OPTICAL STUDIES AT HIGH PRESSURE

by

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The purpose of this paper is to enumerate the salient features of the high-pressure optical cells developed at the University of Illinois and to mention briefly a few of the types of studies practical with the apparatus.

The room temperature optical apparatus has been thoroughly described elsewhere.(1) There are two cells, one useful to 55,000 atmospheres (Fig. 1), the other with a range occasionally exceeding 200,000 atm (Fig. 2), but with a less direct pressure calibration. Each cell involves an outer jacket of AISI 4340 or 6150 steel hardened to 42 Rockwell C, an insert of Solar or Labelle HT tool steel hardened to 59-60 Rockwell C, and jacketed carboloy pistons. In each case the pressure transmitting "fluid" is

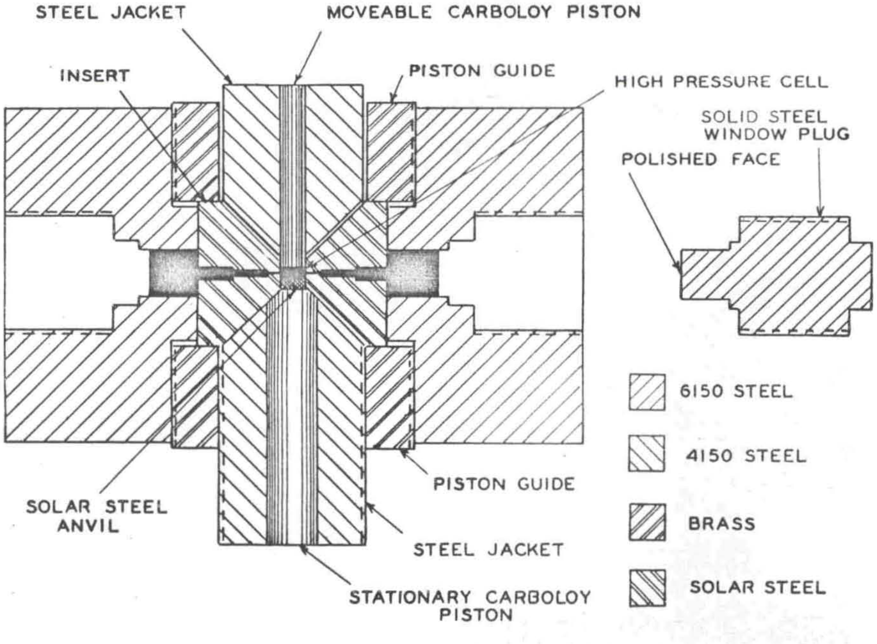


Fig. 1 Diagram of 0-53,000 atm pressure cell.

NaCl. The pistons have a very short bearing area in the cylinder (not over 0.060 inch). This minimizes friction. They are jacketed to within 0.080 inch of the cylinder, and brass guides keep them aligned. The unusual features are described below.

1. The Windows. The windows consist of a series of concentric bales in the insert telescoping towards the center (see Figs. 1 and 2), NaCl is pressure fused in the windows by applying 20,000 atm to heated NaCl crystals, alternately in the window bales of the outer jacket and in the center hole. Ultimately one obtains a strained crystal which transmits light quite well. The strain is such as to cause about 20 per cent depolarization of polarized light, which is a handicap in some experiments. The center pellet can be pressed out and a new pellet inserted containing a new sample. This procedure can be repeated many times. Any cracking of the windows can be repaired by repressing. Cells have been used for over 100 runs without replacing the insert. Usually the insert is discarded because of stretching before the windows give out.

2. The Tapered Piston. In order to reach pressures several times the compressive strength of carboloy some form of support is necessary. The tapered pistons (Fig. 2) are normally 1/2 inch in diameter with a 0.090 inch diameter flat. A taper of 6° proves to be the most efficient when using NaCl as the "fluid." The entire chamber is filled with salt, but the sample is inserted in a small slot between the flats, so it is under uniform pressure. There are several advantages to the tapered piston arrangement. In the first place, only a small area in the center is strained beyond the yield point, and this area is supported by the mass of material not so strained. This is Bridgman's principle of "massive support." In the second place this is a very efficient multistage apparatus. Most two stage setups are already awkward. Here one has essentially an infinite number of supporting stages as each differential layer of salt, going out on the taper, supports the next inner layer which is at a slightly higher pressure. At the maximum average applied pressure of slighly over 50,000 atm, the pressure at the wall is well below this value. Thus the windows and vessel are not strained as highly as in the single-stage apparatus described earlier.

The calibration was accomplished as follows. It was possible to observe optically several phase transitions studied by Bridgman,$^{(2)}$ e.g., KCl--18,000 atm,

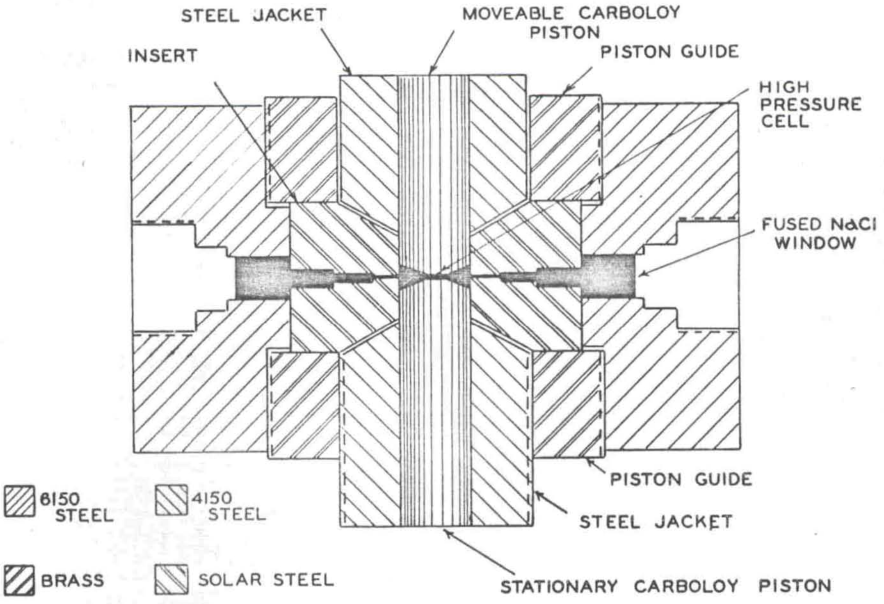


Fig. 2 Diagram of 0-250,000 atm pressure cell.

HgI_2--13,500 atm, AgBr--83,000 atm, AgCl--87,000 atm. (The optical effects due to light scattering at a phase transition are quite dramatic, and, in fact, form the basis for a current study of kinetics and mechanism of phase transitions.) These transitions gave certain fixed points as a function of applied force and center thickness. We then measured the shift of numerous peaks and absorption edges with pressure for various applied pressures and pellet thicknesses. By curve fitting it was possible, for each substance, to predict extrapolated pressures as a function of thickness and applied force. Since the various substances extrapolated to the same pressures ($\pm$ 5000 atm at 200,000 atm pressure) there is a consistency to the calibration. Every substance studied in the cell is run at several pellet thicknesses, and the consistency from thickness to thickness gives a check on the calibration. In its final form, the calibration can be written(3)

$$p_c = p_a \left[1 + \frac{10.8}{p_a^{0.14}} \exp(-0.174\, t_c)\right]$$

where

p_c = center pressure, thousands of atmospheres

p_a = applied pressure, thousands of atmospheres

t_c = center thickness, thousandths of an inch.

Numerous runs have been made as high as 175,000 atm, and a few runs over 200,000 atm, although the accuracy of pressures above about 160,000 to 180,000 atm is much in doubt due to flowing of the carboloy. There is sufficient deformation of the carboloy to require regrinding for every run over about 160,000 to 180,000 atm.

There exists the possibility of significant nonhydrostatic optical effects because of the medium used. We were able to check several shifts obtained in a liquid cell to 10,000 atm. Apparently the strains and dislocations introduced in the sample, which would certainly have measurable effects in an electrical conductivity experiment, introduce optical absorption at too low a level to affect the spectra observed. There are theoretical calculations(4) which indicate that it would take a very high concentration of dislocations to give a large optical absorption.

3. The High-Temperature Optical Cell. The optical cell has been modified to extend to high temperature and pressure.(5) One piston is ground 0.008 inch undersize and insulated from the insert with mica. Salt and pipestone are extruded in the gap to hold the mica in place. The piston is also backed with a sheet of mica. The heater arrangement is shown in Fig. 3. Four holes are drilled, carefully spaced, around the center flat. Graphite is fused in the holes. A wattage-temperature calibration was obtained by observing optically the melting points of a number of substances near atmospheric pressure. The observation of phase transitions at high pressure indicates that the

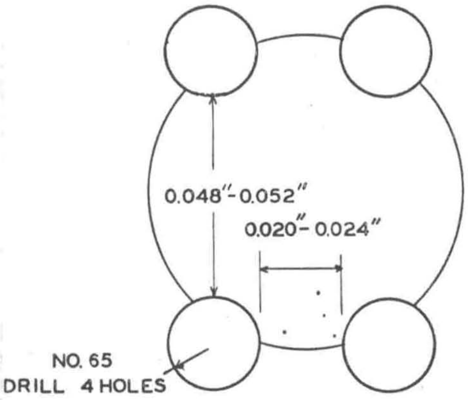


Fig. 3(a) Positioning of resistors in center of pellet.

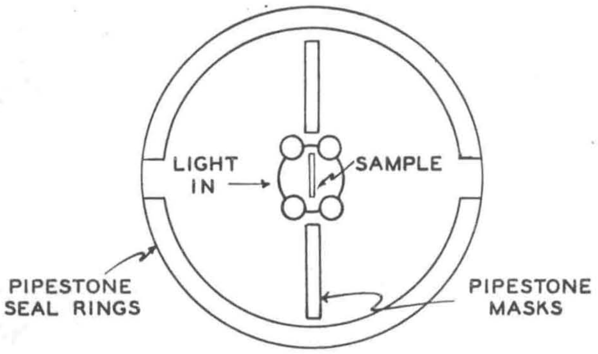


Fig. 3(b) Salt pellets with slots cut for sample and pipestone masks.

calibration is not affected by pressure.

One would expect some pressure redistribution in the salt at high temperature. The pressure at high temperature is obtained as follows. The spectrum of the substance to be studied is run as a function of pressure at room temperature. A spectrum is then taken at elevated temperature and pressure, the cell quenched with an air blast, and a room temperature spectrum run. It is presumed that the high-temperature pressure distribution is quenched in, and the pressure is calculated from the room temperature data. The operation is repeated at successively higher temperatures. A new sample is loaded for each "isobar." There is a considerable pressure correction for temperatures at lower pressures, but above 100, 000 to 120, 000 atm this becomes negligible. In view of the rapid rise of melting point with pressure for NaCl(6) this result is not surprising.

Spectra have been obtained at 500°C and 180, 000 atm. The operation is limited by the fact that the sample cannot be placed inside the heater, and by non-negligible emission from the heaters.

4. Results. It would not be possible to discuss any large fraction of the systems which have been studied optically or which are now under study. Nor could the theory behind any of these be presented in any detail in this paper. A few examples of typical optical studies are presented below under three general categories. Many of these data are discussed in detail elsewhere.

(a) Absorption Edges. One of the most fundamental properties of an insulator is the energy gap between the valence band (the highest band containing electrons) and the conduction band (the lowest empty band of allowed energies). When this gap is large compared with kT one has a normal nonconductor. When this gap is a few kT one has an intrinsic semiconductor. When the bands overlap, the material is a metal. An electron can be excited from the valence to the conduction band by electromagnetic radiation of the appropriate energy. Since this is an allowed transition the crystal will absorb this energy strongly. This steep rise in absorption is known as the "absorption edge." Its shift with pressure tells a considerable amount about the effect of interatomic distance on band structure.

In Fig. 4 is shown the shift of the absorption edge of several elements with density(7) (using Bridgman's compressibility data). It can be seen that they all follow the same pattern, and that by the time the solid is compressed 50 per cent all will be metallic. One can estimate that this will occur, e.g., for selenium at 135, 000 atm, for iodine at 250, 000 atm, and for sulfur by about 400, 000 atm.

Figure 5 shows the effect of pressure on the edge of several substances having the zinc blende lattice.(8, 9) The band structure of these substances is rather complex and cannot be discussed in detail here. Ge, GaAs, and ZnSe are isoelectronic, but Ge is entirely a valence crystal, while ZnSe should have a significant ionic component. All show an increase in gap with pressure at low pressures. The direction of shift ultimately reverses. The magnitude of the initial shift is quite different for Ge and GaAs, and there is evidence that the transition involved in the two cases is quite different.

Ge is directly below Si in the atomic table. GaP should be intermediate in electronic structure, and the shift of the edge with pressure is indeed intermediate. These and related results are very important for our understanding of the behavior of the large class of semiconductors and phosphors having the zinc blende structure.

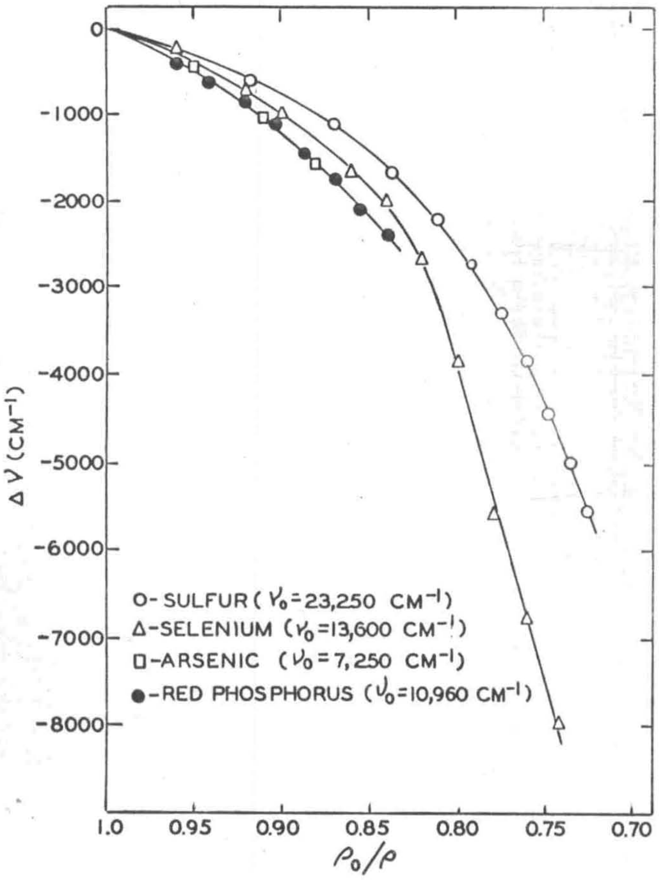


Fig. 4 Shift of absorption edges of some elements with density.

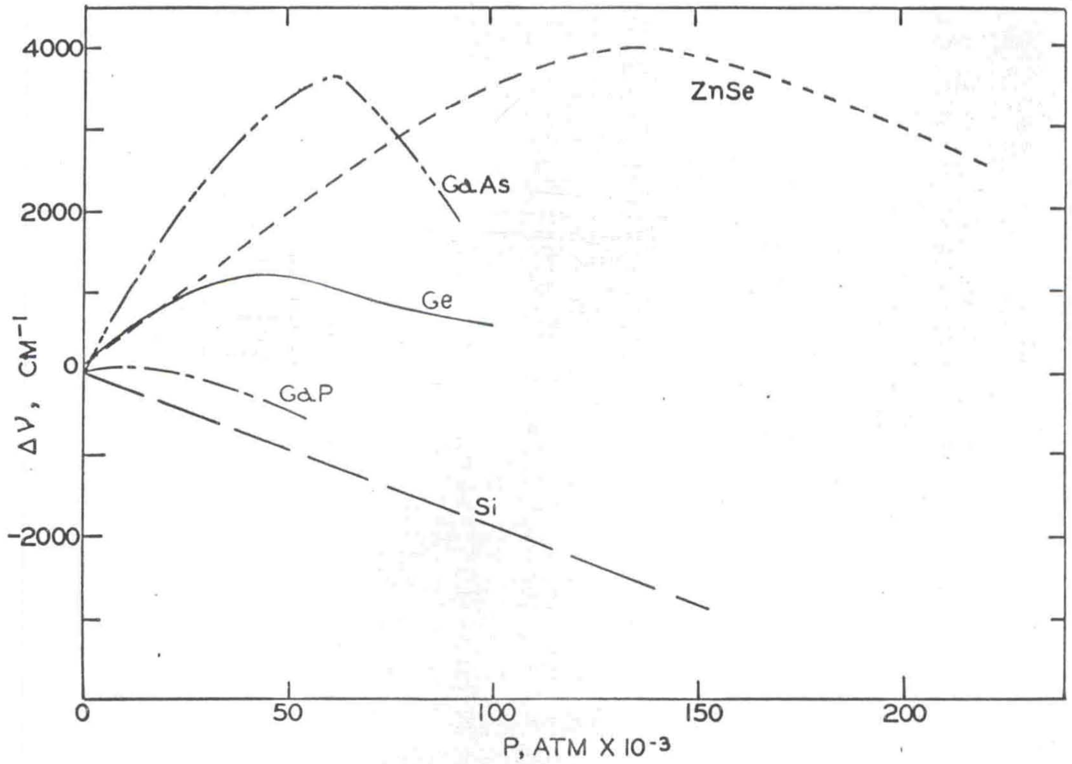


Fig. 5 Shift of absorption edge of semiconductors vs pressure.

The idealized picture of a perfect ionic crystal would involve a valence band constructed entirely from anion wave functions and a conduction band made entirely from cation wave functions. Since one would anticipate a much large deformation of the conduction band than of the valence band with pressure, one would expect the pressure effect to be independent of the anion for lattices with the same band structure. Figure 6(10) shows the shift of the edge for three compounds having the structure O_h^1, and for two compounds having the structure V_h^{16}, and one finds that the assumption is quite good.

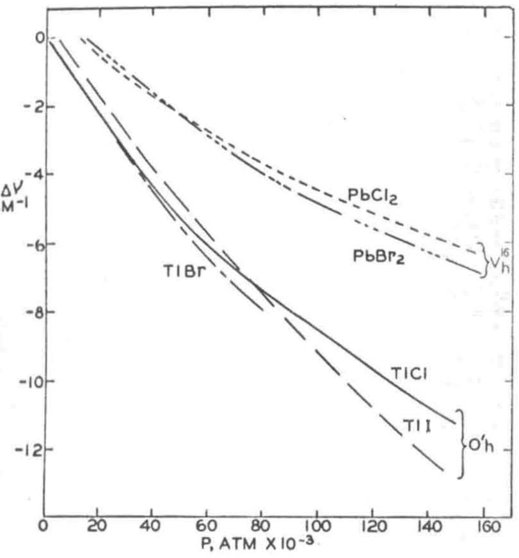
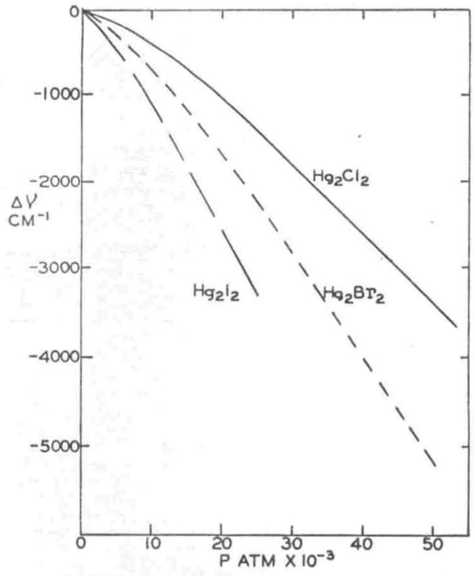


Fig. 6 Shift of absorption edge with pressure-ionic crystals.

On the other hand, a typical molecular crystal shows a good deal of sharing of wave functions in both the valence and conduction bands. Figure 7(11) shows that in this case the shift is quite dependent on the more electronegative atom.

Fig. 7 Shift of absorption edge with pressure-molecular crystals.



At a solid-solid phase transition there are rather spectacular optical effects, including a large discontinuous shift of the absorption edge. One can find out a good deal about electronic structure from a study of these discontinuities. Figure 8(2, 10) shows the shift of the edge vs pressure for several solids having phase transitions. The three silver halides are particularly interesting. AgCl and AgBr are much alike. Both are initially in the f.c.c. structure and show a very small shift of the edge with pressure. At 83,000 to 87,000 atm they show a phase transition, presumably to the SC (CsCl) structure accompanied by a large decrease in the energy gap. The high-pressure phase also shows a small shift with pressure. AgI, on the other hand, starts out in the zinc blende lattice, transforms at 4000 atm to the f.c.c. phase with a large decrease in gap, and shifts rapidly (like most ionic crystals) to 115,000 atm where there is a second phase change, presumably to the SC structure, accompanied by an <u>increase</u> of the gap. The high-pressure phase behaves like AgCl and AgBr. These peculiarities can be related to the unusual optical properties of the silver halides.

(b) Transitions Isolated at a Point in a Lattice. A most interesting set of electronic transitions are those where the ground state and excited state are both on the same entity (usually an atom or ion). The excitation may travel from atom to atom, but there is no electron transfer.

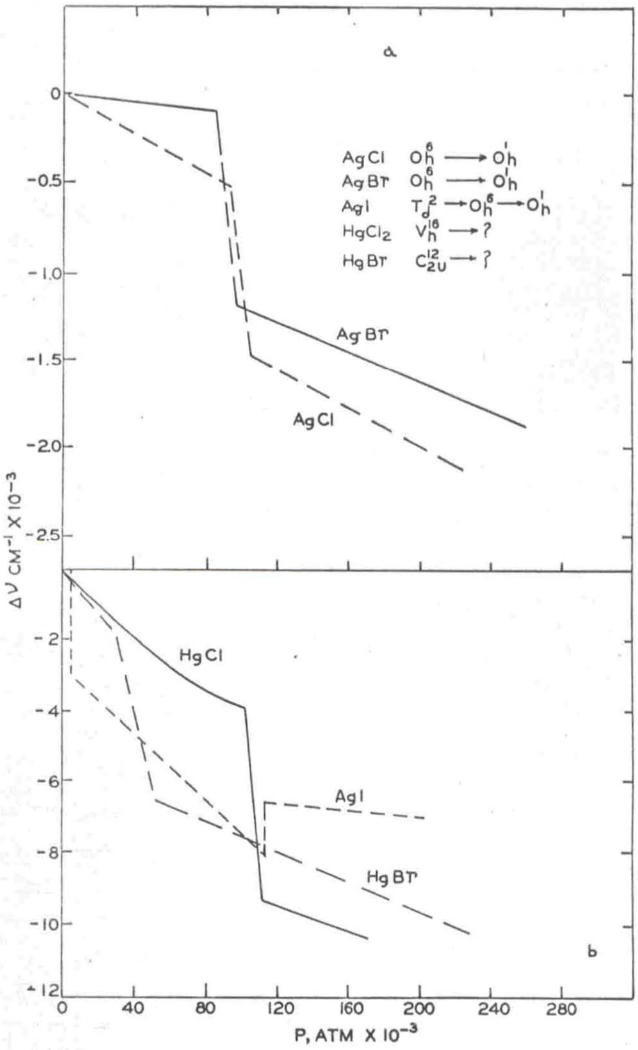


Fig. 8 Shift of the absorption edge at phase transitions.

A simple case of such excitation is the F center in alkali halides, a negative ion vacancy with a trapped electron. The electron jumping from the ground state to the first excited state is responsible for the characteristic color of X-irradiated alkali halides. In the simplest picture this should behave as a particle in the box with $E \sim A_0^{-2}$ (A_0 = lattice constant). Data for a series of alkali halides show that this holds to a fairly good approximation. If one plots the shift of the absorption peak vs relative density (using Bridgman's data) one can then calculate the compressibility of the F center compared with the bulk compressibility. Figure 9(12, 13) is such a plot for NaCl, NaBr, and KCl. At low pressures the F center is about twice as compressible as the lattice. At high pressure the compressibility approaches that of the lattice. These results are quite compatible with the picture of the F center.

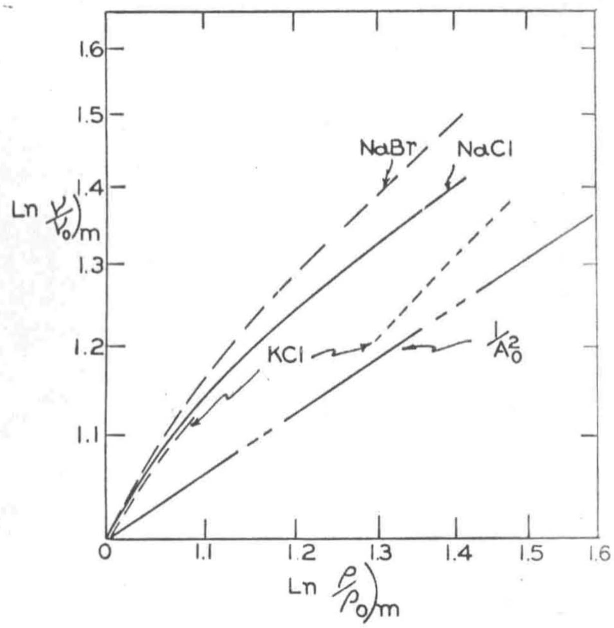


Fig. 9 Color centers in alkali halides.

An important class of phosphors involves a heavy metal ion dissolved in an alkali halide. Examples are Tl^+ and, more rarely, Pb^{++}. There have been a number of indications that these ions interact quite differently with their environment. Figures 10 and 11(14, 15) show the initial shift of the absorption peak with pressure for Tl^+ and Pb^{++}. For Tl^+ the shift depends strongly on the type of lattice involved, and only slightly on the halide. Pb^{++} depends strongly on the halide and only incidentally on the lattice. These results help to confirm the picture that the excitation is rather definitely isolated on the Tl^+ ion in the first case, but that the Pb^{++} ion is strongly complexed with the neighboring halides. Incidentally, at high pressures (over 80,000 atm) both phosphors show a definite shift to lower energy with increasing pressure. This would indicate that in all cases the excited state has a flatter curve with interatomic distance in the region of repulsion than does the ground state.

It might be mentioned in passing that it is quite possible with our apparatus to measure decay rates of phosphors as a function of pressure(16) although no data will be presented here.

An important and interesting class of optical phenomena concerns complexes or crystals involving transition metal ions. These ions are characterized by having a partially filled d shell. In the free ion the d levels are degenerate. In the field of the surrounding ions or molecules the d levels are split into two or more groups of levels

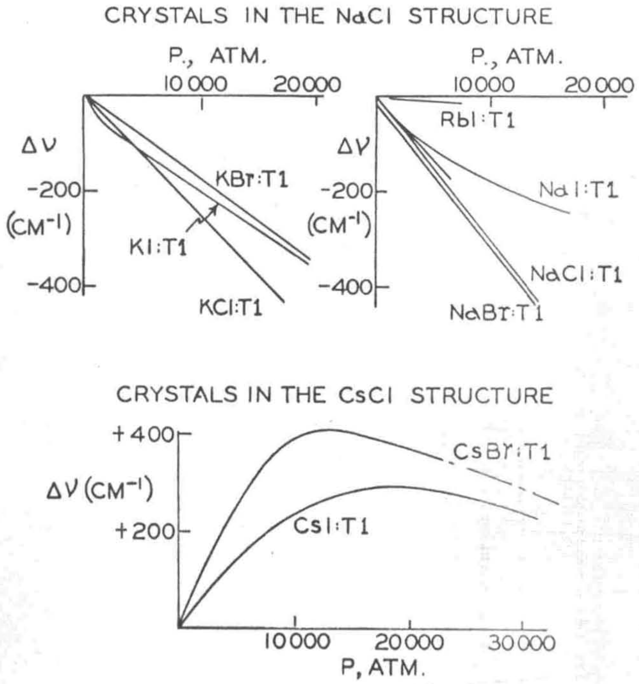


Fig. 10 Initial frequency shift vs pressure ten alkali halides activated by Tl.

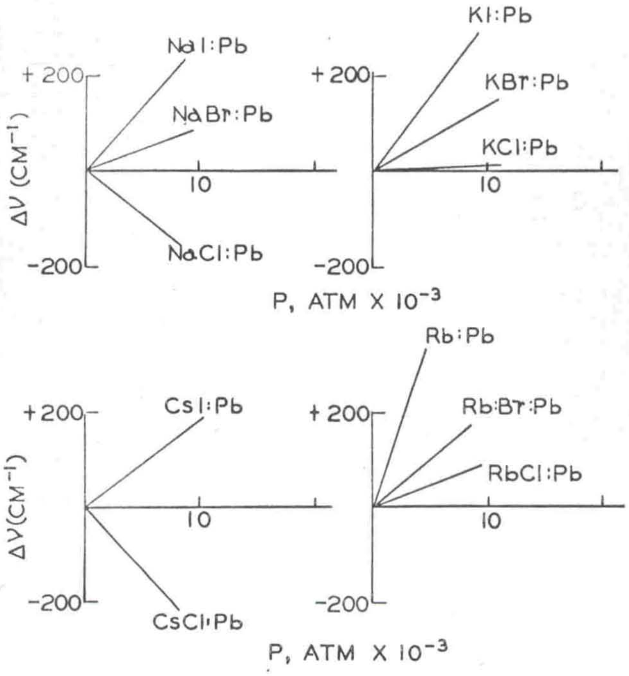


Fig. 11 Initial frequency shift vs pressure eleven alkali halides activated by lead.

having different energies. The characteristic colors are due to transitions between these levels. One of the most active branches of theoretical chemistry is crystal field theory, which attempts to relate these transitions to the intensity of the crystal field. With pressure one varies the ion-ligand distance and thus the strength of the field. This provides a very direct test of the theory. A very extensive program is underway in this area, but only one example is shown here. Figure 12(17) shows the increase of splitting with pressure for two of the peaks in $[Ni(NH_3)_6]Cl_2$. From each of these peaks it is possible to calculate the change of field intensity with pressure. If crystal field theory were rigorous these changes would be the same. From Fig. 12 we see that the theory actually applies quite well. There is a discrepancy of about 2 per cent of the total energy. This is larger than the possible experimental error and indicates the degree to

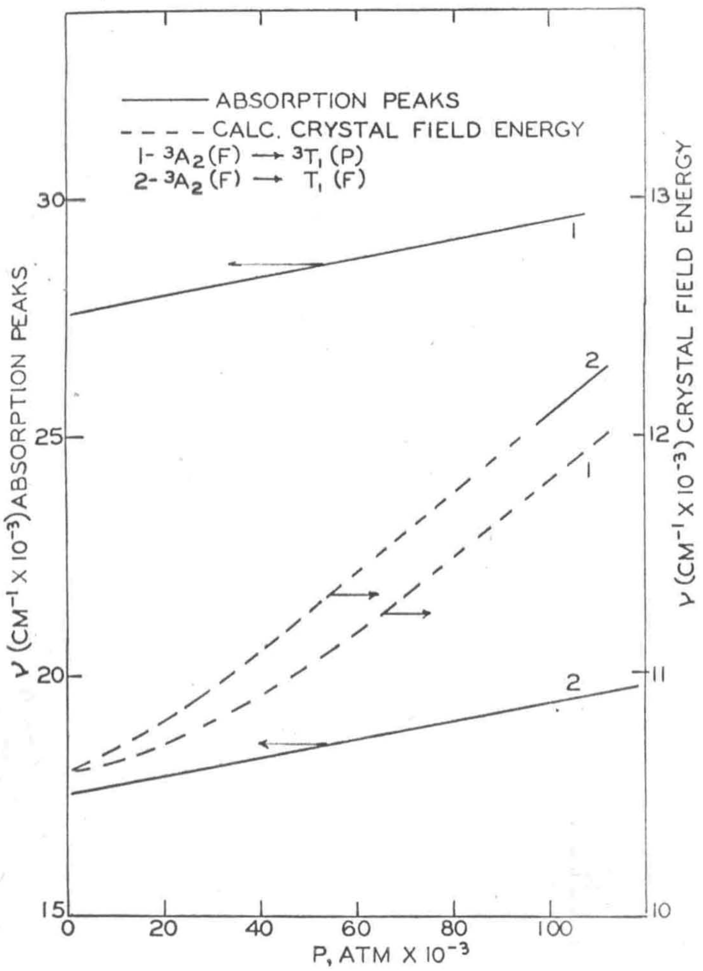


Fig. 12 Effect of pressure on d levels Ni^{++} in $[Ni(NH_3)_6]Cl_2$.

which covalent forces enter in, and to which molecular orbital theory is necessary for a complete explanation.

The rare earths form an interesting group of ions in that they have a partially filled 4f shell, although the 5p and 5s shells are filled. Their characteristic pastel colors are due to weak transitions from one state to another within the 4f shell. The "radius" of the 4f shell is of the order of 0.5 A. The ionic radius is about 1.5 A. The study of pressure effects on these transitions gives a measure of the degree to which external pressure penetrates the inner shells through ionic interaction. There are indeed definite pressure effects which will be discussed in detail elsewhere. One which can be mentioned briefly is the large increase in intensity. The transition occurs because of mixing of the 4f and 5d levels. The increase of intensity, then, is a measure of the increased mixing of levels due to increased overlap of neighboring ions.

(c) Charge Transfer. In addition to the transitions discussed above, a type of electronic interaction occurs wherein there is transfer of an electron from one entity to another. This may be a transfer from one part of a molecule to another, as in organic dyes such as fluorescin or the cyanines and porphyrins or as in the permanganate and chromate ions, or it may be between adjacent molecules or ions.

These are usually very intense transitions. As a matter of fact the absorption edge discussed earlier is a special example wherein both the ground state and excited state belong to the crystal as a whole, rather than to specific molecules or ions. These transitions are very sensitive to molecular configuration and to interatomic or interionic distance, and are thus pressure sensitive. It is quite possible to follow with increasing pressure the change in the character of the transition which may be clearly isolated on a given molecule or molecular ion at low pressure, and gradually become less and less localized until at the higher pressures it is entirely a lattice phenomenon.

The above results illustrate the effect of pressure on electronic structure, as well as the contrast between the effect of pressure and temperature on atomic and ionic interaction. The primary effects of temperature are in the energy of lattice vibrations and on the kinetic energy of electrons, with the expansion a secondary effect, i.e., temperature is primarily a kinetic variable. The primary effect of pressure is to vary the interatomic distance and therefore the interatomic potential. At very high pressures there will be a change of zero point energy, i.e., an increase of the Debye temperature and therefore a redistribution of vibrational frequencies.

It is hoped that this sampling of results will emphasize the importance of optical studies in understanding the effect of pressure on the structure of matter.

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DISCUSSIONS

by A.W. Lawson

I would like to remark that relatively speaking, Professor Drickamer has not received overdue credit for his early entry into the field of superpressures. The wide scope of his activities, while not as flamboyant as some other activities, is quantitatively more interesting and deserves more attention. Recently, at The University of Chicago, we have analyzed his data on absorption of Fe^{++} ions in garnet. We have used a point ion model and Slater antisymmetrized wave functions. If we take Z_{eff}, in the Slater functions to be 20 per cent less than that given by Slater rules we are able to obtain agreement with Clark's data on absorption in almandine-pyrope only if the Si-O bands are very nearly 50 per cent covalent as originally suggested by Pauling. Under those conditions the agreement with Drickamer's measured pressure dependence is within experimental error. This result seems to justify Phillip's recent contention that the effect of distributed charge very nearly cancels the effect of repulsive terms in the potential as indeed do the curves Drickamer shows in his Fig. 12.

by D. Langer

The disadvantage of not having true hydrostatic pressure can not be avoided in your apparatus. For some measurements, however, and especially at lower temperatures this lack might be intolerable. For one of such cases D. Warschauer and myself developed a gas pressure generator. Optical measurements were done up to 16 kilobars at room temperature and up to 12 kilobars at 77°K. Electrical measurements could be done under true hydrostatic pressure up to 18 kilobars at room temperature and up to the freezing point of helium at 77°K. A description of this apparatus will be published in the Rev. Sci. Inst.

by William Paul

I would like to comment on the abscissa used for the display of the data. It is, of course, quite proper to display the experimental data as a function of pressure, and, at low pressures, this can be understood also as a plot against lattice constant. At the pressures reached by Dr. Drickamer, it seems likely that the compressibility is very different at the top pressures from that at atmospheric pressure; yet it is probably the lattice constant that is the more fundamental quantity in what theory exists for these effects. Thus, for example, the linear relation between gap and pressure found for silicon may convert into a non-linear one when compressibility corrections are applied. Since the gap variation in silicon at high pressures is often taken to be indicative of the change with pressure of the (100) energy band minima in group IV and group III-V semiconductors at all pressures, a compressibility correction is not trivial for attempted fits of theory and experiment.

H. T. Hall

DISCUSSION

by W. B. Daniels

We have been investigating the possibilities of doing x-ray structure studies at high pressures in a device similar to that of Drickamer. Lithium hydride is being used as the sample holding and pressure transmitting fluid. This material is quite easy to handle and nearly transparent to x-rays.

Optical Studies at Hi P

Drickamer

PROGRESS IN VERY HIGH PRESSURE RESEARCH
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