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ULTRAPRESSURE MATERIALS SCIENCE

"Final Report, covering the period, Jan. 1, 1982-June 30, 1984
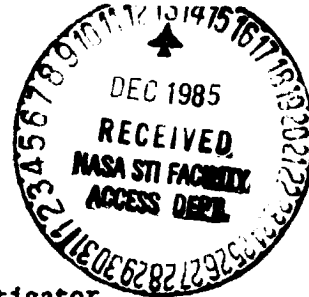
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ABSTRACT

During the grant there were three active areas of research at
ultra pressures: Diffraction Studies with the Cornell High Energy
Synchrotron Source (CHESS), Band Gap and Absorption Edge Effects,
Indentor-Anvil Experiments and Theory and Research to Attain Higher
Pressures. In this research grant we were able to extend the range
over which we actually obtained x-ray diffraction data and absorption
edge data to 700 kbars. Using the indentor technique we were able to
attain pressures of 2.1 Mbars. Our results will be described in the
following sections.

DIFFRACTION STUDIES WITH CHESS

Using energy dispersive x-ray diffraction techniques with CHESS,
we are now able to obtain in one hour (often less), in a successful
experiment, a dozen or so diffraction peaks on a high pressure
polymorph to 700 kbars; with earlier techniques we would have obtained
perhaps three or so peaks in an experiment lasting several hundred
hours. The experimental aspects of this technique are now published.[1]
A summary of results were presented as an invited paper in Bad Honnef,
Germany.[2] These results, along with the diamond indentor-anvil
experiments, were also described at a Special American Chemical Society
Symposium.[3] The work on germanium confirmed the β-Sn tetragonal
structure found by Jamieson.[4] The work on GaAs and GaP led to the
successful determination of the crystal structures of the high pressure

polymorphs for the first time. GaAs has a crystal structure which is an orthorhombic distortion of the sodium chloride structure in which the cell is stretched along one cube axis and compressed along another cube axis. GaP has the β-Sn tetragonal structure with the Ga and P atoms randomly located.[5] The high pressure phase of AlB has the same structure as the high pressure phase of GaAs.[6] This completes the phase of the work to 250 kbars.

The next phase of the diffraction work involved studies on the mercury chalcogenides which carried us into the pressure regime of 500 kbars.

The stable form of HgS at atmospheric structure is cinnabar, a material with a hexagonal structure which is a semiconductor at atmospheric pressure. At high pressure (130 kbar) this material has a phase transition (observed by us for the first time). Figure 1 shows
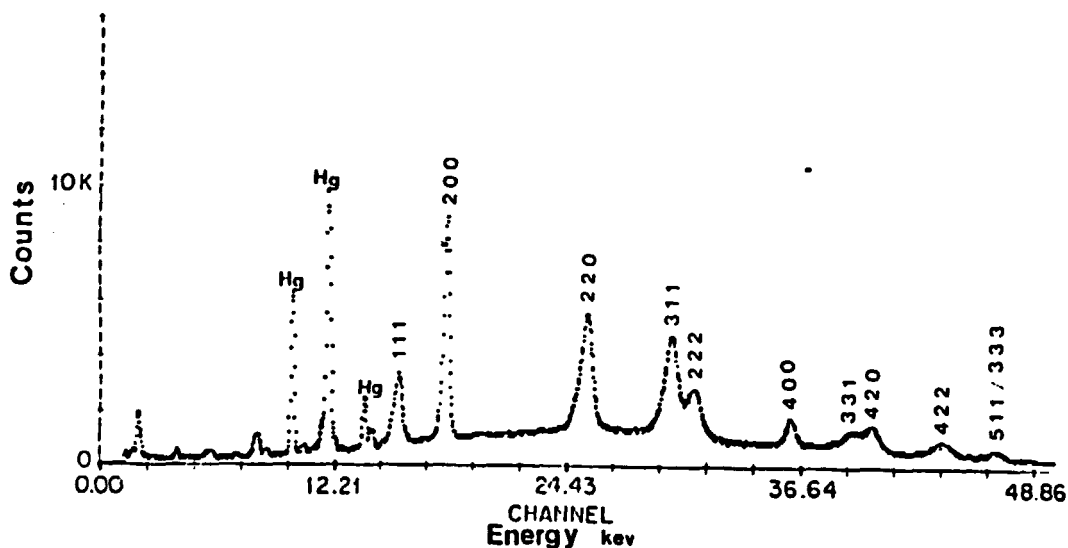

Fig. 1. Diffraction pattern of HgS at 300 kbar.

the diffraction pattern of this new phase at 300 kbars. The pressure medium is $Ch_3OH - C_2H_5OH$.

Table 1 shows the experimental d-spacings, the calculated d-spacing on the assumption that the new structure is a NaCl-type structure, and the observed and theoretical relative intensities. The ten well-indexed peaks at high pressure and the good agreement of the intensities show that <u>quantitative results</u> are possible at high pressure. Similar results were obtained at 400 kbars.[7]

It was known that both HgSe and HgTe transform from the cinnabar structure to a new phase at high pressure. We showed for the first time that the new structure in each case is the NaCl-type structure. Moreover, in each case, we found that at a still higher pressure, the

Table I. The analysis of the diffraction pattern of Fig. 1. NaCℓ crystal structure at 300 kbar based on a=5.070±0.005 A.

Index	Energy(kev)	$d(A)_{obs}$	$d(A)_{cal}$	I_{obs}	I_{cal}
111	15.61	2.930	2.927	32	25
200	18.07	2.531	2.535	87	62
220	25.53	1.792	1.793	100	100
311	29.92	1.529	1.529	76	64
222	31.22	1.465	1.464	43	31
400	36.15	1.265	1.268	13	10
331	39.30	1.164	1.163	10	13
420	40.33	1.134	1.134	14	19
422	44.19	1.035	1.035	11	11
333/511	46.88	0.9757	0.9757	3	4

NaCl-type phase transforms to another crystal structure.[8,9] A paper on
the structures of the high pressure polymorphs of the mercury
chalcogenides was presented at the IX AIRAPT International High
Pressure Conference held in Albany, NY, July 24-28, 1983 and has been
published in the proceedings.[10] It is also discussed in Huang's Ph.D.
thesis.[11] These results are summarized in Table 2. It is pointed out
that this is a fascinating series of compounds with the crystal
structure sequence being zincblende, cinnabar, sodium chloride, β-Sn,
and distorted CsCl (discussed later) which are respectively semimetal,
semiconductor, excellent metal, metal and (probably) metal.

Table 2. Summary of the Pressure-Induced Phase Transitions of Mercury
          Chalcogenides

Phase	I	II	III	IV	V
Structure	Z.B.	Cinnabar	NaCl	b.c.t.*	
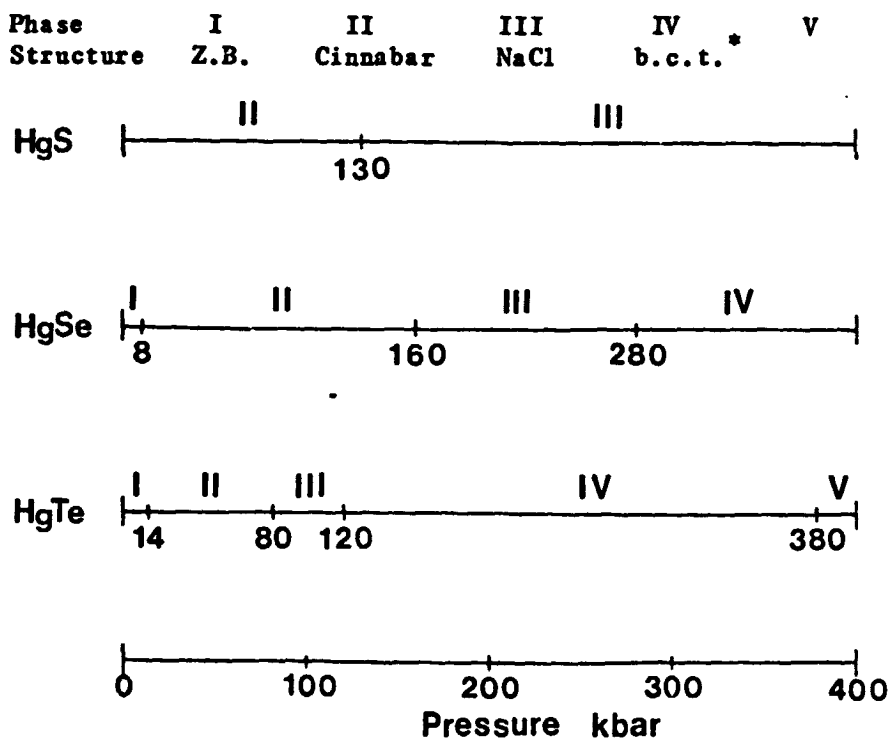
* The ordered compound analog of the β-Sn structure. However,
  the descrepencies with the calculated and the theoretical
  intensities is such that we can not determine the space group
  definitely.

We now enter the third phase of the high pressure diffraction studies which extended the pressure at which diffraction studies are made to 700 kbars and included studies on CsI and BaTe and BaSe. In CsI we found a surprising transition from the cubic CsCl structure to a tetragonal structure which appears to occur at constant volume. This transformation was first reported at the 1983 AIRAPT Conference in July 1983 in Albany, NY.[12] This transformation at 380 kbars is also discussed further in other papers of ours.[11,13] The equation of state was measured to 660 kbars. We will talk about the optical properties of CsI in a later section.

We showed that BaTe and BaSe both transformed from NaCl-type to CsCl-type at 48 and 60 kbars, respectively. We also obtained the equation of state of these materials to 410 and 610 kbars, respectively. These results were presented at the AIRAPT meeting mentioned previously[14] and elsewhere.[11,15,16] They will be used in the next section.

BAND GAP AND OPTICAL ABSORPTION EDGE STUDIES

It was noted by Ruoff[17] that for the rare gas solids, the alkali halides and the alkaline chalcogenides (including oxides), we found a simple relationship between the optical dielectric constant and the optical band gap of the form.

$$\kappa_o \, E_g(eV) = D(eV), \qquad (1)$$

where $D = 21.1$ eV.

Moreover, it was noted that this relationship holds for xenon as a function of pressure. As we become able to independently measure refractive index, n, as a function of pressure ($n^2 = \kappa_o$), this relationship can be tested in more detail. The results at atmospheric pressure are illustrated in Fig. 2. These results were presented at the IX AIRAPT Conference.[17]

This simple relation along with the Herzfeld criterion provides a simple model for the band gap versus volume of the closed shell systems of Figure 2.
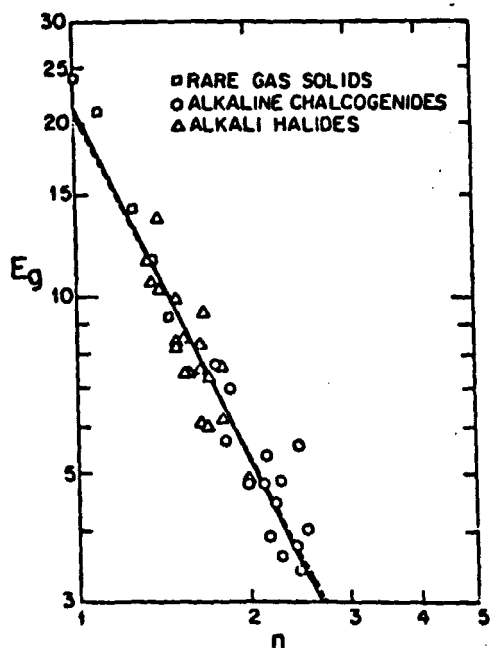

Fig. 2. Plot of the logarithm of the energy band gap versus the logarithm of the refractive index of the rare gas solids, alkali halides and alkaline chalcogenides. The dashed line is the best least squares fit. The solid line is the best least squares fit for the case where the slope is assumed to be -2.

The Herzfeld condition is obtained from the Lorentz-Lorenz equation.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{R}{V} \qquad (2)$$

where R is the molar refraction and V is the molar volume. At zero pressure

$$\frac{n_o^2 - 1}{n_o^2 + 2} = \frac{R}{V_o} ; \qquad (3)$$

metallization corresponds to n → ∞ and hence to

$$1 = \frac{R}{V_m}. \qquad (4)$$

It is assumed that the molar refraction does not vary with pressure, i.e., it is an intrinsic property of the atom or compound, so the Herzfeld condition follows from these two relations:

$$\frac{n_o^2 - 1}{n_o^2 + 1} = \frac{V_m}{V_o} , \qquad (5)$$

[K. F. Herzfeld, Phys. Rev. $\underline{29}$, 701 (1927)]. Here n_o is the refractive index at zero pressure, V_o is the molar volume at zero pressure, and V_m is the molar volume when metallization occurs. The theory is strictly applicable to cubic solids only.

With the same assumption on R we can write

$$\frac{n^2 - 1}{n^2 + 2} = \frac{V_m}{V} . \qquad (6)$$

Combining (6) and (7) we have

$$E_g = D(V-V_m)/(V+2V_m) \qquad (7)$$

This was fitted to our experimental absorption edge data to obtain D = 22.7 eV and V_m/V_o = 0.655 as shown in Figure 3.[16]

Note that our Eg vs. P data was actually combined with our P(V) data from x-ray measurements mentioned in the previous section to get the Eg(V) data in Figure 3.
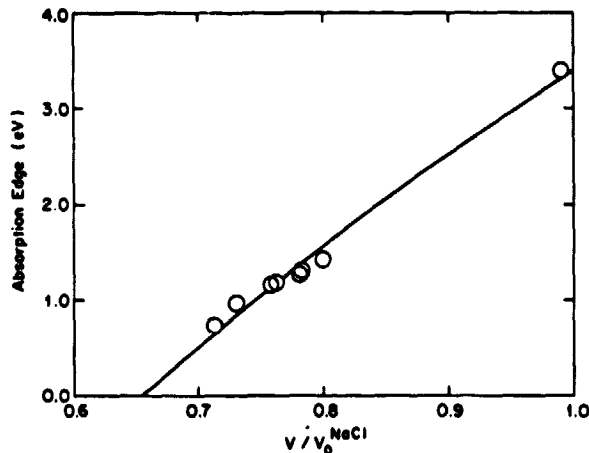

FIG. 3. Absorption edge vs volume fraction at 296 K. The solid line is fitted to Eq. (7).

Note that the D agrees closely with the general D in Eq. (1) while the fractional volume at metallization is close to that predicted from the Herzfeld criterion [Eq. (5)] which is V_m/V_o = 0.623. It is a challenge to theoretical physicists to explain why Herzfeld's assumption apparently works so well.

Figure 4 shows similar data for CsI.[11] Here we have analyzed the data as if it is a direct band gap E_{t_1} and indirect E_{t_2}. The cubic to tetragonal transition mentioned earlier occurs at $V/V_m = 0.54$. We noted it occurs without measurable volume change. Note that there is no noticeable discontinuity in the energy gap either. The extrapolated intercepts are at volume fractions of 0.39 and 0.44. The Herzfeld prediction is at 0.42. The highest pressure point in this data is 710 kbar. The transition pressure is likely to be above 1 Mbar.

INDENTOR ANVIL EXPERIMENTS AND THEORY AND RESEARCH TO ATTAIN HIGHER PRESSURES

Results with the diamond indentor-diamond anvil system have been described in an invited paper at a special American Chemical Society Symposium.[3] A thorough review was given in the leadoff plenary talk at the Eighth AIRAPT Conference on High Pressure at Uppsala.[18] This technique was used in an earlier NASA grant to show that PMMA (polymethylmethacrylate) was still an electrical insulator at a pressure of 1 Mbar [K. S. Chan and A. L. Ruoff, J. Appl. Phys. 52, 5395 (1981)].

In this technique it is necessary to produce interdigitated electrodes of small dimensions. We have succeeded in producing interdigitated electrodes with a spacing of 1400Å and a width of 2000Å (see Figure 5), a considerable improvement over the 0.5 μm electrodes produced previously.
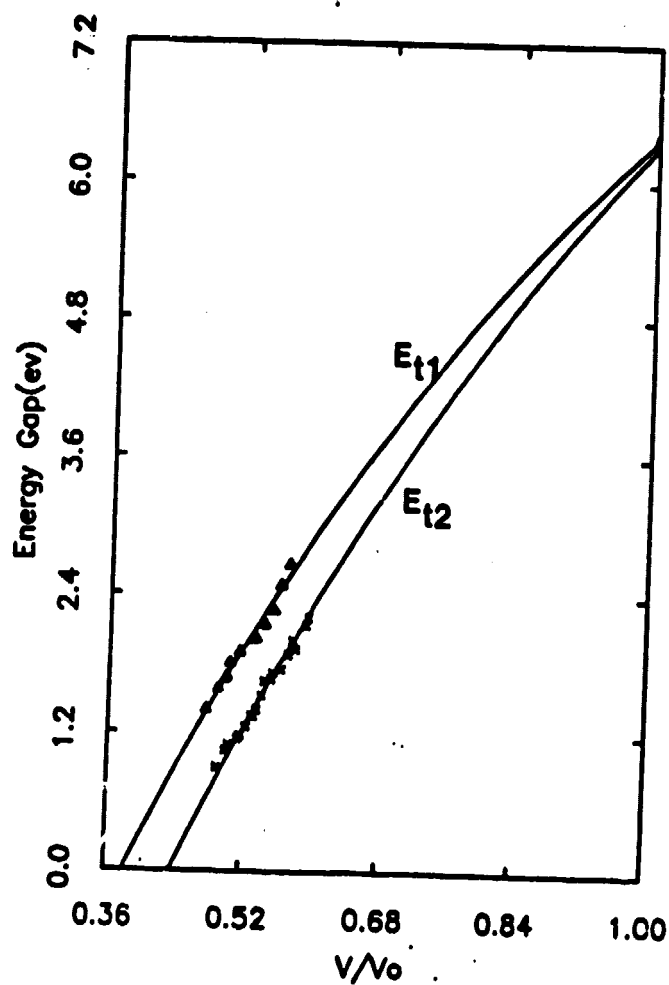
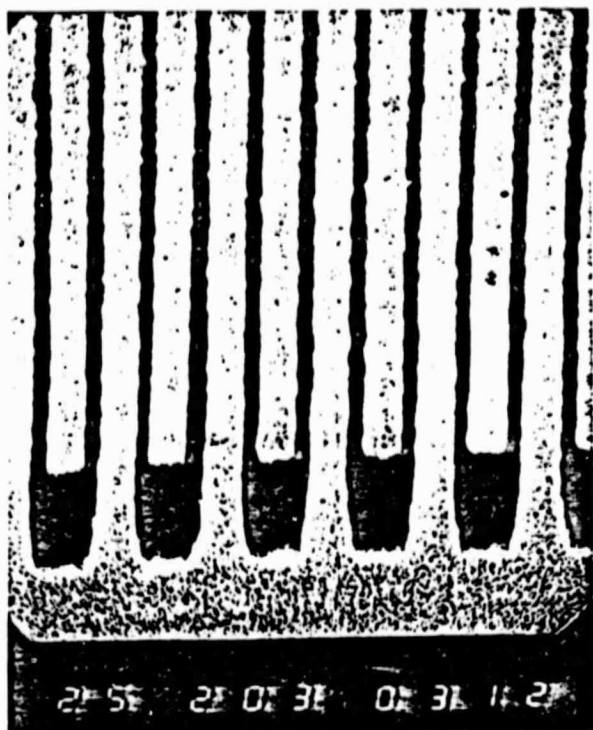Figure 4. Optical Band Gap versus fractional volume for CsI assuming direct (1) or indirect (2) gaps.

Figure 5

Interdigitated electrode of
palladium on diamond produced
by electron beam lithography.
Spacing 1400Å, line width
2000Å.

It is important to note that pressures of 2.1 Mbars were
obtained.[18]

In our studies of indentors we developed a new method for the
observation of ring cracking in electrical insulators,[19] which nicely
compliments optical observation and provides a method of in situ
measurement even if the sample is not transparent.

We carried out an important analysis (finished during this grant)
involving pressure concentrations created by plastic flow of thin discs
between rigid anvils. This gives the maximum attainable pressure and
involves only the compressive flow stress of the crystal (including
strain hardening) and the aspect ratio a/h (where a is the disc radius
and h is the gasket thickness). This gives us a good physical
understanding of how extreme pressures are created in the diamond

window cell.[20] (These attainable pressures are currently limited by the fact that the diamonds are not rigid so the faces become concave under the stress. Hence the diamonds touch at the edges while h at the center is still finite. If the diamonds were rigid and perfectly aligned, then h could be made arbitrarily small and the pressure arbitrarily large if the diamonds also had infinite strength.) In special cases the compressive flow stress of the sample (or gasket) varies strongly with pressure; this problem was also analyzed. This analysis shows that the pressure present in xenon when Nelson and Ruoff observed metallization was greater than 1 Mbar rather than the smaller Hertzian pressure which they assumed.[21] While the obvious conclusion of this analysis is that we had underestimated the pressure, the much more important conclusion is that the diamond indentor-anvil system is capable of much higher pressures than thought previously.

Another important paper by other high pressure workers published recently measured the pressure distribution under spherical tips by observing the ruby shift of ruby powder through the flat diamond as a function of radius [M. I. Eremets, E. S. Itskevich, A. M. Shirokov and E. N. Yakovlev, J. Exp. Tech. Phys. 36 (3), 58 (1982).] The experimental results were in excellent agreement with our theoretical analysis.[20] The experimental pressure distribution with a gasket was of the form $P = P_o(1-r/a)$ where a is the contact radius and r is the distance along the flat from the center of contact. This means that the maximum pressure, P_o, is three times P_{av}. For the Hertz case (no gasket or sample) $P_o = 3 P_{av}/2$. Thus the presence of a plastically deforming gasket has doubled the maximum pressure. In the diamond

anvil cell, the maximum pressure would be three times the average gasket pressure. If, in addition, the yield stress of the gasket material increased strongly with pressure (a case we analyzed in detail[20]), then the pressure intensification can be much higher. Hence this analysis greatly increased our understanding of the role of the gasket in the diamond anvil cell.

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11. T.-L. Huang, "High Pressure Studies on Cesium Iodide and Mercury
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