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THE PHASE BEHAVIOR OF SIMPLE COMPOUNDS

JOHN C. JAMIESON

Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

The phase behavior of simple compounds is not necessarily simple. Several examples are given in which either common approximations fail, or "expected" phases do not appear. These include

1. Introduction

It is of geophysical interest to study the polymorphic behavior of materials, not only to ascertain density changes for equations of state but for more subtle reasons, i.e. to determine the actual solid state physical properties of potential earth-forming materials. The detailed crystal structure determines such physical parameters as the electrical conductivity, magnetic properties, anisotropic elastic constants and the crystal field effect on transition elements with its concomitant effect on radiative transfer. Chemical effects which may be ascribed to detailed structures include solid solubility ranges and reaction kinetics. To point out that simple compounds do not necessarily have simple phase behavior a few specific examples follow:

2. Titanium dioxide

The thermodynamically rigorous condition for one material of fixed composition (compound or element) to exist in two phases in equilibrium at a constant hydrostatic pressure P and temperature T is

$$-\Delta G(P_0, T) = \int_{P_0}^P \Delta V(P, T) dP, \quad (1)$$

in which ΔG is the difference of their Gibb's free energies and ΔV the same difference of their molal volumes. If $\Delta G(P_0, T)$ is measured at $P_0 = 1$ bar and as a function of temperature say by calorimetric means, and the volume behavior of both phases is known over the region of (P, T) space of interest, then the integral may

TiO₂, ZnO and Ag-halides. In addition, an example is given of development of an inhomogeneous stress system in a situation where homogeneity is usually assumed.

be solved in terms of its end-point P and a phase diagram developed. In order to make rough estimates of phase behavior when volume behavior are unknown, frequently ΔV is set equal to a constant, and then eq. (1) becomes simply

$$-\Delta G(P_0, T) = \Delta V(P_0, T) (P - P_0), \quad (2)$$

from which an equilibrium pressure can be obtained. One's intuitive feeling is that errors made in this way are percentage errors, possibly large, but not orders of magnitude. Over large pressure ranges such as 100 kb plus there is still very little compressibility data on *both* phases of any substance exhibiting a polymorphic transition. JAMIESON and OLINGER (1968) have presented such data for TiO₂ in its rutile and α -PbO₂ forms to almost 200 kb using X-ray diffraction. There they found ΔV to be highly non-linear with a minimum at *circa* 140 kb. In terms of an experimental error analysis, the equilibrium pressure for the transition rutile to α -PbO₂ form could be as low as 60 kb or as high as no upper bound at all, i.e. it wouldn't occur at the experimental temperatures (room)! In the absence of actual compression data for all phases under consideration one should be suspicious of the validity of other calculations of this type where a small ΔV and very high pressures are involved. For a large ΔV and small energy differences the approximation may suffice.

3. Zinc oxide

The ambient form of ZnO is in the hexagonal wurtzite structure. BATES *et al.* (1962) discovered that a NaCl

type modification could be quenched from pressures above 100 kb and temperatures above 100 °C. These conversions could only be obtained in the presence of ammonium chloride. This study has the features of many phase studies in geophysical materials. A phase line is developed by exposing the substance to given (P, T) conditions, and a post-mortem analysis is made to see if a reaction has occurred. Almost invariably there is a (lower) cut-off temperature below which no apparent reaction has occurred, and the very plausible explanation is given that the kinetics of the reaction are simply too slow for any products to appear in reasonable experimental times. In a survey of divalent oxides JAMIESON *et al.* (1964) have found this kinetic explanation not to hold for ZnO. We have found the wurtzite-NaCl transition to be *reversible* at room temperature using *in situ* X-ray diffraction. Several runs were made both with and without internal NaCl standards. The runs containing standards gave the pressure of transition in the neighborhood of 90 kb. Quite clear patterns could be indexed as the NaCl structure with all expected lines appearing with $h^2 + k^2 + l^2$ up to 24. The 90 kb transition is in excellent agreement with the extrapolation to room temperature of the data of BATES *et al.* (1962). Actually EDWARDS *et al.* (1959) had earlier optically observed a transition in ZnO at 100000 at which they ascribed to the appearance of the zincblende form. We believe this is actually a transition to the NaCl type as their optical study could not be diagnostic as to structure type.

In the absence of further X-ray studies over a region of (P, T) space it is only speculative to attempt to explain why a structural transition should be rapid enough to be reversible at room temperature, yet sluggish enough to be quenched from higher temperatures but we do suggest two possibilities. One is that the NH_4Cl used as flux may enter into the reaction to stabilize the NaCl structure, or that the elevated temperatures may lead to grain growth of the NaCl phase, and that such larger grains are less likely to undergo a reverse transition to the zincite type. In any event the primary moral to be drawn is that the lack of an observed transition in quench studies is no proof that the material is not in a different structure at high pressures.

An even more complicated situation occurs in rutile types MnF_2 and ZnF_2 in which a new phase (α) appears in quench studies. This phase is not the phase

actually present at elevated pressures but forms on release of pressure. This has been discussed extensively by DANDEKAR and JAMIESON (1969) elsewhere. For MnF_2 at room temperature with increasing pressure we find: rutile $\rightarrow$ tetragonal $\rightarrow$ orthorhombic; while on pressure relief: orthorhombic $\rightarrow$ tetragonal $\rightarrow$ (α). The overall volume change approaches 25%. Needless to say this situation could not have been resolved without *in situ* X-ray diffraction initially performed by VERESHCHAGIN *et al.* (1966) and KABALKINA *et al.* (1968).

4. Silver halides

Sodium, potassium and rubidium halides appearing in the NaCl structure at ambient conditions are known to transform to the CsCl structure at elevated pressures. This is a very reasonable occurrence since the CsCl type has a higher cation-anion coordination. A frequent suggestion for the constitution of the middle and lower mantle is that it is a mixture of oxides. Since the majority of these oxides exist in NaCl structures at one bar, the question arises as to whether or not they will be in a CsCl structure at depth in the earth. We have no direct evidence on this point but we would like to point out that there are substances in which the CsCl structure does not appear as a high pressure form, at least in the range of pressure and temperature studied.

SCHOCK and JAMIESON (1969) have recently studied the high pressure forms of AgCl , AgBr and AgI . The first two transform (reversibly) from their normal NaCl structure to the cinnabar type near 90 kb. This is a distortion of the NaCl type which permits covalent Ag bonding with each Ag having two linear nearest neighbors. The latter, AgI , adapts the NaCl structure above 4 kb, then at 90 kb it transforms to neither the cinnabar structure nor the CsCl. A tentative tetragonal indexing has been offered for this form. Electrical conductivity measurements suggest that it too is more covalent than the NaCl type. The volumes of these high pressure forms are the order of 10% less than their NaCl counterparts. How these would compare with volumes of hypothetical CsCl structures is unknown. But it doesn't seem impossible that divalent oxides at high pressures (and temperatures) might adopt the above or other distortions of the NaCl (or even the CsCl) structure type. This could make interpretation of the earth's structures and coordination numbers quite inaccurate.

5. Pressure intensification

Currently all static ultra high pressure phase studies are made using mechanical mixtures of solids. Either the sample is embedded in a matrix such as pyrophyllite, etc. or admixed with some internal standard to determine pressures. In the final analysis, when a material transforms it is a mechanical mixture of its own two phases. It has been earlier suggested by BOBROWSKY (1963) and later by CORLL (1967) and CORLL and WARREN (1965) that "pressures" would not be uniform in such mixtures. This has been found the case in mixtures of Nb and NaCl by JAMIESON and OLINGER (1968) using *in situ* X-ray diffraction. In this study the compression of Nb at a constant compression of NaCl was found to be a function of the (volume) amount of Nb present. This would seem to have petrological significance when a pressure is assigned to a given rock unit using "indicator" minerals as these minerals may have formed at a pressure different from other areas of the same rock.

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References

- BATES, C. H., W. B. WHITE and R. ROY (1962) *Science* **137**, 993.
BOBROWSKY, A. (1963) Pressure alterations through use of solid containers or jackets in high pressure environment, in: A. A. Giardini and E. C. Lloyd, eds., *High Pressure Measurement* (Butterworth, Washington D.C.).
CORLL, J. A. (1967) *J. Appl. Phys.* **38**, 2708.
CORLL, J. A. and W. E. WARREN (1965) *J. Appl. Phys.* **35**, 3655.
DANDEKAR, D. P. and J. C. JAMIESON (1969) Some high pressure phases of RX_2 fluorides, in: D. B. McWhan, ed., *High pressure symposium volume*, Am. Cryst. Assoc. 1969 meeting.
EDWARDS, A. L., T. E. SLYKHOUSE and H. G. DRICKAMER (1959) *Phys. Chem. Solids* **11**, 140.
JAMIESON, J. C., Q. C. JOHNSON and D. K. SMITH (1964), Unpublished research.
JAMIESON, J. C. and B. OLINGER (1968a) *Science* **161**, 893.
JAMIESON, J. C. and B. OLINGER (1968b) Pressure inhomogeneity, a possible source of error in using internal standards for pressure gages, in: *Symposium on the accurate characterization of the high pressure environment*, Oct. 14-18, 1968, Natl. Bur. Std. (U.S.).
KABALKINA, S. S., L. P. VERESHCHAGIN and L. M. LITYAGINA (1968) *Soviet Phys. "Doklady"* (English Transl.) **12**, 946.
SCHOCK, R. N. and J. C. JAMIESON (1969) *Phys. Chem. Solids*, to be published.
VERESHCHAGIN, L. P., S. S. KABALKINA and A. A. KOTILEVETS (1966) *Soviet Phys. JETP* (English Transl.) **22**, 1181.

* 74 k bar
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