Diffusion in periclase by combination of analytical formulas and thermodynamic model

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Abstract. Analytical formulas for the temperature dependence of elastic constants of MgO combined with a thermodynamic model, which interconnects bulk properties to point defect parameters, can successfully reproduce the self diffusion coefficients of periclase at temperatures representative of the Earth’s mantle conditions.

Although the calculated diffusion coefficients are estimated from a single measurement and cover a broad range of values (i.e. five orders of magnitude), an almost excellent agreement with the experimental ones is observed. The slight discrepancy at the highest temperature lies at error margins.

1 Introduction

In a recent paper (Sarkar et al., 2009), the elastic constants and the bulk modulus for ionic solids of cubic structure such as NaCl, KCl, MgO, CaO have been evaluated at different temperatures by means of analytical formulas based on Murnaghan’s equation of state (Murnaghan, 1944) and Tallon’s (Tallon, 1980) models. Various equation of state for the thermal dependence of elastic properties of solids are reported in literature (Anderson, 1995) and experimental data for the variation of these properties with temperature for a large number of materials can be found in Anderson and Isaak’s book (1995).

Among ionic solids, periclase (MgO) is of great geophysical interest since it is a significant component of the lower mantle. For a better understanding of the rheological properties of the Earth’s interior and of the kinetic mechanisms of underlying solid-state transport, the diffusion equation of MgO in the prevailing temperature conditions of the lower mantle plays an important role. Diffusion controls many dynamic processes in Earth such as mantle convection and phase transition.

Scope of the present work is to show that a combination from one side of the elastic data for MgO at any temperature, obtained by Sarkar (2009) through analytical formulas (Tallon, 1995; Murnaghan, 1944) and from the other side of a thermodynamical model that interconnects bulk properties and defect parameters, leads to the estimation of diffusion coefficients of MgO at any temperature and especially at those dominating in the lower mantle.

2 The thermodynamical $c B \Omega$ model

This model interconnects the Gibbs energy $g_i$ to the bulk expansivity and elastic data (Varotsos, 1976, 1977, 2007; Varotsos and Alexopoulos, 1977, 1978, 1979, 1980a, 1984c, 1986; Varotsos et al., 1978) though the relation:

$$g_i = c_i B \Omega$$  \hspace{1cm} (1)

where “$i$” denotes the different process mechanism, (formation, migration and activation), $c_i$ is a dimensionless constant which can be considered as independent of temperature and pressure, $B$ is the isothermal bulk modulus, $\Omega$ is the mean atomic volume per atom. It has various successful applications in many cases such as in alkali and silver halides (Varotsos and Alexopoulos, 1978, 1979, 1986), in alkali halide mixed crystals (Varotsos and Alexopoulos, 1980b; Varotsos, 1980), but also in seismic electric signals (SES) emitted prior to large earthquakes (Varotsos and Alexopoulos, 1984a, b; Varotsos et al., 1986) from crystalline materials included in
the rocks of the pre-focal area when the increasing tectonic stress reaches a critical value (Varotsos and Lazaridou, 1991; Varotsos et al., 2002, 2003a, b, 2006a, b).

If we introduce Eq. (1) into the following diffusion relation given by Eq. (2) for a single operating mechanism,

\[ D = f a^2 \nu \exp(-g_{\text{act}}/k_B T) \]  

(2)

where \( f \) is a numerical constant depending on the diffusion mechanism and the structure, \( a \) the lattice constant, and \( \nu \) is the attempt frequency we get:

\[ D = f a^2 \nu_0 \exp(-c_{\text{act}} B \Omega/k_B T). \]  

(3)

We note that the Debye frequency \( \nu_0 \) and the attempt frequency \( \nu \) are of the same order of magnitude, and thus \( \nu_0 \) can be used as an approximation to \( \nu \) without considerable changes in the values of diffusion coefficients.

The constant \( c_{\text{act}} \) can be computed from Eq. (3) if for a given temperature \( T_i \) the self diffusion coefficient \( D_i \) is known as:

\[ c_{\text{act}} = -kT_i B_i \Omega_i \ln \frac{D_i}{a_i^2 \nu_0}. \]  

(4)

When \( c_{\text{act}} \) is calculated, the diffusion coefficients \( D_i \) at any temperature \( T = T_i \) can be estimated from Eq. (3) if the appropriate values \( B_i \) and \( \Omega_i \) at each temperature \( T_i \) are known.

### 3 Data and analysis

Here, by using the values of elastic parameters obtained from analytical relations that have been recently deduced (Sarkar et al., 2009), we proceed to the estimation of the self diffusion coefficients of MgO in temperatures prevailing in the lower mantle (1800–2500) K, and for which experimental data are available (Yang and Flynn, 1994). Thus, the values of the bulk modulus \( B \) listed in Table 1 are the reported ones by Sarkar et al. (2009) in their Fig. 7, which were derived by means of the following analytical formulas on the basis of Murnaghan’s equation of state and Tallon’s model. Precisely, Murnaghan’s first and second order approximations for the temperature dependence of the elastic modulus \( C_{ij} \) (Murnaghan, 1944) are given by Eqs. (5) and (6), respectively, as

\[ C_{ij}(T) = [1 + \alpha_D (T - T_D)] + \frac{1}{2} \alpha_D^2 \delta_{ij} (T - T_D)^2 \delta_{ij} \]  

(5)

\[ C_{ij}(T) = [1 + \alpha_D (T - T_D)] + \frac{1}{2} \alpha_D^2 \delta_{ij} (T - T_D)^2 + \frac{1}{3} \alpha_D^3 \delta_{ij} (T - T_D)^3 \]  

(6)

where \( \alpha_D \) is the volume thermal expansion coefficient at initial temperature \( T_D \) close to Debye temperature and \( \delta_{ij} \)

\[ \delta_{ij} = -\left( \frac{\partial C_{ij}}{\partial T} \right)_P \]  

the Anderson Gruneisen parameter associated with the elastic modulus \( C_{ij} \), while Tallon’s equivalent first and second order approximations (Tallon, 1995) are given by Eqs. (7) and (8), respectively,

\[ C_{ij}(T) = \exp \left\{ -\delta_{ij} [\alpha_D (T - T_D)] + \frac{1}{2} \alpha_D^2 \delta_{ij} (T - T_D)^2 \right\} C_{ij0} \]  

(7)

and

\[ C_{ij}(T) = \exp \left\{ -\delta_{ij} [\alpha_D (T - T_D)] + \frac{1}{2} \alpha_D^2 \delta_{ij} (T - T_D)^2 \right\} C_{ij0} \]  

(8)

In the case of MgO and for the parameter values \( T_D = 900 \) K, \( \delta_{D} = 4.86, \alpha_D = 4.42 \times 10^{-5} \) K\(^{-1}\), \( \delta_{11} = 5.38 \) and \( \delta_{144} = 2.49 \), Eqs. (6) and (8) lead to the values of bulk modulus (Fig. 7 of Sarkar et al., 2009) which are also presented in Tables 1 and 2. We remind that \( B = (C_{11} + 2C_{12})/3 \).

### Table 1. The values a, \( \Omega \), \( B \), calculated \( (D_{\text{calc}}) \) and experimental \( (D_{\text{exper}}) \) diffusion coefficients along with their errors for the temperature range (1820–2500) K and for \( c_{(1820)} = 0.7243 \).

<table>
<thead>
<tr>
<th>( T )</th>
<th>( 10^{-8} \text{ cm} )</th>
<th>( 10^{-24} \text{ cm}^2 \text{ s}^{-1} )</th>
<th>( B )</th>
<th>( D_{\text{calc}} )</th>
<th>( D_{\text{exper}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1820</td>
<td>4.399</td>
<td>10.651</td>
<td>116.1</td>
<td>( 1.00 \pm 1.91 \times 10^{-17} )</td>
<td>( 1.00 \pm 0.58 \times 10^{-17} )</td>
</tr>
<tr>
<td>1900</td>
<td>4.409</td>
<td>10.713</td>
<td>114.1</td>
<td>( 6.44 \pm 1.12 \times 10^{-17} )</td>
<td>( 5.01 \pm 2.93 \times 10^{-17} )</td>
</tr>
<tr>
<td>1950</td>
<td>4.416</td>
<td>10.764</td>
<td>112.2</td>
<td>( 2.27 \pm 3.76 \times 10^{-16} )</td>
<td>( 1.26 \pm 0.73 \times 10^{-16} )</td>
</tr>
<tr>
<td>2000</td>
<td>4.422</td>
<td>10.808</td>
<td>111.0</td>
<td>( 6.34 \pm 9.96 \times 10^{-16} )</td>
<td>( 3.98 \pm 3.22 \times 10^{-16} )</td>
</tr>
<tr>
<td>2100</td>
<td>4.435</td>
<td>10.904</td>
<td>108.2</td>
<td>( 4.69 \pm 6.61 \times 10^{-15} )</td>
<td>( 2.51 \pm 1.07 \times 10^{-15} )</td>
</tr>
<tr>
<td>2350</td>
<td>4.468</td>
<td>11.149</td>
<td>101.0</td>
<td>( 3.64 \pm 4.10 \times 10^{-13} )</td>
<td>( 1.00 \pm 0.58 \times 10^{-13} )</td>
</tr>
<tr>
<td>2500</td>
<td>4.488</td>
<td>11.996</td>
<td>96.0</td>
<td>( 3.95 \pm 3.87 \times 10^{-12} )</td>
<td>( 1.00 \pm 0.58 \times 10^{-12} )</td>
</tr>
</tbody>
</table>
Table 2. The values a, c, calculated (D_calculated) and experimental (D_experimental) diffusion coefficients along with their errors for the temperature range (1820–2500) K and for c_{act mean} = 0.7422.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>a (10^{-8} cm)</th>
<th>c (10^{-24} cm^3)</th>
<th>B (GPa)</th>
<th>D_calculated (cm^2 s^{-1})</th>
<th>D_experimental (cm^2 s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1820</td>
<td>4.399</td>
<td>10.641</td>
<td>116.1</td>
<td>0.40_{+1.59}^{−0.75} × 10^{-17}</td>
<td>1.00_{+0.58}^{−0.37} × 10^{-17}</td>
</tr>
<tr>
<td>1900</td>
<td>4.409</td>
<td>10.713</td>
<td>114.1</td>
<td>2.79_{+5.10}^{−1.80} × 10^{-17}</td>
<td>5.01_{+2.93}^{−0.85} × 10^{-17}</td>
</tr>
<tr>
<td>1950</td>
<td>4.416</td>
<td>10.764</td>
<td>112.2</td>
<td>1.02_{+1.75}^{−0.65} × 10^{-16}</td>
<td>1.26_{+0.73}^{−0.47} × 10^{-16}</td>
</tr>
<tr>
<td>2000</td>
<td>4.422</td>
<td>10.808</td>
<td>111.0</td>
<td>2.91_{+4.76}^{−1.81} × 10^{-16}</td>
<td>3.96_{+2.32}^{−0.47} × 10^{-16}</td>
</tr>
<tr>
<td>2100</td>
<td>4.435</td>
<td>10.904</td>
<td>108.2</td>
<td>2.26_{+3.34}^{−1.36} × 10^{-15}</td>
<td>2.51_{+1.07}^{−0.93} × 10^{-15}</td>
</tr>
<tr>
<td>2350</td>
<td>4.468</td>
<td>11.149</td>
<td>101.0</td>
<td>1.95_{+2.28}^{−1.05} × 10^{-13}</td>
<td>1.00_{+0.58}^{−0.37} × 10^{-13}</td>
</tr>
<tr>
<td>2500</td>
<td>4.488</td>
<td>11.299</td>
<td>96.0</td>
<td>2.25_{+2.28}^{−1.15} × 10^{-12}</td>
<td>1.00_{+0.58}^{−0.37} × 10^{-12}</td>
</tr>
</tbody>
</table>

The lattice constant at ambient conditions is considered as a_0 = 4.20 × 10^{-8} cm (Geneste et al., 2009), the atomic volume Ω_0 = (a_0/2)^3 = 9.261 × 10^{-24} cm^3, the constant f = 0.78, while the Debye temperature Θ_D = 927.4 K (Zhao et al., 2007) and consequently v_D = 19.315 × 10^{12} s^{-1}. The linear thermal expansion coefficient for T = 300 K (i.e., 31.2 × 10^{-6} K^{-1}) is taken from Table 1 of Anderson and Zou (1990). The values of a and Ω at different temperatures in the range (1800–2500) K are listed in Tables 1 and 2.

For the estimation of the constant c_{act}, we inserted in Eq. (4) for the lower temperature T = 1820 K the corresponding values (Table 1): a_{(1820)} = 4.399 × 10^{-8} cm, Ω_{(1820)} = 10.641 × 10^{-24} cm^3, B_{(1820)} = 116.1 GPa (Sarkar et al., 2009) and D_{(1820)} = 1 × 10^{-17} cm^2 s^{-1} (Yang and Flynn, 1994 in their Fig. 1) and we obtained c_{act} = 0.7243. Alternatively, we can apply Eq. (4) for all temperatures and associated data listed in Table 2 and get the mean value of c_{act mean} = 0.7422. Since c_{act} is known, the diffusion coefficients are calculated from Eq. (3) and the derived values D_calculated along with their errors (resulting from the uncertainties in the calculation of B and c_{act}) as well the experimental ones D_experimental (Yang and Flynn, 1994 in their Fig. 1) are shown in Table 1 for c_{act} = 0.7243 and Table 2 for c_{act mean} = 0.7422. Plots of log D versus 1/T, which were obtained either for c_{act} = 0.7243 or for the mean value c_{act mean} = 0.7422, are presented in Fig. 1a and b, respectively. Our calculated diffusion coefficients D_calculated reveal a very close accord with experimental ones D_experimental. The observed slight discrepancy at the highest temperature lies within the errors limits when the mean value c_{act mean} is considered (Table 2), while this difference in the case of c_{act} for the lower temperature (T = 1820) is slightly beyond the error range (see Table 1). We note that D_calculated span a broad range of values (i.e., 5 orders of magnitude). Thus, the possibility to estimate, from a single measurement, the diffusion coefficients at different temperatures is of significant importance. Direct measurements of diffusion parameters are extremely difficult to obtain, especially at high temperatures and pressures required to model Earth's interior. However, with the above-mentioned analytical formulas and the c B Ω thermodynamic model, which interrelates defect point parameters to bulk properties, the diffusion coefficients can be successfully predicted at mantle's temperature conditions.

Fig. 1. Temperature dependence of the self diffusion coefficient of O in MgO. Red triangles denote the calculated data and blue dots the experimental ones. (a) for c_{act} = 0.7243 at the lowest T = 1820 K and (b) for the mean value c_{act mean} = 0.7422.
4 Conclusions

The self-diffusion coefficients of MgO at temperatures representative of the Earth’s mantle conditions, can be successfully predicted from the combination of a thermodynamic model which interconnects defect parameters to bulk properties and from analytical formulas through which elastic data can be obtained.

Although the calculated diffusion coefficients are estimated from a single measurement and cover a broad range of values (i.e. five orders of magnitude), an almost excellent agreement with the experimental ones is observed. The slight discrepancy at the highest temperature lies at error margins.

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References