

Crystal chemistry: past, present, and future¹

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Abstract

Crystal chemistry is an important part of the science of mineralogy and describes the relationships of mineral crystal structures with the corresponding physical and chemical properties. Crystal chemistry has evolved over a period of fifty years or more from a purely qualitative endeavor to one that is quantitative and that can provide essential insight to the behavior of minerals under varying conditions of pressure, temperature, and chemical environment. Increased interest in the chemical and physical properties of minerals and how these are related to important problems in the geological and materials sciences makes the future look very promising.

Introduction

Role of crystal chemistry

The study of crystal chemistry is of fundamental importance to the science of mineralogy, as well as to other fields such as materials science and solid-state chemistry. However, it is my perception that mineralogy itself means different things to different people, as do crystallography and petrology, disciplines that are also considered to be official interests of the Mineralogical Society of America and the Society often regulates its activities according to these categories. For example, awards are given each year to promising young scientists, but alternately to crystallographers one year and mineralogists/petrologists the next. I believe that these labels are not really representative of the way in which we apportion our scientific efforts and that another kind of division is more realistic. This division is illustrated in Figure 1 and is characterized by three major parts, descriptive mineralogy, mineralogical applications, and physics and chemistry of minerals. Descriptive mineralogy, involving identification and classification of minerals is really classical mineralogy and describes virtually all mineralogical activity before the 1930's, and still is of great interest to many scientists. Since the 1930's, applications of mineralogical theory and experiment have become more important in the understanding of and application to petrology, geochemistry, and even geophysics. This constitutes the second division in Figure 1 and is also the one in which most people are involved today. The third category, the study of physical and chemical properties of minerals, is one that has seen substantial growth in recent years and one that is becoming increasingly important, not only for the earth sciences, but for many other aspects of science

and technology as well. The subject of this paper, crystal chemistry, embodies aspects of all three areas in Figure 1 and, therefore, should be considered to lie in the overlap region among the different circles.

Evans (1952) defined crystal chemistry as "the study of the relationship of the internal structure of a body to its physical and chemical properties. It aims at interpreting the properties of any substance in terms of its crystal structure, and, conversely, at associating with any structural characteristic a corresponding set of physical and chemical properties. Ideally crystal chemistry should enable us to predict and synthesize chemical compounds having any desired combination of properties whatsoever."

The early development of crystal chemistry was the primary result of experiments and interpretation of W. L. Bragg and coworkers at Manchester in the 1920's and by V. M. Goldschmidt and coworkers in Oslo in the 1930's. Their efforts were characterized by an empirical approach to the understanding of crystal structure through simple models based on observed interatomic distances. Later in the 1930's, Pauling showed that it was important to account for chemical valence and introduced the concept of electronegativity to help account for varying degrees of covalence in chemical bonds. Subsequently, the approach to crystal chemistry has developed along essentially two tracks, one still largely empirical and based on observations of interatomic distances and incorporating relatively simple ideas about valence, coordination, and electronic structure. The second approach is one based on quantum mechanics and has been used mostly for interpretation of spectra or for treatment of molecular structures or hypothetical clusters that simulate configurations found in real minerals.

A major problem for crystal chemists interested in minerals is that most of the important mineral structures are relatively complex and are composed of infinite periodic arrays of individual ions rather than of molecules. Thus, it

¹ Adapted from Presidential Address at the annual meeting of the Mineralogical Society of America, November 6, 1984, Reno, Nevada.

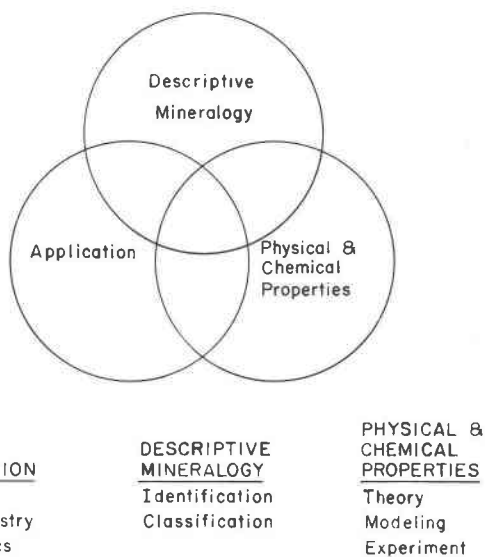


Fig. 1. Circles representing the fields of mineralogy. Crystal chemistry falls in the area of overlap among the circles.

has been difficult to apply the quantum mechanical theory developed by physicists for simple cubic structures or quantum chemistry that has been applied to molecules by chemists. Because of this, the empirical approach of Bragg, Goldschmidt, and Pauling is still being used by many investigators although there has been substantial progress recently in applying quantum mechanical techniques to minerals. A good summary of the latter was made by G. V. Gibbs (1982) in his MSA Presidential Address and today Gibbs, J. A. Tossell, A. Lasaga, their students, and others are making good progress toward combining the cluster calculations with considerations of long-range forces in crystals.

My purpose is to discuss some of the basic concepts of the empirical approach to crystal chemistry, to show how this is being applied to problems in mineralogy and materials science, and to make observations about how the work of crystal chemists will evolve during the rest of the 1980's. It is apparent that there is an enormous amount of published information about crystal chemistry as defined above that has not been compiled or organized in any significant way. The available textbooks are either outdated or emphasize only a small portion of the field. Furthermore, it is clear that treatments of crystal chemistry cannot stop at the boundary between earth science and materials science—I have often noticed a provincialism among some scientists who only want to work on minerals or who are not interested unless a compound has important physical properties that can be sold to a customer. I think this is a bit short-sighted because we all have much to learn about the science of crystal chemistry that encompasses the entire periodic table and it is important that we communicate as much as possible with one another. Today's novelty in one portion of the field can be tomorrow's great discovery in another.

Principles of crystal chemistry

Empirical crystal chemistry is based on the concept of periodic structures containing ions of specific size, charge, and coordination number, with one or two other parameters such as electronegativity helping to account for covalence or metal-metal bonding effects. The coordination groups are combined with each other, resulting in an overall symmetry that can be defined through the unit cell and space group. If the coordinations of the cations by anions are defined, then the coordinations of anions by cations are fixed, as illustrated by the relation for compound ${}^pA_p{}^qB_q{}^rX_r$,

$$rR = pP + qQ$$

where P and Q are the CN's of the cations and R is the CN of the anion. The size of an ion is an arbitrary value depending on what fraction of the spacings between the ion and its neighbors is allocated to the central ion. In mineralogical crystal chemistry, it is most common to use the "hard sphere" model where each ion is considered to be a sphere of a specific size, although molecular chemists often assign a bonding radius and a van der Waal's radius to represent a non-spherical ion.

The charge assigned to ions is usually the formal valence, although even high school chemistry students know that most bonds have a significant degree of covalence and the absolute value of the effective valence in real crystals is less than the formal valence. Various schemes have been proposed for specifying the actual charge on an ion or the degree of ionic character of a bond. Probably the most well-known of these schemes is that of Pauling (1960) who related the degree of ionicity with the electronegativity difference between the two atoms involved. For example, his relation

$$\Delta(\text{Si-O}) = 23(\chi_A - \chi_B)^2$$

indicates that the Si-O bond is about 50% ionic. Even so, it is surprising that the ionic concept works as well as it does. Burdett and McLarnan (1984) emphasized this point in a reinterpretation of Pauling's rules based on band structure calculations. These relatively simple rules have passed the test of time and can still provide valuable insight to crystal chemistry; the application of modern quantum mechanical methods can build on this foundation and carry us still farther toward the understanding of crystalline behavior.

Effective ionic radii

By far, the most important determinants of crystal chemical behavior are size and charge of ions. The concept of ionic radius has been an important part of crystal chemistry since Bragg (1920) first introduced a set of atomic radii that reproduced interatomic distances in various crystals with a variation of about $\pm 0.06\text{\AA}$. Since then, many other papers have been published with radii values derived from crystal structures or calculated using varying degrees of sophistication. Shannon and Prewitt (1968) reviewed previous attempts to derive consistent sets of radii and

presented a new table of effective ionic radii based on 1000 experimental interatomic distances from oxide and fluoride crystal structures. This table was the most comprehensive published up to that time and featured radii values for the known charges of each cation and for the coordinations observed for each ion. In addition, radii values were given for first-row transition metals that occur in both high- and low-spin configurations. Subsequently, these radii have proved to be extremely useful for many different kinds of investigations and the Shannon and Prewitt (1968) paper was featured in *Current Contents* (Shannon and Prewitt, 1981) as a Citation Classic, making it one of the most-cited crystal chemistry references in history. The value of this approach to crystal chemistry is illustrated by the hundreds of applications that have appeared in the literature.

Structural parameters as functions of radii

The fundamental assumption of ionic radii tables is that one can predict the *average* interatomic distance in a coordination polyhedron and that the average interatomic distances will be the same for all similar polyhedra from structure to structure, as long as the cation remains the same. However, Shannon and Prewitt (1968) found that there are additional factors that influence average polyhedral interatomic distances, such as the linkages between polyhedra, relative electronegativity of other cations in the structure, the degrees of distortion of the polyhedra, and metal-metal bonding across shared polyhedral elements. The linkage problem was solved by determining the radii of oxide and fluoride ions as functions of coordination of these ions by cations. Thus, the average interatomic distances in polyhedra increase as the linkages between octahedra increase. Polyhedral distortion will affect the average distance, as was shown by Shannon et al. (1975b). These authors plotted average interatomic distances for Mn-O polyhedra vs. polyhedral distortion showing that the average distances increase with increased polyhedral distortion.

One surprising result of our work was the demonstration that plots of a vs. r or V vs. r^3 are usually found to be linear and that any significant departure from linearity indicates an error in the data or an interesting crystal chemical phenomenon. Figure 2 contains plots of V vs. r^3 for compounds with the olivine and zircon structures (Shannon and Prewitt, 1970a). These structures are ionic in character and the substituting cations do not exhibit any unusual interactions. Figure 3 is an example of a departure from linearity. We interpreted the curvature in the plots relating cell volume to r^3 as a result of the changing effective coordination number of the rare-earth A ion in perovskite structures, i.e., as the size of the A ion increases, the effective coordination number increases from eight normally assigned for the orthorhombic or rhombohedral structure toward the twelve found for cubic perovskite.

Figure 4 indicates another type of relation, that of the Goldschmidt tolerance factor applied to the orthorhombic perovskites where bond length distortion is plotted vs. the tolerance factor, t_{obs} , calculated from observed interatomic distances or from radii tables. Note that the value for

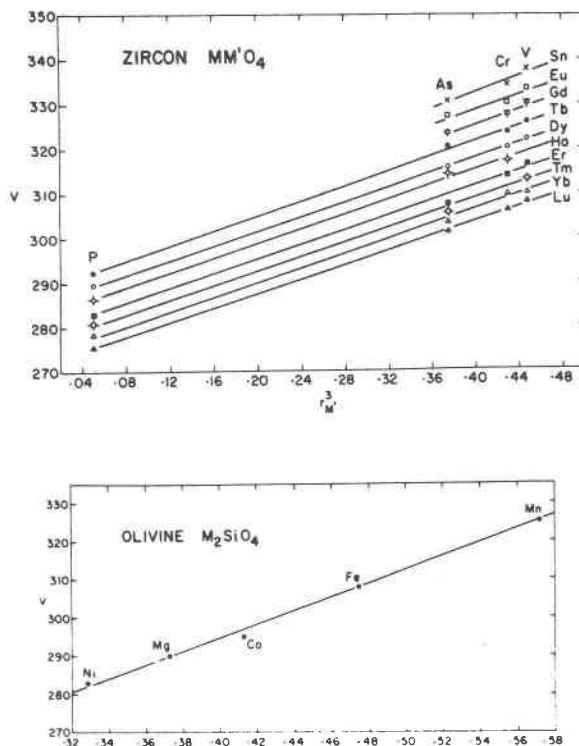


Fig. 2. Plots of cell volume (V) vs. r^3 for cations in the zircon and olivine structures. From Shannon and Prewitt (1970a).

CaTiO_3 does not fall on the smooth trend for titanates. We have re-refined the CaTiO_3 structure (Sasaki et al., ms.) and find that the new values move the point for CaTiO_3 to the linear trend.

Metal-metal bonding

Whenever the formula of a compound does not balance according to the usual valences of cations and anions (e.g., Ni_3S_2 or FeS_2) or when interatomic distances are unusually short, cation-cation or anion-anion bonding is an important feature of the structure. This may also affect the cation-anion bonds and the result is that ionic radii may not predict the actual interatomic distances in the structure. An interesting example of this is seen in compounds with the corundum structure (Fig. 5). Here, each octahedron shares one face and three edges with other octahedra containing identical cations. Pauling's 3rd rule states that "the presence of shared edges, and particularly of shared faces, in a coordinated structure decreases its stability; this effect is large for cations with large valence and small coordination number, and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron." In ionic structures that do contain shared polyhedral elements, the cations repel each other and the O-O distances across the shared element tend to be shorter than others in the structure. Exceptions to this for the corundum structure are shown in Figure 6, a plot of the cation-cation distances as a function of cation radii for

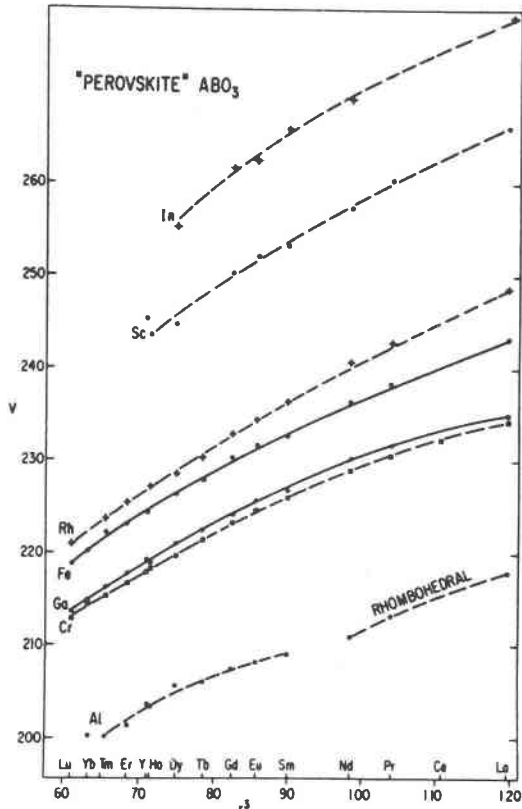


Fig. 3. Cell volumes (V) vs. r^3 of rare-earth ions in the A site for orthorhombic and rhombohedral perovskites. The non-linear features are thought to be a result of changing effective coordination number of the A ions. From Prewitt and Shannon (1969).

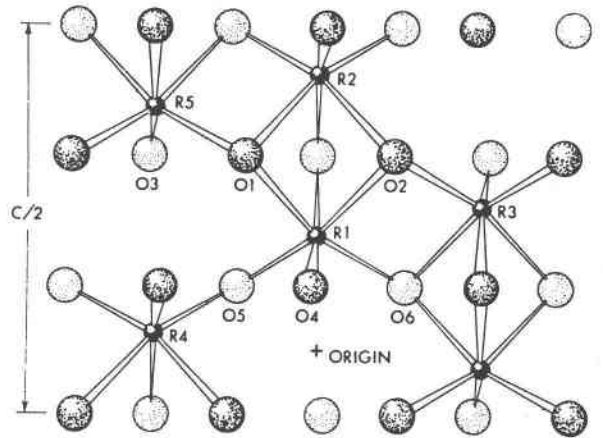


Fig. 5. Corundum structure showing shared faces between octahedra along c , and edges shared between octahedra in the layers normal to c . From Prewitt et al. (1969).

several compositions containing aluminum and transition metal cations. Ti^{3+} contains one d electron and there is strong interaction (contraction) across the shared face. V^{3+} has two d electrons and there is interaction across both the face and the shared edges. Cr^{3+} has three d electrons and there is relatively more shortening across the face than the edge. These interactions become more complicated for cations with more d electrons and for structures containing more than one kind of cation. However, this example does illustrate the importance of metal-metal bonding for certain structures and compositions. A similar situation is found for the rutile structure, shown in Figure 7. Here

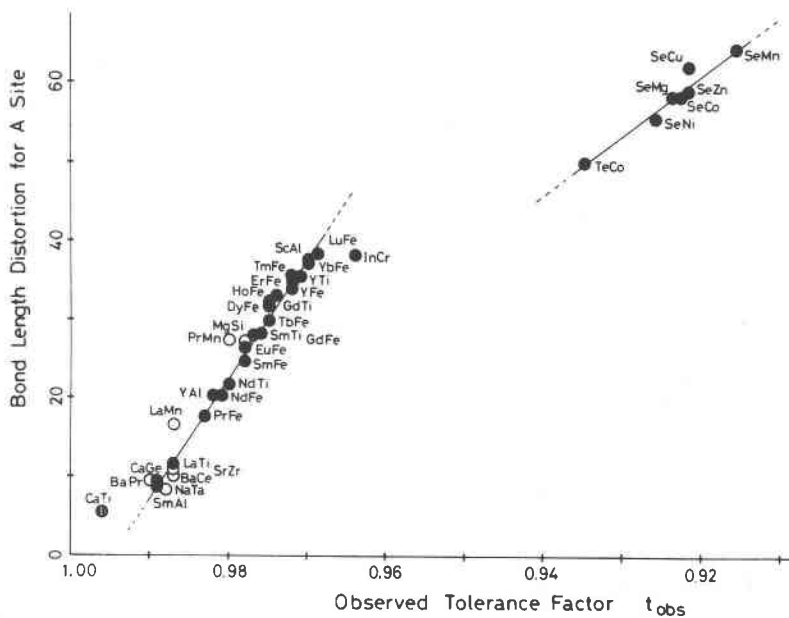


Fig. 4. Bond length distortion vs. Goldschmidt tolerance factor for orthorhombic perovskites. Recent re-refinement of the $CaTiO_3$ structure brings to $CaTi$ point to the linear trend. From Sasaki et al. (1983).

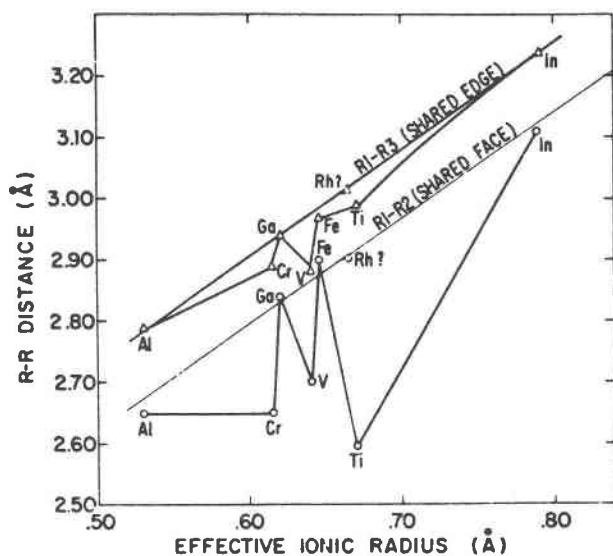


Fig. 6. Cation-cation distances across the octahedral shared face and edges plotted vs. effective ionic radii for compounds with the corundum structure. From Prewitt et al. (1969).

octahedra share edges along c . Figure 8 is a plot of c/a vs. the no. of d electrons on the cation. There are sharp variations in c/a as a function of metal-metal interactions that are somewhat different from those in the corundum-structure example because the cations in rutile are divalent rather than trivalent.

Figure 9 is a plot of V vs. r^3 for compounds with the

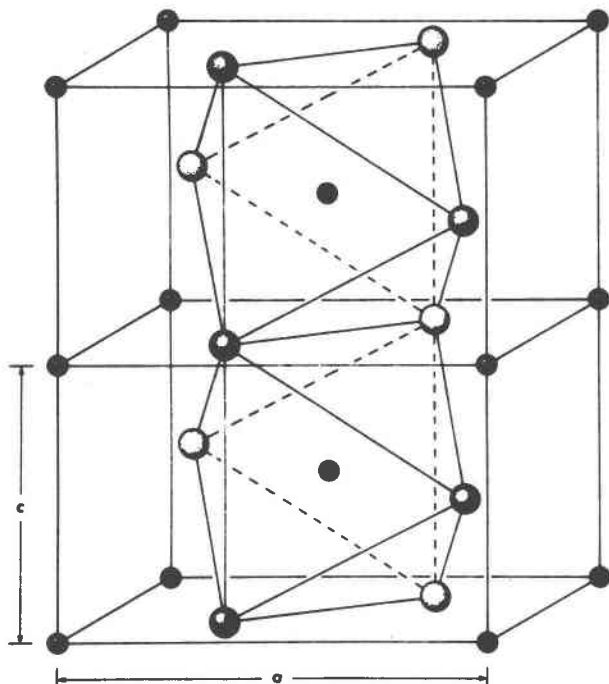


Fig. 7. The rutile structure showing how octahedra share edges in columns parallel to c . From Rogers et al. (1969).

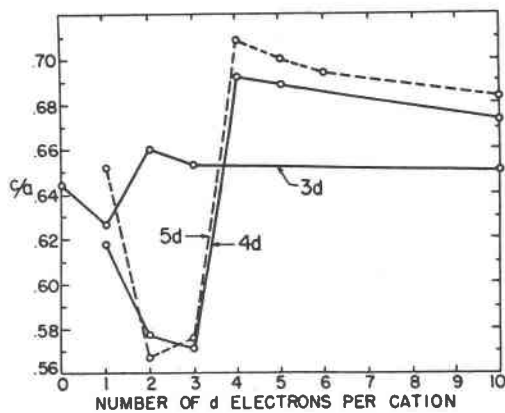


Fig. 8. Plot of c/a vs. number of d electrons for first, second, and third row transition elements in the rutile structure. Apparently, the metal-metal interactions are much stronger for the ions with partly-filled $4d$ and $5d$ shells. From Rogers et al. (1969).

delafossite structure taken from Shannon and Prewitt (1970a). One point illustrated here is that it is often possible to detect faulty structural data by making these plots. The plus signs represent literature data that was improved

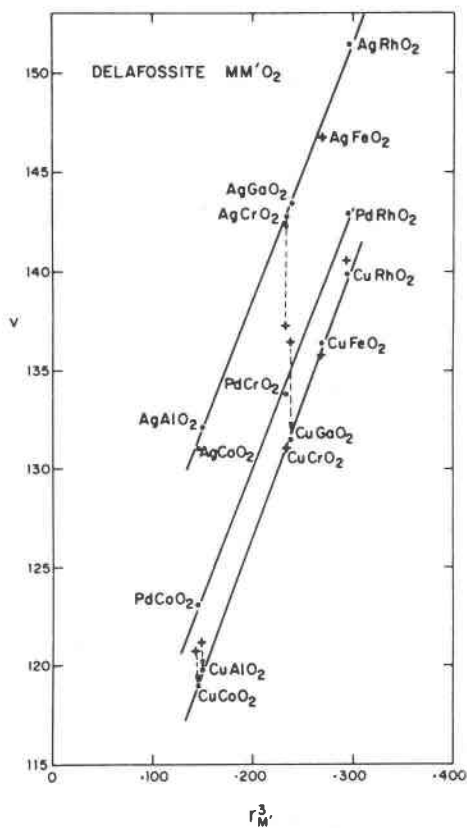


Fig. 9. Delafossite, cell volume (V) vs. r^3 for the M' (octahedral) ions in the delafossite-type structures. The dashed lines show corrections made when cell volumes were re-determined on well-characterized samples. From Shannon and Prewitt (1970a).

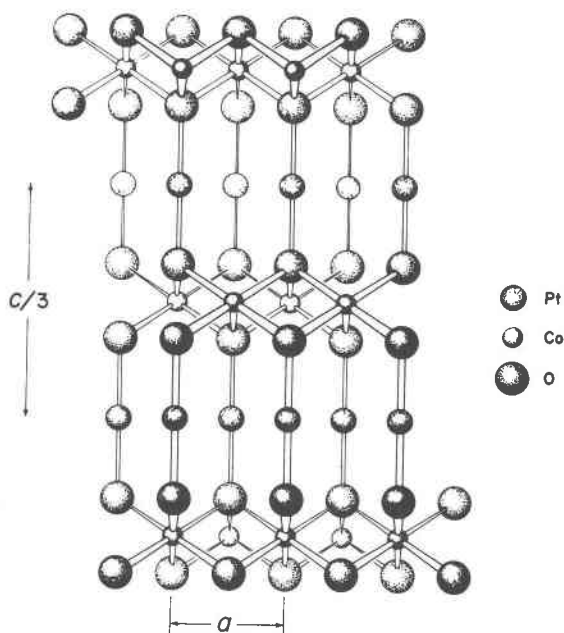


Fig. 10. Delafossite structure for the composition PtCoO_2 . Pt is linearly-coordinated by two oxygens and Co is octahedrally-coordinated. From Prewitt et al. (1971).

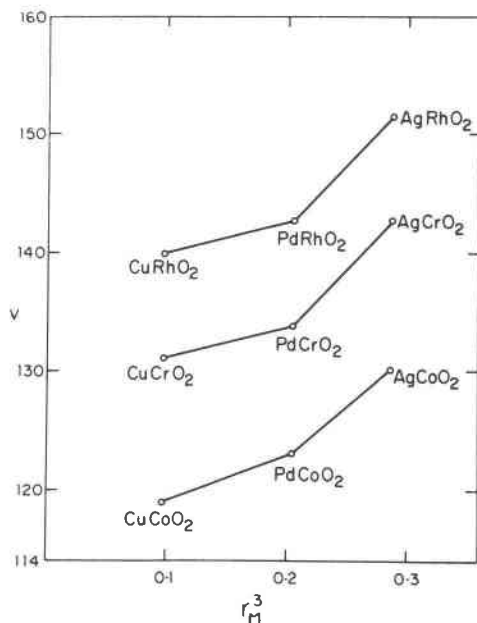


Fig. 11. V vs. r^3 for the linearly-coordinated ions in the delafossite-type structures. The cell volumes for the compounds containing Pd are anomalously low because Pd has an effective valence of 2^+ rather than 1^+ . From Shannon and Prewitt (1970a).

by synthesizing pure crystals and refining their crystal structures. The delafossite (CuFeO_2) structure is shown in Figure 10. Delafossite is a mineral that contains Cu coordinated linearly by two oxygen ions and Fe coordinated octahedrally by six oxygens. The Cu ions are arranged in layers with each Cu surrounded by six other Cu's at a distance of 3.035\AA , making a hexagonal bipyramid together with the two oxygens. However, another compound, PdCoO_3 , contains Pd ions only 2.830\AA apart in the layer, a distance similar to that found in platinum metal. Figure 11 indicates that there is a substantial deviation for compounds containing Pd and Pt. Because the octahedral Co-O distances are exactly right for Co^{3+} and because these ions cannot exist in a 1^+ state, our conclusion is that Pd and Pt are really divalent and that there is a delocalized electron, which is confirmed by the very high conductivity in the metal layer, as opposed to delafossite itself.

Another example where the application of radii has not produced consistent results is for the transition-metal disulfides with the pyrite structure (King and Prewitt, 1979). Figure 12 is a plot of r vs. atomic number for the series of disulfides from Mn through Cu. This plot is entirely consistent with Cu^{2+} in CuS_2 , but no sulfide has ever been confirmed to contain Cu^{2+} and photoelectron spectroscopy (Nakai et al., 1978) shows that Cu in this phase is consistent with monovalent Cu, the only species thus far reported for any copper sulfide. Clearly, this apparent contradiction needs further investigation.

Trace and minor element distributions between phases

Several years ago, Matsui et al. (1977) showed how partition coefficients of elements between a liquid and a crystal

varied as a function of the Shannon and Prewitt (1968) ionic radii. Figure 13 shows a Pc-Ir diagram for an olivine crystal in a fine-grained groundmass. Except for Zn, all ions show parabolic distributions with the maxima at

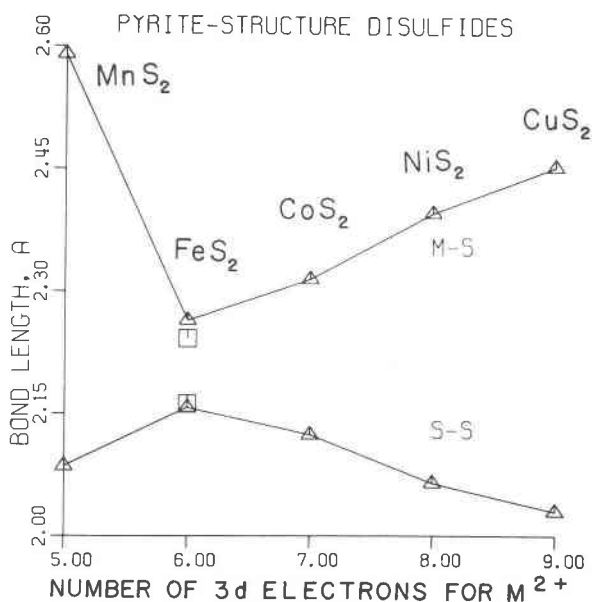


Fig. 12. Effective ionic radius vs. atomic number for disulfides with the pyrite structure. Although the Cu-S bond length in CuS_2 is consistent with Cu^{2+} , other evidence shows that it is really Cu^+ . Data from King and Prewitt (1979).

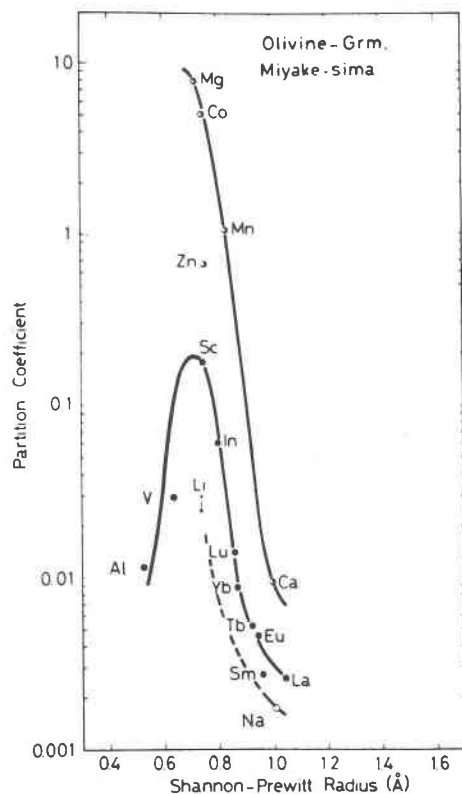


Fig. 13. Partition coefficient vs. effective ionic radius (PC-IR) for olivine-groundmass system in tholeiite basalt. From Matsui et al. (1977).

about the radius of the major cation, Mg. For bronzite, Matsui et al. showed that there are two maxima indicating two M polyhedra that are more different in size than the M polyhedra in olivine, and Figure 14 gives the results for an augite where the peaks are even more pronounced. Evidently, the problems with Zn and Cr are a result of strong tetrahedral preference for the former and strong octahedral crystal field stabilization for the latter. These diagrams are striking examples of how significant information about sizes and chemical characteristics of ions can be obtained. Recently, Yurimoto and Sueno (1984) demonstrated that similar curves for anions could be obtained relatively easily using secondary-ion mass spectrometry (SIMS) as well as curves for cations. One of their plots, reproduced in Figure 15, implies that the ideal sizes for ions in silicate structures (the maxima on the parabolic curves) may not correspond with any actual ionic radii. This observation may not be valid, however, because the radius ratios under conditions of crystallization are probably quite different from those at room temperature.

Another kind of display of partition coefficients was given by Volfinger and Robert (1980) where PC was plotted vs. the difference in size between a polyhedron that would be preferred by the substituting ion with the polyhedron occupied by the major ion in the mica structure.

Figure 16 shows a plot of $\log P_x$ (partition coefficient) vs. $(r_t - d_{A-O} + r_o)$, where r_t is the ionic radius of the trace ion X substituting for the major alkali cation, d_{A-O} is the average bond length for the alkali cation polyhedron, and r_o is the radius of oxygen. This is a very valuable tool for identifying actual sites occupied by trace elements and should be used extensively by geochemists.

High pressure

Crystal structures at high pressure

One of my primary interests is in the crystal chemistry of high-pressure and high-temperature phases. Crystal-chemical principles can help us to understand high-pressure phenomena and are useful as a guide to synthesizing new phases. In recent years the diamond anvil cell has been used to obtain extensive information about crystal structures and phase transformations at high pressure, both with single crystals and powder samples. I will not discuss diamond-cell technology because this has been covered well in reviews by Hazen and Finger (1982), Skelton (1984), Jayaraman (1984), and others. One of the most significant results from single-crystal work is that the same regular kinds of trends we have seen at room pressure are applicable at high pressure. For example, Hazen and

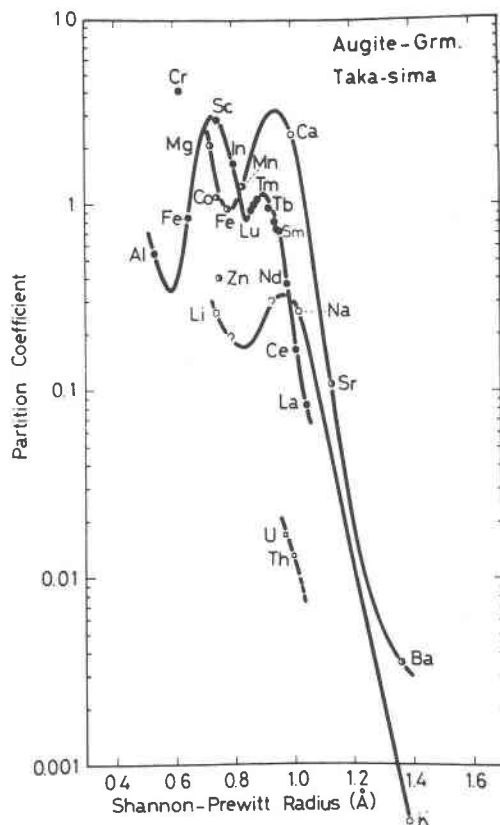


Fig. 14. PC-IR diagram for augite-groundmass system showing two maxima, one corresponding to each M polyhedron in the structure. From Matsui et al. (1977).

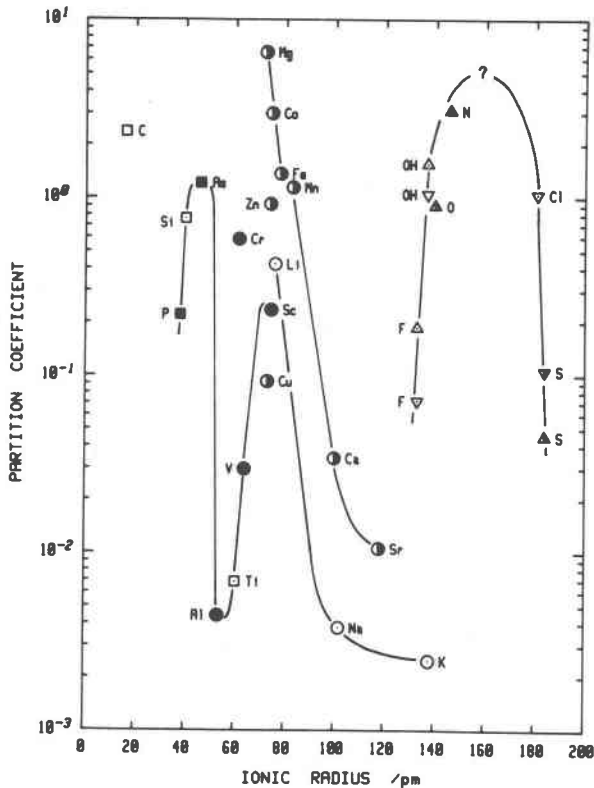


Fig. 15. PC-IR diagram for an olivine-groundmass system constructed using SIMS data. The positions of the maxima correspond to the sizes of cavities for the tetrahedral and octahedral cations, and for the oxygens. From Yurimoto and Sueno (1984).

Prewitt (1977) found that a linear relationship exists for the compressibility vs. size and charge of ions in oxide structures (Fig. 17). A general statement is that polyhedra containing large, low-charge ions are more compressible than those containing small ions with high charge. Hazen and Finger (1979) extended this concept in a comprehensive compilation of data.

A curious consequence of our work on structures at high pressure is contrary to the popular belief that anions are more compressible than cations and that most of the compression in a structure is taken up by the anions. For example, Ida (1976) calculated compressibilities of cations and anions in alkali halides using Born lattice theory combined with experimental values of interatomic distances and bulk moduli. This analysis indicates that the halide anions are substantially more compressible than the alkali ions. Ida extrapolated this result to abundant ions in the Earth's mantle, namely Mg^{2+} , Fe^{2+} , Si^{4+} , and O^{2-} , and concluded that the compressibilities of these cations are negligibly small and that only O^{2-} is effective in determining compressibilities of common silicates. Several other workers (Miyamoto and Takeda, 1980; Matsui et al., 1982) performed molecular dynamic calculations and reached

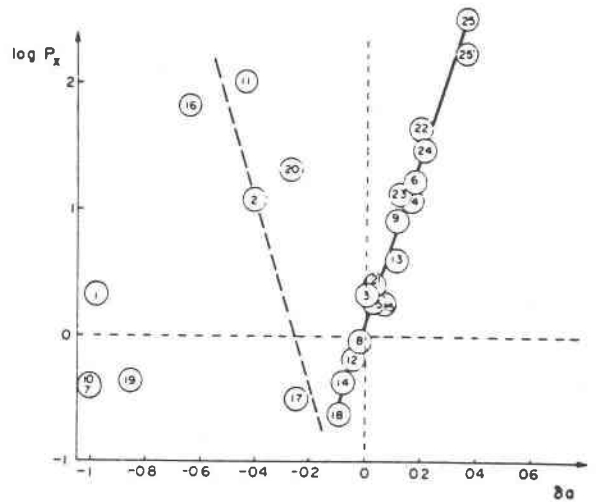


Fig. 16. Partition coefficient between hydrothermal solutions and micas plotted vs. δ where δ is the difference in size between the alkali polyhedron in the mica structure and the polyhedron that normally would be preferred by the substituting ion. The circles on the left-hand branch of the "V" represent cations smaller than the major alkali cation, and those on the right-hand branch represent larger cations. The circles to the far left of the diagram represent ions that occupy smaller interlayer cavities rather than the large alkali site. From Volfinger and Robert (1980).

similar conclusions. However, Prewitt (1982) pointed out that it is hard to reconcile these conclusions with recent determinations of crystal structure parameters determined on oxide structures at high pressure using the diamond-anvil cell. This work shows that cation-oxygen bonds compress and expand more than those with larger bond

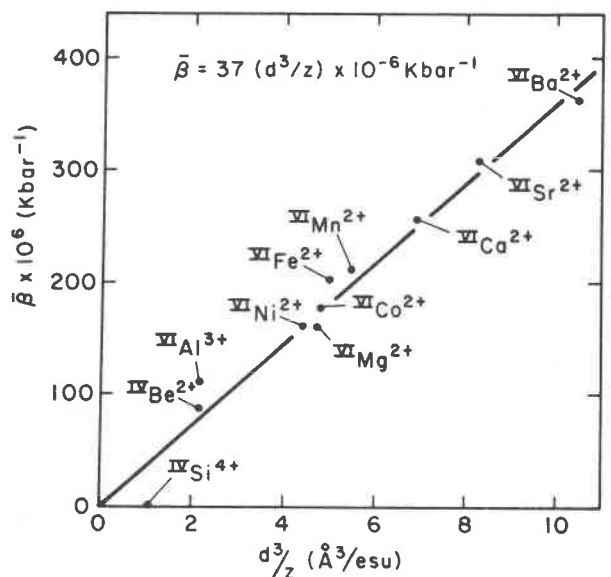


Fig. 17. Linear relationship between compressibility and volume of cation-oxygen polyhedra. From Hazen and Prewitt (1977).

strength; for example, Ca–O bonds compress much more than do Si–O bonds. In fact, when compressibilities of many different cation–oxygen bonds are compared, one could conclude that most compression is taken up by the cations rather than by oxygen, even though this is contrary to the prevailing idea that oxygen ions are rather large and “fluffy”. Examination of the changes in radius with coordination shows that cation radii increase more rapidly with increasing coordination number than do oxygen radii. This leads to the idea that, as far as a single ion is concerned, oxygen is more rigid than at least the large cations. An example of this relationship is shown in Figure 18 where effective ionic radii for Ca^{2+} and O^{2-} are plotted against coordination number. From this diagram, it is apparent that the radius of Ca^{2+} changes at a significantly higher rate than does the radius for O^{2-} . Although this may not be sufficient evidence to prove that oxygen ions are relatively harder than cations, the change in radii with coordination must be explained by any model for the detailed structures of oxides.

I have been interested in mantle mineralogy for a number of years and also in the synthesis of other phases that give interesting crystal chemical information. In a search for rules to guide such synthesis, Shannon et al. (1975a) developed two general rules based on bond strength considerations that extend the applicability of the analog structure concept. Given a composition $\text{A}_x\text{B}_y\text{O}_z$, the two rules are:

1. When the ratio of A cations to B cations (G) is greater than a certain critical value, G_c , the coordination of B is generally tetrahedral. When this ratio is less than ~ 1.0 , the tendency for B to have a CN of five or six is greatly increased. This rule gives an approximate measure of the probability of finding two B cations bonded to the same oxygen ion. The lower the value of G , the greater is this probability and the more unstable the tetrahedral coordination.

2. The greater the A–O bond strength, the greater the tendency for six-coordination of B. High A–O bond strengths imply for A: (a) high formal charges, (b) small

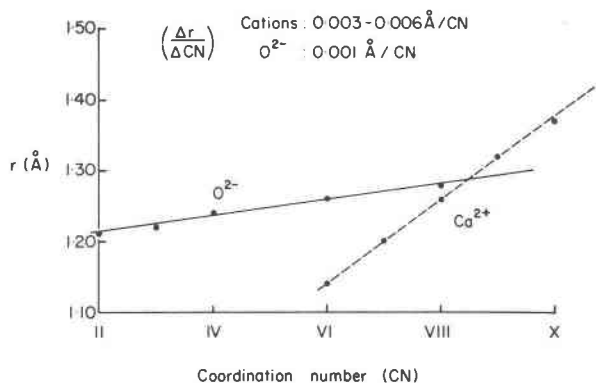


Fig. 18. Plots of ionic radius vs. coordination number for Ca^{2+} and O^{2-} . The slopes of these curves may be related to the compressibilities of the ions. From Prewitt (1982).

ionic radii, and (c) high electronegativities. These parameters are intimately related. The electronegativity need be considered only when the size and charge of A ions are similar, e.g., for the pairs Mg^{2+} – Co^{2+} , Sc^{3+} – In^{3+} , or Ca^{2+} – Cd^{2+} . This rule is related to Pauling’s ionic bond strength modified by the electronegativity factor.

Rule 1 can be illustrated with transformations of germanates and silicates having formulas ABO_3 ($G = 1$) and A_2BO_4 ($G = 2$). For example, MgSiO_3 (clinoenstatite) transforms to a structure with six-coordinated Si (ilmenite) at a lower pressure (20 GPa) than does Mg_2SiO_4 (spinel), which disproportionates to perovskite plus periclase at almost 30 GPa (Ito, 1977). Rule 2 easily explains why Si in P_2SiO_7 is six-coordinated at low pressures, but does not explain completely the transformation of alkaline-earth metagermanates to the perovskite structures. SrGeO_3 transforms to cubic perovskite at 5.0 GPa, and BaGeO_3 at 9.5 GPa. Nevertheless, this kind of approach to the crystal chemistry of high-pressure phases can provide interesting and valuable insight as to why a particular transition takes place as it does. It appears that much more of this kind of analysis can be done with data already available.

Spin crossover

One interesting possibility for a phase transition in the mantle that has been discussed by a number of authors, but never observed experimentally for iron oxides, involves a transition from high-spin to low-spin iron. Such a change has been called “spin crossover” by chemists (Gütlich, 1981) and has been well-documented for molecular organometallic compounds, but no good review for this effect in solid-state materials has been made. Several authors have suggested that increasing pressure can induce a transition from high spin to low spin in oxides and sulfides, and Ohnishi (1978) has given a theoretical treatment of the temperature and pressure effects on spin crossover. Figure 19, a plot of radius vs. atomic number for the divalent first-row transition elements taken from Shannon and Prewitt (1968), illustrates the reason for this transformation. Here, the upper branch of the curve follows the radii of high-spin ions and the lower branch the low-spin ions. Because pressure favors higher density, spin crossover from high spin to low spin can occur as pressure increases. Table 1 adapted from Prewitt and Rajamani (1974) shows how increasing pressure, temperature, and ligand field can induce spin crossover in transition-metal ions.

With regard to minerals, spin crossover could, for example, result in a 13% increase in zero-pressure density for Fe_2SiO_4 . However, no such transitions have been observed and proven for iron in an oxide material. Apparently, at high pressure the oxygen coordination around Fe increases before the crystal field becomes large enough to force a change to the low-spin state. Several years ago, Yagi and Akimoto (1982) reported a phase change in Fe_2O_3 at about 55 GPa and from the X-ray powder pattern it looked as though the high-pressure phase volume was consistent with LS Fe. However, subsequent Mössbauer work indicates that there are two or more crystallographic sites in this

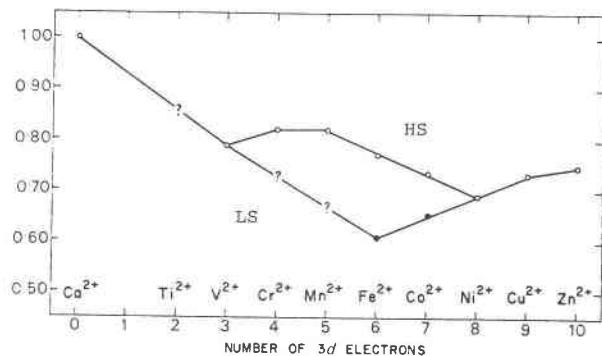


Fig. 19. Effective ionic radii vs. number of *d* electrons for first-row transition elements. The two branches indicate different radii for high-spin and low-spin ions. From Shannon and Prewitt, 1968.

high-pressure phase and it is possible that it contains Fe in a higher coordination (Syono et al., 1984).

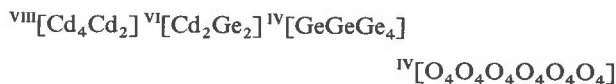
It is possible that experimentalists have been looking at the wrong material and that a silicate olivine or spinel with a small amount of Fe would be the most likely to exhibit spin crossover. This is in analogy with the experiment of Barger et al. (1971) where 2% Fe in MnS₂ showed crossover at about 40 kbar. It is possible that a HS to LS transition would occur in olivine or spinel at very high pressures and it might be instructive to examine analog phases containing HS Co where the transition would take place at much lower pressures. Thus far, the only reported experimental work on a cobalt oxide exhibiting spin crossover is for Co₂O₃ (Chenavas et al., 1971).

Cubic-anvil cell

In the 1950's and 1960's there was great interest among geochemists and geophysicists in high-pressure synthesis of new phases that provided important new information about minerals and conditions in the Earth's mantle. This interest was also shared by materials scientists who were engaged in synthesis of new phases for the purpose of making new materials with unique properties (e.g., synthetic diamond). However, two things happened that reduced the amount of activity (except for Japan and possibly the USSR) in large-volume, high-pressure research: (1) Very few new materials were found that could be produced on an economic basis for commercial applications, and (2) the diamond-anvil cell was invented and perceived by many scientists and administrators as an economical substitute that could perform most of the experiments formerly carried out with the large-volume apparatus. Nevertheless, we learned an enormous amount about systematic crystal chemistry and physical properties of materials through the synthesis of quenchable high-pressure phases with the latter equipment. Foremost in the earth sciences at that time were the Ringwood group at Australian National University and Akimoto's laboratory at the University of Tokyo where many germanate and silicate phases were synthesized and used to interpret the structure of the Earth's mantle. In the USA, a number of laboratories also

were performing significant high-pressure research related to geology and geophysics. Only a few of the laboratories were working at pressures in excess of 40–50 kbar, e.g., those of Kennedy at UCLA, Boyd at the Geophysical Laboratory, and Sclar at Lehigh University. Several other laboratories not directly involved with earth science nevertheless produced results that were of considerable help in understanding mineralogical problems, e.g., those at Bell Telephone, Du Pont, Air Force Cambridge Research Center, Brigham Young University, and Cornell University.

I was involved in high-pressure crystal chemistry in the 1960's and was involved with two experiments that have been of lasting importance to the understanding of mantle mineralogy. One of these experiments was the synthesis of single crystals and structure determination of CdGeO₃ with the garnet structure (Prewitt and Sleight, 1969). Powder samples of this phase had been made previously by Ringwood and Seabrook (1963), but they were unable to index the complete X-ray pattern. We found that the cell was tetragonal and that Cd was ordered into the dodecahedral and octahedral sites, and that Ge was ordered into octahedral and tetrahedral sites. The structural formula can be written showing each crystallographically-distinct ion species:



This formula indicates a wide range of possibilities for substitution of different ions in the tetragonal garnet structure without changing the overall symmetry. To my knowledge, no systematic investigations have been made of these possibilities.

A silicate with this kind of distorted garnet structure was subsequently found in meteorites and named majorite (Smith and Mason, 1970). The other phase synthesized by Prewitt and Sleight (1969) was CaGeO₃ with the perovskite structure. This had also been synthesized previously by Ringwood and Major (1963), and attempts had been made to index powder patterns of both samples using cubic unit cells. Later, we obtained single crystals and found that the material was orthorhombic and with a structure similar to that of MgSiO₃ perovskite (Sasaki et al., 1983). It is clear that high pressure permits the synthesis of an almost unlimited number of new phases that can

Table 1. Effect of temperature, pressure, and ligand field on spin crossover of first-row transition elements

P	T	Ligand	Mn	Fe	Co	Ni ³⁺
		F	HS	HS	HS	HS
↓	↑	O	HS	HS	HS/LS	LS
		S	HS	HS/LS	LS	LS
		S ₂	HS/LS	LS	LS	LS

provide insights to mineral chemistry that cannot be made in any other way. In the late 1970's and 1980's, many of the American high-pressure facilities in geoscience departments became inactive, and although the diamond cell was used extensively in the USA and abroad, most of the significant large-volume syntheses were done in Japan. Figure 20 contrasts the capabilities of the cubic-anvil devices with the diamond-anvil cell. There are at least nine ultra-high-pressure laboratories operating in Japan and two more are under consideration. Except for laboratories in the USSR, the only other such equipment in the World is in a new facility in Ringwood's lab in Australia. The success of the Japanese program is illustrated by the recent book edited by Akimoto and Manghnani (1982) containing papers given at the U.S.-Japan Conference on High Pressure in Geophysics, and by Sunagawa's (1983) book on Materials Science of the Earth's Interior. These reported the results of many important investigations of the chemical and physical properties of materials synthesized at temperatures and pressures that cannot be duplicated with current apparatus available in the USA.

At Stony Brook, with support from NSF and SUNY, we are undertaking the construction of a new ultra-high-pressure facility featuring a Sumitomo 2000 ton press and cubic anvils of the split-sphere type, similar to equipment now being used at the Institute for Thermal Spring Research in Misasa, Japan (cf., Ito, 1982). This apparatus must be used in a two-stage arrangement where the six steel anvils press on the face of a cube that is itself divided into eight tungsten carbide subcubes, each of which is truncated on one interior corner to form an octahedron. Ito has

been able to achieve pressures and temperatures in excess of 20 GPa and 2000°C in his laboratory and we expect to do as well. We believe that this facility will be an extremely powerful too for investigating mantle materials, for experimental petrology, and for synthesizing many previously-unknown phases of varying composition. It will also provide the opportunity for expanding our knowledge of crystal chemistry phenomena at high pressures and temperatures.

Summary and conclusions

In conclusion, I am optimistic about the future of crystal chemistry and how it fits in with other disciplines in the earth sciences. There needs to be more coordination and cooperation among the various people involved to make really significant progress, but I think this can be done. It is clear that momentum is building for more support of mineral physics and mineral chemistry efforts on a national level and I think this will be of benefit to us all. One further comment: Returning to mineralogy and MSA, I have an impression from this meeting, more than in any before, that very substantial changes are in store for us during the 1980's and 1990's. Greater understanding of mineral chemistry and mineral physics, improved experimental techniques, and, above all, the revolution in microcomputers and supercomputers are going to introduce major changes in the way that we teach and conduct research in the mineralogically-related sciences. These changes are already beginning to take place and it is up to us to adapt and to be sure that we and our Society are participants and leaders in this revolution.

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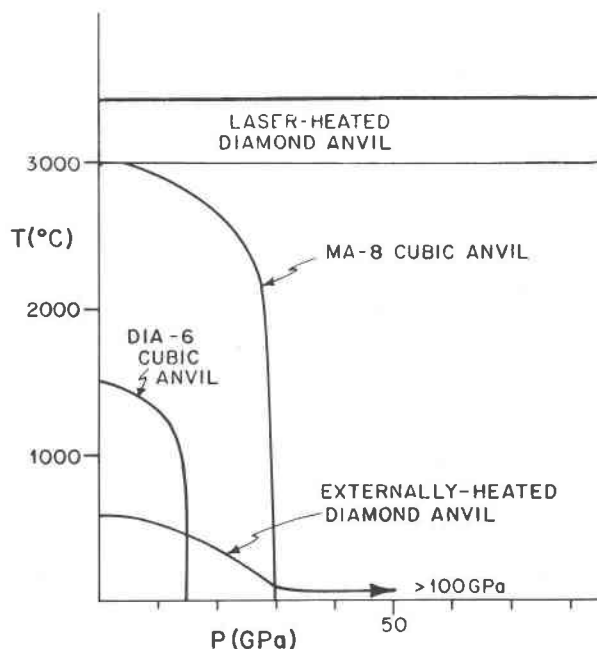


Fig. 20. Approximate pressure-temperature regimes accessible with different kinds of high-pressure apparatus. The DIA-6 is a single-stage cubic anvil device and the MA-8 has two stages.

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