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ELECTRONIC STRUCTURE, ELECTRONIC TRANSITIONS, AND THE HIGH PRESSURE CHEMISTRY AND PHYSICS OF SOLIDS

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INTRODUCTION

The basic effect of high pressure is to increase the overlap between electronic orbitals on adjacent atoms or molecules. There are a number of consequences of this increased overlap. Perhaps the simplest is the broadening of allowed energy bands and the resulting increase in electron mobility. This is a major factor in the "red shift" (shift to lower energy) of the absorption edge observed as a function of pressure in many crystals. It may ultimately lead to an overlap between the valence and conduction band, and thus to metallic conductivity as observed, for instance, in iodine (1).

In the second order, one observes a relative shift of one orbital energy with respect to another. Since orbitals of different quantum number may differ in radial extent, orbital angular momentum (orbital shape), or diffuseness or compressibility, these relative shifts are rather common. In terms of the band picture of solids, one may observe a shift of the center of gravity of one band with respect to another which can either augment or counteract the broadening effect mentioned above.

High pressure experiments measuring the shifts of various parts of the conduction band with respect to the valence band have been instrumental in understanding the structure of the conduction band and the nature of the deformation potential in silicon, germanium, and the III–V and II–VI semiconductors (1, 2). In the alkali, alkaline earth, and rare earth metals, the relative shifts of various parts of the conduction band can lead to drastically different electronic behavior, as discussed below.

Of more direct interest to chemists generally are the relative shifts of orbital energies involving more localized electrons. We mention three classes of such transitions. The π-π^* transitions in aromatic hydrocarbons and related materials generally shift rather strongly to lower energy with increasing pressure. Shifts of $\frac{1}{3}$–1 eV in 100 kbar are not uncommon (1, 3). This implies a higher dipole moment in the excited state, i.e. a greater charge separation with increasing pressure. To the extent that the decrease in the relative energy of the π^* levels vis à vis the π levels indicates a greater occupation of the excited state at high pressure, the implication is that the volume of the system as a whole decreases with increased occupation of the π^* orbitals. We make use of this fact later. Offen (4–12) has made extensive studies of the effect of pressure to 30 kbar on π-π^* and n-π^* transitions and on fluorescence in aromatic molecules in the solid state and as dilute solutes dissolved in plastics.

A second type of localized electronic transition of interest here is the internal rearrangement of the $3d$ electrons of transition metal ions. In a field of octahedral symmetry the $3d$ orbitals split into a higher energy doublet of σ symmetry (e_g) and a lower energy triplet of π symmetry (t_{2g}). In molecular orbital language, the e_g orbitals are strongly antibonding, while the t_{2g} orbitals are nonbonding or slightly antibonding. The occupation of these orbitals depends on the magnitude of the splitting compared with the energy involved in pairing spins. Optical transitions measure the magnitude of the ligand field (Δ) and of the Racah (interelectronic repulsion) parameters B and C. For high spin systems the ligand field increases with pressure, approximately as R^{-5} where R is the ligand-metal distance (13, 14). The Racah parameters decrease by 5–10% in 100 kbar. Qualitatively similar observations have been made for symmetries other than octahedral. These parameters have been very little studied as a function of pressure for low spin systems. There are, however, indications that for some such systems Δ may decrease with pressure and B may increase (15).

There is a third type of transition where a relative shift with pressure has been observed. This excitation involves the transfer of charge from one type of entity to another. Molecular electron donor-acceptor complexes have been widely studied both experimentally and theoretically (16). A variety of these complexes have been observed as a function of pressure (17). The energy of the donor-acceptor transition decreases with pressure, as indicated by the red shift of the optical absorption peak. There is also a decrease in electrical resistance (18).

Coordination compounds of transition metals also may exhibit charge transfer spectra. The transfer may be from the predominantly ligand π orbitals to the metal nonbonding $3d$ orbitals, or from the metal orbitals to the empty ligand π^* orbitals. The available data indicate that both metal-to-ligand and ligand-to-metal charge transfer peaks usually shift to lower energy with increasing pressure (19), with few exceptions (20). The fact that both transitions shift to the red reflects the large decrease in the π-π^* energy with increasing pressure.

There is a third consequence of increased orbital overlap. For a wide variety of systems there exists an excited state which lies not too high in energy above the ground state. The relative displacement of orbitals with pressure may be sufficient to establish a new ground state for the system or to modify drastically the properties of the ground state by configuration interaction as shown schematically in Figure 1. We call this type of event an electronic transition. It may occur at some definite pressure at a given tempera-

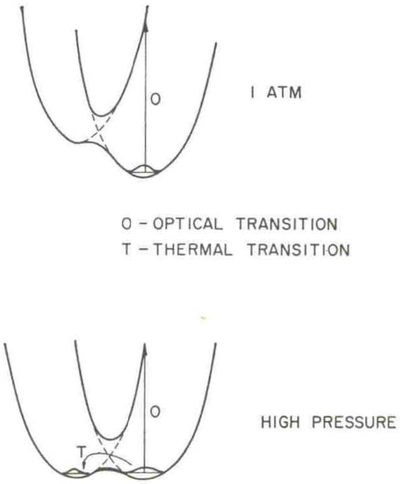


FIGURE 1. Schematic configuration coordinate diagram.

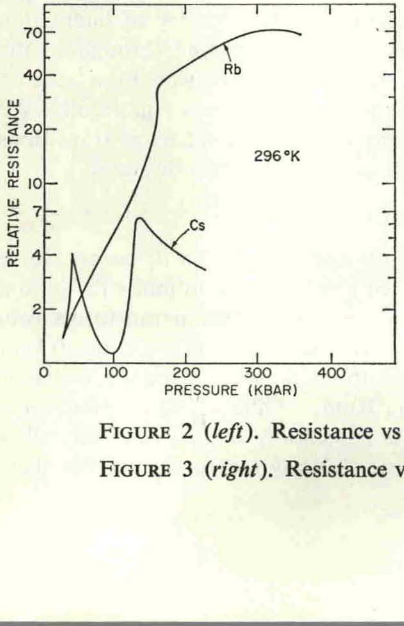
ture, accompanied by a volume discontinuity, i.e. it may involve a first order transition. Alternatively, the two states may be present over a large range of pressures with the amount of conversion changing with pressure as in a chemical equilibrium. The bulk of this article is devoted to a discussion of electronic transitions, their physical and especially their chemical consequences. In the first section, we discuss electronic transitions in alkali, alkaline earth, and rare earth metals. Then we mention briefly insulator-metal transitions. The third section describes the chemical consequences of electronic transitions in aromatic hydrocarbons and their complexes. Finally, we discuss at some length a variety of changes in the electronic structure of ferric and ferrous iron. All these electronic transitions involve a degree of interaction among adjacent sites; in the metals the interactions extend throughout the lattice. These have in common, however, the feature that they are in some sense describable in terms of the states of the individual atoms or molecules. We omit from this discussion such purely cooperative phenomena as transitions between paramagnetic and ferromagnetic or antiferromagnetic states.

METALS

The concept of the electronic transition was first applied to metals. Some twenty-five years ago Bridgman discovered a volume discontinuity (21) and a cusp in the resistance (22) of cesium near 40 kbar. Since cesium transforms from bcc to fcc at 22 kbar, Sternheimer (23) proposed that the event at 40 kbar involved the promotion of the 6*s* electron to the 5*d* shell (or rather, a change from *s* to *d* character in the conduction band). While his calculations were approximate, it appears that his analysis is basically sound. Hall, Merrill & Barnett (24) have demonstrated by means of X-ray measurements that there are two closely spaced volume changes associated with the 40 kbar transition, but that the structure remains fcc. After 1960 a considerably larger pressure range became available. It was then discovered that the resistance started to rise again near 100 kbar, and exhibited a maximum near 135 kbar (25, 26) (see Figure 2). There are speculations that the higher pressure transition introduces *f* character to the conduction band, but no really satisfactory analysis has been performed. It is of considerable interest that the phase present above 100 kbar is superconducting, as shown by Wittig (27). This is the first example of a superconducting alkali metal, a phenomenon which at one time was considered impossible.

Rubidium has a transition near 60 kbar, apparently from the bcc to the fcc structure. Near 145 kbar there is a very sharp rise in resistance (1, 28, 29) as shown in Figure 2. This would appear to be associated with an electronic transition changing the conduction band character from 5*s* to 4*d*. The maximum near 300 kbar may be associated with a further electronic rearrangement.

At room temperature potassium (29) exhibits only a continuous increase in resistance with pressure above about 20 kbar (by a factor of 30–40 in 500 kbar). This is in itself anomalous, as most metals exhibit a modest decrease in resistance with increasing pressure due to reduced amplitude of the lattice vibrations. At 78°K there is a sluggish transition at 230–240 kbar, probably from bcc to fcc structure, then a very sharp rise in resistance near 280 kbar (see Figure 3). The magnitude of the rise decreases with increasing temperature, so that it disappears near 250°K. The sluggish transition at lower pressure is not observed either. The sharp transition could well be the $4s \rightarrow 3d$ electronic



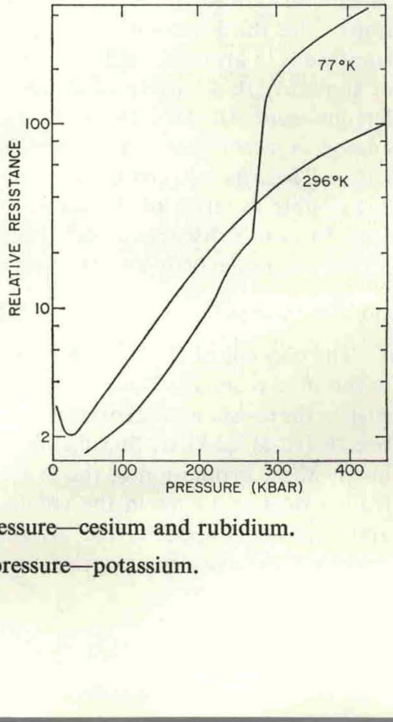


FIGURE 2 (*left*). Resistance vs pressure—cesium and rubidium.

FIGURE 3 (*right*). Resistance vs pressure—potassium.

transition which may disappear in a critical point as discussed for cerium below.

It has been long known (30) that cerium exhibits a discontinuity in resistance (31) and in volume (32) with no change in structure at room temperature and a few kilobars pressure. Jayaraman (33) has shown that the magnitude of the discontinuity decreases with increasing temperature until it disappears. It has been frequently proposed (30, 32) that the transition involves transfer of a $4f$ electron to the $5d$ shell. Recent calculations by Ramirez & Falicov (34) indicate that a transfer of a $4f$ electron to the conduction band is probably involved. It has been shown (1, 35) that a variety of other rare earth metals show very distinct resistance anomalies at high pressure and that these transitions become sharper, rather than more sluggish, at 78°K. The transfer of an electron from the $4f$ shell to the $5d$ shell or to the conduction band must be a common phenomenon.

It has been pointed out that barium and europium exhibit a very similar resistance behavior (1), particularly in the region 100–150 kbar. There appear to be reasons to associate the transition in barium with $s \rightarrow p$ or $s \rightarrow d$ transitions. It is quite possible that europium, with a half-filled $4f$ shell, undergoes a similar transformation.

Interestingly, Jayaraman et al (36) have observed resistance anomalies in compounds of samarium (SmS, SmSe, SmTe) which they associate with the $4f \rightarrow 5d$ electronic transition, so that these transitions may occur in compounds as well as in the elements. In SmSe and SmTe these transitions occur over a considerable range of pressure, rather than discontinuously.

Another type of electronic transition takes place in certain crystals of atoms with filled shells such as calcium, strontium, and ytterbium. These materials are metallic because their conduction band is an s-p-d hybrid such that the Fermi surface intersects the Brillouin zone boundary in a complex manner. As pressure is increased these materials become semiconductors or semimetals (1, 37), i.e. the resistance decreases with increasing temperature. At sufficiently high pressure they again become metallic. There have been extensive theoretical analyses of calcium. Cracknell (38) reviews the theory up to 1969. Calcium, and probably also strontium, are semimetals rather than semiconductors. A recent study by McCaffrey, Papaconstantopoulos & Anderson (39) is also consistent with this viewpoint. Calcium becomes semimetallic near 200 kbar and transforms back to the metallic state near 300 kbar. The corresponding transitions occur at much lower pressures for strontium and ytterbium so that more extensive experimental evidence is available for them. McWhan, Rice & Schmidt (40) have made a particularly thorough study and analysis for ytterbium. Although its resistance behavior is very similar to calcium it becomes semiconducting rather than semimetallic. Very small variations in the relationship of the Fermi surface to the Brillouin zone boundary are sufficient to establish this difference. Important contributions to the study of these two compounds have also been made by Hall & Merrill (41), Souers & Jura (42), Jerome & Rieux (43), and McWhan & Jayaraman (44).

NONMETAL-METAL TRANSITIONS

As mentioned in the introduction, one of the primary effects of decreased interatomic distance is to broaden the bands of allowed energy states. It is easy to visualize that this broadening, possibly accompanied by a relative displacement of one band with respect to another, could transform an insulator into a metal. Such transformations with no apparent discontinuities in resistance or structure have been observed in iodine (1, 45); in crystals of certain aromatic hydrocarbons such as pentacene, hexacene, and violanthrene (46) at temperatures below 200°K; and apparently in the thallous halides (47).

One might expect that a relatively open structure could undergo a first order phase transition to a more closely packed structure, and that this structure could be metallic although the open structure was insulating or semiconducting. Such transitions, accompanied by very large discontinuities in resistance, have been observed in silicon, germanium, and numerous III–V and II–VI compounds with the zinc blende structure (1, 48, 49). X-ray analysis (50–53) indicates that in many cases the high pressure structure is that of white tin or the diatomic analog. Recently van Vechten (54) has been successful in calculating the transition pressure in silicon and germanium.

The foregoing discussion of insulator-metal transitions has been based on the elementary consideration of an empty conduction band and a filled valence band separated by a forbidden energy gap. This picture does not predict the insulating properties of transition metal oxides like NiO or V_2O_3. Since the partially filled atomic 3*d* shell should give rise to a partially filled band, these materials ought to be metals. While a number of theories have been proposed to describe this phenomenon, the most widely discussed is that due to Mott (55). Basically he argues that the problem is one of electron-electron correlation. Above a certain electron density, the material is metallic; for lower densities it is an insulator. Adler (56) has reviewed a wide variety of related theories. While discontinuous transitions from insulator to metal are not uncommon as a function of temperature and pressure, they generally lack the precise characteristics of a true "Mott transition."

Probably the most interesting and informative experiments in this area have been those performed at Bell Laboratories by McWhan et al (57–60). They have studied the properties of crystals of the form $V_{1-x}Cr_xO_3$ and have shown that, in particular, the crystal $V_{0.96}Cr_{0.04}O_3$ exhibits essentially all of the characteristics of a Mott transition, with regions of temperature and pressure where it is a paramagnetic insulator, an antiferromagnetic insulator, or a metal. They have also demonstrated very clearly the equivalence of changing composition and pressure on the electronic properties as shown in Figure 4. Even for this material, the transition may not be a pure "electron-electron" interaction as demanded by the Mott theory, as it is probably phonon assisted. Mott, in fact, now believes (61) that the transition precisely as described by his theory may not be experimentally obtainable. Nevertheless, the proposal has given rise to much interesting work, both theoretical and experi-

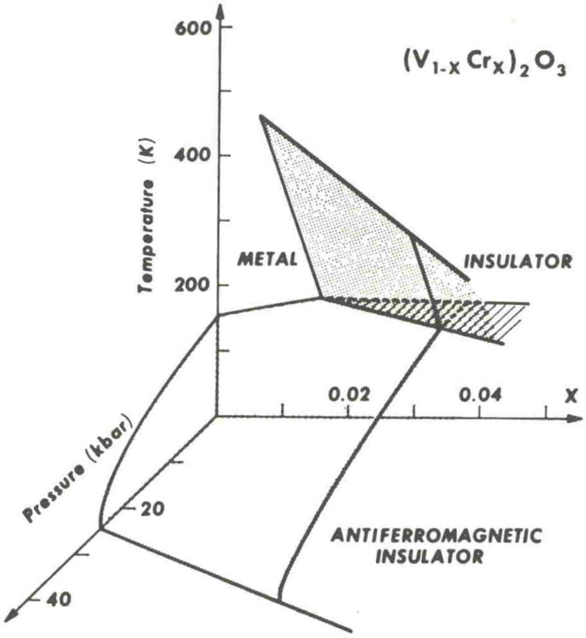


FIGURE 4. Pressure-temperature-composition phase diagram $V_{1-x}Cr_xO_3$.

mental. The work at Bell Laboratories has elucidated important concepts and presented an interesting class of materials.

AROMATIC CRYSTALS

Rather different electronic transitions occur in crystals of some aromatic hydrocarbons and in their charge transfer complexes with a variety of electron acceptors (62–66).

Aromatic hydrocarbons are planar molecules distinguished by their π orbitals which are conjugated to form an electron path around the molecular periphery. They form crystals of a characteristic herringbone structure. The ground state of the molecule is nonpolar and, in the solid at least, is rather unreactive. The excited states are polar and may be more reactive. The energy for optical excitation to the lowest excited state depends strongly on the length of the conjugated path. In anthracene, with three rings, $\nu_{\max}$ is at 26.4 kK (kiloKayser); in tetracene, with four rings, it lies at 21.1 kK; and in pentacene, with five rings, it is at 17.1 kK. With increasing pressure the optical excitation energy decreases rapidly, as shown in Figure 5. ($V/V_0 = 0.7$ corresponds to about 50 kbar.) By 100 kbar the shift approaches 6–9 kK (0.8–1.1 eV). The electrical resistance also decreases with increasing pressure by 12–16 orders of magnitude in 300 kbar. Anthracene and tetracene remain semiconductors at

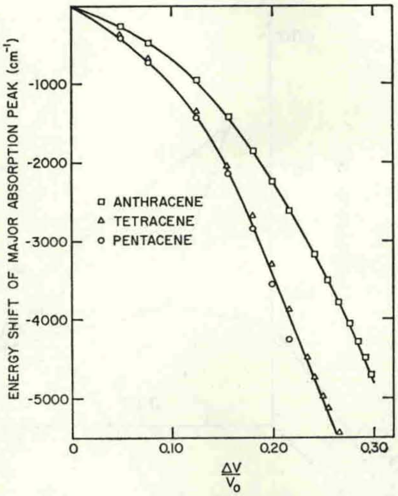


FIGURE 5. Shift of low energy optical absorption peaks with V/V_0—aromatic hydrocarbons.

all available pressures, although the activation energy for carrier production diminishes considerably with pressure. Their behavior is entirely reversible. At low temperature (~78°K) for pentacene the activation energy goes to zero above 200 kbar and the material becomes a metal or semimetal. Below 200°K this behavior is reversible. At high pressures and temperatures above 200°K, the resistance tends to drift upward with time and this behavior is irreversible. The material can be recovered in milligram quantities. Ordinary pentacene is a bluish-black crystalline material which sublimes easily at 120°C in a vacuum. Its electronic absorption spectrum shows peaks in the region 14–18 kK. As mentioned above, these relatively low energies are associated with the long conjugation path. Its infrared spectrum in the C–H stretching region shows only typical aromatic frequencies. The high pressure product is reddish brown and amorphous. It will not sublime at 350°C in a vacuum. The low-lying peaks in the electronic spectrum have disappeared, although there are absorptions which correspond to shorter conjugation paths. The infrared spectrum shows, in addition to the aromatic C–H stretch, a second peak of about equal intensity in the region associated with aliphatic C–H stretching vibrations. There are other drastic differences in the infrared spectrum. It seems clear that the pentacene has polymerized, although the small amounts of material and its extreme insolubility make it difficult to characterize the polymer precisely.

A reasonable mechanism is as follows. The shift of the π^* state to lower energy (vis à vis the π ground state) is sufficient that at high pressure the electrons are largely in this more reactive state. (The two states are probably mixed by configuration interaction as shown in Figure 1.) The reaction may also be stimulated by electron transfer between adjacent molecules (self complexing). For anthracene and tetracene the excited state may be too high initially to be sufficiently occupied at high pressure, or there may not be sufficient self-complexing action. Reaction does occur in molecules like hexacene and violanthrene with sufficiently low-lying π^* orbitals. This is, then, an example of an electronic transition with distinct chemical consequences. A number of aromatic hydrocarbons such as anthracene, pyrene, and perylene form electron donor acceptor complexes with electron acceptors like iodine, tetracyanoethylene, etc. These complexes typically have optical absorption peaks of energy 10–25 kK (1–3 eV) which decrease in energy with increasing pressure. Many of these complexes show irreversible electrical behavior at high pressure (64). The products have not yet been well characterized, but it is clear that sometimes both donors and acceptors have reacted and sometimes just the donors, so that the acceptor is recovered in its original condition. The prime purpose of the acceptor is to provide a low-lying excited state, so that its decrease in energy with pressure is sufficient to establish a new reactive ground state of the donor at high pressure. It would be very desirable to be able to characterize the products accurately, as it might be possible to design complexes with appropriate geometry and electronic structure to give desired products, and thus to establish a new solid state organic chemistry at high pressure.

CHEMISTRY OF IRON

The coordination chemistry of transition metal ions has been a very fruitful field of study. The splitting of the 3*d* orbital energies, the radial extent of these orbitals, and the spin state of the electrons in the orbitals depend on the symmetry and strength of the field due to the ligands and the degree of covalent bonding, which is a function of both the character of the ligand and the oxidation state of the metal ion. The behavior of iron is of considerable interest because of its importance in biology and geophysics as well as in chemistry and physics. The study of iron compounds at high pressure is significantly facilitated by the possibility of using Mössbauer resonance as well as optical absorption. With the latter technique one measures the difference in energy between a ground state and some excited state of an electron along a particular path. Changes in the optical excitation energy with pressure are helpful in understanding high pressure chemical processes. There are three types of excitations which are useful in connection with the high pressure chemistry of iron. Excitations from one state to another within the 3*d* shell measure the change in the field which the ligands impose on the metal 3*d* orbitals, and changes in the interelectronic repulsion (Racah) parameters. From changes in the energy associated with exciting an electron from one ligand state to another (usually $\pi \rightarrow \pi^*$ transitions) one can infer modifications of the ground state configuration of the ligands and, therefore, changes in bonding to the iron. From the energy of the ligand-to-metal charge transfer peaks one can infer the probability of electron transfer between ligand and metal, and thus the change in oxidation state of the metal. The direction and magnitude of these optical shifts were discussed in the early part of the paper.

Mössbauer resonance is helpful in identifying the electronic ground state of the iron ion. Two parameters are important: the isomer shift and the quadrupole splitting. The isomer shift measures the *s* electron density at the iron nucleus; the quadrupole splitting measures the interaction of the nuclear quadrupole moment with an electric field gradient at the nucleus. These gradients arise, in the first order, from an asymmetric occupation of the 3*d* orbitals and, in the second order, from a noncubic arrangement of the ligands.

The factors determining the isomer shift have been summarized by Erickson (67). For high spin ions the major variable is the oxidation state, i.e. the number of 3*d* electrons which shield the 3*s* electrons from the nucleus. Typically, high spin ferric ions have isomer shifts in the range 0.25–0.50 mm/sec, while the values for the high spin ferrous ion lie in the range 0.9–1.4 mm/sec (both given relative to iron metal). Within each group the variation of isomer shift can be related to several factors, including the degree of spreading of the 3*d* orbitals (central field covalency), occupation of the 4*s* orbitals, overlap of metal 3*s* orbitals by ligand σ orbitals, and backdonation of metal 3*d* electrons into empty ligand π^* orbitals. This last phenomenon is especially important for Fe(II) ions. We shall discuss the effect of pressure on the isomer shift and quadrupole splitting only to the extent necessary to explain the various electronic transitions which occur.

The high spin ferrous ion can be distinguished from the high spin ferric ion not only by the difference in isomer shift but also by the difference in quadrupole splitting. The high spin Fe(II) exhibits a large quadrupole splitting (2.0–3.0 mm/sec) because of the asymmetric $^5T_2$ ground state, while high spin Fe(III), with a $^6A_1$ ground state, usually shows a splitting near 0.5–0.7 mm/sec. If the splitting due to the ligand field is large enough to overcome the spin pairing energy, one may obtain a low spin ground state. The low spin ferrous state is characterized by a relatively low isomer shift ~ 0.0 mm/sec relative to metallic iron, and little or no quadrupole splitting because of the $^1A_1$ symmetry. Thus, transitions from high spin Fe(III) to high spin Fe(II) and between the high spin Fe(II) and low spin Fe(II) are easy to identify. It is more difficult to obtain quantitative information on low spin Fe(III), as its isomer shift is very close to low spin Fe(II). As we shall mention later in the report, it may be possible to identify states of intermediate spin or mixed spin in molecules with lower symmetry. It seems desirable to analyze the possibilities and limitations involved in making quantitative high pressure Mössbauer resonance measurements.

For these experiments (68) the sample is made from iron enriched to 70–95% in ^{57}Fe, and the compounds are diluted (5/1 to 10/1) with boron and pressed into a hole 0.3 mm in diameter in a pellet of boron plus lithium hydride 2 mm in diameter (other diluents such as Al_2O_3 or graphite did not seem to affect the results). The pressure calibration is by X-ray diffraction. The problems in making quantitative measurements and in their interpretation fall into three categories: those connected with Mössbauer resonance; those connected with nonhydrostaticity and shear; and those associated with metastability, which may be inherent in solid state reactions.

The relative amounts of the various states are established from the area measured by fitting the data with Lorentzian or pseudo-Lorentzian peaks. It is necessary to assume equal *f* number at the two sites. This is always a possible source of error. Self absorption in the sample can change the apparent relative amounts of two states. This may be a source of significant error in the earlier work where the degree of dilution was not closely controlled. If high dilutions are used and care is taken to run a series of similar compounds at the same dilution, this error can be eliminated. A third possible inaccuracy arises from fitting asymmetric peaks as in the hemiporphyrins. Under the best conditions the conversions can be reproduced to $\sim \pm 2\%$.

The pressure is clearly not completely hydrostatic. Under these conditions there is a question of the degree to which conversions are due to shear rather than pressure. There are a number of reasons to believe that pressure per se is the major factor in the great majority of cases:

1. Isobaric runs show a large effect of temperature on conversion at constant pressure. With no change in pressure, change in shear should be minimized.
2. Studies involving a series of related compounds with apparently similar shear properties sometimes gave very different conversions, conversions which correlated well with other electronic differences, as discussed below.
3. For some compounds with distinctive shear products it is possible to make pressure runs where little or no shear product is produced at any pressure.
4. The change in integrated intensity (area) under optical charge transfer peaks with pressure mirrors the conversion obtained by Mössbauer studies. Shear is minimized in the optical apparatus.
5. The conversions were generally in some sense reversible. When the applied pressure is removed there is still considerable strain in the pellet. However, for some systems (hemin, hematin) the spectrum on releasing all the applied pressure was substantially identical with the atmospheric. For most systems the spectrum was returned 60–80% of the way to the original. It is possible to cut the center from the pellet and to relieve the strain by chopping it with a sharp blade, although with such a small amount of material the efficiency of the operation is low. This chopped material exhibits an 80–100% return to the original spectrum for most materials.

Except possibly for one or two systems it is probable that the lack of immediate reversibility is primarily due to stored strain in the crystals because of modified local geometry, especially at high conversions. This raises the question of establishing true equilibrium in solid state systems where electron transfer or other chemical processes involving local deformation occur. The conversions were not time dependent in the sense that readouts over a period of time at the same pressure gave the same conversion, even over periods of several days. However, if two states of only moderately different energy are separated by a reasonably high potential barrier, the system could stay metastably in the higher energy state for an indefinite period.

We discuss three types of electronic transitions in iron compounds: $\mathrm{Fe(II)_{HS}} \rightarrow \mathrm{Fe(II)_{LS}}$; $\mathrm{Fe(II)_{LS}} \rightarrow \mathrm{Fe(II)_{HS}}$; and $\mathrm{Fe(III)_{HS}} \rightarrow \mathrm{Fe(II)_{HS}}$. In the high spin to low spin transition the increase in ligand field with pressure is sufficient to cause a rearrangement of electrons among the 3*d* orbitals. For the low spin to high spin transition the ground state of the ligand is modified at high pressure by significant thermal occupation of the ligand π^* orbitals by ligand π electrons. This reduces the possibility of metal $d_\pi \rightarrow$ ligand π^* back-donation, which decreases the ligand field so that a high spin state becomes more favorable. Ferric iron reduces to ferrous iron because the energy of the metal d_π orbitals reduces vis à vis that of the ligand nonbonding orbitals so that thermal electron transfer takes place.

Spin changes.—According to Hund's rule the ground state of a free ion is that of maximum multiplicity. This configuration also obtains in many crystals, since the repulsive energy involved in pairing spins is larger than the splitting among orbitals of different symmetry due to the ligand field. Since, for high spin compounds, the ligand field increases with pressure by as much as 15–20% in 150 kbar, ultimately it may become energetically economical to pair spins. For systems of octahedral symmetry Griffith (69) has shown that the intermediate spin configuration is higher in energy than either the high or low spin states. For systems of lower symmetry an intermediate spin ground state is possible, as we shall discuss later.

An example of the high spin to low spin transition is the behavior of Fe(II) as a dilute substitutional impurity in MnS_2 (70). MnS_2 has a cubic structure isomorphous to FeS_2. Iron in FeS_2 is low spin at all pressures. Since the lattice parameter of MnS_2 is significantly ($\sim 10\%$) larger than that of FeS_2 it is not surprising that the Fe impurity is high spin even though there is probably local relaxation near the iron. At a pressure of about 40 kbar a measurable amount of low spin appears. By 130 kbar the iron is completely converted to low spin. The process is reversible in the sense discussed above.

The complexes of ferrous iron with 1,10-phenanthroline form a widely studied series of compounds (71–73). There are two types of octahedral or nearly octahedral complexes. The bis complexes involve two phenanthrolines each coordinated to the iron through the nitrogens, plus two other ligands to fill out the six positions. The tris complexes have the iron coordinated to three phenanthroline molecules with the anions outside the coordination sphere. The bis complexes usually have ligand fields of 10–13 kK, just below the crossover value of ~ 14 kK, and are high spin. The tris complexes have ligand fields in the range 16–19 kK and are low spin. These complexes form an excellent basis for a systematic study of electronic properties, because it is possible to vary the field at the iron in a controlled manner by varying the extra ligands on the bis complexes or by substituting different groups (e.g. CH_3, Cl, NO_2) at various positions on the phenanthrolines. Two such studies have recently been published (3, 74). With increasing pressure, the high spin bis complexes tend to convert to low spin, as can be seen in Figure 6. The pressure at which conversion initiates correlates with the size of the ligand field at 1 atm, as one might expect. The surprising feature is that at 40–80 kbar the high spin to low spin conversion stops and at higher pressures there may actually be a net low spin to high spin conversion with increasing pressure. Similarly, the low spin tris complexes convert partially to high spin at high pressure.

At first a low to high spin transition seems difficult to understand either on electronic or thermodynamic grounds. It is normal for the ligand field to increase with pressure, which should increase the probability of the low spin state. For most compounds the effective ionic radius of a low spin Fe(II) ion is smaller than that of the high spin ion.

The bonding of phenanthroline to iron has a component common to many ligands which have empty orbitals of π symmetry lying not too far above metal d_π orbitals. The metal tends to donate electrons into these π^* orbitals, which increases the bonding and tends to stabilize the metal d_π orbitals and thus to increase the ligand field. The difference in ligand field between the tris and bis complexes and within each group are primarily associated with differences in backdonation. If the π^* orbitals tend to be occupied by ligand π

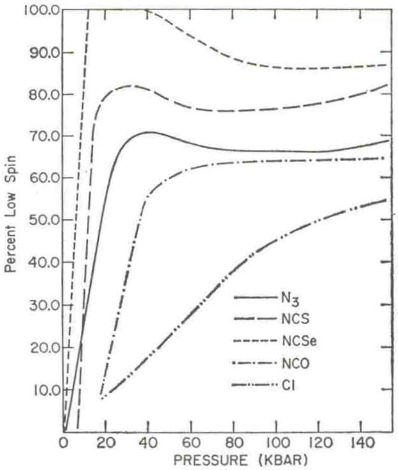


FIGURE 6. Conversion to low spin vs pressure—ferrous bis phenanthroline complexes.

electrons at high pressure they are less available for backdonation. Any reduction in backbonding would reduce the size of the ligand field and, therefore, the probability of the low spin state.

To the extent that the π orbital is emptied by π-π^* transfer it becomes available for metal d_π to ligand π backdonation. This form of backdonation would, however, tend to *destabilize* the d_π orbitals and thus to *reduce* the ligand field.

The lowest allowed π-π^* optical transitions lie in the range 2–4 eV. They shift rapidly to lower energy with increasing pressure. While the red shift implies increased occupation of the π^* orbital at high pressure, the shift is still only a small fraction of $\nu_{\max}$. It appears that one must postulate a large difference between optical and thermal transition energies to obtain significant occupation of π^* orbitals with π electrons in the requisite pressure range. The difference between thermal and optical transitions are discussed in more detail in a later section.

It is also possible that the compressibility of the system is greater when the iron is high spin, or that the arrangement of the molecules when the iron is high spin allows a closer packing. It is important to remember that the criterion for increase of conversion with pressure is that the volume of the system as a whole decrease with increasing conversion at constant p and T. This may come about due to the shortening of bonds or the closer packing of the complexes due to changes in their electronic structure. It is, of course, not necessary that every bond in the system shorten to accomplish this objective.

As indicated above, the probability of the low spin state is related directly to the size of the ligand field. The low energy tail of the charge transfer peak tends to obscure the ligand field peaks. Since the charge transfer peak tends to shift red with pressure, it is not practical to measure the ligand field optically as a function of pressure. However, Erickson (67) has demonstrated an excellent correlation between the low spin isomer shift and the ligand field Δ; the larger the ligand field the smaller the isomer shift. This is inherently reasonable, as the lower isomer shift results from larger backbonding, greater delocalization of the 3*d* electrons, and less shielding of the 3*s* electrons. In Figure 7, we see the very satisfactory correlation between low spin isomer shift and fraction low spin ferrous ion present for a series of substituted phenanthrolines (74). The data presented in the figure are for 100 kbar, but similar correlations apply at other pressures and for other groups of phenanthrolines, as discussed in the original papers.

A second group of low spin ferrous compounds where backdonation is important are the ferrocyanides (75). Since these involve relatively large ligand fields (Δ = 30–35 kK), one would not anticipate a ready conversion to the high spin state. At room temperature indeed no conversion occurs, below 200 kbar, at least. However, at 110°C and 150 kbar $Cu_2Fe(CN)_6$ exhibits 65%

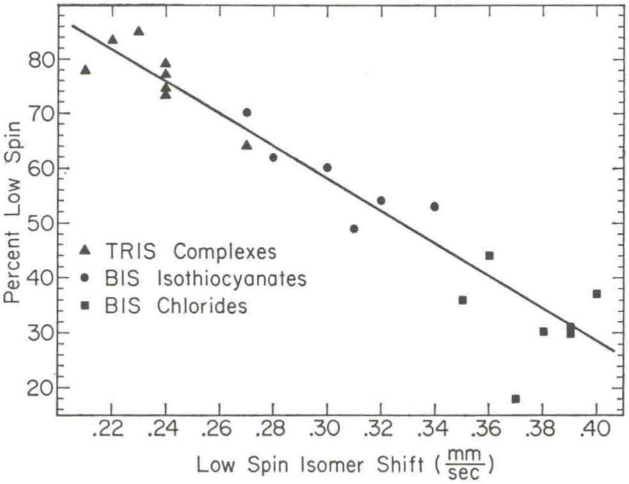


FIGURE 7. Low spin ferrous isomer shifts vs percent low spin at 100 kbar—phenanthrolines.

high spin ferrous ion, and $Ni_2Fe(CN)_6$ exhibits 18–20%. The isomorphous $Zn_2Fe(CN)_6$ and the sodium and potassium salts, with a slightly different structure, exhibit no conversion. At 150°C and high pressure the zinc salt exhibits ~25% conversion to high spin, and the sodium and potassium salts show small traces (<10%). Since the conversion depends so sharply on the cation it is apparent that the occupation of the ligand π^* orbitals at high pressure involves both cyanide and cation π electrons.

A third set of systems where one observes spin change is that involving substituted ferrous phthalocyanines (76). The planar molecule consists basically of four pyrrole rings bridged by nitrogens. The ferrous ion lies in the plane in a site of D_{4h} symmetry. The substitutions studied involve the axial addition of pyridine, substituted pyridines, or piperidine above and below the plane. The order of the orbitals is apparently (with increasing energy) d_{xz}, $d_{yz}(e_g)$; $d_{xy}(b_{2g})$; $d_{z^2}(a_{1g})$; and $d_{x^2-y^2}(b_{1g})$. In the unsubstituted molecule the splitting between d_{z^2} and $d_{x^2-y^2}$ is sufficient that one obtains an intermediate spin ferrous ion. The addition of axial ligands raises the energy of the d_{z^2} orbital sufficiently to give a low spin iron. For the pyridines and substituted pyridines this effect is reinforced by backdonation from the metal d_π orbitals to the ligand π^* orbitals. This is reflected in the order of the metal-to-ligand charge transfer peaks. The piperidine has no empty π^* orbitals but exhibits very strong σ bonding as exemplified by the very large acid dissociation constant of the piperidine derivative.

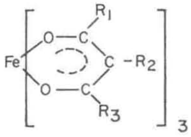
With increasing pressure the low spin compounds transform partially to intermediate spin, but the conversion levels off above ~100 kbar. For the pyridines and picolines the conversion to intermediate spin is primarily due to decrease in backdonation both to the axial and planar ligands, just as with the phenanthrolines and cyanides. This decrease in backdonation raises the energy of the metal d_π orbitals. This tendency is balanced by the spreading of the $3d$ orbitals which is accentuated by the thermal occupation of the π^* orbitals by ligand π electrons at high pressure. Since these π^* orbitals are concentrated farther out on the periphery of the molecule than the π orbitals this increases the possibility of $3d$ expansion. The piperidine complex, which exhibits backbonding only to the phthalocyanine nitrogens, converts only modestly to intermediate spin at low pressure, and the amount of intermediate spin actually decreases at high pressure.

Change of oxidation state.—The most general electronic transition discovered in compounds of iron is the reduction of ferric iron to the ferrous state. The mechanism involves the transfer of an electron from a ligand nonbonding level to the metal d_π orbitals. The first observations were published in 1967 (77), and since then reduction has been observed in perhaps 40–50 compounds including halides, cyanides, hydrates, salts of organic acids, and a variety of organometallic compounds. Higher oxidation states, as in the ferrates (78), also reduce with pressure. The optical absorption peaks corresponding to electron transfer from ligand to metal usually have maxima in the range 2–4 eV. They shift to lower energy by as much as 0.2–0.3 eV at 150 kbar. This red shift is associated with the spreading of the $3d$ electrons which is also reflected in the decrease of isomer shift and of the Racah parameters with increasing pressure. The data published up to 1970 have been summarized elsewhere (79). Much of the earlier data must be regarded as qualitative because of difficulties in perfecting experimental techniques. In any case, there is no easy way of comparing the electronic properties of many of the ligands. There are some general results. First, the reduction increases with pressure, but does not go to completion. For many compounds over a considerable range of pressure and conversion, the data can be approximated by the expression:

$$K = \frac{C_{\text{II}}}{C_{\text{III}}} = AP^M \qquad 1.$$

where C_{II} and C_{III} are the concentrations of ferrous and ferric ions, P is the pressure, and A and M are constants. Second, the reduction generally increases with temperature. Third, the process is reversible in the sense discussed earlier.

We shall restrict our detailed discussion here primarily to a recent study of a series of substituted acetylacetonates (19). This study utilized refinements



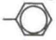
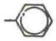
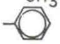
LIGAND	R_1	R_2	R_3
1. ACA	$-CH_3$	$-H$	$-CH_3$
2. DBM		$-H$	
3. DPM	$-C(CH_3)_3$	$-H$	$-C(CH_3)_3$
4 BA		$-H$	$-CH_3$
5. TFACA	$-CF_3$	$-H$	$-CH_3$
6. FTFA	$-CF_3$	$-H$	
7. TTFA	$-CF_3$	$-H$	
8. BTFA	$-CF_3$	$-H$	
9. MACA	$-CH_3$	$-CH_3$	$-CH_3$
10. PACA	$-CH_3$		$-CH_3$
11. NACA	$-CH_3$	$-NO_2$	$-CH_3$
12. EACA	$-CH_3$	$-C_2H_5$	$-CH_3$

FIGURE 8. Characteristics of substituted acetylacetonates.

of technique to minimize effects of shear and of other experimental artifacts. The compounds used, listed in Figure 8, provided a systematic variation of electronic properties which could be correlated with the conversion.

The substituted acetylacetonates form a series of rather covalent complexes with ferric iron. (The Racah parameter B is of the order 500 cm^{-1} compared with a free ion value of 900 cm^{-1}.) They provide a useful basis for studying the relationships between the electronic structure of the ligands, covalency, σ and π overlap, and pressure. These are discussed in some detail in the original paper. We introduce this discussion here only to the extent it bears directly on the conversion as a function of pressure. We shall therefore discuss the properties only in the region 40–180 kbar.

The essential feature is the correlation of electron donor ability of the ligand with degree of conversion. Data were available for a number of the ligands (or for their complexes with copper) on such measures of donor ability as pK_a (acid dissociation constant), polarographic half-wave potential, appearance potential from mass spectrometric studies, and Hammett σ, all evaluated at 1 atm, of course. These correlated quite well with the ferric isomer shift at 1 atm, i.e. a smaller isomer shift corresponds to greater probability of transfer of an electron from the ligand. As discussed in the original paper there is a reasonable correlation between conversion and isomer shift for a group of six of the compounds which are all poor π acceptors.

The isomer shift depends in a complex way on both σ and π orbital overlaps, while the reduction of Fe(III) depends on the ability of the ligand π orbitals to transfer an electron to the metal d_π orbitals. In general the $\pi_L \rightarrow d_\pi$ orbital energy difference decreases with increasing pressure and thus reduction proceeds. Among a series of related compounds it is to be expected that the relative increase in conversion with pressure will depend on the relative change of the electron donor ability as measured by the ferric isomer shift. In Figure 9 we plot the increase of conversion with pressure between 60–160 kbar versus the change in isomer shift over the same range. We see that the correlation holds quite well, i.e. those compounds which show a relatively large increase in donor ability, as measured by a large decrease in isomer shift, show a large increase in conversion, while those complexes which exhibit a relative decrease in donor ability (increase in isomer shift) show a relatively small increase in conversion.

Optical absorption peaks appear in the visible and near-uv spectra of these compounds which are assigned to charge transfer transitions. None of these is the $\pi \rightarrow t_{2g}$ transfer directly involved in the reduction. Nevertheless, the area under the charge transfer peak should reflect the concentration of ferric sites present. Indeed, the relative area under the charge transfer peaks decreases with increasing pressure, by an amount that closely parallels the conversion measured by Mössbauer resonance.

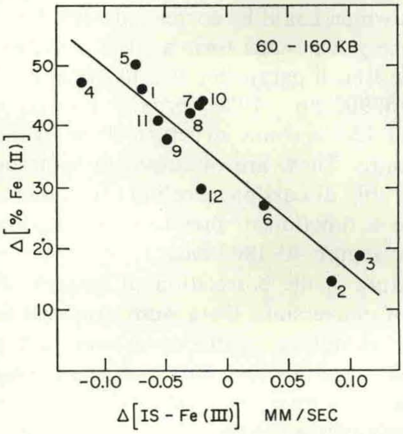


FIGURE 9. Change of ferric isomer shift vs change of conversion [Fe(III) → Fe(II)]. Twelve acetylacetonate derivatives.

Finally, there is a set of compounds which undergoes change of both oxidation state and spin state. These are the iron porphyrins, which consist of four pyrrole rings with methine bridges, and various substituents on the outer pyrrole carbons. In hemoglobin there are four protoporphyrin IX molecules coordinated to imidazole groups of the globin protein. High pressure studies have been made on ferric protoporphyrin derivatives: hemin and hematin, which have respectively one Cl^- or one OH^- coordinated axially to the iron; and imidazole protoheme (80), with two imidazoles in the axial positions. In hemin and hematin the iron is about 0.5 Å out of the molecular plane and is high spin. In the imidazole complex it is nearly in the plane and is low spin.

The iron reduces with pressure in all three crystals but more easily in hemin and hematin than in the imidazole complex. At room temperature the ferrous iron formed from the imidazole protoheme is in an intermediate spin or mixed spin state. At elevated temperature, where it reduces at low pressure, low spin ferrous iron is formed, which transforms to intermediate spin with increasing pressure. The increase in spin is associated with a reduction in back-donation such as discussed earlier for other systems. In hemin and hematin the high spin ferric iron apparently reduces directly to intermediate spin or mixed spin ferrous iron. The high spin state is possible only as long as the iron is well out of the molecular plane; since pressure forces the iron back towards the plane, it reduces the probability of the high spin state. The behavior of the Mössbauer parameters, in particular the large increase in the quadrupole splitting of the ferric iron, is consistent with this interpretation.

The high pressure data supplements the information obtained by changing the substituents on the periphery of the molecule and illustrates the use of pressure to increase our understanding of atmospheric pressure chemistry.

Thermal vs optical transitions.—In the low spin to high spin transition discussed above we postulated that there was significant thermal occupation of the ligand π^* orbitals by ligand π electrons at high pressure. In the reduction process we postulated that an electron was transferred thermally from a ligand nonbonding π orbital to a metal d_π orbital. Optical transitions have been observed in many of these materials from the ligand π to the π^* orbitals, and from ligand π to metal d_π orbitals. For both of these transitions $\nu_{\max}$ lies in the range 2–5 eV, with the charge transfer transition somewhat the lower in energy. In both cases the peak shifts significantly to lower energy with pressure. This implies an increased probability of occupation of the "excited" state at high pressure, so that the volume of the system as a whole must be smaller after electron transfer.

However, the red shifts observed (0.2–0.7 eV in 100 kbar) are only a modest fraction of $\nu_{\max}$, while significant conversion is frequently noted by 50–75 kbar pressure. Thus, the thermal process must require considerably less energy than the optical process. Large differences between the thermal and optical energy requirements have been observed for other systems. Color centers in alkali halides typically absorb in the region 2–4 eV. Yet they can be thermally bleached at moderate temperatures (sometimes as low as 100°K) (81). Analogous results have been observed in a variety of chemical electron transfer processes, the theory for which has been reviewed by Marcus (82). In the special case of oxidation-reduction coupling of ions in solutions (e.g. $Fe^{+3} - Fe^{+2}$; $V^{+3} - V^{+2}$; $Cr^{+3} - Cr^{+2}$) the thermal energy is independent of which ion an electron is on ($E_{th} = 0$), yet the optical absorption gives ν_{max} in the range 2–3 eV.

There are a number of reasons for the difference in energy between optical and thermal transitions. First, optical transitions are subject to the Franck-Condon restriction, i.e. they must occur vertically on a configuration coordinate diagram while thermal transitions are not subject to this limitation (see Figure 1).

Second, in the high pressure thermal process the volume is the relevant configuration coordinate, while the optical process in general will involve more coordinates. This factor could act to increase further the difference between the optical and thermal energies.

A third factor which can increase the difference between optical and thermal transition energies is configuration interaction as illustrated in Figure 1. This is caused by partial breakdown of the Born-Oppenheimer approximation due to spin orbital coupling. The conditions have been discussed for color centers by Henry & Slichter (83) and for electron transfer processes by Marcus (82) and Hush (84). The latter author has shown that the separation between energy surfaces should increase significantly with increased orbital overlap, as would obtain at high pressure.

In the fourth place, there is the matter of selection rules. For allowed optical transitions a change in parity between states is required. In the charge transfer process the metal d_π states are of g symmetry, so the optically observed transition must be from a ligand state of u symmetry. However, for ligands with filled p orbitals the highest filled molecular orbital has t_{1g} symmetry, and the thermal transfer, which is not subject to the selection rule, will be from this orbital. Jorgenson (85) has shown that for halide ligands the energy difference between π (t_{1g}) and π (t_{1u}) is typically 0.75–1.0 eV. For the π-π^* transition on the ligand apparently, in general, no selection rule limits the optical transition from the highest filled to the lowest empty level.

A fifth factor is also operative in the case of reduction of Fe(III) to Fe(II): the crystal field stabilization energy. For the ferrous state the lowest $3d$ level is lowered in energy by 0.4Δ, where Δ is the ligand field strength. There is no corresponding shift for Fe(III).

One can make a crude estimate of the difference between optical and thermal transition energies from a relationship derived from the work of

Marcus (86), Hush (87), and Henry & Slichter (83) to include the effect of pressure (88):

$$E_{th} = h\nu_{\max} - \frac{1}{16 \ln 2} \frac{(\Delta\nu_{1/2})^2}{kT} \left(\frac{\omega'}{\omega}\right)^2 \qquad 2.$$

Here E_{th} is the difference in thermal energy of the two states, $\nu_{\max}$ the optical absorption frequency, $\Delta\nu_{1/2}$ the peak half-width, and ω and ω' the force constants for the ground and excited state potential wells. The relationship assumes a Gaussian shape for the optical absorption peak. Using experimental data for the $\pi \rightarrow \pi^*$ transition in phenanthroline complexes one obtains the results of the Table 1, assuming $\omega' \simeq \omega$. The calculation is approximate, but the change of sign for E_{th} occurs in the pressure region where the low spin to high spin transition initiates, and thus where significant thermal occupation of the π^* orbital would be expected.

An analogous calculation applies to the reduction process. For the acetylacetonates, the charge transfer peaks observed in the spectrum are definitely not assigned to the ligand to metal $\pi \rightarrow t_{2g}$ transition responsible for the reduction. A series of compounds where the charge transfer peak may have such an assignment are the ferric hydroxamates: tris(acetohydroxamato) iron(III)(AHA); tris(benzohydroxamato) iron(III)(BHA); tris(salycilhydroxamato) iron(III)(SHA); and the related biological hydroxamate ferrichrome A (FA) (89). Table 2 shows the calculated thermal energies based on Equation 2.

TABLE 1. Thermal vs optical transitions π - γ^* for phenanthroline

Pressure (kbar)	$h\nu_{\max}$ (eV)	$\Delta E_{1/2}$ (eV)	E_{th} (eV)
0	4.6	0.95	+1.35
50	4.45	1.05	+0.45
100	4.30	1.14	−0.40
150	4.20	1.20	−0.98

TABLE 2. Optical versus thermal transitions: ferric hydroxamates and ferrichrome A for 10% reduction of Fe(III)

Compound	Pressure (kbar)	$h\nu_{\max}$ (eV)	$\Delta E_{1/2}$ (eV)	E_{th} (eV)
AHA	125	2.80	0.90	−0.11
BHA	105	2.70	0.875	−0.06
SHA	70	2.54	0.84	−0.02
FA	37	2.65	0.835	+0.11

Both the peak location and width affect the amount of reduction, and the reduction appears to initiate approximately where the calculated value of E_{th} changes sign.

These transformations in iron typically do not go to completion at a fixed pressure. In fact, the conversion may not be complete at any pressure; there can actually be a maximum in the pressure-conversion curve. Slichter & Drickamer (90) have accounted for this behavior with a thermodynamic treatment which has analogies in regular solution theory and molecular field theory of magnetism. As noted earlier, metastability may be a serious limitation on a thermodynamic treatment of solid state chemistry, but the analysis predicts all of the essential features observed. The free energy of the mixture is written

$$G = N_0[(1 - C)G_0(P, T) + CG_1(P, T) + \Gamma(P, T)C(1 - C)] - T\sigma_{\text{mix}} \quad 3.$$

where

$$\sigma_{\text{mix}} = k[N_0 \ln N_0 - N_0C \ln N_0C - N_0(1 - C) \ln N_0(1 - C)] \quad 4.$$

is the usual entropy contribution due to the variety of ways of choosing converted sites. G_0 and G_1 are the free energies of the pure components and Γ is a term which measures interaction among sites. A little manipulation gives:

$$\ln K = -\frac{1}{kT}[\Delta G + \Gamma(P, T)(1 - 2C)] \quad 5.$$

where

$$\Delta G = G_1 - G_0$$

Three cases were considered: 1. noninteracting sites ($\Gamma = 0$) with linear elastic behavior; 2. noninteracting sites with nonlinear elastic behavior; and 3. interacting sites. The first of these treatments involves only a balancing of volume and compressibility effects; we shall not elaborate on it here.

In the nonlinear theory the Helmholtz free energy is expressed in the form

$$F = \sum_m \frac{A_m}{V^m} \quad 6.$$

where the coefficients A_m depend on temperature but not on volume. One can use this expression to evaluate other thermodynamic properties. In the first order one can describe the physics of the situation with three terms involving $m = 1/3$, $5/3$, and $9/3$, corresponding to electrostatic, covalent, and repulsive interactions. With the use of the Murnaghan equation of state:

$$\frac{V_0}{V} = \left(1 + \frac{nP}{B}\right)^{1/n} \quad 7.$$

where B is the bulk modulus, one obtains the relationship:

$$\ln K = -\frac{\Delta G_1}{kT}(1 + y)^{1/16}\left[1 + \frac{\Delta G_5}{\Delta G_1}(1 + y)^{1/4} + \frac{\Delta G_9}{\Delta G_1}(1 + y)^{1/2}\right] \qquad 8.$$

where $y = nP/B$ and the ΔG values correspond to the three types of interaction mentioned above. Reasonable values of ΔG indeed predict a pressure-conversion dependence qualitatively similar to experiment. The fact that the conversion spreads over a large range of pressure depends on the relative importance of the three terms in various pressure regions. The fit to the data, however, requires rather close cancellation between ΔG_1 and ΔG_5 which seems fortuitous for so many compounds over a large pressure range.

For a really satisfactory discussion of the data, it is necessary to assume interacting centers. One expands Γ:

$$\Gamma(P_1T) = \Gamma_0(T) + P\Gamma_1(T) + P^2\Gamma_2(T) \qquad 9.$$

The results of this analysis are most striking in establishing reasonable pressure and temperature dependence for the equilibrium constant.

$$\frac{d\ln K}{d\ln P} = \left[\frac{1}{1 - \frac{\Gamma_0}{kT}\left[\frac{2K}{(1 + K)^2}\right]}\right]\left(\frac{d\ln K}{d\ln P}\right)_{\Gamma_0=0} \qquad 10.$$

for $K = 1$ this reduces to

$$\frac{d\ln K}{d\ln P} = \frac{1}{\left(1 - \frac{\Gamma_0}{2kT}\right)}\left(\frac{d\ln K}{d\ln P}\right)_{\Gamma_0=0} \qquad 11.$$

Relatively small values of Γ_0 affect the slope significantly, e.g. for a repulsive interaction with $\Gamma_0 = -0.05$ eV the slope is cut in half. The introduction of Γ makes it possible to fit a wide variety of data rather easily. For the temperature dependence one obtains

$$\frac{d\ln K}{d(1/T)} = -\frac{1}{k}\left[\frac{\Delta H + \left(\frac{1 - K}{1 + K}\right)\left(\Gamma - T\frac{d\Gamma}{dT}\right)}{1 - \frac{2\Gamma}{kT}\frac{K}{(1 + K)^2}}\right] = -\frac{\Delta H_{\text{eff}}}{k} \qquad 12.$$

So that if the interaction is repulsive (Γ-negative) the effective heat of reaction is reduced. For attractive interaction the possibility exists that the denominator might go to zero, which corresponds to a discontinuity in conversion at some temperature. This phenomenon has been observed by König & Madeja (71) for the spin transition in certain ferrous phenanthrolines.

This analysis lends itself to rather extensive graphical presentation which appears in Slichter and Drickamer's paper. It is possible to establish the effects of both attractive interaction, which enhances conversion, and repulsive interaction, which inhibits it. The possibilities of hysteresis and of a discontinuity in the degree of conversion at some temperature and pressure are also illustrated.

SUMMARY

Pressure has profound effects on the electronic structure of solids. One of the most general and significant of these is the relative shift in energy of one type of orbital with respect to another. For a wide variety of materials there exist excited states which lie sufficiently near the ground state so that this relative shift can create a new ground at high pressure or greatly modify the ground state by configuration interaction. These new ground states may have very different properties which lead to new electronic and chemical phenomena. A study of this new chemistry and physics can also enhance our understanding of atmospheric pressure chemical and physical phenomena.

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