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Pressure and Electronic Structure

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Experimentation at high pressures is essential to an understanding of the electronic structure of solids.

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Two of the basic properties which help determine the electronic structure of solids are the arrangement of the atoms (or ions) and the equilibrium interatomic distance. Pressure is a variable of prime importance for determining these two parameters. Experimentation at high pressures is, then, significant because it permits one to test theories where the variation of a property with interatomic distance is critical and because, on occasion, new polymorphic forms appear which permit one to study the relationship between atomic arrangement and electronic properties.

The range of pressure to be used depends on the type of measurement to be made, the degree of accuracy to which the data (and the pressure) must be known, and the degree of hydrostaticity required. The recent book *Solids Under Pressure* (*1*) gives a general review of experiments in this field. Techniques are discussed in a review article by Swenson (*2*) and in the book by Wentorf (*3*).

In this article I review some exploratory experiments on optical absorption and electrical resistance at relatively high pressures—in the optical work, to 160 kilobars (1 kilobar = 0.986 atmosphere); in the electrical measurements, to over 500 kilobars.

The pressures, especially in the electrical work, are rather imprecisely known. A complete understanding of the electronic structure would require a much wider variety of experiments. In particular, accurate knowledge of the interatomic distance as a function of pressure, and of the structure and lattice parameters of the new phases which appear at high pressure, would be desirable. Nevertheless these experiments have contributed to the understanding of a variety of problems and have unearthed a large number of new and interesting phenomena. I have selected a few illustrations which give some notion of the power and versatility of the techniques.

The energy states of an electron on a free atom or ion can be described in terms of its four quantum numbers. The lowest of these states is the ground state. These states are determined experimentally either by measuring the absorption of (usually electromagnetic) energy or by the emission of energy as an excited electron returns to the ground state. In this discussion we are concerned only with outer electrons, generally called valence electrons because they are involved when chemical reaction takes place. Only the ground state and the excited state nearest above it are important in the phenomena considered here.

When an atom or ion appears in a crystal, the electronic energy states are affected to a degree which depends on the interaction between the wave functions which describe the state in question and the wave functions of the other electrons in the crystal.

Both the ground state and the excited state may remain closely associated with the original atom. In this case, the energy states may be perturbed by the potential of the surrounding atoms and affected, because this potential has less than spherical symmetry. The optical absorption which represents transitions from the ground state to the first excited state still shows discrete peaks, perhaps somewhat broadened by the interaction described. In some cases, a single peak in a free ion may be split into two or more peaks in the crystal. This sort of effect can be observed in transition-metal ions in crystals, or in the spectra of some crystals of fused-ring aromatic compounds. An impurity in an insulating crystal may have highly localized states. The phosphor made by dissolving the Tl^+ ion in alkali halides is an example. Since, in both the ground state and the excited state, the electron is highly localized, one obtains no electrical conductivity in such systems.

As the wave function becomes a little more delocalized it is no longer practical to think of slightly perturbed atomic levels. Solution of the Schrödinger equation to determine the periodic potential of the lattice gives what is known as a Bloch function. This is of the form

$$\psi = u(r)\ \exp\ (i\mathbf{k}\cdot\mathbf{r})$$

where $u(r)$ has the symmetry of the lattice and the exponential expression represents a wave motion. Vector $\mathbf{k}$ is a reciprocal lattice vector which is called the crystal momentum since $\hbar\mathbf{k}$ represents the momentum of the wave. Solution of the wave equation indicates that there are bands of closely spaced allowed states separated by relatively

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large energy gaps, whereas, in a perfect crystal, there are no allowed states. Each of the states in the band can accommodate two electrons of opposite spin.

In a crystal made of atoms or ions having filled electronic shells (for example, Na$^+$ and Cl$^-$ or I$_2$), each state in the band is filled. Since the next available level is far out of reach, when an electrical potential is applied there are no available empty states and therefore there can be no net displacement of electrons. Thus one has an electrical insulator. One can get significant conductivity by supplying energy to excite electrons across the gap to the next empty (conduction) band, or by adding impurities which will supply conduction electrons or will trap electrons from the valence band, leaving it a partially filled band. In the absence of these effects the only conducting electrons will be those which can escape as a result of fluctuations in thermal energy. It can be shown that the number of these is proportional to exp ($\Delta E/2kT$), where ΔE is the difference in energy between the top of the valence band and the bottom of the conduction band. Thus the temperature coefficient of electrical conductivity gives a measure of this energy gap. As mentioned earlier, it is possible to excite electrons across the gap by absorption of electromagnetic radiation of appropriate energy. By measuring the wavelength at which the very sharp increase in absorption due to this allowed transition begins, one has a second measure of the energy gap. In many practical cases there are complications in interpreting these measurements, due to impurities, due to complex band structure, and due to bound excited states below the conduction band, but the general picture still has definite experimental validity.

At room temperature these gaps can be as large as 5 to 6 electron volts (1 electron volt equals 23 kilocalories), as in sodium chloride or in diamond. On the other hand, the gap can be vanishingly small. When the gap is so small that the resistivity is of the order of 10^4 ohm-centimeter or less, the material is called a semiconductor. Both insulators and semiconductors are characterized by an exponential decrease in resistivity with increasing temperature (provided impurity concentrations are not too high).

Let us return now to our picture of the energy levels in the valence band and consider a crystal made from atoms which do not have filled shells. (Typical examples are copper, silver, gold, and the alkali metals.) The valence band would, in these cases, be only half full. Since there are now states to which an electron can easily move, an electrical potential results in a flow of electrons, and one thus obtains a typical metal. The electrons can no longer be associated at all with individual atoms but belong to the molecule as a whole (the piece of metal), much as the so-called "pi electrons" in benzene belong to the molecule as a whole. For the noble metals the electrons have almost the characteristics of free electrons. It can be shown that a perfectly periodic array of atoms would offer no resistance to electronic motion. In a real lattice the atoms are vibrating about an equilibrium position, and these displacements tend to scatter electrons. Under these circumstances, the resistivity should increase linearly with temperature, and this actually obtains for many metals. Impurities give additional scattering, and complications in band structure can grossly modify this "almost free electron" picture. Even the sign of the temperature coefficient of resistance may be changed. One can speak of "typically metallic behavior," but one cannot simply characterize all metals from their resistivity behavior.

Finally, it is not necessary that a gap exist between the highest filled band and the next empty band at the equilibrium interatomic distance. These two bands may overlap and produce typically metallic behavior in a solid of closed-shell atoms. The crystals of the alkaline earths provide an example of such behavior.

In general, the effect of pressure is to reduce the interatomic distance. In a pressure range of several hundred kilobars, salts such as the alkali halides may decrease in volume as much as 40 to 50 percent, while even such metals as silver compress by 20 percent or more, so the changes in interatomic distance are significant.

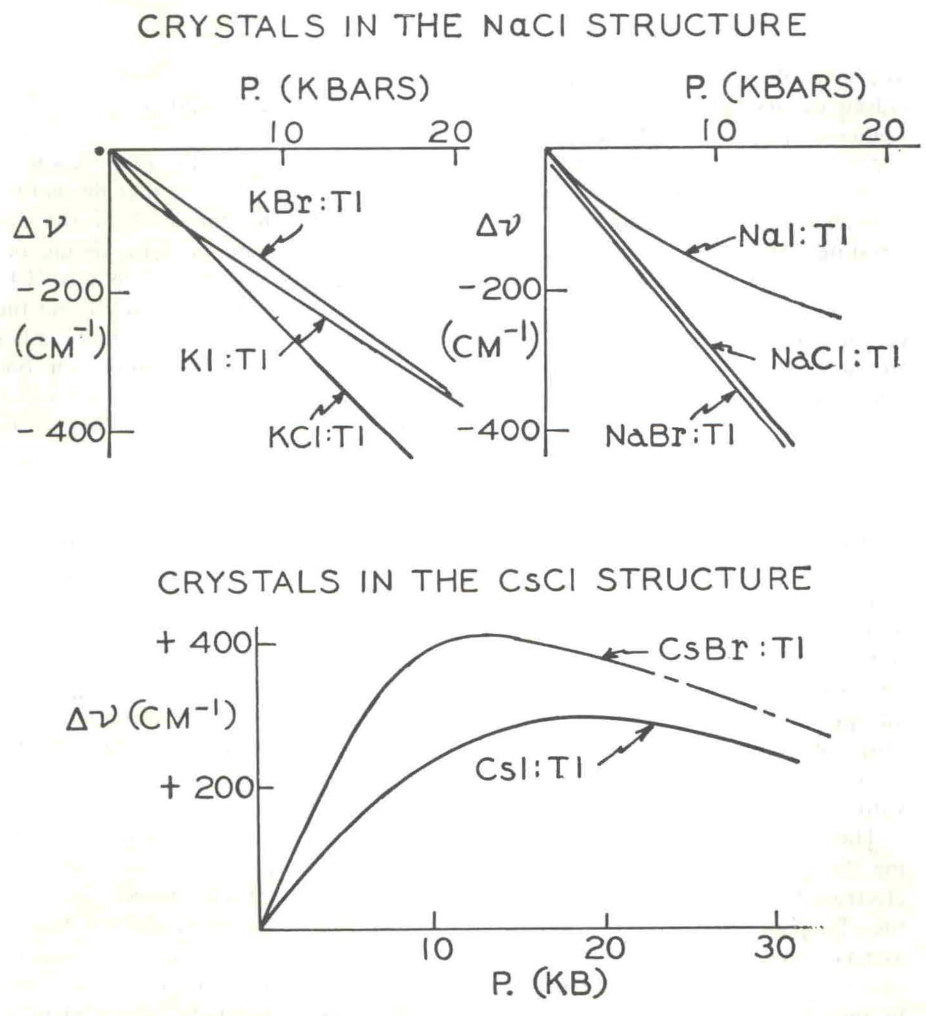
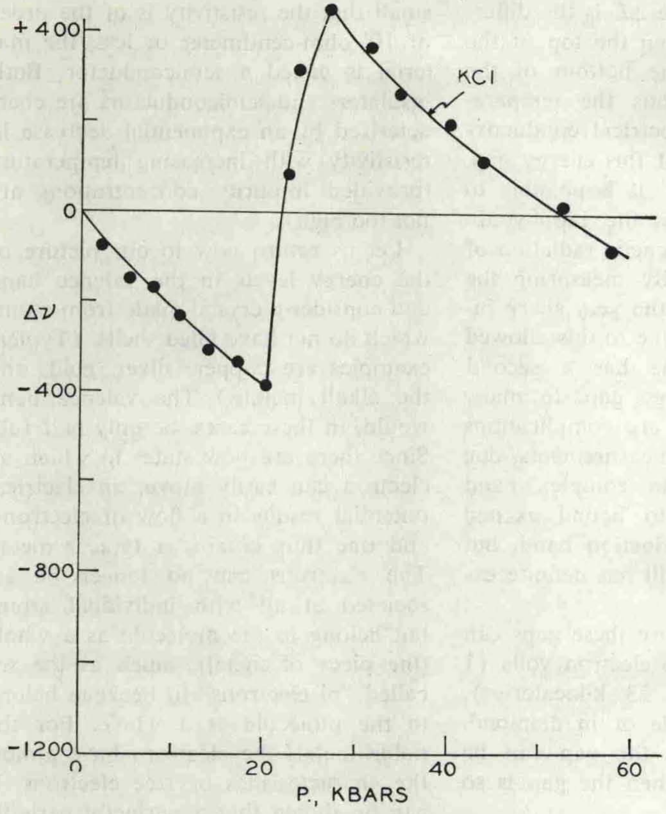


Fig. 1. Initial frequency shift plotted against pressure for alkali halides activated by Tl$^+$.

In the case of internal transitions, the effect of increasing pressure is to



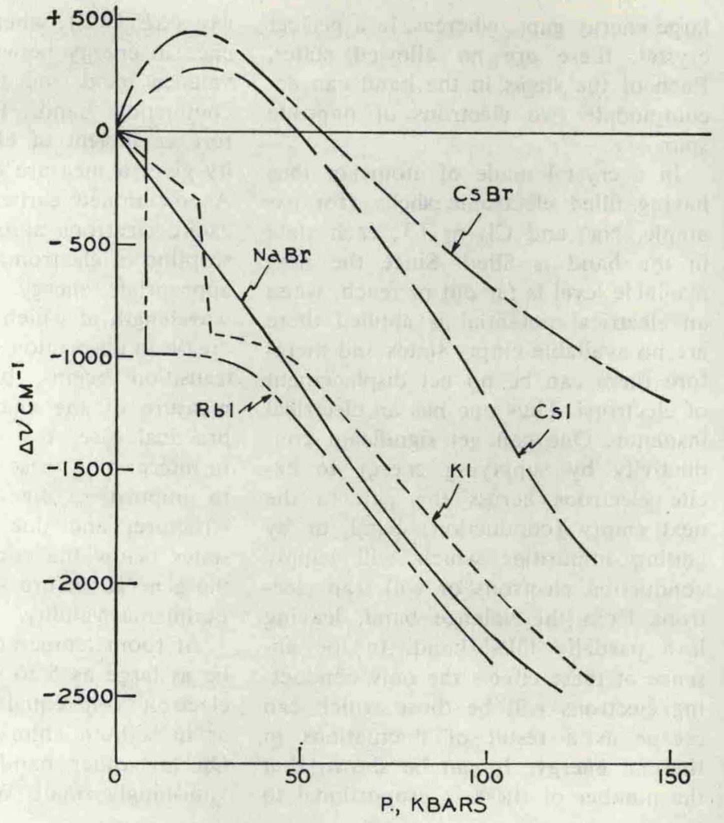


Fig. 2 (left). $\Delta\nu$ plotted against pressure for potassium chloride with Tl^+. **Fig. 3 (right).** $\Delta\nu$ plotted against pressure for Tl^+ in alkali halides.

increase the perturbing effect of the field provided by the lattice. Where a theory predicts the effect of the field, this effect can provide a quantitative test of the theory. Where two theories predict different effects of increasing field intensity, pressure experiments provide the basis for a choice between theories.

For typical semiconductors of simple band structure, the effect of pressure should be to reduce, and ultimately to eliminate, the gap between the conduction and valence bands, and thus to convert an insulator or semiconductor into a metal. This may take place with no change in crystal structure, or it may take place through a polymorphic transition to a new phase, in which case the change in gap is discontinuous. For semiconductors of complex band structure, such as germanium or gallium arsenide, the changes in gap with pressure can help elucidate the structure.

In the simplest picture, the effect of pressure on the resistance of a metal can be directly analyzed qualitatively. The decrease in interatomic distance should result in a decrease in the amplitude of vibration and "stiffen" the structure. Thus, increasing the pressure acts in the opposite direction from increasing the temperature and should result in a decrease in resistivity. This indeed occurs for such metals as gold, studies of polymorphic transitions having' a variety of possible effects on silver, copper, and many others. In a significant number of metals the effects teresting. Here, pressure experiments of interatomic distance on band structure are more complex and more in- can add much to our understanding. In addition, there exist possibilities for electronic structure.

Alkali Halide Phosphors

One of the most useful and most thoroughly studied types of phosphors consists of an alkali halide crystal with a fraction of a percent of Tl^+ ion dissolved in it. The Tl^+ ion substitutes for an alkali ion at a lattice site. There is an optical absorption band in the near-ultraviolet and an emission peak in the visible spectrum. Here we are concerned with the nature of the absorption band.

The two extreme viewpoints concerning this absorption are (i) that it is an electron transfer, or sharing, between the Tl^+ and neighboring halide ions and (ii) that it is an internal transition localized on the Tl^+ ion and perturbed by the crystal field imposed by its nearest neighbors. Actually, there are limitations on either viewpoint, as discussed by Knox and Dexter (*4*).

One could say, if the first viewpoint were essentially correct, that the nature of the state and the shift of the absorption peak with pressure should depend strongly on the halide ion (Cl^-, Br^-, or I^-) and only secondarily on the symmetry of the lattice. On the other hand, with the second approach one would predict a pressure shift which would be essentially independent of the halide ion but might depend strongly on the lattice involved. Williams and his co-workers (*5*) have developed a semiquantitative formulation of the second viewpoint, as applied to potassium chloride in particular. To summarize his results, the theory predicts a shift to lower energies with increasing pressure. This should be true for all alkali halides with the face-centered cubic structure, but not necessarily for the simple cubic (cesium chloride) structure. Figure 1 (see *6*) shows the low-pressure shift for a series of these compounds. Energy shifts are shown in wave numbers (1000 waves per centimeter equal 2.88 kilocalories). Indeed, it may be seen that the predicted red shift prevails for all the face-centered cubic structures quite independent of the halide ion involved. Williams's calculations tell nothing explicit about the simple cubic structure, but one can see from the initial blue shift that there is a marked effect of crystal symmetry. Potassium chloride has a transition at a pressure of 19 kilobars to the simple cubic structure. On the basis of the results at low pressures and of William's theory, one would expect a discontinuous shift to higher energy for the absorption peak at the transition. Figure 2 shows that just such a shift occurs—a finding which also confirms the basic features of the picture.

Finally, in Fig. 3 is shown the shift of the absorption peak at high pressure for a series of alkali halides having both the sodium chloride and the cesium chloride structure. One can see that there is a remarkable similarity in the slopes at high pressure, all showing a large shift to lower energy. While there is as yet no theory which predicts the behavior at very small interatomic distances, it is clear that any such theory must predict that the ground state and the first excited state get closer together in energy under these conditions, quite independent of the crystal lattice.

We see, then, that the results at high pressure allow us to choose between available simple theories, although we must understand that these may be oversimplified. Secondly, the results present a test for any theory formulated to describe the potential energy surfaces at small interatomic distances.

Approach to the Metallic State

A second type of problem where optical and electrical measurements at high pressure make a unique contribution involves the approach to the metallic state at high pressure. As discussed earlier, in an insulator or semiconductor there is a filled valence band, separated by an energy gap, which is large compared with the fluctuations in thermal energy of the electrons, from an empty band available for electrical conduction.

In the absence of impurities the process of supplying electrons capable of moving through the lattice involves excitation of electrons across this gap. The smaller the gap the more likely it is that this can occur by thermal excitation, and the higher the conductivity. This excitation is an activation process. Theory shows that the activation energy is half the energy of the gap. Thus one can obtain a measure of the gap width from the temperature coefficient of the electrical resistance at constant pressure. In a solid of simple band structure one would expect the bands to broaden with increasing pressure, and the gap to narrow accordingly. Thus one would expect a rapid decrease in electrical resistance with increasing pressure, accompanied by a decrease in the temperature coefficient of resistance.

In addition to exciting electrons by thermal fluctuations it is possible to excite electrons across the energy gap by means of electromagnetic radiation of the appropriate energy. The conductivity obtained thus in the presence of light of the right wavelength is known as photoconductivity. The very intense absorption of light of the energy of the gap is called the absorption edge of the crystal. It provides an independent measure of the size of the gap.

In recent years my associates and I have made both optical and electrical measurements as a function of pressure on iodine crystals (7). Iodine forms a base-centered orthorhombic crystal with the I_2 molecules lying in the *ac* plane. It is quite practical to grow single crystals of usable size from the vapor phase.

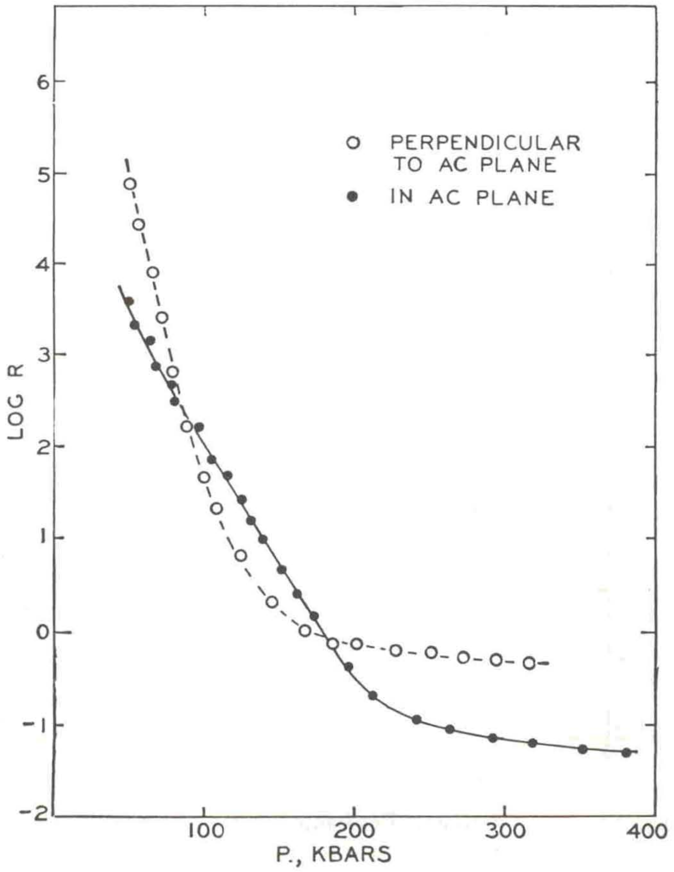
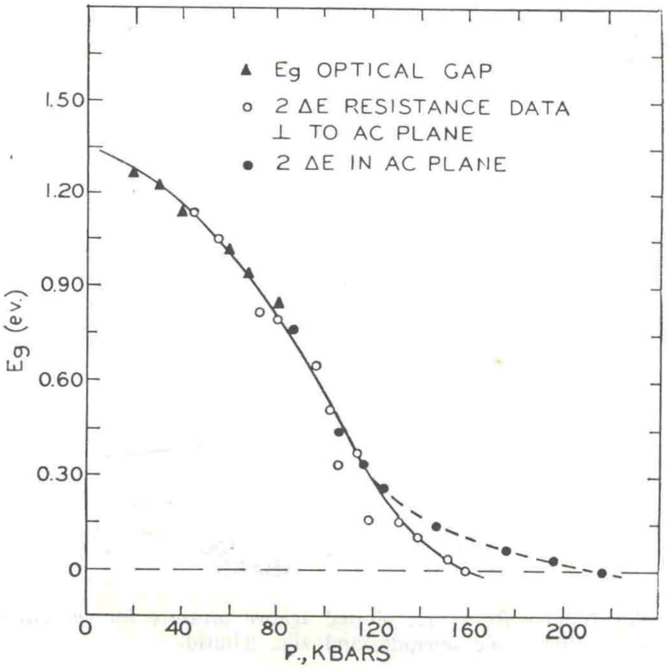


Fig. 4 (left). Log resistance plotted against pressure for iodine.

Fig. 5 (below). Energy gap plotted against pressure for iodine.



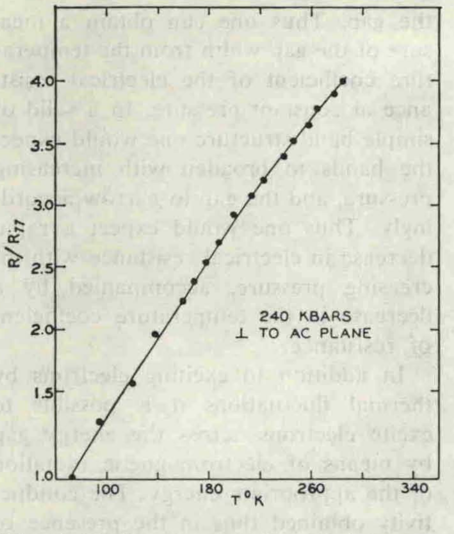


Fig. 6. Resistance plotted against temperature for iodine.

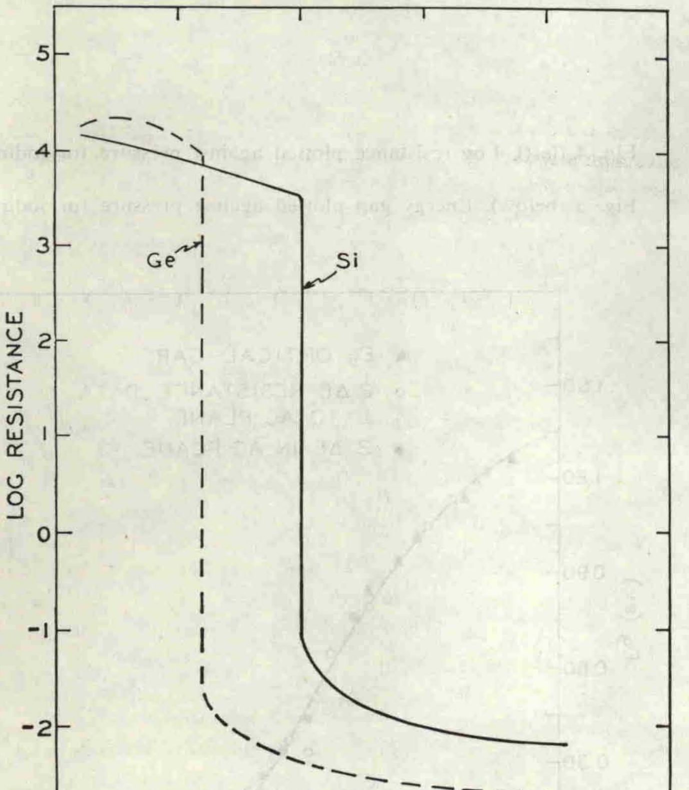
The measurements we have made include (i) optical absorption measurements (location of the absorption edge) as a function of pressure to about 90 kilobars, (ii) measurements of electrical resistance both parallel and perpendicular to the molecular plane as a function of pressures to over 400 kilobars, and (iii) measurements of the temperature coefficient of resistance between 77° and 296°K at pressures from 60 to 400 kilobars.

Figure 4 is a plot of resistance versus pressure, measured both perpendicular and parallel to the molecular plane. In our apparatus it is not possible to correct for contact resistance, so the curves have been placed relative to each other by correcting for sample geometry only. Below 50 kilobars the resistances are too large to be measured in our apparatus, but they must be decreasing by many orders of magnitude. For measurements made in the *ac* plane, the rapid drop continues to pressures of about 230 to 240 kilobars, where there is a relatively sharp break. Beyond this pressure the resistance decreases at a rate which would be anticipated for a relatively compressible metal.

The broken curve of Fig. 4 represents measurements made perpendicular to the *ac* plane. The curve is qualitatively like the curves just discussed, but the break comes at 160 kilobars. In the high-pressure region the resistance perpendicular to the *ac* plane is apparently 5 to 7 times greater than in the other direction; corrections for contact resistance could alter this number.

Figure 5 shows the measured optical absorption edge (triangles) as a function of pressure. Compared with this is shown the activation energy for electrical conductivity measured (open circles) in the *ac* plane and (solid circles) perpendicular to the *ac* plane. In the pressure region where both optical and electrical measurements could be made, the agreement is excellent, confirming that the simple band picture is a reasonable description for iodine. The activation energy measured perpendicular to the *ac* plane vanishes at 160 kilobars, where the break in the resistance-pressure curve occurs. As one would expect, below 160 kilobars the activation energy is independent of direction. Above 160 kilobars the activation energy in the *ac* plane tails off to zero by about 220 kilobars.

Figure 6 is a plot of resistance versus temperature at 240 kilobars, measured perpendicular to the *ac* plane. It shows the linear increase of resistance with temperature which one would expect for a typical metal. Essentially identi-



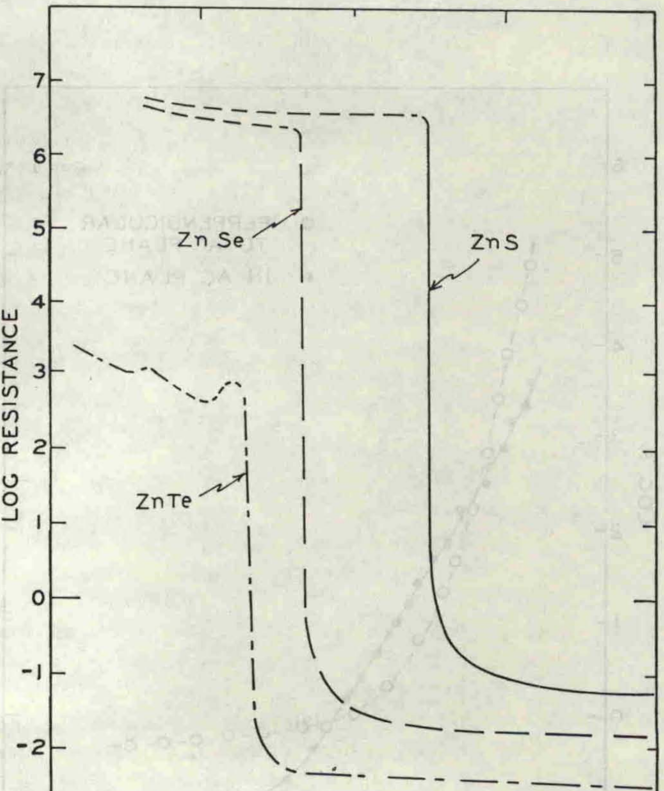
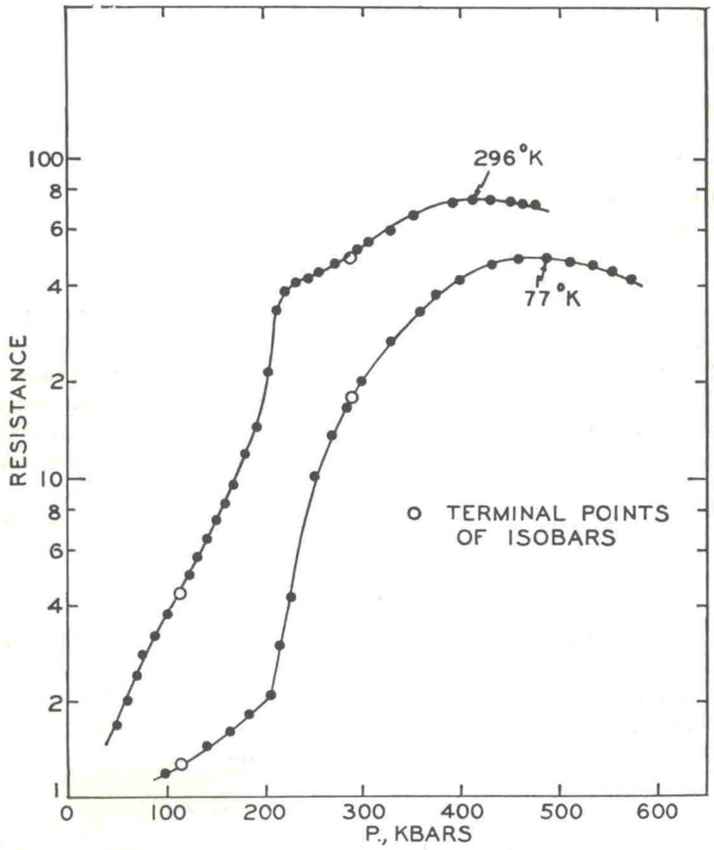


Fig. 7 (left). Resistance plotted against pressure for germanium and silicon. Fig. 8 (right). Resistance plotted against pressure for zinc sulfide, zinc selenide, and zinc telluride.



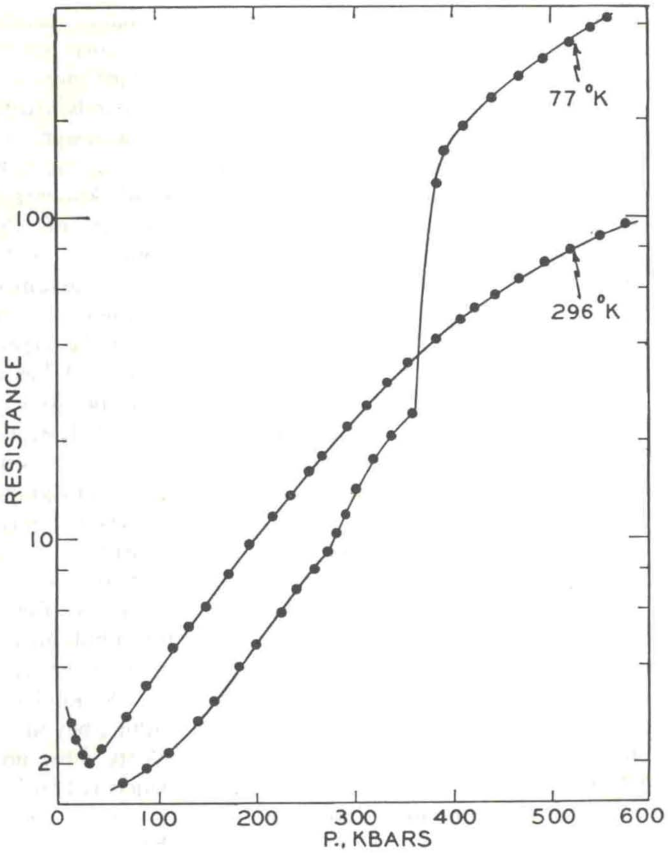


Fig. 9 (left). Resistance plotted against pressure for rubidium. Fig. 10 (right). Resistance plotted against pressure for potassium.

cal curves were obtained at pressures from 170 to 400 kilobars, indicating that the transition to the metallic state occurs in a very small pressure range. Above 240 kilobars measurements in the *ac* plane also revealed typical metallic behavior. In the region between 160 and 220 kilobars the electronic properties are very highly directional, in a general way analogous to the behavior of single-crystal graphite.

At room temperature and atmospheric pressure an array of atoms assumes the crystalline configuration in which cohesive and repulsive energy are balanced. Often different structures differ in energy by relatively small amounts. Because their valence electrons form strongly directionalized orbitals, silicon and germanium crystallize in the diamond lattice, having four neighbors located tetrahedrally, with rather tight binding. Zinc sulfide, zinc selenide, and zinc telluride are much more ionic in character than silicon and germanium, but they crystallize in the zinc blende lattice, which differs from diamond only in that alternate neighbors are anion and cation.

These are relatively open structures with only four nearest neighbors, so that one might expect to obtain, at sufficiently high pressure, a first-order phase transition to a more efficient packing.

In Fig. 7 are shown the resistances of germanium and silicon as a function of pressure (*8*). Germanium exhibits a maximum at 30 kilobars, a finding which is consistent with optical observations (*9*). The explanation is well understood, but it is complex and need not be given here. At 120 kilobars there is a precipitous drop in resistance, by many orders of magnitude. Beyond this pressure the resistance drops slowly, as one might expect of a metal. The high-pressure phase indeed exhibits metallic behavior (*10*). Jamieson (*11*) has shown that the structure is the same as that of white tin; thus the transition is quite analogous to the well-known transformation of grey tin to white tin.

Silicon shows a small continuous drop in resistance with pressure in the low-pressure phase. Again this is consistent with measurements on the shift of the absorption edge (*9*). At 190 to 195 kilobars there is a very large drop in resistance. The high-pressure phase is metallic and has the white-tin structure.

Figure 8 shows resistance-pressure curves for zinc sulfide, zinc selenide, and zinc telluride (*12*). The sulfide and selenide have very high resistances in the low-pressure phase. Hence the dotted lines show merely the resistance of the cell. The curve for zinc telluride is, again consistent with optical measurements (*13*). For each of these materials there is a transition accompanied by a very large drop in resistance. These transitions occur at 135, 165, and 240 kilobars, respectively. In each case the high-pressure phase behaves like a metal (*10*). Recent unpublished x-ray measurements indicate that zinc telluride, zinc selenide, and possibly zinc sulfide have, at high pressure, the simple cubic structure of cesium chloride. Thus we see that it is possible for a single material to behave as an insulator, a semiconductor, or a metal, depending on the interatomic spacing. The transformation may take place continuously, or it may be accompanied by a first-order phase transition.

Electronic Transitions in Metals

As discussed in the opening paragraphs, the normal effect of pressure on the electrical resistance of a metal is a modest decrease in resistance due to the stiffening of the lattice. There are a variety of exceptions to this rule. Of interest is one class of exceptions which illustrate, again, a case where pressure is a unique tool for investigating electronic structure.

The periodic table of the elements and the corresponding periodic properties are built up by adding electrons according to the rules of quantum mechanics. The electrons are classified according to their four quantum numbers. Each electronic shell, characterized by a principal quantum number (*14*), contains subshells classified according to their angular-momentum quantum numbers, $l = 0,1,2,3 \ldots n-1$. These latter states are generally labeled $s(l = 0)$, $p(l = 1)$, $d(l = 2)$, $f(l = 3)$, and so on. The electrons build up regularly from element to element, filling first the $1s$ shell (2 electrons), then the $2s$, $2p$ shell (6 electrons), and so on, up to potassium. In potassium, however, the last electron enters the $4s$ state, leaving the $3d$ shell empty; calcium has two $4s$ electrons and an empty $3d$ shell. Similarly, the valence electrons on the rubidium and strontium atoms are in the $5s$ state, while the $4d$ shell is empty, and cesium and barium have $6s$ valence electrons with an empty $5d$ shell. The transition metals are characterized by partially filled $3d$, $4d$, or $5d$ shells, with two electrons in the s shell of next higher principal quantum number. In the rare-earth elements there are $6s$ electrons with an empty $5d$ shell and a partially filled $4f$ shell.

Let us now look at the electronic structure of an alkali metal, say cesium. The lattice is body-centered. There is a spherically symmetric band which is related to the $6s$ atomic level and contains one electron per atom. This is, of course, the conduction band. In the free atom the $5d$ shell is fivefold degenerate—that is, it contains five substates of equal energy, each capable of containing two electrons. In the crystalline field of the lattice two bands appear, connected with the $5d$ shell; one is capable of containing six electrons per atom and one has a capacity of four electrons. Both these bands are higher in energy than the band arising from the $6s$ shell and, of course, contain no electrons.

Bridgman (*15*) measured the volume and electrical resistance of cesium as a function of pressure. He found a volume discontinuity at 22 kilobars, doubtless a first-order transition to a cubic close-packed structure. There is a further large-volume discontinuity at 41 kilobars, accompanied by a very definite cusp in the electrical resistance. Sternheimer (*16*) has suggested that the bands arising from the $5d$ shell become lower in energy, with pressure, vis-à-vis the $6s$ band, and that the events at 41 kilobars are associated with the transfer of the conduction electron from the $6s$ to the $5d$ band. Sternheimer assumed a single, spherically symmetric d band, so his calculations cannot be rigorously correct. Recently Ham (*17*) has shown that the situation must be somewhat more complicated. Nevertheless, the notion of this "electronic transition" is probably sound and is very intriguing.

Very recently Stager and I (*14*) have measured the electrical resistance of rubidium and potassium to very high pressures. Figure 9 shows the results for rubidium at 77° and 296°K. There is a sharp rise in resistance at 190 to 200 kilobars, and there is a maximum beyond 400 kilobars. These events show no lag at 77°K, a finding which is consistent with the notion that this is an electronic transition rather than a diffusion-controlled rearrangement.

In rubidium the separation in energy between the $5s$ and the $4d$ atomic states is much larger than the $6s$–$5d$ separation in cesium, so it is reasonable to conclude that it would take a higher pressure to effect the electronic promotion.

In potassium the $3d$ energy is even further above the $4s$ state, so one would expect any electron transfer to occur at very high pressure. Figure 10 shows the curves for resistance and pressure. The resistance at room temperature rises by a factor of 50 with a change in pressure of 600 kilobars. It seems very likely that there is a maximum at still higher pressures. At 77°K the features at low pressure are similar. The very sharp rise at 360 kilobars is the result of a martensitic transition, the details of which are not germane to this article.

One would expect that there would be electronic transitions in the rare earths, involving promotions of $4f$ electrons to bands arising from the empty $5d$ shell. Indeed, one such transition in cesium has been studied in much detail (*18*). More recently, evidence that a similar transition takes place in ytterbium has been reported (*19*).

It seems probable that this is not an uncommon event in the heavier elements, where empty and filled bands do not differ greatly in energy. These radical changes in the character of the valence electrons offer the possibility that new chemical valences, and, conceivably, radical changes in chemical reactivity, can be achieved.

Summary

In this article (*20*), pressure as a variable in elucidating electronic structure is discussed. It is shown that measurements of optical absorption at high pressure can provide a satisfactory explanation of the characteristics of alkali halide phosphors. Data on optical absorption and on electrical resistance at high pressure are combined to illustrate the mechanisms whereby an insulator or a semiconductor can become a metal. Also discussed is the notion of an electronic transition in metals wherein distortion of the bands at high pressure can result in electron transfer between atomic shells and in new valence states for some elements.

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