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NEGLECTED ROLE OF METASTABILITY IN HIGH PRESSURE RESEARCH

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INTRODUCTION

Full-page advertisements(1) proclaim to an international public that "A diamond is forever." Thermodynamics, of course, tells us precisely the opposite: that while graphite might last 'forever' on this earth, diamond will not. Diamond is, at ambient 'p' and 't', a metastable phase. So, of course, are all the new true high pressure phases which have been 'quenched' to the laboratory ambient during a decade of accelerated high pressure research.

A metastable phase is one which has a chemical potential or Gibbs free energy higher than that for any other known* phase of the same composition**, and which is separated from the stable phase (of minimum free energy) by a finite barrier or activation energy. The familiar representation of Fig. 1(a) has served for decades to describe the free energy temperature relations between the two polymorphs of a compound. The importance of the activation energy barrier which prevents the metastable phase from reaching the lowest energy state is also crucial and this is expressed in the standard representation of Fig. 1(b). The metastable phase may suffer finite, even large excursions of free energy without transforming into the stable phase. This is so, even when the free energy difference between stable and metastable conditions is very small; indeed, quite generally the activation energy bears no relation to the free energy differences. In fact, the familiar sketch of Fig. 1(b) is grossly misleading, since near a transition pressure or temperature, the free energy difference is vanishingly small (at T_{tr}, $\Delta F = 0$) whereas the activation energy

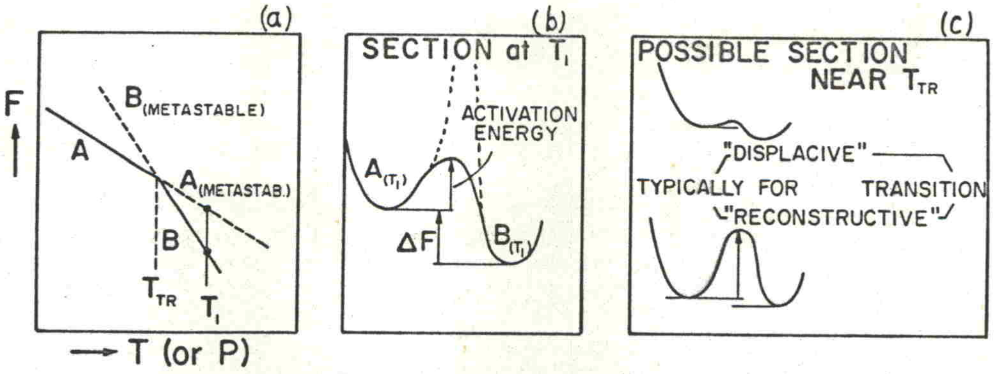

Fig. 1 Note dashed lines in (b) which are more representative of most real cases than the typical solid line.

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*At a given point in history; it is impossible to be certain that a more stable structure will not be found later.

**As a first approximation, we will ignore very small changes in stoichiometry, as well as the question of point defects as compositional units.

may be of the order of 10-50 kcal. Two cases with very small and typical activation energies are shown in Fig. 1(c) to represent the situation: the rapid, displacive, and the sluggish, reconstructive types of transitions respectively. In the case of solid phases of the same composition, the most common source of energy whereby a metastable phase transforms to the stable one is usually thermal excitation energy kT. At low temperatures, therefore, it is probable that the same chemical entity may form, exist, and persist (if not "forever", for very long times by experimental standards) in any one of several metastable arrangements. It should be noted then, that neither formation, existence, nor persistence is a sufficient criterion as an indicator of thermodynamic stability. In high pressure research, we encounter precisely those conditions which conduce to the formation or persistence of metastable phases. By the use of volume changes, catalysis, shearing stresses and bond breakage, one is able to bring about structural changes under conditions where the normal means of attaining the thermodynamically stable arrangement are absent, since kT may be very low indeed. It is, therefore, to be expected that in all high pressure research (especially near room temperature) the probability of metastable reactions occurring and giving rise to metastable phases will be recognized as being very high. Regrettably, this has not been the case. Indeed, high pressure research seems to have suffered from a singular lack of concern for this vital aspect of the problem, well known to those more typically concerned with phase transformations as a function of temperature.

Another reason why it is in high pressure studies that metastability is of particular importance is the enormous rate with which the intensive variable (p) may be changed in the shock (or dynamic pressure) experiments. Chemical kinetics demands attention to the role of transport of atoms from one spatial arrangement to another, and time is a most important parameter in real phase transformations. In the case of micro-second pulses to megabar pressures, it is clearly absurd to expect the attainment of thermodynamic equilibrium except in cases with especially favorable structural relationships. Yet it is not exceptional to find in the high pressure literature attempts to find congruence and agreement between p-t transformation data obtained from static data and those for shock work.

Finally, related to the problem of metastability, is the question of the role of shearing stresses and other 'catalysts' in high pressure kinetics. Eight years ago in ISRS-IV, the author presented(2) new experimental data on the role of shear and bond breakage on enhancing the rates of high pressure reactions. Although considerable similar data has accumulated since then, we are not much further along in our understanding of the phenomena involved.

SOME F-T-P RELATIONSHIPS

Figure 2 is a schematic free energy-temperature representation for the system, SiO_2, the most complex known, with several solid phases and various kinds of transformations (categorized roughly in the small insets) among them. We wish to draw attention here to the metastable persistence to ambient conditions of several crystalline and non-crystalline solids. Moreover, as also illustrated in Fig. 2, certain starting materials may react to yield any one--or in sequence, all--the metastable phases.

The known metastable phases which are stable in some temperature range (at 1 atm) include cristobalite, tridymite, high quartz and liquid (which becomes 'glass'). All except high quartz can all be retained at room temperature 'indefinitely'. "Cristobalite" may be made directly from starting materials such as silica gel or "H_2SiO_3" by heating to 1400°C, or at much lower temperatures as in nature where millions of tons of cristobalite have existed for millions of years. Clearly, neither formation nor persistence under a given set of p, t conditions has a sufficient index of thermodynamic stability. Cristobalite also illustrates beautifully the case of a metastable phase undergoing, in its

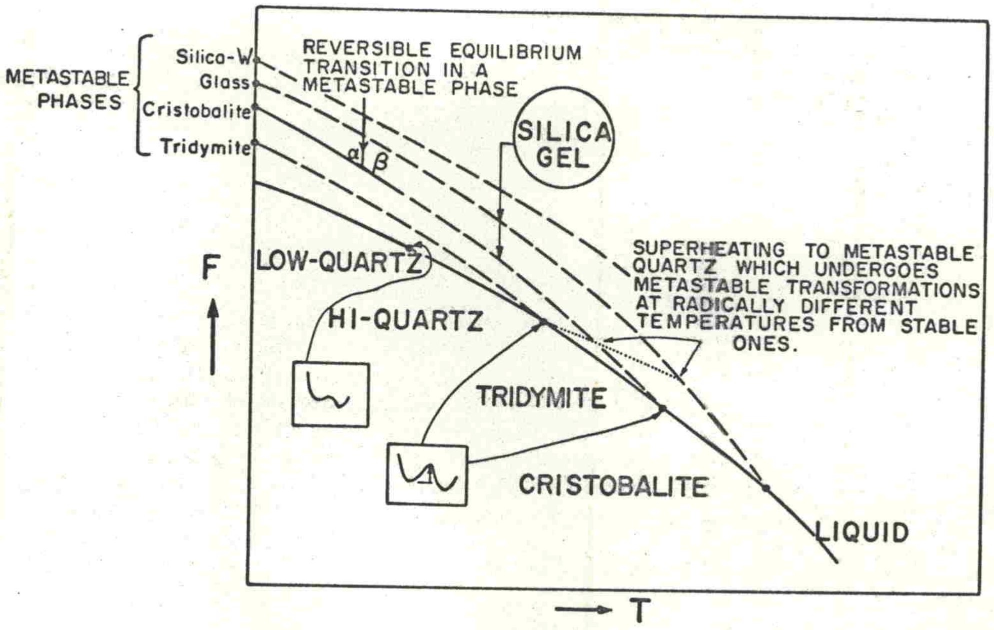

Fig. 2 Free energy-temperature diagram for the system SiO_2. Note metastable extensions and transitions in both the up and down temperature directions.

α-β transition at 268°C, a reversible, equilibrium phase transformation, which obeys all the laws of equilibrium thermodynamics, although both phases are metastable. Here we distinguish between metastable, reversible, equilibrium, processes and stable reversible equilibrium processes--the latter occurring only among phases each of which has the lowest free energy at that particular p, t. Finally, we note also the existence of wholly metastable phases--one of which corresponding to Silica-W (SiS_2 structure) is shown schematically in Fig. 2. Silica-W is not stable under any conditions of p-t, but can be formed, quenched and studied nevertheless. We have treated this F-T example in detail because on the basis of this familiar analogy we can now examine the relationships among solid phases as a function of pressure.

HIGH PRESSURE TRANSFORMATION OF STABLE→STABLE PHASES

The simplest assumption about an experimentally located phase transition under pressure is that it corresponds to the transition from one thermodynamically stable phase to the phase stable at the higher pressure. Some such cases are actually observed. Thus the widely used calibrants such as Bi_{I-II} and Bi_{II}-Bi_{III} or the transitions in Ba and Tl almost certainly belong here. The criteria appropriate to decide whether a non-quenchable transition belongs in this stable→stable category are: (i) Reversibility within a very small pressure range (in principle, of course, there must be a finite departure from the equilibrium value). (ii) Rapid change in both directions. (iii) Probably a small ΔV. (iv) Structural change, where known, is minor, involving usually only the displacement of atoms.

However, the assumption that any observed transition belongs to this family, is dangerous in the extreme, since it proves to be inaccurate in the vast majority of cases. A variety of other possibilities such as those categorized below often intervene, and especially in cases of "quenchable" or sluggish transitions must always be considered.

TRANSFORMATIONS OF STABLE→METASTABLE PHASES

When phase transformations are effected by temperature, it is only rarely that the low temperature phase can be "superheated" substantially, and even rarer is the case that this metastably persisting high temperature phase undergoes a transformation in the metastable regime. In Fig. 2, we have, however, shown one such example where SiO_2-quartz may easily be superheated beyond the equilibrium 870°C transition and indeed may be 'melted' as shown where the two metastable extensions of the F-T lines of the "supercooled" liquid and the "superheated quartz" intersect. Likewise, in the related tektosilicates, $NaAlSi_3O_8$ (albite) and $KAlSi_3O_8$ (orthoclase), we have examples of solids which can be 'superheated' several hundred degrees above their equilibrium melting points. The reason for this particular persistence is to be found in the major 'reconstruction' required of the structures and the relationship of the bond strength of the Si-O and Al-O bonds to the kT available. It is then not unexpected in atmospheric temperature, high pressure work, that except where the phase transition is of the displacive type (Buerger's[(3)] terminology) the general case will very probably involve the over-riding of stable transitions along a metastable free energy curve for substantial and easily measured pressure ranges. This experience is almost universal. Most of the substances whether metals, ionic solids, semiconductors, glasses, etc. can be 'superpressured' easily into structural state which is not the equilibrium one for the given pressure. The next reaction may involve either a rapid transition from the 'superpressured' state to the stable phase (Fig. 3(a)) or a reversible equilibrium transition occurring between two phases both of which are metastable (Fig. 3(b)). (The temperature analogue has been cited above in the α-β cristobalite case.) Both

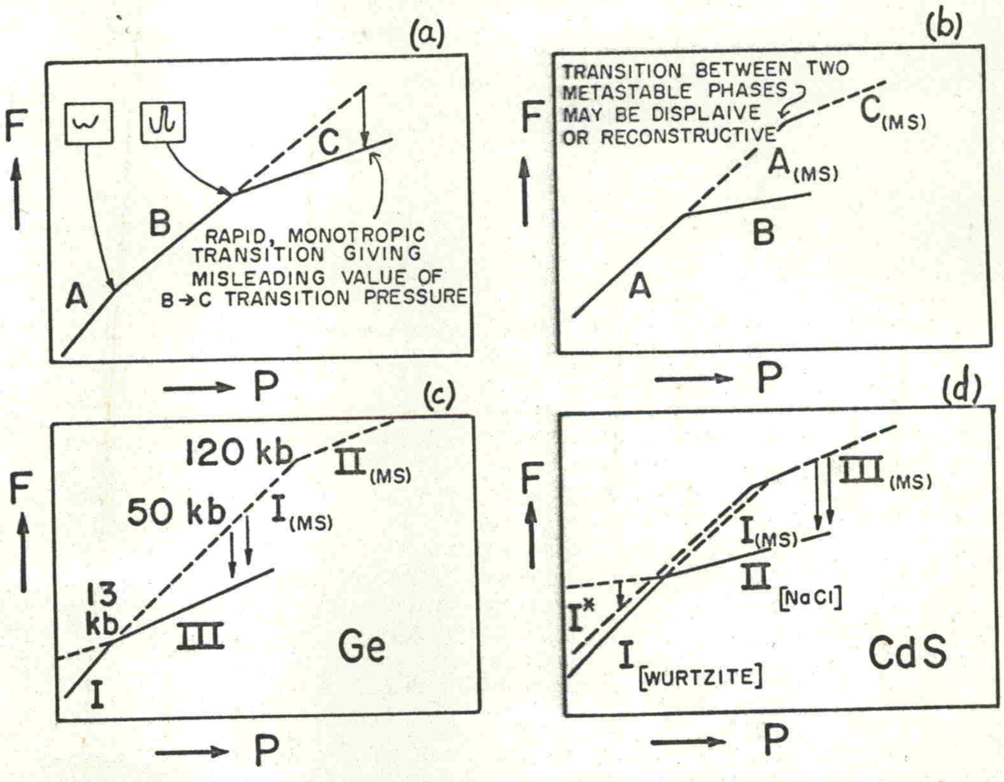

Fig. 3 Schematic F-P plots of transitions from metastable phases, and corresponding real examples.

these phenomena are very commonly encountered. In Figs. 3, the illustrations are chosen from the systems Ge (3c), and CdS (3d). In Ge the I form can and is most easily "superpressured". In the work of Bates, Dachille and Roy(4), it was shown that the lowest pressure equilibrium transformation from I-III (a tetragonal phase) at room temperature was at about 13 kbars, whereas previous work located the first transition at about 120 kbars.(5) This latter transition then from I→II (White tin(6) structure) is of the class illustrated in Fig. 3(b). Moreover, a reaction of the type generalized in Fig. 3(a) also occurs in Ge, in shorter runs as shown in Fig. 3(c). It takes literally weeks or months for the transition I-III to be accomplished near the equilibrium pressure at temperatures below about 200°C. But Ge-I may be "superpressured" to above 50 kbars at room temperature,(7) where in five or 10 minutes some Ge-III starts to form. In Fig. 3(d) is presented the case of CdS, studied in detail by Miller, Dachille and Roy(8). Here again wurtzite (4c. n.) structure CdS, under stable equilibrium conditions transforms to an NaCl structure phase at about 13 kbars at room temperature. However, single crystals or powdered CdS characteristically undergo a remarkably sharp change of resistivity at 25-30 kbars. This would at first sight be thought to represent a monotropic reaction of I_{ms}→II of the type in Fig. 3(a), although as the authors have shown, it may in fact be a I→III transition as shown in Fig. 3(d).

It is probably safe to estimate that the vast majority of atmospheric temperature high pressure reactions observed are of the 3(a) or 3(b) with substantial 'superpressuring' over the equilibrium value, and hence non-reversibility at the same pressure. Thus even in the classical example of the [NaCl]* ⇄ [CsCl] transition in RbCl, we see in Fig. 4 the very large reproducible hysteresis between the up and down-pressure transitions as studied by Frushour and Roy(9). There is, moreover, no a priori reason why the equilibrium value should be symmetrically located in a hysteresis loop, and the not-impossible F-P relations are shown in Fig. 4(b), where the equilibrium value is not the average of T_p ↑ and T_p ↓.

One need hardly cite further examples since nearly every chemical entity is likely to show behavior of the type represented in Fig. 3(a) if there is a transition at all. Thus it is well known that SiO_2 quartz may be easily 'superpressured'(10). The following table shows the data of Zeto(10) on quartz. The equilibrium pressure at 450°C is near 20 kbars, yet the quartz persists metastably at five times this value for eight hours.

However, the absence of a transformation is less apt to mislead than the occurrence of a metastable one of the Fig. 3(c) type. We have alluded to the diamond structure transitions. While the simplest crystal chemical principles require a change of coordination from four to six with pressure, the assumption that most stable diamond-structure phases transform to stable [NaCl] phases is clearly unjustified. Similarly, the expectation on electronic structure grounds of a "semi-conductor"→metal transition (often diamond-white tin) tends to produce oversimplified pictures of the high pressure polymorphism; thus the generalizations of Klement and Jayaraman(11) in which such direct, stable transitions are implied (see for example, Fig. 29, Ref. 11) for almost all 3:5 and 2:6 compounds has already been shown to be in error for those cases where it has been studied in detail. Results on CdS(8), Ge(4) are noted above. For InSb, Banus and Lavine(12) show at least four crystalline phases. The phase equilibrium diagram for almost every system including even the simplest elements is revealing a fantastic complexity, difficult to resolve with certainty even after years of detailed work. In the sulfur system, under study in our laboratory, there is

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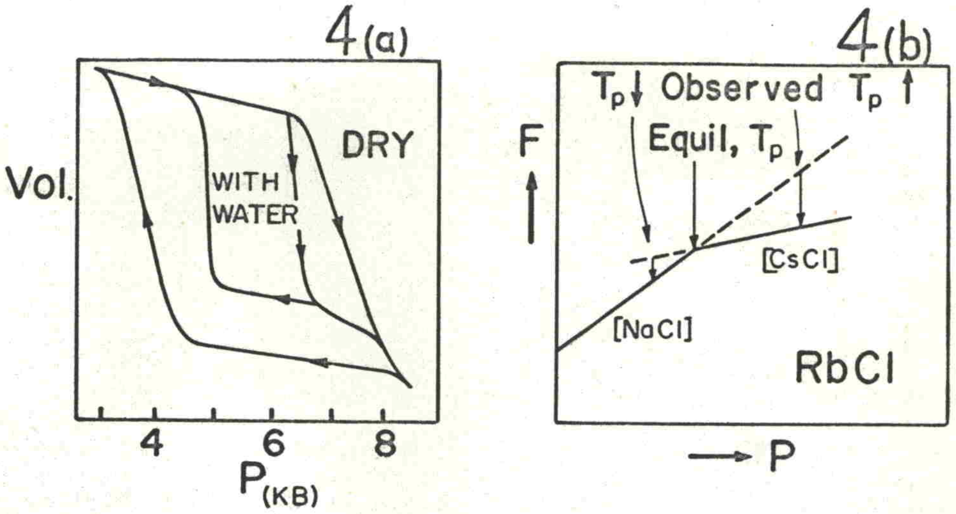
*Due to the confusion caused in studies involving a chemical entity which also gives its name to a particular structure, square brackets are used around a formula to denote "structure". Thus [NaCl] indicates the sodium chloride structure.



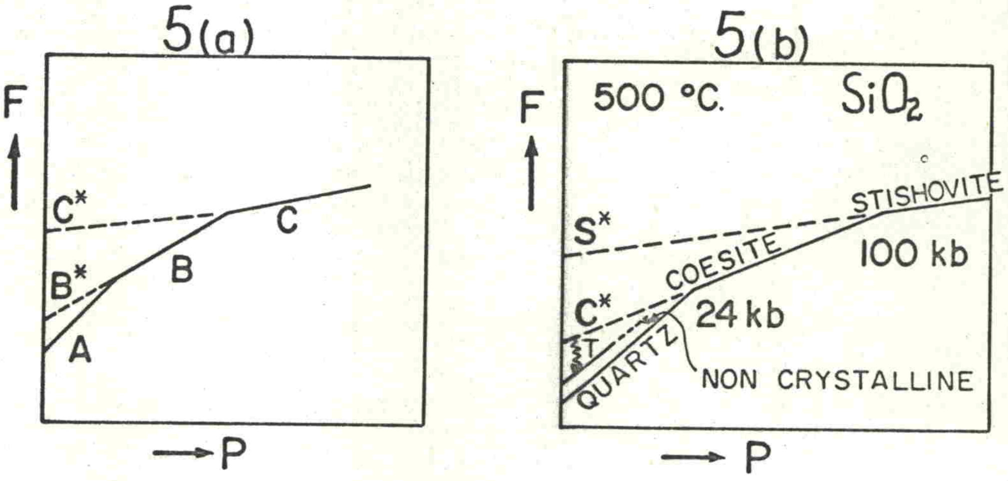


Fig. 4 (a) Shows the change in volume indicating the hysteresis in transition in RbCl, and the influence of a trace of water on it. (b) Shows not-impossible asymmetric distribution of up and down pressures about equilibrium value.

Fig. 5 Schematic (a), and real (b), examples of metastable persistence reactions.

evidence for four new high pressure crystalline phases and two or three non-crystalline ones.

THE RETENTION AND PERSISTENCE OF METASTABLE PHASES

The analogous phenomenon in the temperature case has been discussed above. It is well known that especially in reconstructive transitions if the temperature is "quenched" quickly enough, a higher free-energy form may be preserved metastably. All the so-called high-pressure phases, diamond, coesite, stishovite Ge-III, Ge-IV, jadeite, kyanite, etc., etc., are examples of such phases formed where they are thermodynamically stable, but preserved by "rapid" pressure (and possibly temperature) quenching. The F-P relations in the general case are shown in Fig. 5(a) and for the real case of SiO_2 in Fig. 5(b).

Table 1

Transformation of SiO_2-Quartz to SiO_2-Coesite
Quartz Initially Dried at 130°C (after Zeto[10])

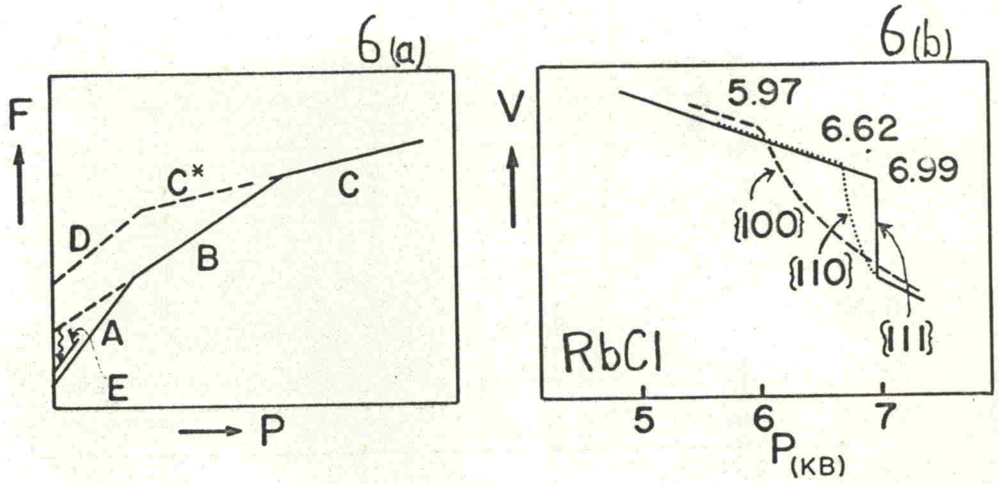
Pressure (Bars)	Temperature (deg. C.)	Time (Hours)	Products
60,000	440	15	No Reaction
60,000	450	20	No Reaction
60,000 (quartz exposed to lab air)	450	20	93% Coesite
80,000	450	10	Trace Coesite
100,000	450	8	No Reaction

While the existence of such "high pressure phases" is taken for granted, what is not fully recognized is that there are widely differing degrees of "persistence". Thus the properties of diamond may be studied with excursions along its own F-T or F-P curves of, say, 1000°C or 20,000 atm during which excursions it may attain reversible (repeatable) thermodynamic equilibrium. This does not alter in any way the fact that diamond is metastable with respect to graphite in this p-t range but indicates that the activation energy for conversion is very high. Dachille, Zeto and Roy(13) have compared stishovite and coesite in this respect. Persistence is clearly not related to "stability" in any simple way.

TRANSFORMATION OF METASTABLE→METASTABLE PHASES

We have already discussed one class of such reactions (shown in Fig. 3(c)), which can occur in the up-pressure direction. Precisely the same type of transformation can occur in the down-pressure cycle. The general case is shown in Fig. 6(a), where the C* formed possibly by the stable A→stable B→C reaction can persist metastably for a short pressure range and then undergo another displacive transition to a second metastable phase D. In Fig. 6(a) is also shown another type of metastable→metastable change whereby a pressure-quenched metastable phase, B*, may transform monotropically to a second metastable phase of lower free energy. (This type of reaction may be cited as an example of the more or less self-evident generalization sometimes called Ostwald's Stepwise Rule.) Examples of this type must be quite common. However, it is extremely difficult to establish with certainty the details of the F-P relationships in such cases. For example, the B→C reaction may be extremely sluggish and the C*→D quite fast. The results of post-exposure examination only record the A→D net reaction and even the existence of C may not at first be suspected. It appears possible from our latest work on Ge that the relationship of Ge-II - Ge-IV may be of this type, where the metastable II transforms if quenched at high pressures and very low temperatures to the IV phase.

In real substances, the metastable phase, E in Fig. 6(a), formed as a result of room temperature transformation of another, B*, even higher free energy phase, frequently turns out to be either poorly crystalline or non-crystalline. The case of non-crystalline products is treated below. An example of the "poorly crystalline" case is to be found in CdS, whereby the [NaCl] phase--in the absence of Cl^---reverts to a structure which is a highly disordered polytype. This disordered phase is commonly confused with the 3C or [sphalerite] stacking. However, careful examination shows that the material is in fact only a randomly stacked array, with no hkl reflections. The F-P relations have already been shown in Fig. 3(d).



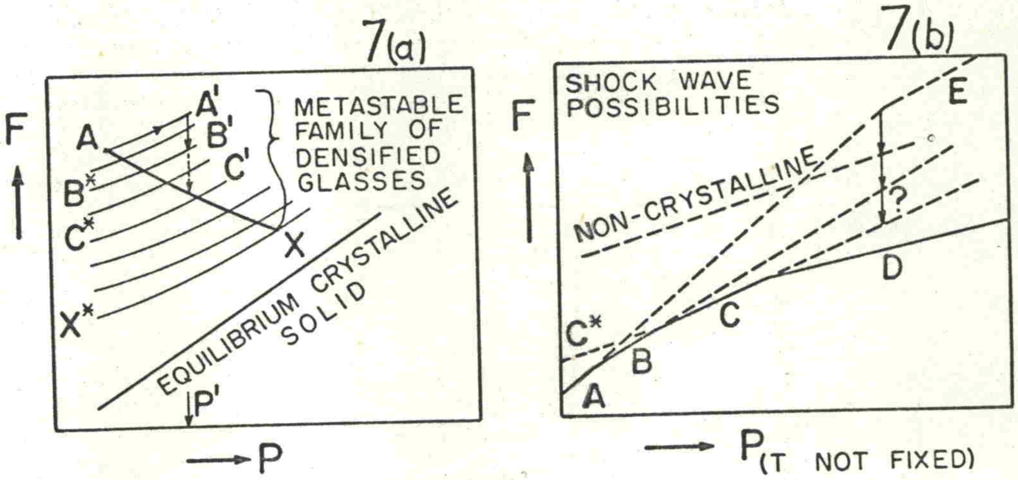


Fig. 6 (a) Typical metastable, equilibrium transitions $C \rightleftharpoons D$, and monotropic change $B^* \to E$. (b) Directional dependence of transition in RbCl after Frushour and Roy(9).

Fig. 7 (a) F-P relations among members and formation of family of densified glasses. (b) Possible metastabilities encountered under dynamic pressures.

NON-CRYSTALLINE METASTABLE PHASES FORMED IN HIGH PRESSURE REACTIONS

All non-crystalline phases are metastable. High pressure reactions should and do provide a novel way to prepare such phases. In Fig. 6(a), the monotropic reaction of metastable B can lead to a phase E, which could be non-crystalline. Exactly this happens in the case of Ge. When Ge-IV, metastable at room temperature, is heated to 200-300°C for appropriate lengths of time, one obtains non-crystalline Ge.(4, 7) Recently we have achieved the same effect starting with Ge-III. Zeto, Dachille and Roy(13) obtained non-crystalline SiO_2 from both metastable coesite and metastable stishovite. DeCarli and Jamieson(14) have reported the transformation of quartz (and feldspars) into a non-crystalline form by shock wave exposure to 350 and 600 kbars. This result must constitute an example of this type (See Fig. 7(b)) as indeed these authors proposed as a possible explanation of their data. Regrettably the influence of the actual temperatures realized is unknown, since the glass recovered has much too low a density to have been formed at 600 kbars.

STRUCTURAL TRANSFORMATIONS AMONG NON-CRYSTALLINE SOLIDS (GLASSES)

Cohen and Roy(15-17) generalized the work of Bridgman and Simon(18) showing that metastable phases such as glasses with only short range order may undergo at equilibrium, continuous structural change as a function of pressure. Moreover, the whole series of phases may be retained metastably at room temperature and pressure, so that as shown schematically in Fig. 7(a), an entire band of non-crystalline solids, continuously varying in structure, became available for study. While, initially, the surprising phenomena reported by Cohen and Roy were questioned, there is now universal agreement that such a series of dense glasses can be prepared for every composition. We have, in effect, a metastable second-order structural transition in the glasses from A→X. Figure 7(a) illustrates the progress of the structural change in the metastable glass, starting at, say, A. Typically there will be metastable elastic compression along a A→A' for a given pressure p'. Given enough time and/or activation energy the structural transition will proceed towards the metastable equilibrium structure for that pressure at C'. Due to the sluggishness of the reaction it may only go part way in the process to B'. Upon "quenching" the pressure, each of them will proceed along different elastic equilibrium paths to appear as new dense glasses at B or C. It is not surprising in the nature of the case, where low temperatures and high bond strength materials are the only ones that are concerned that at present there is still some disagreement on the quantitative location of AX (or the analogous volume-pressure line for important glass compositions).

THE RELATION OF DYNAMIC (SHOCK) PRESSURE TO STATIC PRESSURE DATA

From the foregoing, although we have not dealt with the kinetics of the fastest transition reactions, it is quite clear that it is wholly absurd to look to shock data to provide any indication whatsoever of the equilibrium structures at any pressure. The search for correspondence between certain "breaks" in property-pressure curves, obtained under shock conditions with transitions observed in static apparatus which is still common(11) perpetrates a false idea. It is quite certain that with maximum shock durations of milliseconds, the vast majority of solids will follow the metastable 'superpressure' phase F-P lines of the form of Fig. 3(a) and (b), with the scale of 'superpressuring' considerably expanded from the static cases. Most insulators and metals withstand excursions of a few hundred kilobars without revealing many transitions, if any, in a range where the static equilibrium work when done carefully reveals a multiplicity of new phases and exceedingly complex relationships. Thus consider the system shown in Fig. 7(b) in which it is envisaged that there are four static-equilibrium high pressure phases, A, B, C and D. Under dynamic loading conditions, it is certain that 'superpressuring' along AA' for, say, 200 kbars is easily achieved without any structural change. The first change A→E may occur rapidly enough that it can even be detected in the shock apparatus. There is then the temptation to relate the pressure of this transition A→E to the equilibrium value for the first static stable transition A⇌B. Alternatively, with sufficiently 'long' 'superpressuring' the metastable phase may undergo the typical 3(a) monotropic reaction as shown in 7(b), but at a pressure which will bear no relation whatsoever to the equilibrium pressure, indeed which may exceed it by an order of magnitude. The conversion of quartz to coesite, or of graphite to diamond are cases in point: they require 'superpressuring' by factors of 5-20 times under shock conditions. The general case may be even more complex since due to structural similarities the transition A'→C' may occur and C may be preserved metastably, instead of B or D.

THE ROLE OF SHEAR STRESSES AND 'CATALYSTS' IN ELIMINATING METASTABILITY

The problem of the influence that the substitution of a pure shear strain for the hydrostatic strain would have on the F-P curves is far from resolution. There is, however, no doubt whatsoever that shear stresses and those leading to fracture, greatly increase the kinetics of a transformation, thus preventing great 'superpressurizing' of phases, and facilitating the conversion of metastable phases to the stable ones. A discussion of this subject is outside the scope of this paper. In a study of structural factors which can influence the kinetics of a high pressure transformation, Frushour and Roy(9) were able to demonstrate a remarkable directional dependence of the rate of transformation with the 'superpressuring' required in the [NaCl] $\rightleftharpoons$ [CsCl] transition in RbCl. The data are shown in Fig. 6(b), where single crystals oriented in the [CsCl]-111 direction transformed virtually instantaneously as expected from a consideration of the structures. The same authors also showed that in the same transition a trace of water narrowed the hysteresis very substantially (see Fig. 4(a)), i. e., lowered the metastable persistence in both up and down directions. Zeto(10) had demonstrated much earlier the same profound influence which even a trace of water has on the quartz $\rightleftharpoons$ coesite equilibrium (see Table 1). It would appear that all these 'devices' aid the nucleation of the high pressure phase on a surface, and thereby 'tunnel' through the activation energy barrier.

LIMITATIONS ON METASTABILITY

We are concerned with any limits to metastable persistence of a phase, and whether there are any transition pressures which cannot be over-driven. Displacive transitions are in general much more difficult to 'superpressurize' by static techniques (i. e., by more than several degrees or 1-2 kb.) However, Barsch(19) has discussed the elastic mode-failure transitions as an entire class of reactions which cannot be over-ridden. In Fig. 8(a) we show schematically the behavior of the elastic constant C_{44} of NaCl and RbCl. P_{mf} represents the critical pressure at which one of the elastic constants goes to 0 and infinitesimal displacements cause structural disintegration. In practice, an equilibrium transition may precede the mode-failure transition, but if such an equilibrium transition is 'superpressurized', the metastable persistence of such a phase is

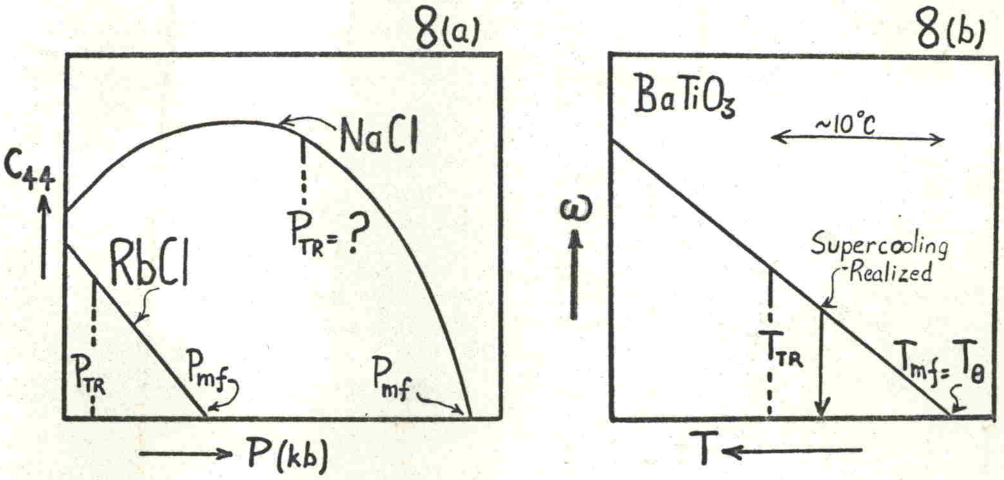


Fig. 8 Relation of equilibrium transitions (P_{tr}, T_{tr}) to mode-failure transitions (P_{mf}, T_{mf}) which set an upper limit to persistence of metastable phases of the type shown in Fig. 3(a). (Note distorted scale in 8(a).)

limited by P_{mf}, which is 90 kbars for RbCl while P_{tr} is near 6.0 kb and the usual over-riding is about 1 kbar. The temperature analogue is shown for the well-known case of $BaTiO_3$ in Fig. 8(b) where the optical mode vanishes at a (extrapolated) Curie temperature, T_{mf}, but is preceded about 10°C earlier by the equilibrium transformation, which may be overridden experimentally by a few °C. Barsch(19) has calculated a value for the persistence limit of [NaCl]-NaCl of about 400 kbars (not far from a shock wave indication of a transition), and 1.1 Mbars for [CsCl]-CsCl. It would appear very reasonable, therefore, to assume that in high bond strength materials, the elastic instability pressure (or temperature) sets an upper limit to metastable persistence, and further that one may well look for near agreement between such instabilities and some of the breaks in shock-wave property measurement.

Acknowledgments

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DISCUSSION

R. J. Zeto: I would like to comment on the remark made by Dr. Roy with regard to the location of the equilibrium pressure within a pressure hysteresis loop. I agree that there is no *a priori* reason why the equilibrium value should be symmetrically located in a hysteresis loop, i.e., halfway between the upstroke and downstroke of the transition. In our laboratory we have made experiments on the bismuth I-II transformation under hydrostatic pressure to specifically examine this relationship. For this transformation the pressure hysteresis is about 0.7 kbar wide and the equilibrium pressure was found to be appreciably removed from the center of the hysteresis. The equilibrium pressure was measured to be only about 0.15 kbar lower than the pressure of the I-II transformation.