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Accurate Thermal Expansivity Measurements in the Range 1500–2000 K Are Needed for Minerals[1]

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It is shown that the future high-temperature thermodynamic computations for minerals now hinge on the extension of the measurement of the volume thermal expansivity, β, up to 2000 K. At present many measurements of β end at about 1200–1500 K, but the extrapolations to 2000 K are fraught with large errors. A few years ago, the missing thermodynamic parameter at high temperatures was the bulk modulus (or its reciprocal compressibility). Now that measurements of the bulk modulus are being accurately measured at 1800 K, attention is focused on improving measurements of β at higher temperatures.

KEY WORDS: high-temperature data; minerals; thermal expansivity; thermodynamic computations.

1. INTRODUCTION

For the determination of the thermodynamic properties of solids, certain measurable physical properties are needed. They include the specific heat, C_p; the adiabatic bulk modulus, K_S; the pressure derivative of $K'_S = (\partial K_S/\partial P)_T$ at $P = 0$; the specific volume, V; and the volume thermal expansivity, β.

An example of what is meant by a thermodynamic property is the Gruneisen parameter, Υ, a dimensionless parameter used to relate pressure and temperature along an adiabat.

$$\Upsilon = (\beta K_S)/(\rho C_p) \qquad (1)$$

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Other thermodynamic properties defined by these physical property measurements are the Anderson–Gruneisen parameter, a dimensionless parameter to relate temperature to bulk modulus.

$$\delta_s = -(1/\beta K_S)(\partial K_S/\partial T)_P \tag{2}$$

Also needed is the thermal pressure, which is the temperature correction of pressure when the equation of state is calculated at absolute zero conditions.

$$P_{TH} = \int_0^T \beta K_T \, dT \tag{3}$$

Other important thermodynamic properties are the entropy, $S(V, T)$; the internal energy, $U(V, T)$; and the Helmholtz free energy, $F(V, T)$.

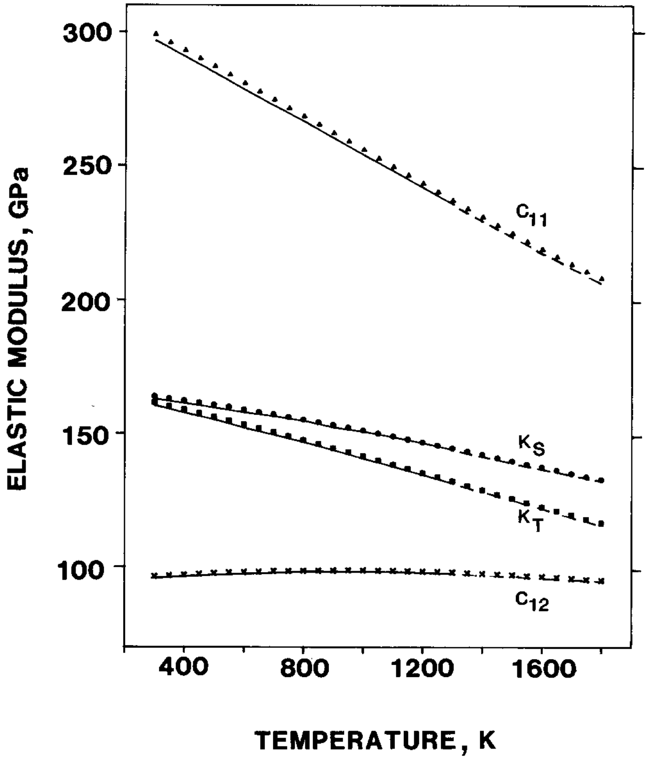

Fig. 1. The elastic constants of MgO versus T, as measured by Isaak et al. [6]. Note, in particular, that the actual measurements extend to temperatures up to 1800 K.

For minerals with a high Debye temperature, such as, for example, Mg_2SiO_4 and Al_2O_3, accurate measurements of the basic physical properties (C_p, V, K_S, β) at high temperature are all needed to obtain thermodynamic properties at high temperatures (that is, above about 1500 K).

C_p is tabulated in standard references up to 3000 K; for example, see JANAF [1] for Mg_2SiO_4 and CODATA [2] for MgO. Until recently K_S was not known beyond about 800 K, but advances in resonance ultrasound measurements have yielded good measurements of all elastic constants up to 1825 K [3–6]. Such measurements are currently being done in my laboratory at UCLA, and an example of the results for MgO is shown in Fig. 1.

From these measurements the isothermal bulk modulus at high T is readily calculated versus T. It is through the volume measurement at high T that β at high T is determined. At this stage of development, I find that the measurement of β for minerals is the least well defined. For many minerals, little agreement is found above 1200 K. The lack of data above about 1200 K, or the lack of agreement of data above about 1000 K, precludes the determination of many thermodynamic properties at higher T for many minerals. Available high-T data are reviewed in the following section.

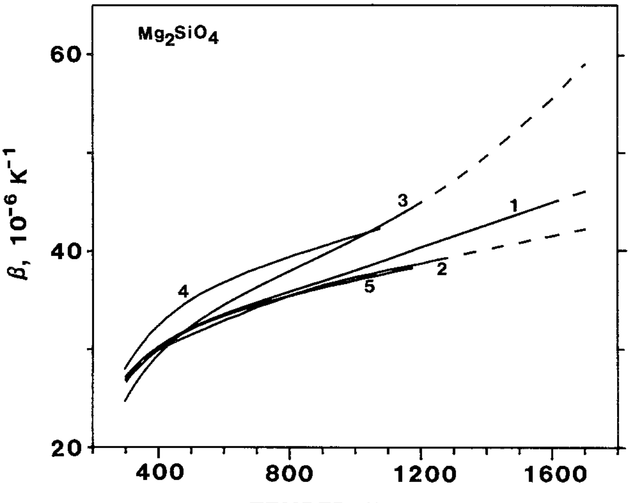

Fig. 2. The coefficient of thermal expansion of Mg_2SiO_4, versus temperature, according to the compilation of Isaak et al. [4]. Reports by Suzuki et al. [7], curve 3; Suzuki [8], curve 5; White et al. [9], curve 2; Matsui and Manghnani [10], curve 4; and Kajiyoshi [11], curve 1. The point is that extrapolations of these various curves to 2000 K lead to great discrepancies in β.

2. REVIEW OF HIGH-*T* DATA FOR β

2.1. Mg_2SiO_4

Figure 2 shows the high-temperature data for β of forsterite as reported by five different studies since 1975. In 1984 Suzuki et al. [7] reported measurements of β of this mineral to 1200 K in the UCLA Mineral Physics Laboratory, as shown by curve 3. This departed from β, as reported by Suzuki in 1975 [8], curve 5. The use of the β data of curve 3 led to values of Υ and βK_T which had unusual behavior. White et al. [9] measured β in 1985, by curve 2, obtaining values in good agreement with those of Suzuki. Matsui and Manghnani [10] reported values of β which are in agreement with the Suzuki and Anderson data at 1200 K but significantly higher than all other data at 600 K, curve 4. Kajiyoshi [11] subsequently reported β in his Master's thesis, curve 1, which is in agreement with the data of White et al.

The spread of extrapolated values at 1800 K covers a large range and leads to wide variation in calculated thermodynamic properties at 1800 K.

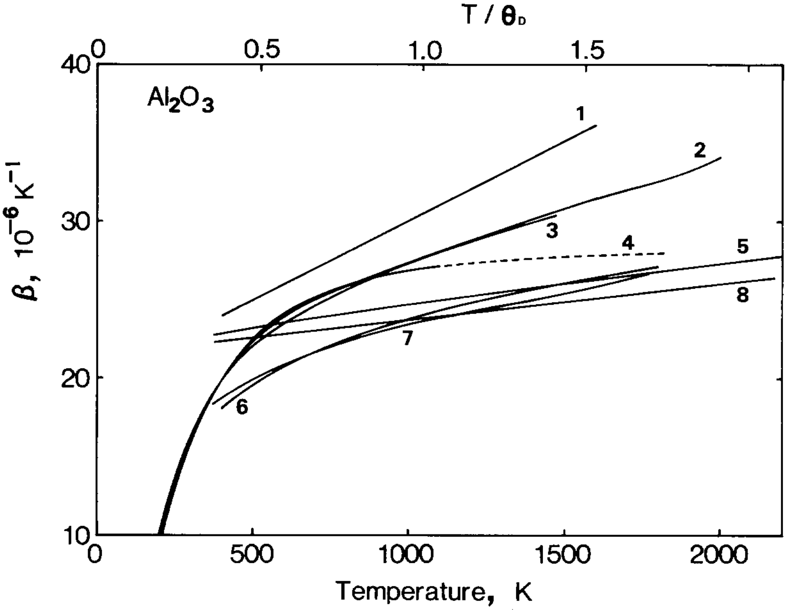

Fig. 3. The spread of values for β for Al_2O_3, as reported by Goto et al. [5]. Primary data on β are as follows: curve 1, Eckart and Bradt [18]; curve 2, White and Roberts [19]; curve 3, Schauer [20]; curve 4, Wachtman et al. [21]; curve 5, Aldebelt and Traverse [22]; curve 6, Petukhov et al. [23]; curve 7, Fitzer and Weisenburger [24]; curve 8, Baldock et al. [25].

2.2. Al_2O_3

Figure 3 illustrates the spread of values of β for corundum [5]. Again, there are wide discrepancies among the data sets. Extrapolation to 1800 K produces even larger discrepancies because of the differences in slopes of the various data.

The problem is illustrated by computing the Gruneisen parameter for each case shown in Fig. 3. The result, as shown in Fig. 4, includes variations as large as 10%.

One of the important thermodynamic tests for many properties is whether or not $(\partial \Upsilon / \partial T)_{P=0} = 0$. We see that this is approximately true for the lower curves, but some valid criteria for selection of this curve are necessary.

If $(\partial \Upsilon / \partial T)_V$ is zero, then the derivation of pressure, as taken from statistical mechanics, is greatly simplified because the thermal pressure is then proportional to the thermal energy divided by V. This validates the Mie–Gruneisen equation of state, which is ordinarily considered a gross approximation.

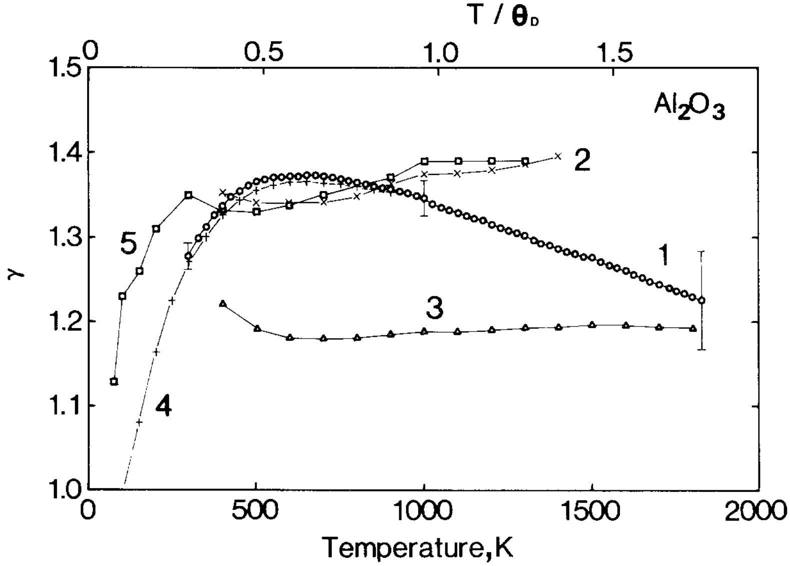

Fig. 4. The calculation of the Gruneisen parameter versus T for single-crystal Al_2O_3 using the author's data on bulk modulus, K_S [5], and the data on thermal expansivity from a few of the sources plotted in Fig. 3: circles, curve 1, using β from Wachtman et al. [21]; crosses, curve 2, using β from White and Roberts [19]; triangles, curve 3, using β from Petukhov et al. [23]; plus signs, curve 4, using β from Schauer [20]. The squares, curve 5, are calculations by Chung and Simmons [26], using their own data on polycrystalline Al_2O_3 for K_S, and values of β at low T from Wachtman et al. [21] and at high T from Schaurer [20].

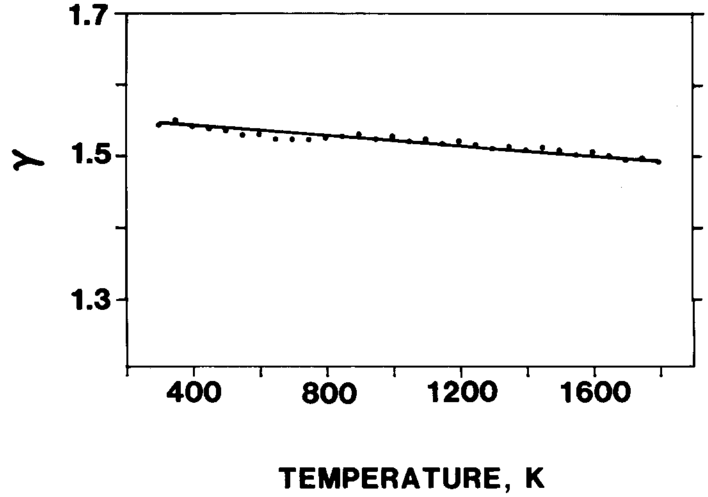

Fig. 5. The variation of Υ with T for MgO according to Isaak et al. [6]. The experimental results for β, K_S, C_p, and ρ are sufficiently constrained that a conclusion about the temperature behavior of Υ can be made. We see that Υ is slowly decreasing with T.

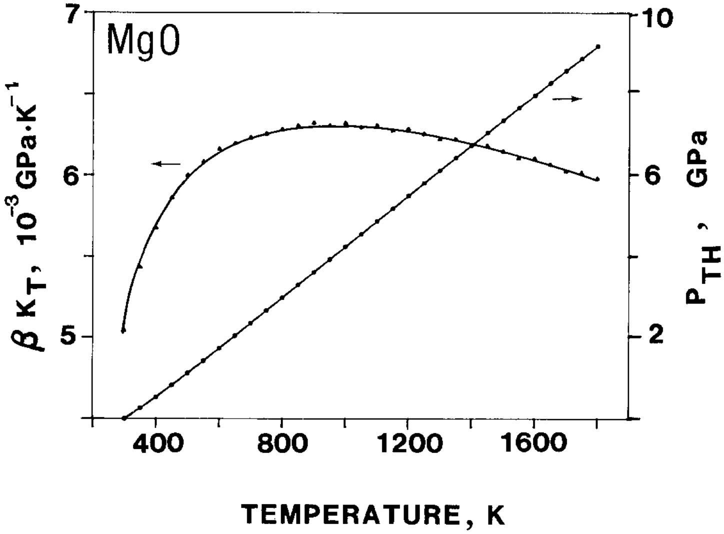

Fig. 6. The variation of βK_T and P_{TH} with T for MgO according to Isaak et al. [6]. We see that βK_T is decreasing slightly with T in the high-temperature range but that the thermal pressure is virtually a straight line in the high-temperature range.

2.3. MgO

For MgO, the various data on β are in sufficiently close agreement that there is not a wide divergence of the 1800 K extrapolated values [6]. It is possible to compute thermodynamic data with an acceptable uncertainty using these extrapolated values of β. The high-T values of Υ, calculated from Eq. (1), are shown in Fig. 5 and indicate a slight decrease in Υ with T. The variation found in calculations of Υ using the other data sets is 6% at the high-T end.

In order to calculate the thermal pressure, P_{TH}, the product βK_T must be known. This product and its integral, P_{TH}, are shown in Fig. 6 for the case of MgO. The fact that P_{TH} is virtually a straight line is a very important result for equation of state calculations.

When the relationship between P_{TH} and T is linear, or very nearly linear, then the solid is purely classical in its thermodynamic behavior. In the region of temperature where quantum mechanical effects are important, the relationship between P_{TH} and T is quite nonlinear (in this regard P_{TH} versus T resembles an enthalpy curve).

When the results of β, C_p, and K_S are combined by means of the appropriate formulas, entropy can be calculated [12]. Figure 7 shows the results of such a calculation for MgO over a wide range of pressures and temperatures. Note that the temperature range is about 2000 K and the compression range is up to V/V_0 (about 150 GPa in Fig. 7), which is necessary for modeling earth conditions at depths of up to 3000 km.

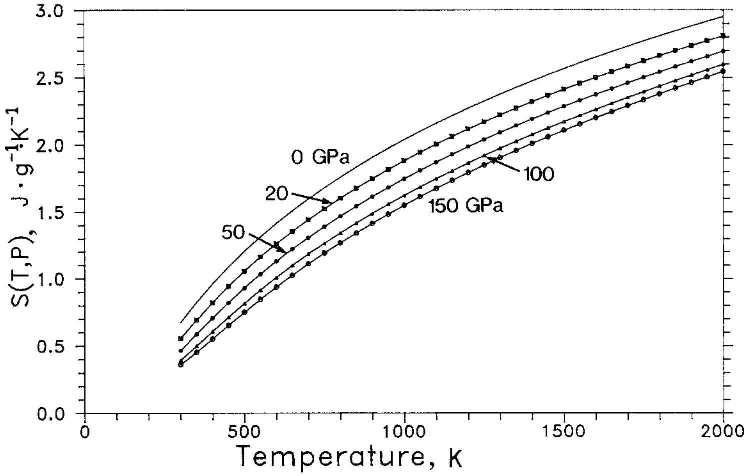

Fig. 7. The entropy of MgO over a wide pressure and temperature range, as calculated by Anderson and Zou [12]. This calculation is possible because of the agreement of various authors on the thermal expansivity of MgO.

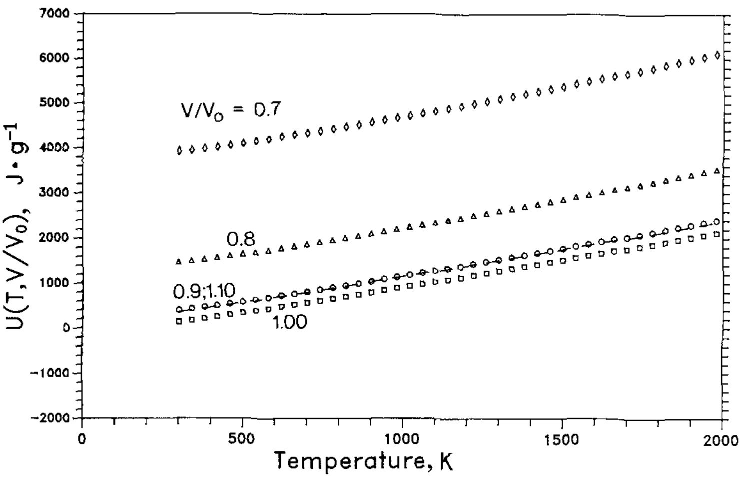

Fig. 8. The enthalpy of MgO over a wide temperature and wide compression range, as calculated by Anderson and Zou [12].

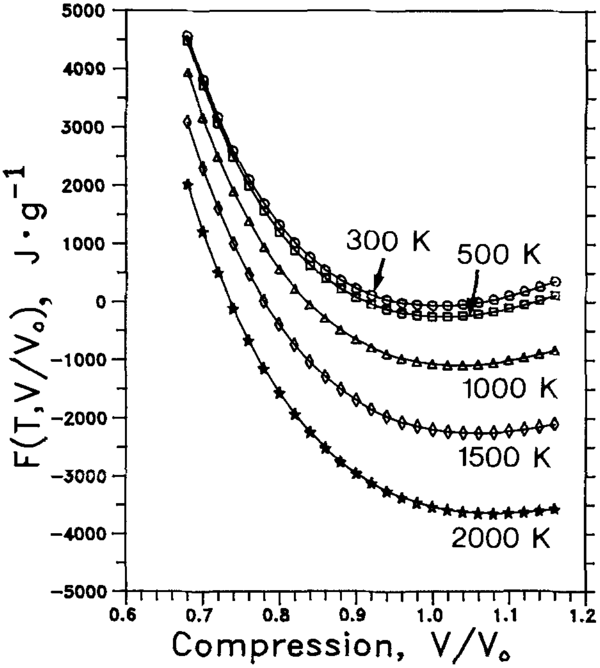

Fig. 9. The Helmholtz energy of MgO over a wide compression range for five isotherms resulting from the entropy and internal energy calculations made by Anderson and Zou [12].

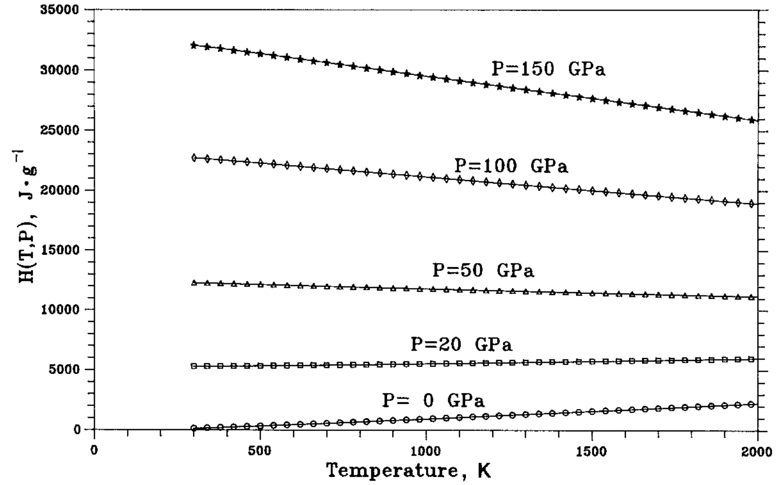

Fig. 10. The enthalpy of MgO over a wide pressure and temperature range, calculated from the primary data according to equations developed by Anderson and Zou [12].

When the results of the calculated entropy and the calculated thermal pressure are combined with the equation of state at 0 K (which must be made if P_{TH} is used this way), the internal energy can be computed over a wide range of compression and temperature, [12] as shown in Fig. 8.

Once the entropy and internal energy are known, the Helmholtz energy is determined by the equation $F = U - TS$. The free energy so determined for MgO [12] is shown in Fig. 9.

Figure 10 shows the calculation of enthalpy versus P and T for MgO, which can be determined from entropy and internal energy by manipulation of standard thermodynamic equations [12].

3. SUMMARY

It is very important to try to compute the free energy of a solid over a wide T and V/V_0 range, in order to test the *ab initio* calculations of physical properties of a solid made by theorists. A typical calculation starts with the Schroedinger equation of quantum mechanics, and by assuming the potential between adjacent atoms, taking due care of the crystallographic symmetry, arrives at the Helmholtz free energy F [13–16]. F is then used to derive mechanical properties versus V/V_0 and T.

Experimentally we are in a position to compute the Helmholtz free energy, to test the corresponding values derived by theorists. The most pressing experimental requirements are good determinations of β at high T. This situation presents an important and urgent challenge to the thermal expansivity community. It is necessary to measure the thermal expansivity of minerals in the 1200 to 2000 K range. That this can be done is shown by the results of the measurement of β on metals at very high T demonstrated by Miiller and Cezairliyan [17] (see this issue also).

Successful measurements of β in the 1200–2000 K range may require laser interferometry such as Miiller and Cezairliyan [17] have used in their experiments. In this temperature range, all mechanical and electrical diagnostic tools will probably be rendered useless. This suggests that only light can be used as the metrology device for the specimen at high T. The experiments must be done in a vacuum in order that convection currents will be eliminated.

The most urgent need is for expansivity data for Mg_2SiO_4, Fe_2SiO_4, CaO, and FeO.

ACKNOWLEDGMENTS

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NOTE ADDED IN PROOF

A referee has drawn my attention to CODATA Bulletin No. 59 (1985), "Thermophysical Properties of Some Key Solids" (G. K. White and B. Minges, eds.), and the associated compilation by G. K. White and R. B. Roberts (*High Temp. High Press.* **15**:321, 1983), which show that the selected data with aluminum or sapphire as a reference standard are in much closer agreement up to 2000 K than Fig. 3 suggests and that gamma is a sensible constant, with a value of 1.35 to 1.4 above 1000 K.

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