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THE EFFECT OF SOLID SOLUTIONS UPON THE BULK MODULUS AND ITS PRESSURE DERIVATIVE: IMPLICATIONS FOR EQUATIONS OF STATE*

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Following Liu, equations relating the bulk modulus and its derivatives with composition for systems in which solid solution occurs are presented. It is shown that these equations adequately represent the available data for the system $MgAl_2O_4$-γ-Al_2O_3, and α-Al_2O_3-α-Cr_2O_3. The important equation of state parameters K and dK/dP (bulk modulus and its pressure derivative) may be computed from data available for any two compositions in a solid solution. Using these equations and available data, these parameters have been calculated to be K = 1.36 mbar and dK/dP = 1.8 for fayalite.

1. Introduction

Interpretations of and models for the interior of the earth rest upon three pillars. These are observational geophysics, laboratory experimentation, and theoretical development. The latter is an important guide for understanding and utilizing the information from both sources. It is the purpose of this paper to present results of data obtained in the laboratory, and to show how the parameters in the Murnaghan equation of state can be calculated for the case of solid solution.

Many results on the direct measurement of the sound velocities of geological materials and of their pressure and temperature derivatives have been reported. The work of the Lamont group has recently been summarized by Anderson et al. [1]. Among others that have been reporting such data are Chung and Simmons [2], Manghnani [3], Spetzler [4], and Kumazawa et al. [5]. The significance of these data which are obtained upon single phase materials is that they provide the experimental parameters for predicting the behavior of these materials over a wide regime of pressure and temperature, thereby yielding an experimental control upon models constructed on the basis of inference and theory.

Equations of state relate thermodynamic properties. For velocity data to be useful in this respect, it is necessary to obtain a thermodynamic property from them. Liu [6] suggests an approach for dealing with such a property determined from measured sound velocities in solid solutions, and this is the compressibility (β).

For a system in which solid solution exists, we may express the volume of the solution of overall composition j, as the sum of products formed by the molar volume of the pure constituents forming the solution and the mole fraction appropriate to each constituent, plus a volume change on mixing if the mixing is not ideal. This may be expressed as

$$V_j = \sum_{i=1}^{n} V_i X_i + \Delta V_j \qquad (6)$$

where V_j is the molar volume of solution of composition j, V_i the molar volume, and X_i the mole fraction of the component of the solution. If the solution is

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ideal, then $\Delta V = 0$. Following Liu [6], upon differentiating with respect to pressure at constant temperature and composition, we obtain

$$\left(\frac{\partial V_j}{\partial P}\right)_{T,X} = \sum_{i=1}^{n} X_i \left(\frac{\partial V}{\partial P}\right)_{T,X} + \left[\frac{\partial(\Delta V_j)}{\partial P}\right]_{T,X} \quad (2)$$

and, if ΔV_j is a function of *composition* only, then we can write, after some algebra

$$V_j\beta_j = \sum_{i=1}^{n} X_i V_i \beta_i \quad (3)$$

where $\beta = \left(-\frac{1}{V}\frac{dV}{dP}\right)$ is the appropriate compressibility.

We can take this one step further, by differentiating again with respect to P at constant T and X

$$\frac{\partial(V_j\beta_j)}{\partial P} = \sum_{i=1}^{n} X_i \frac{\partial(V_i\beta_i)}{\partial P}$$

to obtain an expression involving the volume, bulk modulus, K, (reciprocal compressibility), and pressure derivatives of the bulk modulus

$$\frac{V_j}{K_j^2}\left(\frac{\partial K_j}{\partial P} + 1\right) = \sum_{i=1}^{n} X_i \frac{V_i}{K_i^2}\left(\frac{\partial K_i}{\partial P} + 1\right) \quad (4)$$

where in eq. (3) and (4) all of the terms are experimentally determinable numbers.

Analogous equations are readily derived for the temperature derivatives of the volume. For temperature, eq. (3) and (4) become

$$\alpha_j V_j = \sum_i X_i V_i \alpha_i \quad (5)$$

$$V_j\left[\left(\frac{d\alpha_j}{dT}\right)_P + \alpha_j^2\right] = \Sigma_i X_i V_i \left[\left(\frac{\partial \alpha_i}{\partial T}\right)_P + \alpha_i^2\right] \quad (6)$$

where α is the volume expansivity.

2. Results

Data in two systems were examined to explore the ideas developed so far. These are in the systems $MgAl_2O_4$-γ-Al_2O_3 and α-Al_2O_3-α-Cr_2O_3. In the former system, solid solution occurs over a range of 100% $MgAl_2O_4$ to 85% of α-Al_2O_3; however, the phase in solution with spinel is not α-alumina, but γ-alumina. In the latter system, complete solid solution is formed between the two end members [7]. Further in this system, the mean atomic weight, a parameter defined by Birch [8] and which serves as a parameter in equations of state [9, 10], varies continuously from 20 (Al_2O_3) to 30 (Cr_2O_3).

The data for members of the $MgAl_2O_4$-γ-Al_2O_3 system were taken from the literature. Data for three compositions are reported, in which all the specimens are single crystals. These are for the compositions $MgAl_2O_4$ [11], $MgAl_2O_4 \cdot 1.6Al_2O_3$ [12], and $MgAl_2O_4 \cdot 2.5Al_2O_3$ [13]. The compressibilities in all three cases were determined from velocity measurements using the precise acoustic techniques. The pressure derivatives of the bulk modules are available for only one of these compositions [12]. For the system α-Al_2O_3-α-Cr_2O_3, the velocities of transmission of P and S waves through polycrystalline specimens of both the end members and intermediate members of the solid-solution series have been measured and reported by Rossi [14]. These measurements were performed upon a large number of hot-pressed specimens which Rossi prepared. In order to obtain the best values for each composition, he performed the velocity measurements upon a number of specimens which varied from less than 1% to several per cent of theoretical density. These were used to obtain an extrapolated value of the velocities at theoretical densities. The values for the theoretical

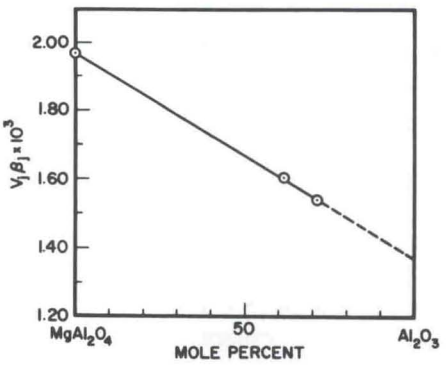


Fig. 1. Parameter $V_j\beta_j$ as a function of composition in the system $MgAl_2O_4$-γ-Al_2O_3.

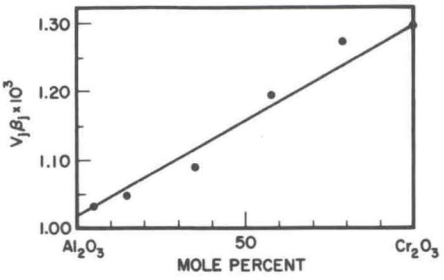


Fig. 2. Parameter $V_j\beta_j$ as a function of composition in the system α-Al_2O_3-α-Cr_2O_3.

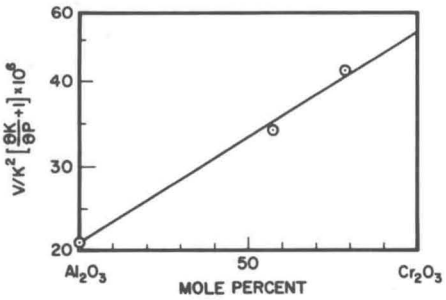


Fig. 3. Parameter
$\frac{V}{K^2}\left(\frac{\partial K}{\partial P}+1\right)$
as a function of composition in the system α-Al_2O_3-α-Cr_2O_3.

densities of the specimens of different composition were obtained from X-ray lattice parameter determinations. The method used to measure the velocities was the pulse superposition technique of ultrasonic interferometry due to McSkimin [15]. Several of these specimens of different composition were generously presented to this writer who measured the pressure derivatives of the P and S velocities, using the same method of ultrasonic interferometry. The pressure apparatus and the electronic system used have been described elsewhere [16]. The specimens selected for the pressure measurements were within 1% of theoretical density, and no corrections were made for porosity effect (which has been demonstrated to be sufficiently small for such low values of porosity (Anderson et al. [1]; Chung and Simmons [2]).

In fig. 1, $V_j\beta_j$ is plotted as a function of the composition for the system $MgAl_2O_4$-γ-Al_2O_3, and in Fig. 2, for the system α-Al_2O_3-α-Cr_2O_3. The data appear to satisfy eq. (3) quite well. In fig. 3,

$$V_j/K_j^2\left[\left(\frac{\partial K_j}{\partial P}\right)_T + 1\right]$$

is shown as a function of compositon, and it can be seen that these data are adequately represented by eq. (4). Unfortunately, there is very little data on thermal expansivity in solid-solution systems, and that found by the author is internally inconsistent, generally having been determined by different investigators, separated by years in time, on natural samples rather than carefully prepared synthetic materials.

3. Conclusions

In the present work, the composition-compressibility relation first derived by Liu [6] has been used to develop equations for the pressure and temperature derivatives of the volume. These relationships include the bulk modulus and thermal expansivity, respectively.

Several equations of state have been presented in the geological literature for predicting the volume behavior of geologic materials at pressures equivalent to great depths in the mantle. Notable among these are the Birch equation of state [17] and the Murnaghan equation of state [18]. Recently, a new equation of state due to Thomsen [19] has been reported. A characteristic of all these equations of state is that the bulk modulus and its pressure derivatives are the necessary parameters. Determination of these values, at low pressures in the laboratory, is sufficient to allow utilization of such equations for pressures greater than can be obtained presently in the laboratory, as has been demonstrated, for example, by Anderson [20].

As an example of the applicability of the results presented here, it is of interest to compute the bulk modulus and its pressure derivatives for fayalite. Data for single crystal forsterite are available [5, 21]. Kumazawa [5] has also reported data for an olivine single crystal of composition $Fo_{0.93}$-$Fa_{0.07}$. Forsterite-fayalite forms a complete solid solution with ideal mixing [22], and so with these data on two compositions within the system, one can com-

pute the bulk modulus and its pressure derivative for any composition. No data for fayalite are known to the author; however, from the Voigt-Reuss-Hill averages of Kumazawa's data, the averaged values computed for fayalite are:

Bulk modulus $K = 1.36$ mbar

Pressure derivative of the bulk modulus:

$$\left(\frac{\partial K}{\partial P}\right)_T = 1.8.$$

The errors in the above computation, based on those given by Kumazawa are 1% and 10% for the bulk modulus and its pressure derivative, respectively.

The computed value of dK/dP is surprisingly small. For all other materials of geologic interest for which dK/dP has been measured, the value is greater than 3.9 [1]. The significance of the results to considerations of the mantle will be discussed elsewhere.

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References

[1] O.L.Anderson, E.Schreiber, R.C.Liebermann and N.Soga, Some elastic constant data on minerals relevant to geophysics, Rev. Geophys. 6 (1968) 491.

[2] D.H.Chung and G.Simmons, Pressure derivatives of the elastic properties of polycrystalline quartz and rutile, Earth Planet. Sci. Letters, in press.

[3] M.H.Manghnani, Elastic constants of single crystal rutile under pressures to 7.5 kb, J. Geophys. Res., in press.

[4] H.Spetzler, Equation of state of polycrystalline MgO to 9 kb and 1000°K, submitted for publication.

[5] M.Kumazawa and O.L.Anderson, The elastic moduli, pressure and temperature derivatives of single crystal olivine and single crystal forsterite, J. Geophys. Res., in press.

[6] L.Liu, Isothermal compression of magnetism garnets up to 300 kilobars and its implications to the earth's mantle, M. S. thesis, Department of Geology, University of Rochester (1968).

[7] E.M.Levin, C.R.Robbins and H.F.McMurdie, Phase Diagrams for Ceramics (The American Ceramic Society, Columbus, Ohio, 1964).

[8] F.Birch, Composition of the earth's mantle, Geophys. J. Roy. Astron. Soc. 4 (1961) 295.

[9] D.L.Anderson, A seismic equation of state, Geophys. J. Roy. Astron. Soc. 13 (1967) 9.

[10] O.L.Anderson and J.Nafe, The bulk modulus volume relationship for oxide compounds and related geophysical problems, J. Geophys. Res. 70 (1965) 3951.

[11] M.F.Lewis, Elastic constants of magnesium aluminate spinel, J. Acoust. Soc. Am. 40 (1966) 728.

[12] E.Schreiber, Elastic moduli of single-crystal spinel at 25°C and to 2 kbar, J. Appl. Phys. 38 (1967) 2508.

[13] R.K.Verma, Elasticity of some high density crystals, J. Geophys. Res. 65 (1960) 757.

[14] L.Rossi, The elastic properties of oxide solid solutions; the system Al_2O_3-Cr_2O_3, Ph. D. thesis, S.U.N.Y. College of Ceramics, Alfred University, Alfred, N.Y. (1966).

[15] H.J.McSkimin, Pulse superposition method for measuring ultrasonic waves in solids, J. Acoust. Soc. Am. 33 (1961) 12.

[16] E.Schreiber and O.L.Anderson, Pressure derivatives of the sound velocities of polycrystalline alumina, J. Am. Ceram. Soc. 49 (1966) 184.

[17] F.Birch, Elasticity and consitution of the earth's interior, J. Geophys. Res. 57 (1952) 227.

[18] F.D.Murnaghan, The foundations of the theory of elasticity, Proc. Symp. Appl. Math. 1 (1949) 167.

[19] L.Thomsen, On the fourth-order anharmonic equation of state of solids, submitted for publication.

[20] O.L.Anderson, Two methods for estimating compression and sound velocity at very high pressures, Proc. Natl. Acad. Sci. 54 (1965) 667.

[21] E.K.Graham and G.R.Barsch, The pressure derivatives of the elastic constants of forsterite, Trans. Am. Geophys. Union 50 (1969) 101.

[22] I.C.Jahanbagloo, X-ray diffraction study of olivine solid solution series, Am. Mineralogist 54 (1969) 246.