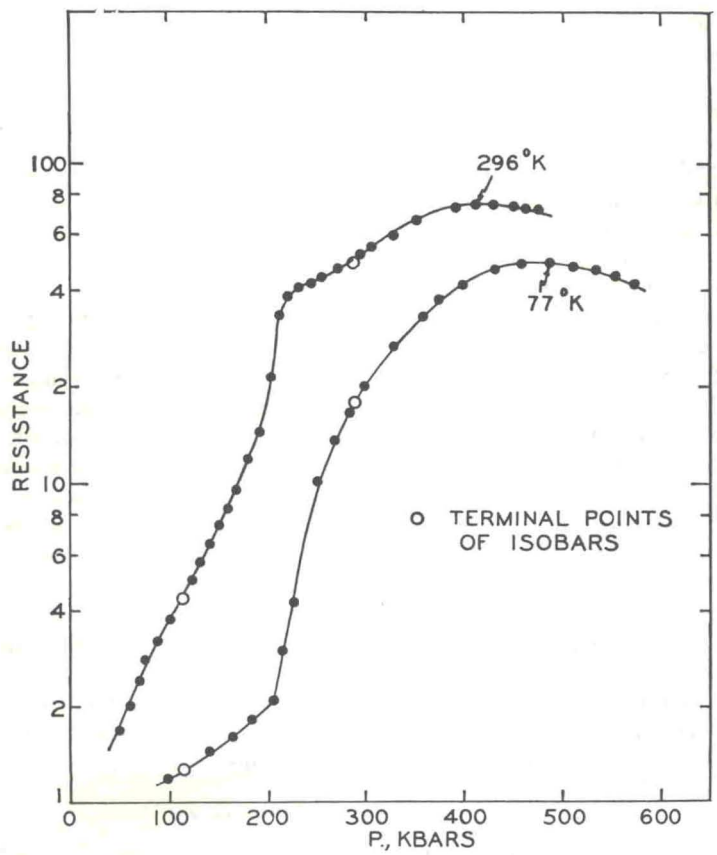

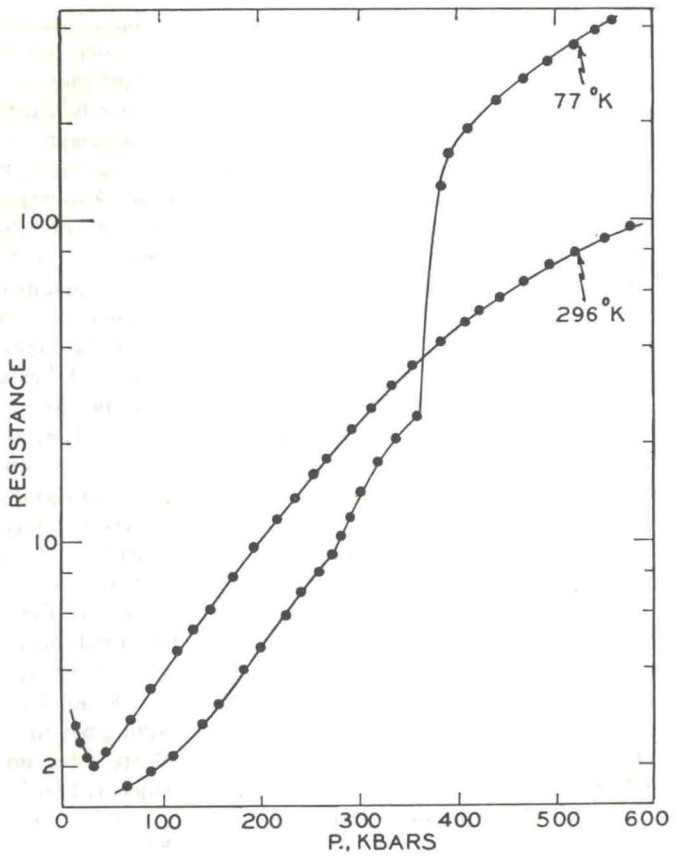

Fig. 9 (left). Resistance plotted against pressure for rubidium. Fig. 10 (right). Resistance plotted against pressure for potassium.

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 1*s* shell (2 electrons), then the 2*s*, 2*p* shell (6 electrons), and so on, up to potassium. In potassium, however, the last electron enters the 4*s* state, leaving the 3*d* shell empty; calcium has two 4*s* electrons and an empty 3*d* shell. Similarly, the valence electrons on the rubidium and strontium atoms are in the 5*s* state, while the 4*d* shell is empty, and cesium and barium have 6*s* valence electrons with an empty 5*d* shell. The transition metals are characterized by partially filled 3*d*, 4*d*, or 5*d* shells, with two electrons in the *s* shell of next higher principal quantum number. In the rare-earth elements there are 6*s* electrons with an empty 5*d* shell and a partially filled 4*f* 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 6*s* atomic level and contains one electron per atom. This is, of course, the conduction band. In the free atom the 5*d* 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 5*d* 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 6*s* 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 5*d* shell become lower in energy, with pressure, vis-à-vis the 6*s* band, and that the events at 41 kilobars are associated with the transfer of the conduction electron from the 6*s* to the 5*d* 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 5*s* and the 4*d* atomic states is much larger than the 6*s*–5*d* separation in cesium, so it is reasonable to conclude that it would take a higher pressure to effect the electronic promotion.

In potassium the 3*d* energy is even further above the 4*s* 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 4*f* electrons to bands arising from the empty 5*d* 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.

References and Notes

1. W. Paul and D. M. Warschauer, Eds., *Solids Under Pressure* (McGraw-Hill, New York, 1963).
2. C. A. Swenson, in *Solid State Physics*, vol. 11, F. Seitz and D. Turnbull, Eds. (Academic Press, New York, 1960).
3. R. H. Wentorf, Jr., Ed., *Modern Very High Pressure Techniques* (Butterworths, London, 1962).
4. R. S. Knox and D. L. Dexter, *Phys. Rev.* **104**, 1245 (1956).
5. F. E. Williams and P. D. Johnson, *J. Chem. Phys.* **20**, 124 (1952); F. E. Williams, *ibid.* **19**, 457 (1951); P. D. Johnson and F. E. Williams, *Phys. Rev.* **95**, 69 (1594).
6. R. A. Eppler and H. G. Drickamer, *Phys. Chem. Solids* **6**, 180 (1958); ———, *ibid.* **15**, 112 (1960); see also H. G. Drickamer and J. C. Zahner in *Advances in Chemical Physics*, vol. 4, I. Prigogine, Ed. (Wiley, New York, 1963).
7. B. M. Riggleman and H. G. Drickamer, *J. Chem. Phys.* **38**, 2721 (1963); ———, *ibid.* **37**, 446 (1962); see also A. S. Balchan and H. G. Drickamer, *ibid.* **34**, 1948 (1961); H. L. Suchan, S. Wiederhorn, H. G. Drickamer, *ibid.* **31**, 355 (1959).
8. S. Minomura and H. G. Drickamer, *Phys. Chem. Solids* **23**, 451 (1962).
9. T. E. Slykhouse and H. G. Drickamer, *ibid.* **7**, 210 (1958).
10. S. Minomura, G. A. Samara, H. G. Drickamer, *J. Appl. Phys.* **33**, 3196 (1962).
11. J. C. Jamieson, *Science* **140**, 72 (1963).
12. G. A. Samara and H. G. Drickamer, *Phys. Chem. Solids* **23**, 457 (1962).
13. A. L. Edwards and H. G. Drickamer, *Phys. Rev.* **122**, 1149 (1961).
14. R. A. Stager and H. G. Drickamer, *ibid.*, in press.
15. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **76**, 55 (1948); **81**, 165 (1952).
16. R. Sternheimer, *Phys. Rev.* **78**, 238 (1950).
17. F. S. Ham, *ibid.* **128**, 2524 (1962).
18. P. W. Bridgman, *Proc. Am. Acad. Arts. Sci.* **79**, 149 (1951); A. W. Lawson and T. Y. Tang, *Phys. Rev.* **76**, 301 (1949); I. Likhter, N. Riabinin, L. F. Vereschaguin, *Soviet Phys. JETP* (*English Transl.*) **6**, 469 (1958); R. Herman and C. A. Swenson, *J. Chem. Phys.* **29**, 398 (1958).
19. H. T. Hall, J. D. Barnett, L. Merrill, *Science* **139**, 111 (1963); R. A. Stager and H. G. Drickamer, *ibid.*, p. 1284.
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