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The Pressure Variable in Materials Research

Experiments at high pressure reveal trends in crystal structure, superconductivity, and magnetism.

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The variation of physical properties with pressure provides new insight into materials at 1 atmosphere, and the pressure variable adds a new dimension to the synthesis of materials. Building on the pioneering work of P. W. Bridgman and sparked by the successful synthesis of diamonds in the laboratory, the field of research at high pressure has expanded at a rapid rate during the last decade. It is now possible to carry out a wide variety of sophisticated experiments at ever increasing ranges of pressure and temperature. In order to convey the flavor of this field, I will concentrate in this article on the tip of the iceberg, namely, the elements of the periodic table and will illustrate the effect of pressure on only a few properties. Clearly, many more fascinating things can occur in the vast number of compounds that can be made.

It has been found that the application of pressure tends to smooth out differences in crystal structure, density, and compressibility in the elements and that, with increasing pressure, many insulators are transformed into metals which are often superconducting at low temperatures. At high pressure the simple metals such as the alkali metals have properties similar to those of typical transition metals, and the onset of magnetic ordering in the 3*d* transition metals is very sensitive to pressure. These are only a few samples, and more detailed information on specific topics of research at high pressure can be found in other review articles (*1*–*8*). I will not discuss the experimental aspects of research at high pressure except to comment that with the present technology it is possible to achieve pressures of several hundred kilobars (1 kilobar = 987 atmospheres) at temperatures ranging from about 1° to about 1000°K. In many cases it is possible to design small, inexpensive equipment, thus making large high-pressure installations unnecessary.

Trends in the Periodic Table

Many physical properties of the elements exhibit a marked periodicity with increasing atomic number; for example, the cohesive energy, density, and bulk modulus are shown in Fig. 1 (*9*). The fact that the least dense elements are also the most compressible has led to the speculation that the periodicity in density will be smoothed out at pressures of about 10 megabars (*10*). It now appears that the pretransition elements become discontinuously less compressible at high pressure and thus the periodicity in compressibility is also reduced. This discontinuous change and its implications are discussed below.

In the absence of phase transitions, the properties plotted in Fig. 1 are smooth functions of pressure, and the available compression data can be represented by a two-parameter equation if we assume a linear dependence of the bulk modulus B on pressure P:

$$B = (\partial P/\partial \ln V)_T = B_0 + B_0' P \quad (1)$$

where V is the volume, T is the temperature, and B_0 and B_0' are the bulk modulus and its first pressure derivative in the limit of $P \rightarrow 0$ [see the curve for tungsten in Fig. 2 (*11*)] (*12*).

The curve (Fig. 2) for cesium is markedly different from that for tungsten. Between the phase transitions at 42.5 and 120 kilobars the bulk modulus increases dramatically (*13*). At a pressure of 120 kilobars the ratio of the bulk modulus of tungsten to that of cesium has been reduced from the value of 200 at 1 atmosphere to 3. This type of anomaly is not limited to cesium; almost all of the pretransition elements and many of the *d* and *f* transition elements near the beginning of each series also have abrupt increases in bulk moduli. For example, in the 4*d* transition series the anomalies occur at 330 kilobars (strontium), 460 kilobars (yttrium), 530 kilobars (zirconium), and 860 kilobars (niobium) (*14*). These anomalies occur in elements with partially filled *d* bands, and they may reflect electronic transitions in which electrons are transferred from *sp* bands to *d* bands (*14, 15*).

This abrupt increase in bulk modulus may be contrasted to the larger bulk moduli of the *d* transition metals compared with those of the *sp*-bonded elements at 1 atmosphere (see Fig. 1). In both cases the larger bulk moduli coincide with the higher densities, a result which suggests that their origin may lie in the interaction of the ion cores with the bonding electrons.

The present theory of cohesion in metals does not account for these large bulk moduli. In the simple metals the kinetic energy of the conduction electrons is lower than that of the isolated atoms because the electrons can move throughout the metal. This freedom of motion allows the electrons to take better advantage of the potential energy of the ions and results in a lower energy in the metal than in the isolated atoms,

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that is, a cohesive energy. This effect is balanced by the Pauli exclusion principle which says that electrons of identical spin and momentum may not occupy the same volume (*16*). The increased cohesion in the transition metals is attributed to the broadening of the atomic *d* levels into a band as the atoms are brought together. The average energy of the total *d* band is the same as that of the atomic levels; however, for an unfilled *d* band the average energy is lower, and this leads to additional cohesive energy. This simple picture gives approximately the observed energy and its parabolic variation with the number of 4*d* or 5*d* electrons (*17*). It does not include a repulsive term which can account for the observed bulk moduli, however. If the origin of this term is the interaction between the conduction electrons and the ion cores, then it may be more profitable to study the simple metals at high pressure. In this way the interaction could be increased in a controlled manner.

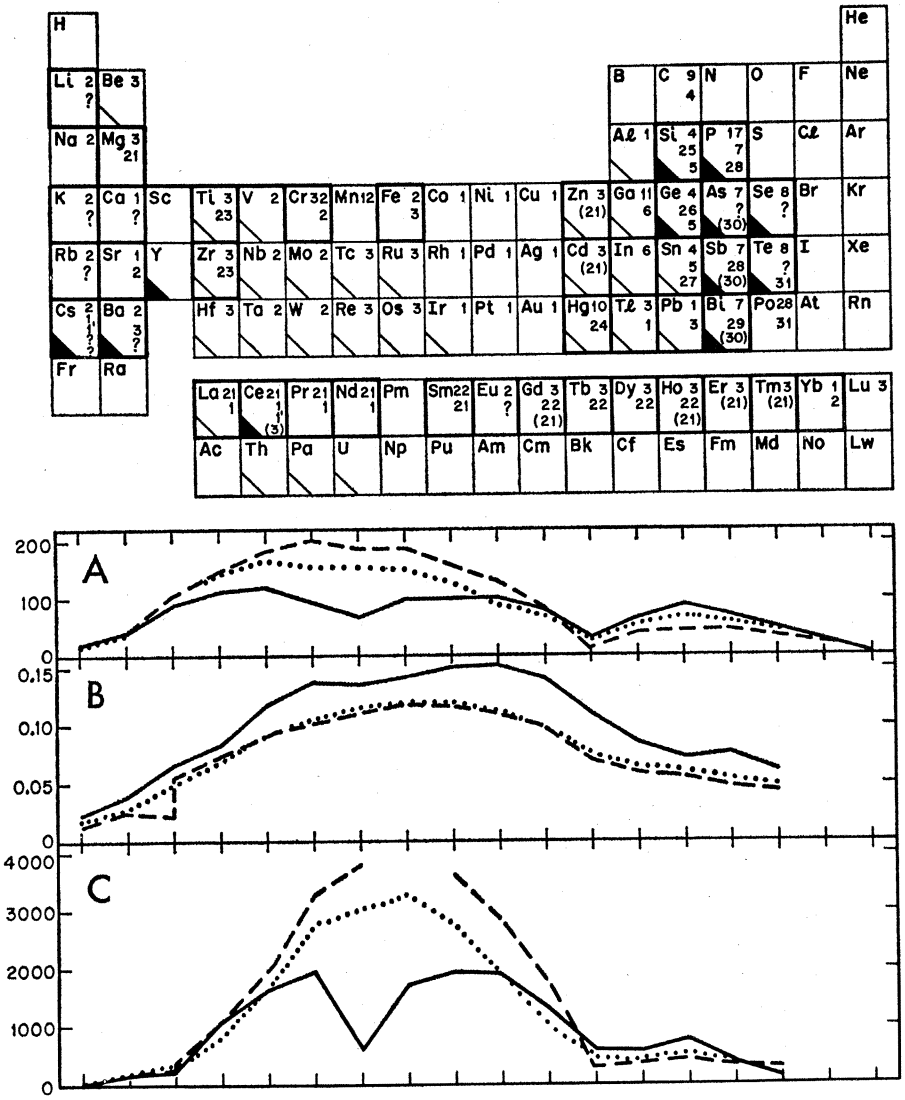


Fig. 1. Periodic table showing the occurrence of phase transitions (heavy borders) at room temperature and pressures up to several hundred kilobars. The occurrence of superconductivity at low temperatures is indicated by diagonal lines (1 atmosphere) or solid triangles (only at high pressure). The curves below the periodic table show the periodic variation in (A) the cohesive energy (in kilocalories per gram atom), (B) density (in gram atoms per cubic centimeter), and (C) bulk modulus (in kilobars) with atomic number: (solid lines) potassium through krypton; (dotted lines) rubidium through xenon; (dashed lines) cesium through radon. The vertical step in the curves for cesium through radon is the lanthanide contraction from lanthanum to lutetium. The crystal structurse are designated by numbers. The Structurbericht notation is used for structures 1 through 20, that is, 1 ≡ A1 (face-centered cubic), 2 ≡ A2 (body-centered cubic), 3 ≡ A3 (hexagonal close-packed), and so forth; 21, double hexagonal close-packed; 22, samarium structure; 23, ω phase related to body-centered cubic; 24, tetragonal; 25, cubic-intermediate high pressure phase; 26, tetragonal-intermediate high pressure phase; 27, tetragonal distortion of body-centered cubic; 28, simple cubic; 29, monoclinic related to A5; 30, similar but unknown structure; 31, simple rhombohedral; 32, antiferromagnetic, orthorhombic distortion of body-centered cubic. The data are from (*9, 18–23, 30*).

The band-broadening model for cohesion in the transition metals does not work even at 1 atmosphere for the 3*d* series. The elements in the series which are magnetic have lower cohesion energies than one would expect on the basis of a scaling with the 4*d* and 5*d* series. The very low value of cohesive energy for manganese implies that it is much more atomic-like and that it does not gain the band energy which contributes to the cohesive energy of the solid. Perhaps under pressure manganese becomes more band-like, and experiments at very high pressures would be an important way to study the delocalization of the 3*d* electrons.

Trends in Crystal Structure

Physical properties are often structure-sensitive, and trends in structure as a function of pressure are a useful guide for the synthesis of new materials with a given structure or property. Over one-third of the elements have phase transitions at room temperature and pressures of a few hundred kilobars. The available data are summarized in Fig. 1. Evidence for the occurrence of a transition is taken from x-ray diffraction studies (*18*), resistivity measurements (*19*), and the discontinuous appearance of superconductivity at low temperatures (*20*). In favorable cases the high-pressure phase may be retained in a metastable state at 1 atmosphere (*21*). The elements with phase transitions are indicated by the dark borders, and the structures are designated by numbers with the highest pressure phase on the bottom. The numbers in parentheses indicate that the structure is not known unambiguously (*22*).

There is a clear trend for elements in any given group of the periodic table to adopt similar structures at high pressure. In the transition metals only α manganese is not isostructural with the rest of its group, but it is anomalous in most of its properties, as indicated above (*23*). The data in Fig. 1 (which admittedly are incomplete and cover a limited pressure range) lead to the speculation that, if enough pressure were applied to the elements in each group of the periodic table, the elements would become isostructural. This idea implies that it is possible to construct generalized phase diagrams for each group as shown for the group V elements phosphorus, arsenic, antimony, and bismuth (Fig. 3) (*24*) and the rare-earth metals (Fig. 4) (*25*).

The diagram for the group V elements is speculative and probably would not be valid for alloys made from other than adjacent elements because of size differences. However, there is a clear trend both with increasing pressure and with atomic number from a semiconductor to a semimetal with a distorted simple cubic structure to a metallic, simple cubic phase. This metallic phase and the higher pressure phases all become superconducting at low temperatures.

A series of structures involving only different stacking sequences of hexagonal close-packed layers of atoms is found in the rare-earth metals (*26*). Here there is a relation between the volume at which a certain phase exists and the atomic number (or number of $4f$ electrons).

The theoretical analysis of phase stability is very complicated because of the small energy changes involved in most phase transitions (*27*). There are roughly two classes of transitions: those involving major changes in bonding character, as exemplified by the group V elements (Fig. 3), and those involving slight distortions from simple structures or small changes in volume, as in the rare-earth metals (Fig. 4). Little real progress has been made in understanding the former class of transitions, but perhaps some of the recent extensions of Pauling's concept of "ionicity" will lead to new insight into this area (*28*). In the latter class of transitions it may be possible to separate a structure-determining factor because many of the contributions to the total energy of each phase are mainly volume-dependent. In one reasonably successful model the structure-determining factor is assumed to be the contribution to the total energy arising from the electronic band structure (*29*). The energy spectrum of the electron gas will be perturbed by the lattice. In many cases a distortion or change in the stacking sequence of simple structures can lower the band structure energy, and in this way many of the observed structures and phase transitions have been rationalized (*29*).

A Dozen New Superconductors

The occurrence of numerous phase transitions at high pressure has led to the discovery of many new superconductors. At the present time it is known that one-third of the elements that become superconducting are superconducting only at high pressure. This information is summarized in the upper part of Fig. 1 where the diagonal lines indicate the superconducting elements and the solid triangles designate those that are superconducting only at high pressure (*30*). In some cases it is possible to quench the high pressure phases [for example, antimony (*31*)] and to study the superconducting properties at 1 atmosphere, but this possibility is more common in compounds than it is in the elements. The compounds containing elements from groups III and V, such as InSb (*32*), were among the first to be quenched, and recently reasonably high transition temperatures (15° to 17°K) have been observed in some carbides that were synthesized at high pressure and then quenched to ambient conditions (*33*). In the case of the elements it has been necessary to carry out experiments under the difficult conditions of simultaneous ultrahigh pressures and ultralow temperatures. These studies have led to a much broader view of superconductivity than one might have had a decade ago. Not only does superconductivity occur in some transition elements and in a few elements like tin and lead, but it has been found at high pressure even in the alkali [cesium (*34*)] and alkaline-earth [barium (*35*)] elements and in many of the elements on the right side of the periodic table [selenium (*36*) and tellurium (*37*), for example]. There appears to be a general trend in which the superconducting transition temperatures increase in successive high pressure phases; for example, the sequence in bismuth is 3.9°, 7.1°, and 8.3°K (*38*). In essentially all cases the appearance of superconductivity is accompanied by a change in crystal structure. This result further emphasizes the sensitivity of many phenomena to structure. [In the case of yttrium there is no evidence for a phase transition, but high pressure x-ray studies have not been made (*34*).] Studies at high pressure have not yet led to a definitive answer to the question of how or whether superconductivity is destroyed by pressure in a given structure. In many materials the superconducting transition temperature decreases with pressure. Whether it approaches zero exponentially or linearly as a function of volume is difficult to decide experimentally. This investigation would be an interesting test of some aspects of the theory of superconductivity.

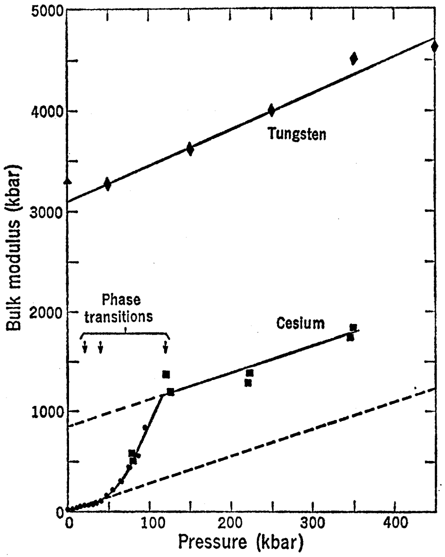


Fig. 2. A plot of bulk modulus versus pressure for tungsten and cesium showing a linear increase in tungsten and anomalous stiffening in cesium between phase transitions at 42.5 and about 120 kilobars. Below and above these transitions cesium has a linear increase in bulk modulus with pressure. Circles and triangle are from static compression measurements, and squares and diamonds are from shock-wave experiments, as discussed in the text and (*11, 13*).

Onset of Magnetism in Transition Metals

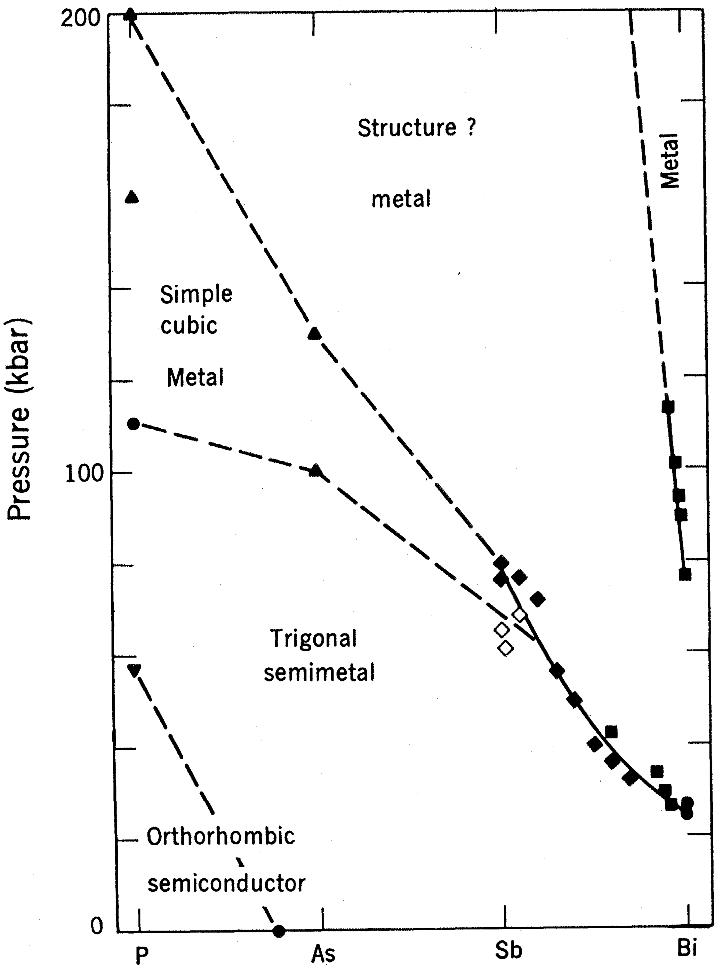
Although superconductivity is a very common phenomenon among the elements, magnetism is limited to the $3d$ metals chromium, manganese, iron, cobalt, and nickel and to the rare-earth metals with partially filled $4f$ states. In an effort to understand the origins of magnetism, the onset at chromium has been studied extensively. The magnetic properties of chromium are very sensitive to the detailed shape of the Fermi surface which proves, in turn, to be very pressure-sensitive.

Chromium is probably the unique example of itinerant antiferromagnetism; that is, above a Néel temperature T_N of 312°K there is no evidence for the existence of localized magnetic moments such as are found, for example, in the rare-earth metals. The Fermi surface is such that there are pockets of electrons and holes of similar size and shape. It is believed that the attractive coulomb interaction between the electrons and holes in the matching pockets causes them to condense into electron-hole pairs with parallel spin (triplet excitons) at low temperatures. This condensation is a cooperative effect which results in a spin density wave whose periodicity may or may not be commensurate with the lattice (*39*). The fact that the electron-hole pairs have a lower energy at low temperatures results in the formation of a temperature-dependent energy gap in the electronic spectrum. The density of states at the Fermi surface is reduced as the excitons condense. This causes the electrical resistivity to increase below T_N. By studying the electrical resistivity as a function of temperature at different pressures, the dependence of T_N on pressure may be determined as shown in Fig. 5 (*19, 40*). In addition, by scaling the resistivity in the paramagnetic region of two curves at widely different pressures, the magnetic contribution to the resistivity below T_N may be obtained. This contribution may be interpreted in terms of the temperature-dependent energy gap and the fraction of the Fermi surface that is destroyed by the magnetic ordering (*40*). This is shown in the inset in Fig. 5. The energy gap at $T = 0°K$, obtained from fitting the data to the theoretical curve (solid line in the inset), is close to that observed directly in optical measurements (*41*).

The Néel temperature of chromium is much more strongly pressure-dependent than that of any of the other elements which order magnetically, with $(d \ln T_N)/(d \ln V) = 26.5$ for chromium and 0 to 2 for other elements (*4*). Furthermore, the pressure dependence is not linear but follows the relation

$$T_N = T_N(0) \exp(-26.5\Delta V/V_0)$$

where $T_N(0)$ and V_0 refer to quantities in the limit of $P \rightarrow 0$. This exponential variation is predicted by the theory for high temperatures (*40*). In the available pressure range ($P < 80$ kilobars) the antiferromagnetism in chromium cannot be completely suppressed, but, by alloying chromium with small amounts of vanadium or molybdenum, it is possible to lower the critical pressure into the experimentally observable range. This result is shown in Fig. 6 for three alloys for which the magnetic contribution to the resistivity in the limit of $T \rightarrow 0°K$ is plotted versus pressure (*41, 42*). Theoretically it has been



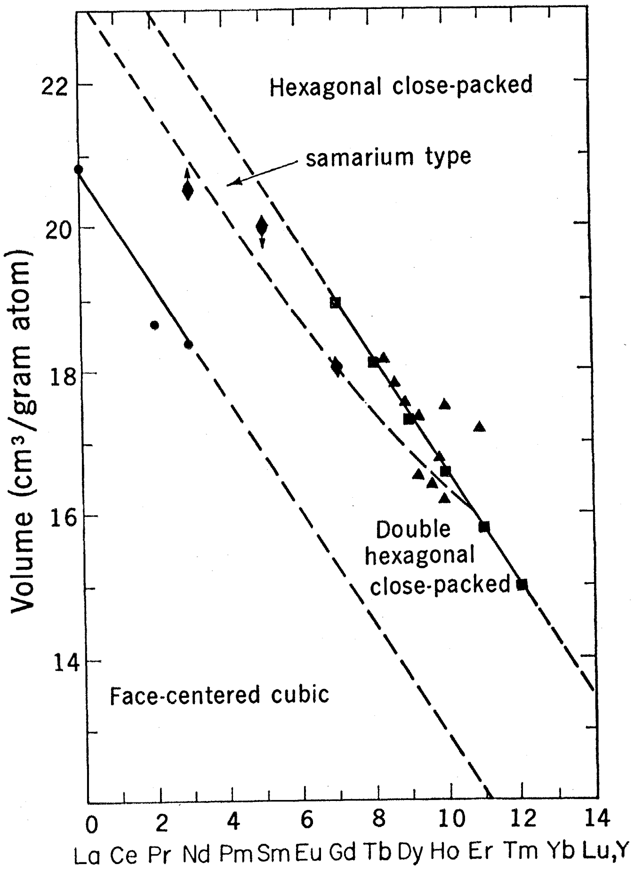


Fig. 3 (left). Tentative generalized phase diagram for the group V elements showing the trend with increasing pressure or atomic number from semiconductor to metal. Squares and diamonds are from resistivity measurements of McWhan and Kolobyanina *et al.* (*24*), respectively; open and solid symbols designate different phase transitions; triangles are the pressures at which discontinuous changes in the superconducting transition temperature occur; circles are from x-ray measurements; the inverted triangle is from Bridgman's resistivity measurements [see (*13*)]. Fig. 4 (right). Tentative generalized phase diagram for the rare-earth metals showing the sequence of close-packed phases as a function of volume and of the number of 4*f* electrons or atomic number (*25*); (circles) face-centered cubic to double hexagonal close-packed transition; (diamonds) samarium type to double hexagonal close-packed transition; (squares and triangles) hexagonal close-packed to samarium type transition in elements and alloys, respectively.

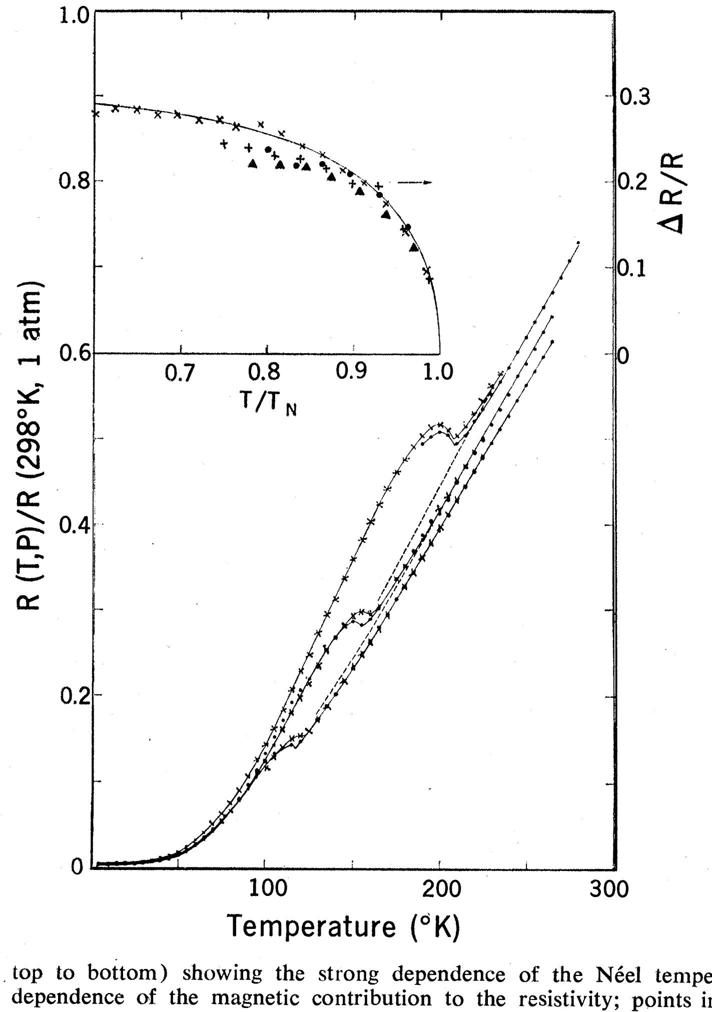
shown that at low temperatures the band structure of the group VI elements (chromium, molybdenum, and tungsten) leads to anomalies in the one-electron band susceptibility (*43*). As a result of these so-called "Kohn cusp-type" anomalies, it has been predicted that the Néel temperature as $T_N \rightarrow 0$ should be a linear function of $(P - P_c)$, where P_c is the critical pressure for the suppression of antiferromagnetism (*41*). In alloys there are depairing effects (that is, breaking up of electron-hole pairs by impurities) which tend to smear out the anomalies and to change the pressure dependence. The available results on a series of alloys strongly suggest that in pure chromium T_N will go to zero linearly in agreement with the theory. The shape of the magnetic resistivity curves shown in Fig. 6 is much more difficult to calculate. A large change in slope is expected between the low- and high-temperature regions because of the impurity depairing effects, but the detailed shape of the curve is not understood (*42*).

Pure chromium has a periodicity that is incommensurate with the lattice, but the addition of manganese to chromium results in a discontinuous jump to a commensurate structure. A similar transition as a function of an external variable such as pressure was predicted theoretically on quite general grounds (*44*). Recent experiments show a sharp change in the pressure dependence of T_N as a function of pressure in a series of chromium-manganese and chromium-ruthenium alloys, in agreement with the theoretical prediction (*42*). By mapping out the temperature-pressure phase diagram for these alloys, it has been possible to determine experimentally the change in T_N resulting from the depairing effects of the impurities. Thus significant contributions to the understanding of magnetism in chromium have been made by the use of the pressure variable.

Semimetal-Semiconductor Transitions: The Group V Elements

The magnetism in chromium is dependent on a subtle matching of parts of the Fermi surface, and the magnetism is very pressure-sensitive. It is also possible to have electronic transitions that involve not cooperative effects but the crossing or uncrossing of the conduction and valence bands as a function of pressure at temperatures above 0°K. This type of semimetal-semiconductor transition seems to occur in the face-centered cubic, divalent metals calcium (*19*), strontium (*45*), and ytterbium (*45, 46*) and also in some of the group V elements. In an effort to illustrate the variety of phenomena that can occur, I will discuss the group V elements in more detail.

The crystal structures of arsenic, antimony, and bismuth at 1 atmosphere may be viewed as a rhombohedral distortion of a simple cubic structure in



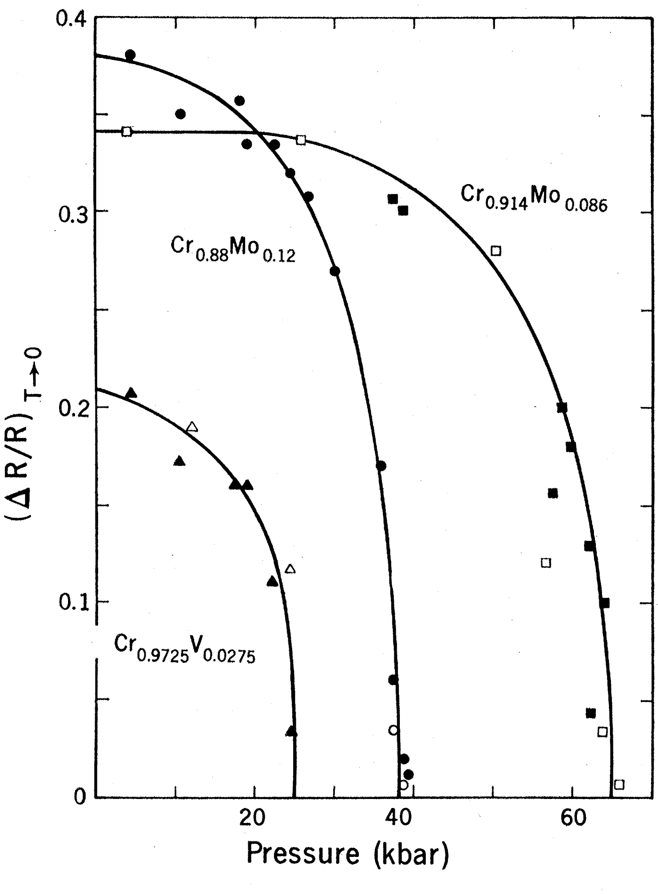


Fig. 5 (left). A plot of resistance R versus temperature for chromium at pressures of 26.5, 45.7, and 64.9 kilobars (from top to bottom) showing the strong dependence of the Néel temperature on pressure (from *40*). The inset shows the temperature dependence of the magnetic contribution to the resistivity; points in the inset are the difference between the solid and scaled dashed curves in the main figure (see text). The solid, theoretical curve in the inset is calculated as described in the text and (*40*). Fig. 6 (right). Variation of the magnetic contribution to the resistivity with pressure at 4.2°K for several chromium alloys showing the suppression of the itinerant antiferromagnetic state with pressure [from (*42*)]. Distinct symbols represent separate experiments.

which there are two atoms per unit cell at the positions ± (u,u,u). If the rhombohedral angle, α, equals 60° and the positional parameter, u, equals ¼, then the structure is simple cubic. The parameters for the group V elements are in the range $\alpha = 54°$ to $57°$ and $u = 0.23$ to 0.24 with the distortion from the simple cubic structure decreasing as one goes from arsenic to bismuth (*47*). Both α and u approach the cubic values with increasing pressure (*48*). This increase in α toward 60° with decreasing volume, $(V_0 - V)/V_0$, is illustrated for antimony and arsenic in Fig. 7 (*49*).

Although the structural properties of the group V elements show a marked similarity with increasing pressure, their electrical properties vary quite differently. The temperature coefficient of electrical resistivity of bismuth becomes negative at high pressure (see Fig. 8), thus suggesting that bismuth has a continuous transition from a semimetal with a small overlap of the valence and conduction bands to a semiconductor (*50, 51*). Measurement of the pressure dependence of both the frequency of the de Haas–Shubnikov oscillations (*52*) and the residual resistivity (*51*) confirms that the Fermi surface shrinks to zero at $P = 25$ kilobars.

The Fermi surface of bismuth consists of separated pockets of electrons and holes in momentum space, whereas that of arsenic consists of holes and pockets that are connected (*53*). If the pockets become disconnected, thereby changing the topology of the Fermi surface, then the resulting electronic transition will cause anomalies in many of the physical properties (*54*). From measurements of the pressure derivative of the de Haas–van Alfen frequencies and from band structure calculations, it has been shown that this transition occurs in arsenic as a function of pressure at 1.8 kilobars and 1.1°K (*55*). The elastic properties of arsenic are much more anisotropic than those of antimony and bismuth as illustrated in Fig. 7 (*56*). Initially the rhombohedral angle increases rapidly and then approaches the slope observed for antimony (*57*). It is possible that this result reflects the electronic effects observed at low temperatures, and further work on arsenic may lead to new insight into this type of electronic transition.

In both bismuth and arsenic the Fermi surface shrinks with increasing pressure, making them less metallic. In antimony, however, which lies between arsenic and bismuth in the periodic table, the number of carriers increases with increasing pressure, making it more metallic (*58*). This is illustrated in Fig. 8 where the temperature dependence and magnitude of the resistivity of antimony are those corresponding to metallic behavior even at 45 and 60 kilobars (*59*). Using band structure calculations based on the pseudopotential method, one can fit the experimental Fermi surface data at 1 atmosphere, but one cannot at present explain the differences in the pressure dependence of the Fermi surfaces of arsenic, antimony, and bismuth (*60*).

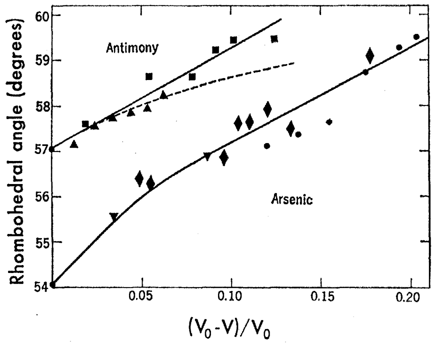


Fig. 7. Variation of the rhombohedral angle of the unit cells of antimony and arsenic with volume, showing the approach toward an undistorted simple cubic cell ($\alpha = 60°$). Triangles are from linear compression measurements, and other symbols are from x-ray measurements (*49*). The initial slopes for antimony and arsenic are calculated from elastic constant and x-ray measurements, respectively (*56*). The dotted curve for antimony is from Kolobyanina *et al.* (*18*).

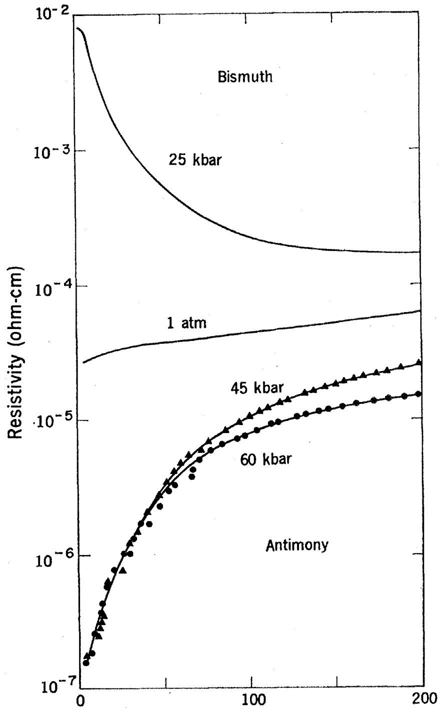


Fig. 8. Resistivity versus temperature at different pressures for bismuth (*51*) and antimony (*59*) showing how bismuth becomes less metallic and antimony becomes more metallic with increasing pressure. Curves for bismuth are for 25 kilobars and after releasing pressure.

New Transition Metals?

A more fundamental change in band structure as a function of pressure is thought to occur in some of the pretransition elements and the light rare-earth metals. It appears that under pressure these elements become similar to *d* transition metals. The most complete data are available for cesium and cerium for which it is believed that 6*s* and 4*f* electrons, respectively, are promoted to 5*d* states. Recent experiments on both metals suggest that a single transition to *d* states does not take place but that an intermediate phase exists.

Cesium is the most anomalous of the alkali metals with respect to the effects of pressure. It has a maximum in its melting point as a function of pressure and a subsequent minimum at the 42.5-kilobar transition (*61*). At a pressure of 42.5 kilobars there are actually two closely spaced transitions. At the first there is no change in structure, but there is a 12 percent change in volume and an increase of a factor of 2 in the electrical resistivity (*62*). When the pressure has increased by less than 1 kilobar, there is another transition accompanied by a phase change to an unknown structure and a drop in the resistivity to the value observed for the first phase (*62*). Both the first and third phases have an anomalously large T^2 term in the resistivity which peaks at the transition in each phase (*63*). There are further anomalies in the behavior of cesium near 120 kilobars. As shown above, the bulk modulus rises anomalously between 42.5 and 120 kilobars. Superconductivity has been observed only above 120 kilobars (*34*). Finally, there is a large rise in resistivity at 120 kilobars. A similar rise in resistivity has been observed at higher pressures in the other alkali metals with available *d* states (for example, rubidium and potassium) (*64*). These results suggest that the conversion to a *d* transition metal starts at 42.5 kilobars, but that it is not complete until 120 kilobars.

The transition from rare-earth metal to *d* transition metal in cerium appears to take place in stages. At a pressure of 1 atmosphere cerium has one localized 4*f* electron, and it orders antiferromagnetically at low temperatures. At 7 kilobars there is a transition with no change in structure and an 11 percent change in volume (*18*). However, cerium becomes superconducting only at 50 kilobars where there is another phase transition (*65*). The structure of the higher pressure phase resembles that found in the group IV elements titanium, zirconium, and hafnium, which is the structure cerium would have if it had completely lost its 4*f* electron (*18*, *22*). The intermediate phase appears to be a transitional one between localized 4*f* states and 5*d* states, as it is neither magnetically ordered nor superconducting (*66*).

Summary

In this article I have touched on only a few of the areas of research in which the pressure variable has led to new insight into materials at 1 atmosphere. Clearly in compounds other trends in structure and physical properties are significant, and many of them have been studied extensively. One example is in the transition from metal to insulator which occurs in several transition metal oxides. The combination of doping experiments and experiments at high pressure has shown that V_2O_3 must be considered as part of a more general phase diagram for metal-insulator transitions (*67*). It has been argued that the transition involves a fundamental change from band states in the metal to localized states in the insulator (*67*) and that it is a "Mott" transition (*68*). As theoretical interest in the pressure variable increases, it is reasonable to look forward to the continued growth of research at high pressure.

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22. For example, structure changes involving different stacking arrangements of hexagonal close-packed layers (magnesium, zinc, cadmium, gadolinium through thulium). Similar anomalies in resistivity were observed in magnesium, zinc, and cadmium but only in magnesium was there evidence from x-ray diffraction. There are conflicting reports on zinc and cadmium [D. B. McWhan, *J. Appl. Phys.* **36**, 664 (1965)]. Bismuth III and antimony III are isostructural, but the structure is unknown; a recent suggested structure {S. S. Kabalkina, T. N. Kolobyanina, L. F. Vereshchagin, *Zh. Eksp. Teor. Fiz.* **58**, 486 (1970) [*Sov. Phys. J. Exp. Theor. Phys.* **31**, 259 (1970)]} does not fit the data of R. M. Brugger, R. B. Bennion, T. G. Worlton, W. R. Myers, [*Trans. Amer. Crystallogr. Ass.* **5**, 141 (1969)] or satisfy the deWolff reliability test [P. M. deWolff, *Acta Crystallogr.* **14**, 579 (1961)]. Early reports of a phase of tellurium with the arsenic structure are apparently incorrect. The data for cerium above 50 kilobars do not fit a hexagonal close-packed structure as well as expected, but the earlier suggestion of yet another face-centered cubic phase is not confirmed.
23. X-ray measurements up to pressures in excess of 100 kilobars showed no evidence for a phase transition in α manganese.
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25. Figure 4 was constructed from the data in Fig. 1 and bulk compression data (D. B. McWhan, paper presented at the 6th Rare Earth Research Conference, Gatlinburg, Tenn., 1967). Included are points for the pure elements and for alloys of the heavy rare-earth elements with each other and with yttrium which is assumed to be similar to lutetium.
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Transmissible Multiple Drug Resistance in Enterobacteriaceae

The structure, replication, and mode of action of drug-resistance episomes are discussed.

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Ever since the introduction of antibiotics as a means of controlling infectious disease, bacterial strains have emerged that are resistant to a variety of chemotherapeutic agents. The examination of the mechanism of resistance in resistant strains which have been isolated from nature or derived in the laboratory has revealed a variety of ways in which microorganisms can survive in the presence of antibiotics. According to the tenets of microbial genetics, mutant strains should acquire resistance to only one antibiotic at a time, and organisms resistant to several drugs should arise in nature only by the accumulation of successive mutations. It is therefore quite extraordinary that there has been a dramatic increase in the frequency of occurrence of Enterobacteriaceae with multiple drug resistance in essentially all countries in which the problem has been examined.

In general, the multiple resistance of these microorganisms does not seem to have arisen in a series of discrete steps; but rather, resistance to all of the drugs appears to have been acquired simultaneously. Genetic analysis has revealed that multiple drug resistance is specified by an extrachromosomal element, which is referred to as a drug-resistance factor or R factor. Over the past decade, R factors have been studied extensively throughout the world because of their theoretical and practical consequences. We will review a number of their properties, particularly those that are related to the biochemical mechanism of multiple drug resistance and to the ways in which the level of drug resistance of host bacteria may be varied by the replication and the dissociation and reassociation of the components of R factors.

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