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.

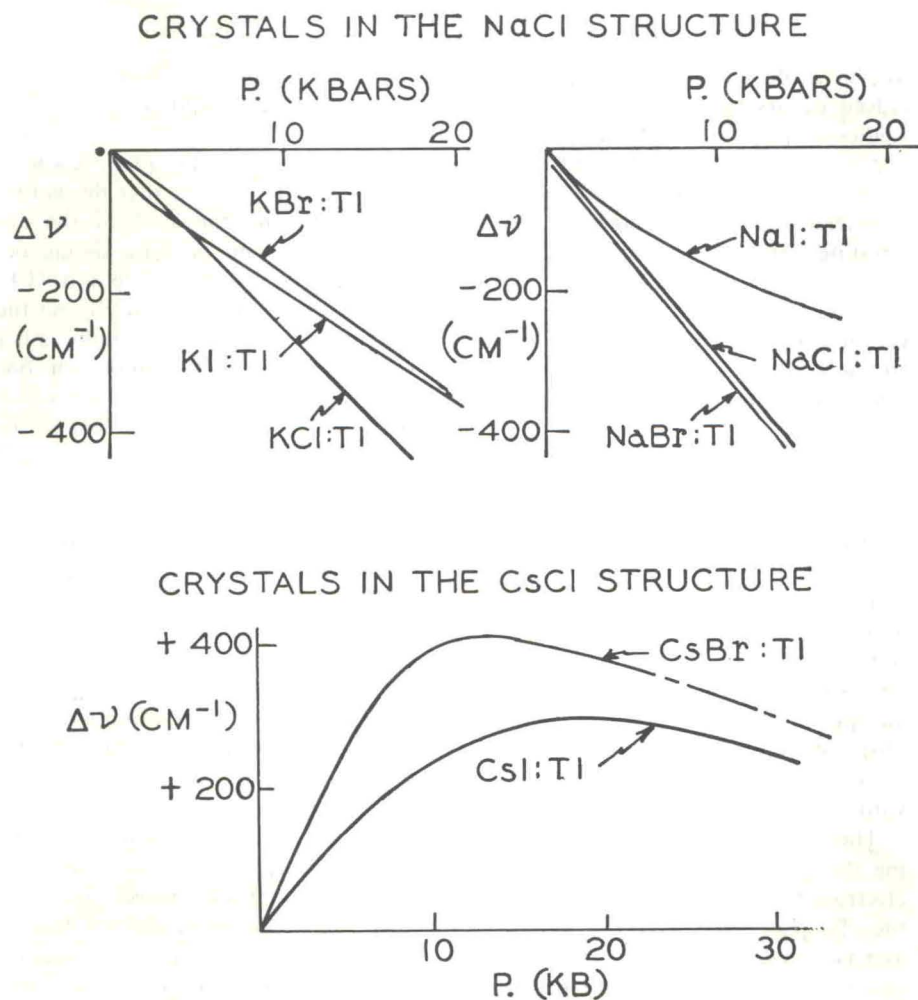In the case of internal transitions, the effect of increasing pressure is to

CRYSTALS IN THE NaCl STRUCTURE

CRYSTALS IN THE CsCl STRUCTURE

Fig. 1. Initial frequency shift plotted against pressure for alkali halides activated by Tl⁺.
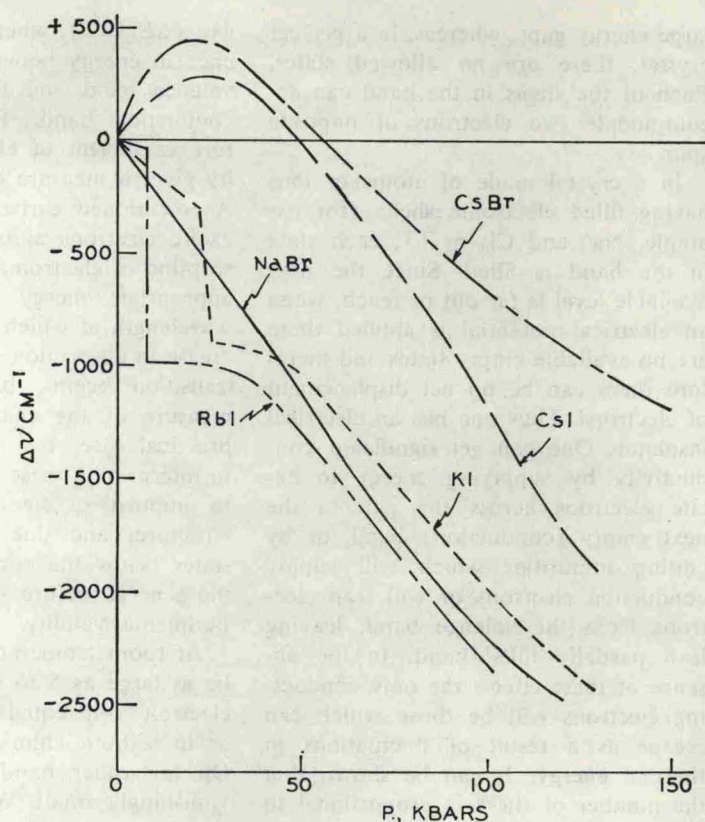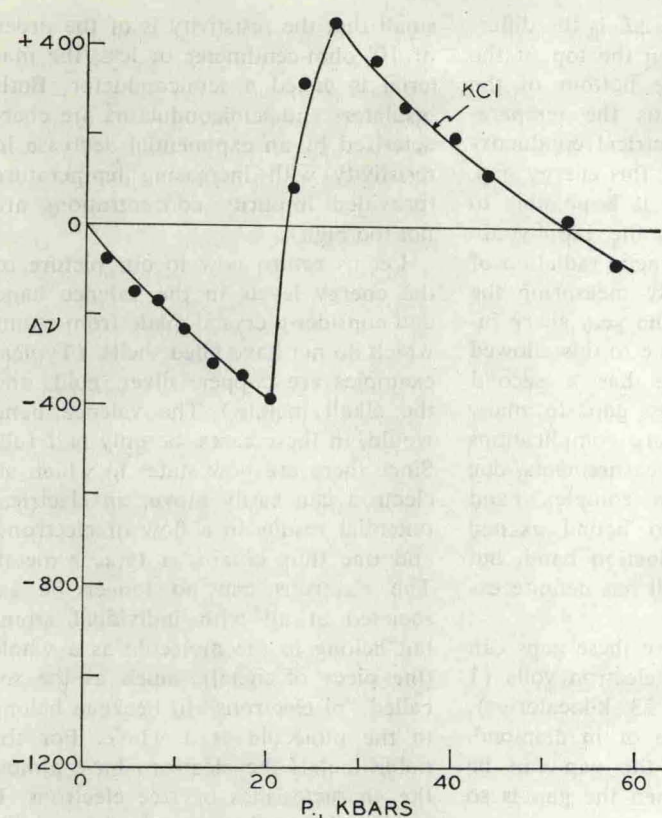
Fig. 2 (left). Δ_ν plotted against pressure for potassium chloride with Tl^+. Fig. 3 (right). Δ_ν plotted against pressure for Tl^+ in alkali halides.

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 re-

sult 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 near-

est 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

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