atm, it indicates an initial energy level about 700 wave numbers, or 0.09 ev, above the lowest energy level at 1 atm. The interpretation of this picture is that the minimum energy gap in GaSb at 1 atm is at the zone center, and that the conduction band minima in the [111] direction are about 0.09 ev above that at the zone center. Zwerdling, *et al.*⁸ showed through oscillatory magnetoabsorption measurements that the transition in GaSb is direct. If it is assumed that the [100] conduction band minima move down at the rate of about $-0.0015 \text{ ev/kilobar}$, the leveling off of the shift at about 45 kilobars indicates that the [100] minima are about 0.4 ev above the [000] minimum at atmospheric pressure. Ehrenreich and Olechna⁹ conclude that a consistent picture for GaAs places the [111] minima 0.25 ev above the [000] minimum, and the [100] minima about 0.5 ev above the [000] minimum. It is quite likely, then, that GaSb has the same relative order of conduction band states as GaAs.

InP and InAs can be assumed to have similar band structures since Weiss¹⁰ has found that in mixed crystals of the form $\text{In}(\text{As}_y\text{P}_{1-y})$, there is a linear relationship between y and the size of the forbidden energy gap. This

⁷ J. H. Taylor, Bull. Am. Phys. Soc. **3**, 121 (1958).

⁸ S. Zwerdling, B. Lax, K. J. Button, and L. M. Roth, J. Phys. Chem. Solids **9**, 320 (1959).

⁹ H. Ehrenreich and D. J. Olechna, Bull. Am. Phys. Soc. **5**, 151 (1960).

¹⁰ H. Weiss, Z. Naturforsch. **11a**, 430 (1956).

is in contrast to the situation for mixed crystals of the form $\text{Ga}(\text{As}_y\text{P}_{1-y})^{11}$ and for Ge-Si alloys,^{12,13} for which the relationship between composition and the size of the energy gap is not linear. In those cases the shift with pressure was also quite different, comparing GaP with GaAs, or Si with Ge. In the case of InP and InAs, the shifts are quite similar, both having slopes of about 0.0047 eV/kilobar obtained for InAs by Taylor⁷ from 0–2 kilobars. Work done by Lax¹⁴ indicates that the conduction band minimum is probably at the zone center in InAs. Calculations by Kane¹⁵ of the absorption constant associated with direct transitions in the vicinity of the zone center agree fairly well with the experiments of Fan and Gobel.¹⁶ The change in slope of the shift of the absorption edge of InAs with pressure is additional evidence that the initial transition is direct, since the same effect was observed in the case of GaSb.

B. II-VI COMPOUNDS

The effects of pressure on the optical spectra of CdS, CdSe, and CdTe have been measured, and the results are presented and discussed below. In each case, the shift of the optical absorption edge with pressure was measured, and a phase change observed.

1. Experimental Results

CdS was obtained from E. C. Stewart of the Harshaw Chemical Company, in the form of large single crystals and polycrystalline masses, having the wurtzite structure. Spectra were obtained on the DUR Spectrophotometer, using a tungsten lamp source and an RCA 7102 photomultiplier detector. The results of a $\frac{1}{8}$ -in. bomb run, and two $\frac{1}{2}$ -in. bomb runs are shown in Fig. 6. The shift with pressure was measured from an initial value of 19 140 wave numbers at an absorption coefficient of 30 cm^{-1} . The edge shifts red irreversibly when the sample is initially pressed in, to a point about 230 wave numbers red from the location of the absorption edge measured at one atmosphere. The slope of the shift from this point is 0.0033 eV/kilobar. A phase transition occurs, starting at about 27.5 kilobars, and is essentially complete at about 40 kilobars. The absorption edge shifts red about 6000 wave numbers over the transition. In the high-pressure form, the absorption edge shifts very little up to 50 kilobars, then begins to shift red. Between 60 and 160 kilobars, the average slope is about -0.0007 eV/kilobar. On reduction of pressure, the reverse phase transition begins at 10 kilobars, and does not appear to be complete at 1 atm even after letting the bomb stand for several days. The

¹¹ O. G. Folberth, *Z. Naturforsch.* **10a**, 502 (1955).
¹² E. R. Johnson and S. M. Christian, *Phys. Rev.* **95**, 560 (1954).
¹³ R. Braunstein, A. R. Moore, and F. Herman, *Phys. Rev.* **109**, 695 (1958).
¹⁴ B. Lax, *Revs. Modern Phys.* **30**, 122 (1958).
¹⁵ E. O. Kane, *J. Phys. Chem. Solids* **1**, 249 (1956).
¹⁶ H. Y. Fan and G. W. Gobeli, *Bull. Am. Phys. Soc.* **6**, 298 (1956).

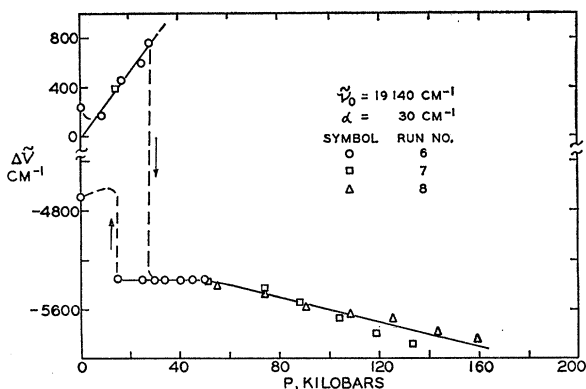


FIG. 6. Shift of CdS absorption edge with pressure.

absorption edge moved back part way, but is still about 4150 wave numbers red from the initial value. The progress of the phase transition was followed by measuring the change in intensity with pressure of the light transmitted by the sample at 10 000 wave numbers. Figure 8 is a plot of such data for a typical run involving a phase change in CdSe, which behaves very much like CdS.

X-ray powder diffraction patterns for 3 CdS samples which had been under 50 kilobars pressure for several minutes showed a faint line corresponding to a planar spacing of 2.915 Å, which could be due to the 200 plane of the zincblende structure. Other strong lines in zincblende pattern correspond too closely to strong lines in the wurtzite pattern to be definitely identified. The lines in the diffraction patterns are much more diffuse than in a pattern for a crushed CdS sample which had

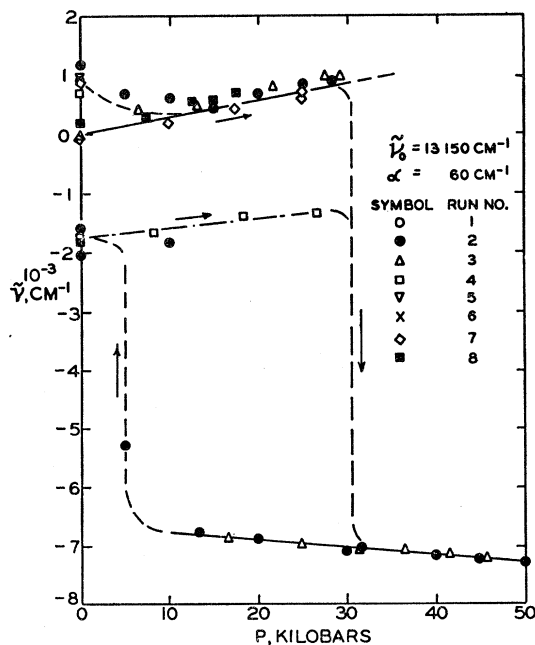


FIG. 7. Shift of CdSe absorption edge with pressure.

not been under pressure, indicating that the high pressure results in a much smaller particle size.

CdSe was obtained from Dr. R. H. Bube, of the RCA Laboratories, Princeton, New Jersey, in the form of small needles and plates having the wurtzite structure. Spectra were obtained on the infrared spectrometer with a tungsten lamp source and PbS detector. The shift was measured from an initial value of 13 150 wave numbers, at an absorption coefficient of 60 cm^{-1} . The results are quite similar to those for CdS, and are shown in Fig. 7. There is an initial irreversible red shift of about 750 wave numbers when the sample is pressed in, followed by a reversible blue shift with pressure of $0.0037 \text{ ev/kilobar}$. A phase transition begins at about 27 kilobars, and is complete at about 37 kilobars, as shown by a plot of light intensity vs pressure at 6500 wave numbers, Fig. 8. The absorption edge of the new phase is about 8000 wave numbers red from that of the wurtzite phase. In the high-pressure phase, the edge shifts red reversibly with a slope of $-0.0015 \text{ ev/kilobar}$ up to 50 kilobars. The absorption edge returns to about 11 400 wave numbers, about 2500 wave numbers red from the original location, and 1750 from the zero point of measurement.

In an investigation to determine the factors affecting the initial irreversible red shift, several samples were repeatedly bent to a strain of 0.2% in the outer fibers, but this does not significantly affect the location or shape of the absorption edge. Another sample was polished in several steps, from a thickness of 14.7 to 7.1 mils, taking spectra at each step. This also does not significantly affect the location or shape of the edge, with the sample thickness taken into account. Another sample was loaded into the $\frac{1}{8}$ -in. bomb between thin plates of AgCl, which has much less shear strength than NaCl, in an effort to reduce the shearing effect on the sample during the initial pressing in. In this case, the irreversible red shift took place in much the same way as for runs in which the sample was loaded in the usual way.

CdTe was obtained from Dr. A. A. Giardini, of the U. S. Army Signal Research and Development Laboratory, in the form of small pieces of single crystal material with the zinblende structure. Spectra were obtained on the infrared spectrometer, with a tungsten lamp source and a PbS detector. As in the case of CdS and CdSe, there is an initial irreversible red shift on being pressed in, so the shift was measured from an initial value of 11 630 wave numbers at an absorption coefficient of 100 cm^{-1} . The edge shifts reversibly from this point with a slope of $0.0044 \text{ ev/kilobar}$, up to about 35 kilobars, where a phase transition begins to occur. Since the edge shifts at least 8000 wave numbers red, beyond the range of the instrument, no spectra could be obtained above 39 kilobars. On reduction of pressure, the reverse transition begins at about 20 kilobars, and the absorption edge returns to about 10 630 wave numbers.

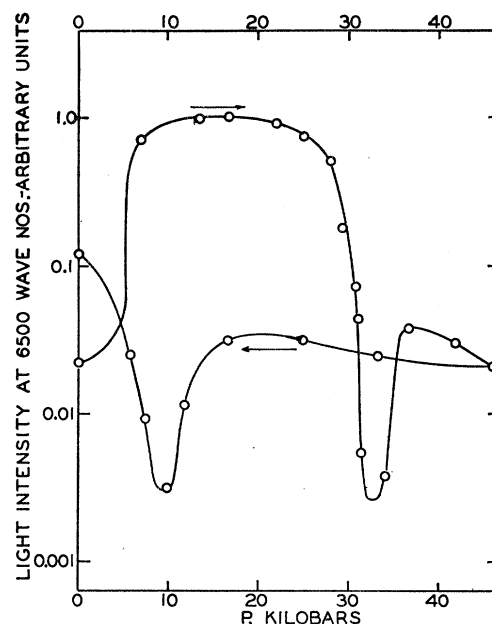


Fig. 8. Light intensity vs pressure for CdSe phase changes.

From this point, increasing results in a blue shift with a slope of $0.0048 \text{ ev/kilobar}$ up to about 35 kilobars. The data appear in Fig. 9. In several runs, a small absorption band appeared on the tail of the absorption edge, centered at about 10 700 wave numbers, with a maximum absorption coefficient of about 10 cm^{-1} . This peak increases in size above 35 kilobars, but is hidden by the red shift due to the transition.

The effects of pressure on CdS, CdSe, and CdTe appear to be quite similar, although the first two com-

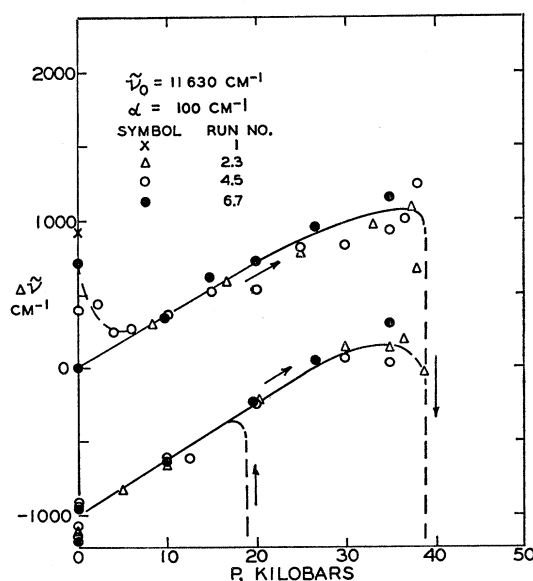


Fig. 9. Shift of CdTe absorption edge with pressure.

pounds have the wurtzite structure, while CdTe has the zincblende structure. This difference must be considered in comparing the results for CdS and CdSe with those for CdTe and those for the group III-V compounds considered above.

The results for CdS and CdSe indicate that the band structures are similar. This would also follow from the results of Khanseverov, Ryvkin, and Ageeva,¹⁷ who found that the energy gap varies in a smooth curve with composition for solid solutions of CdS and CdSe. Thomas, Hopfield, and Power¹⁸ measured the absorption coefficient of CdS from 10 to 300 cm⁻¹ in polarized light, from 20° to 300°K, in the region of the absorption edge, and concluded that the transition was direct at the zone center. However, Boer and Gutjahr,¹⁹ from measurements of the absorption constant at 90° and 300°K, concluded that an indirect transition involving phonons was responsible. The shift of the absorption edge of CdS with pressure up to 4 kilobars was measured by Gutsche²⁰ who found a slope of 0.0044 ev/kilobar, compared with the value 0.0033 ev/kilobar obtained in this work. He also obtained a compressibility ($-dV/VdP$) of 0.00166 per kilobar up to 4 kilobars. Preliminary calculations on the band structure of CdS have been started by Cohen and Reitz.²¹ The shifts with pressure of the absorption edges of the high pressure forms resemble the shifts of the corresponding group I-VII compounds much more than those of the corresponding group III-V compounds.

The blue shift of the absorption edge of CdTe indicates that the initial transition is probably to a conduction band minimum either in the [111] direction or at the zone center. An analysis of the shape of the absorption edge according to the theory of Bardeen, Blatt and Hall,²² was carried out for CdTe by Davis and Shilliday²³ at various temperatures. The results indicate that the lowest conduction band minima are in [111] directions, and 1.440 ev above the valence band maximum at room temperature, and that the [000] conduction band minimum is at 1.505 ev, or 0.065 ev higher.

The irreversible red shifts which occur in CdS, CdSe, and CdTe on being pressed in, may conceivably be due to strain and shear, although the experiments with CdSe failed to produce this effect outside the bomb, or prevent it from occurring in the bomb. The samples are very brittle, and many cracks probably develop when they are pressed into the sample chamber of the bomb.

¹⁷ R. I. Khanseverov, S. M. Ryvkin, and I. N. Ageeva, *Soviet Phys.-Tech. Phys.* **3**, 453 (1958).

¹⁸ D. G. Thomas, J. J. Hopfield, and M. Power, *Phys. Rev.* **119**, 570 (1960).

¹⁹ K. W. Boer and H. Gutjahr, *Z. Physik* **155**, 328 (1959).

²⁰ E. Gutsche, *Naturwissenschaften* **45**, 486 (1958).

²¹ D. A. Cohen and J. R. Reitz, *Bull. Am. Phys. Soc.* **5**, 162 (1960).

²² J. Bardeen, F. G. Blatt, and L. J. Hall, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley & Sons, New York, 1956), pp. 146-154.

²³ P. W. Davis and T. S. Shilliday, *Phys. Rev.* **118**, 1020 (1960).

The phase transitions occurring in CdS and CdSe under pressure are quite similar, both in the pressure at which they take place and in their effect on the location of the absorption edge. The actual thermodynamic transition points are probably about 19 kilobars in each case, with a region of indifference of about 8-12 kilobars on either side of the thermodynamic point. This can be seen in Fig. 8, for a typical CdSe run. With either increasing or decreasing pressure, the transitions require about 10 kilobars to become essentially complete, once they have begun. The transitions do not progress at constant pressure, but only for a few seconds after each pressure increase. This might indicate that the transitions are of the diffusional type, requiring a shear or strain mechanism to progress rapidly.

Although no direct identification of the high-pressure phases has been made, the x-ray patterns for CdS which has been subjected to high pressure do show some evidence of a small amount of the zincblende form being present. The shifts of the absorption edges after the transitions look considerably like the pressure shifts of the zincblende phases of CuCl, CuBr, and CuI, which will be presented and discussed below.

The phase transition in CdTe results in a form with an energy gap no larger than about 0.35 ev, which could be wurtzite, a distorted zincblende structure, or even the liquid form. On using approximate values of the heat of fusion and volume decrease on melting for CdTe of 10 ± 5 kcal/mole and $10 \pm 4\%$, respectively, the pressure required to bring the melting point from 1041° to 27°C is 120 ± 90 kilobars, so that melting is possible. The large volume decrease is reasonable, since the average coordination number in the melt would probably be 6 or 8 compared to 4 in the solid.

C. I-VII COMPOUNDS

The effects of pressure on the optical properties and lattice stability of the group I-VII compounds CuCl, CuBr, and CuI have been measured, up to pressures of 160 kilobars. Each compound underwent at least two phase transitions under pressure, and the shifts of the absorption edges were measured in each phase. The phase transitions in CuCl and CuBr were studied in the

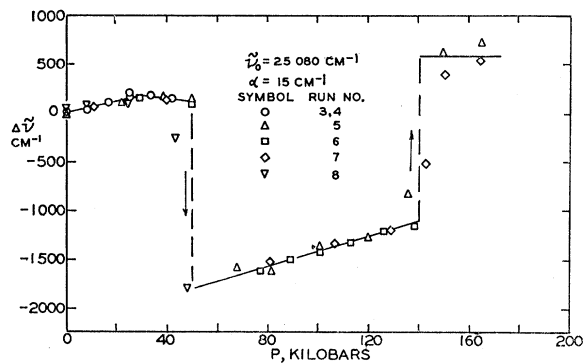


FIG. 10. Shift of CuCl absorption edge with pressure.

high-temperature modification of the $\frac{1}{2}$ -in. bomb, and the phase boundaries determined up to 160 kilobars and 400°C. A small peak on the absorption edge of CuCl was observed up to 50 kilobars, and the shift and change in intensity measured. These results are presented and discussed below.

Reagent grade CuCl from Fisher Scientific Company was repurified, and runs made in the $\frac{1}{8}$ -in. bomb, the $\frac{1}{2}$ -in. bomb, and the high-temperature modification of the $\frac{1}{2}$ -in. bomb. Spectra and light intensity changes with pressure and temperature were obtained on the DUR Spectrophotometer, using a tungsten lamp source and a 1P28 photomultiplier detector. The shift of the absorption edge with pressure was measured from an initial value of 25 080 wave numbers at an absorption coefficient of 15 cm^{-1} . The results are shown in Fig. 10. The initial slope of the shift is 0.0007 eV/kilobar, leveling off at about 30 kilobars, and shifting red from 30 to 50 kilobars. A phase transition occurs at about 54 kilobars, accompanied by a change in the location of the absorption edge of -1900 wave numbers. In the new structure, the edge shifts blue with a slope of 0.0010 eV/kilobar, until a second phase change, beginning at 100 kilobars, causes a change in the location of the absorption edge of 1800 wave numbers. The direction of shift could not be obtained in the highest pressure form, because of the over-all loss of light due to the previous transitions. The purer the sample, the lower were the transition pressures. One sample, which had been stored in a light-tight bottle in a desiccator for only a few days after repurification, required pressures up to 100 kilobars to complete the first transition, and did not begin the second transition until 135 kilobars had been reached.

The results of the combined high-temperature high-pressure runs are shown in Fig. 11. The transitions were located by following the changes in light intensity with increasing temperature, with the pressure applied to the $\frac{1}{2}$ -in. bomb remaining constant, and also taking spectra at intervals to locate the absorption edge. The samples did not clear up completely after each transition, and the defects seemed to hinder the following transition, so that some transitions were difficult to

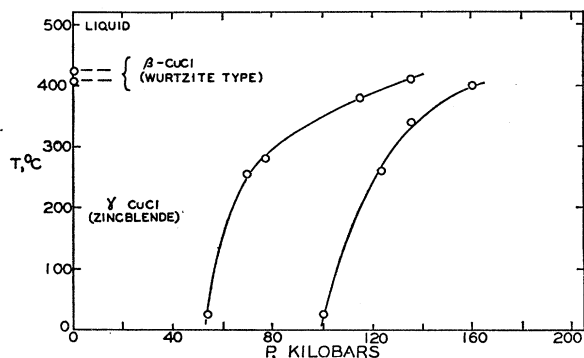


FIG. 11. Phase equilibrium diagram for CuCl.

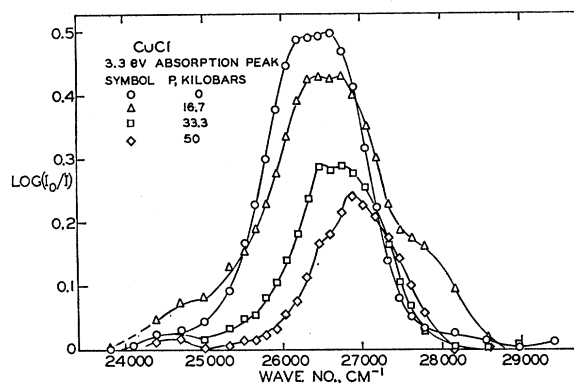


FIG. 12. Pressure effect on the 3.3-eV absorption peak in CuCl.

find. Fig. 11 is probably correct only within about 10% due to inaccuracies inherent in the method.

A small absorption peak on the absorption edge was studied in the $\frac{1}{8}$ -in. bomb, with a sample 10 mils thick containing 10% CuCl and 90% NaCl. The background absorption was corrected for by subtracting a linear tangent between 23 000 and 29 000 wave numbers, on a plot of $\log(I_0/I)$ vs wave number. The results are shown in Fig. 12. It appears that the peak has at least two components, which change in relative strength with increasing pressure. The peak, as a whole, shifts about 300 cm^{-1} blue, and decreases in strength by about 60-65% at 50 kilobars. Similar results were obtained in a previous run made by T. E. Slykhouse in this Laboratory.

CuBr Regent Grade powder was obtained from Matheson, Coleman, and Bell Company, repurified, and the same types of runs made as for CuCl, using the same equipment. The shift of the absorption edge with pressure was measured from an initial value of 22 740 wave numbers, at an absorption coefficient of 15 cm^{-1} . The results are shown in Fig. 13. The absorption edge shifts slightly blue up to 10 kilobars, then shifts red with a slope of about -0.0010 eV/kilobar up to 50 kilobars. One or more phase changes occur near 50 kilobars. The reverse transition, on reduction of pres-

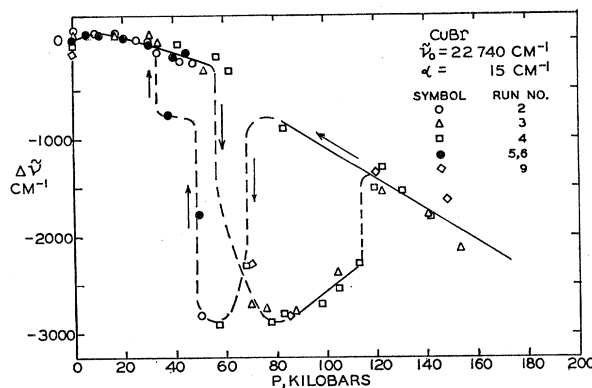


FIG. 13. Shift of CuBr absorption edge with pressure.

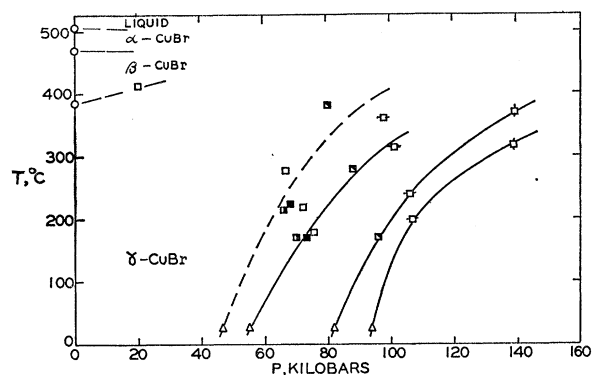


FIG. 14. Phase equilibrium diagram for CuBr.

sure, clearly involves two separate steps, spaced about 5 kilobars apart, with the absorption edge returning only part of the way at each step. Completion of the transitions with increasing pressure results in a total change in the location of the absorption edge of -2600 wave numbers. The absorption edge in the new form appears to shift blue with pressure. Between 80 and 95 kilobars, what appear to be two separate transitions take place, moving the absorption edge about 1700 wave numbers blue. In the highest pressure form, the absorption edge shifts red, with a slope of about 10.0019 ev/kilobar.

The phase equilibrium diagram obtained for CuBr is shown in Fig. 14. Because of the many phase transitions, the high-temperature runs were more difficult to analyse, although the large difference in the absorption edges, between the phase stable from 55 to 80 kilobars at room temperature, and the lowest and highest pressure forms, was helpful in determining the occurrence of transitions. The curves drawn in Fig. 13 are probably accurate within 10–15%.

Purified Reagent Grade CuI was obtained from Fisher Scientific Company, and room temperature pressure runs made up to 150 kilobars, with the same equipment used for CuCl and CuBr. The shift of the absorption edge with pressure was measured from an initial value of $23\,550$ wave numbers at an absorption coefficient of 15 cm^{-1} , and is shown in Fig. 15. Three distinct phase transitions took place, as indicated both by discontinuities in the shift of the edge, and by measurement of light intensity changes with pressure. These transitions occurred at 14, 41, and 80 kilobars, with changes in the location of the edge of 1300, 150, and 0 wave numbers, respectively. The slopes of the shift in the four separate phases were -0.0041 , -0.0079 , -0.0061 , and -0.0022 ev/kilobar, in order of increasing pressure.

The direction and slope of the absorption edge shifts in the zinblende form of CuCl and CuBr are somewhat different and the shift of CuI quite different, than those of the corresponding group II–VI compounds, ZnS and ZnSe, which had blue shifts up to very high pressures,

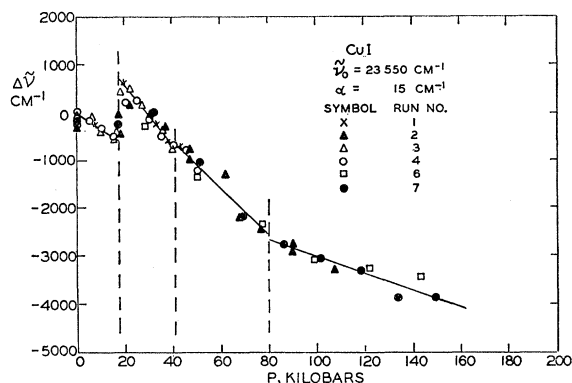


FIG. 15. Shift of CuI absorption edge with pressure.

with slopes of 0.0057 and 0.0060 ev/kilobar, respectively.² However, the shifts of the edges are similar to those observed in the high-pressure forms of CdS and CdSe, which may have the zinblende structure. This would indicate that the band structure picture used in interpreting the results for the group IV elements Si and Ge and the group III–V compounds GaP and GaAs, and AlSb, GaSb, InP, and InAs cannot be carried over without modification, to the heavier and more ionic group II–VI compounds or any of the group I–VII compounds, which are quite ionic. Herman²⁴ has indicated that this is the case, because of the way the size of the energy gap changes in isoelectronic sequences. CuCl, CuBr, and CuI have smaller energy gaps than would be obtained from a reasonable extrapolation from the other members in the isoelectronic sequences, as do the high-pressure forms of CdS and CdSe, which may have the zinblende structure.

Fesefeldt and Gyulai²⁵ observed absorption peaks on the edges of CuCl, CuBr, and AgI, at $26\,870$, and $25\,320$, and $23\,600\text{ cm}^{-1}$, respectively. The peak in CuCl is largest. Gross and Kaplyanski²⁶ observed this peak in a mixture of 10% CuCl in NaCl at 77°K , and found it to consist of a narrow component at $26\,000\text{ cm}^{-1}$ and a broad component from $26\,450$ to $26\,970\text{ cm}^{-1}$. The room temperature locations found here were $26\,260$ and $26\,600\text{ cm}^{-1}$ for the two components of the peak, indicating little or no temperature dependence of the peak energies.

Seitz²⁷ states that the peaks in CuCl and CuBr are probably due to d^{10} to d^9s transitions in the Cu^+ ion, which are allowed due to the tetrahedral symmetry of the lattice.

There is undoubtedly a crystal field splitting of these levels due to the lattice symmetry, and the effect of pressure may be further complex splitting and shifting, resulting in the observed blue shift. The loss in strength

²⁴ F. Herman, J. Electronics **1**, 103 (1955).

²⁵ H. Fesefeldt and Z. Gyulai, Göttingen Nachr. 226 (1929).

²⁶ E. F. Gross and A. Kaplyanski, Optika i Spektroskopiya **2**, 204 (1957).

²⁷ F. Seitz, Revs. Modern Phys. **23**, 328 (1951).

of the peak with increasing pressure could be due to many possible effects, including the changes in the background absorption, pressure effects on lattice vibrations, production of lattice defects, or effect from the NaCl matrix in which the CuCl particles are dispersed. A d^{10} to d^9s transition requires a mixing of symmetrical and antisymmetrical states, which is already present in the zincblende structure, but is somewhat increased by lattice vibrations.

For complete understanding of the band structure, a wide variety of measurements would be necessary on

each compound. It is hoped that these optical measurements will promote some general understanding of the band arrangement of compounds of the same crystal structure, and of the effects in going from a purely valence crystal to a largely ionic compound.

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Ferromagnetism in Dilute Solutions of Cobalt in Palladium

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Measurements of the magnetic properties of solid solutions of cobalt in palladium show that ferromagnetism exists in solutions as dilute as 0.1 at. % of cobalt, when the cobalt atoms are about 10 at. diam apart. The ferromagnetic Curie point is established in this alloy by three different methods as 7°K. Bohr magneton numbers are determined for the whole series of alloys, and the moment associated with one cobalt atom is found to increase with dilution from 1.7 Bohr units in pure cobalt to a limit of 9 to 10 units in the greatest dilution. Lattice constants measured at room temperature show the effect of the onset of ferromagnetism at about 10 at.% cobalt. A simple model explains the magnitude and variation of the cobalt moment.

CONSTANT,¹ and more recently Gerstenberg,² have shown that dilute solutions of cobalt in palladium are ferromagnetic, and that the moment associated with one cobalt atom (the total ferromagnetic moment divided by the number of cobalt atoms) is greater than the atomic moment of pure cobalt. Working at temperatures above 80°K, ferromagnetism was observed^{1,2} in alloys as dilute as 5 at. % cobalt. Crangle,³ working to 20°K, has found ferromagnetism in solutions of iron in palladium as dilute as 1.25 at. % iron. If it is assumed that the total moment is carried by the iron atoms the moment per atom must be more than 7 Bohr magnetons. As Gerstenberg and Crangle point out, it must be concluded that some of the moment resides on the Pd atoms.

The present work was undertaken to find out how dilute the cobalt alloys could be made and still remain ferromagnetic. As shown below, the most dilute alloy studied, 0.1 at. % of Co in Pd, was found to be ferromagnetic even though the distance between Co atoms is about 10 at. diam. Interpretation is given of the high moment per cobalt atom, and of ferromagnetic interaction over these long distances.

MATERIALS AND MEASUREMENTS

The palladium used was of 99.999% purity, the greatest impurities being 0.0002% each of Fe and Cu. The purity of the electrolytic Katanga cobalt was 99.91%, the principal impurities being 0.04% Fe and 0.04% Si. The constituents were melted in argon in pure fused silica and raised to about 1800° with high-frequency heating. After cooling they separated from the silica with no sign of corrosion. The loss in weight during melting was usually less than 0.1%. Spectroscopic analysis of the specimen containing 0.1 at. % Co showed a trace of silicon and iron to the extent of less than 0.001%; photometric analysis of Co gave 0.10 at. %.

Magnetic moments were measured in fields up to 12 koe at temperatures down to 1.3°K, as previously described.⁴ The moment per atom of alloy was determined by extrapolation to $T=0$, $H=\infty$, except that in the most dilute alloys the paramagnetic moment of pure palladium was subtracted before extrapolation. Curie points were determined by the classical Weiss-Forrer method and also by the method of plotting⁵ H/σ_m vs σ_m^2 , σ_m being the magnetization per mole.

⁴ R. M. Bozorth, H. J. Williams, and D. Walsh, *Phys. Rev.* **103**, 572 (1956).

⁵ K. P. Belov and A. N. Goriaga, *Fiz. Metal. i Metalloved. Akad. Nauk S.S.S.R.* **2**, 3 (1956); A. Arrott, *Phys. Rev.* **108**, 1394 (1957); J. S. Kouvel, C. D. Graham, and J. J. Becker, *J. Appl. Phys.* **29**, 518 (1958).

¹ F. W. Constant, *Phys. Rev.* **36**, 1654 (1930).

² D. Gerstenberg, *Ann. Physik* **2**, 236 (1958).

³ J. Crangle, *Phil. Mag.* **5**, 335 (1960).