Diffusion of aluminum in MgO: A thermodynamic approach study*

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We have applied a thermodynamical model to calculate the diffusion coefficient of aluminum in MgO with the aid of bulk elastic properties. Our calculated diffusivities as a function of temperature and pressure are compared with the existing results derived from experimental or theoretical investigations. We find that the present model provides a satisfactory estimation for the activation volume and the activation enthalpy.

Keywords: MgO, diffusion, aluminum, $cB\Omega$ model

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1. Introduction

Periclase, MgO, is a material of key importance to Earth sciences and solid-state physics: it is one of the most abundant minerals in Earth's lower mantle and has the simplest structure (NaCl-type structure) for a large group of ionic oxides, thus it can serve as an excellent prototype for developing theoretical models of the physical properties of oxides.[1–6] In addition, MgO is frequently used as an industrial ceramic and especially as an ideal pressure standard in *in-situ* X-ray diffraction high pressure experiments[7–9] due to its wide pressure-temperature stability range.[10]

A detailed knowledge about the physical and chemical properties of MgO, particularly defect and diffusion, is crucial for our understanding of the mantle rheology, as the dominant deformation mechanism in the deep interior is thought to be diffusive in nature. The high-pressure high-temperature behaviors of MgO have long been a subject of great interest for experimental and theoretical investigations, the elasticity,[7–16] deformation,[17,18] defect structure,[2,4,5,19] diffusion,[1,3,6,20,21] and electrical conductivity[22,23] have been studied. Nevertheless, few experiments or theories have been carried out on the diffusion of cationic impurities in periclase at high-pressure and high-temperature. It should be noted that trivalent cations (e.g., Al^{3+}, Cr^{3+}, and Fe^{3+}) are significantly soluble in periclase,[24] and the cation diffusion is considerably more rapid in periclase than that in silicate perovskite.[21,25] As a consequence, periclase might enhance the bulk diffusive transport in Earth's lower mantle because the impurities directly control the diffusion process of the other species in periclase.

Van Orman *et al.*[21,26] reported experimentally determined aluminum diffusion coefficients in periclase at 1577–2273 K in the pressure range from 1 atm to 25 GPa. Their data suggested that cation vacancies are strongly attracted to Al in periclase and form bound pairs which have a strong influence on the Al diffusion. More recently, a first-principles calculation[27] has been performed on the diffusion of Al in periclase. Although the results of those different studies are roughly similar, the number of data points is very limited, especially at high pressure. In addition, neither experimental nor theoretical investigation has constrained well the pressure dependence of Al diffusion in MgO. In this study, a thermodynamic approach, as described previously,[28–30] is employed to examine whether the diffusion coefficient of aluminum in MgO can be successfully reproduced in terms of the bulk elastic and the expansivity data.

2. Theoretical consideration

Defect parameters can be directly estimated by using a macroscopic elastic thermodynamic model, the so-called $cB\Omega$ model, which interconnects the Gibbs energy g^i with the bulk expansivity and the elastic data of the solid through the relation[31–40]

$$g^i = c^i B\Omega, \tag{1}$$

where c^i is practically a constant which can be considered as independent of temperature and pressure to the first approximation,[36,41] B is the isothermal bulk modulus, and Ω is the mean atomic volume per atom. Superscript i in Eq. (1) refers to the defect process under consideration, i.e., i = f, act, and m, standing for formation, self-diffusion activation, and migration processes, respectively. The validity of the $cB\Omega$ model has been checked for different defect processes (i.e., formation, migration, and activation processes) in various categories of solids, including metals,[32,34,38,42]

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rare gas solids,[35,36] alkali and silver halides,[36,41,43,44] fluorides,[31,36,45,46] as well as diamond.[30,47] It is also found to satisfactorily provide a basis for the understanding of the compensation rules in carbon subgroup crystals[48] and the diffusivity-density scaling function for viscous liquids.[49] Furthermore, this model is successfully applied to refine the self-diffusion and heterodiffusion coefficients for silicate minerals of geophysical interest.[28–30,50–52]

For a single operating mechanism, the self-diffusion process at different temperature T is described in terms of activation Gibbs energy $g^{\rm act}$ as[53]

$$D = fa^2\nu \exp\left[-g^{\rm act}/(k_{\rm B}T)\right], \tag{2}$$

where f is a geometrical factor, a stands for the jump distance, ν is the jump frequency (usually taken to be the Debye frequency $\nu_{\rm D}$[36]), $k_{\rm B}$ is the Boltzmann constant, T is the absolute temperature, and $g^{\rm act}$ denotes the Gibbs free energy for the activation process.

Considering $g^{\rm act}$ is proportional to quantity $B\Omega$, by inserting Eq. (1) into Eq. (2), we have

$$D = fa^2\nu \exp\left[-c^{\rm act}B\Omega/(k_{\rm B}T)\right]. \tag{3}$$

Clearly, for a given temperature T_1 (or pressure P) and a constant pressure P (or temperature T), if the self-diffusion coefficient D_1 is known, the value of $c^{\rm act}$ can be estimated from the formula

$$c^{\rm act} = \frac{k_{\rm B}T_1}{B_1\Omega_1}\ln\frac{fa_1^2\nu_1}{D_1}, \tag{4}$$

where subscript 1 stands for the value of each quantity measured (a_1, ν_1, B_1, and Ω_1) at $T = T_1$ (or $P = P_1$). Once $c^{\rm act}$ is determined through Eq. (4), Eq. (3) permits the refinement of the diffusion coefficient D at any temperature (or pressure) provided that appropriate values of f, a, ν, B, and Ω corresponding to the temperature are available.

In the application of the above-mentioned method to the case of impurity diffusion (heterodiffusion), we must emphasize that the jump frequency ν depends roughly on the mass of the diffusant for a given matrix.[29,36,42,43,52] As a consequence, ν can be reasonably given by

$$\nu = \nu_{\rm D}(m_{\rm m}/m_{\rm i})^{1/2}, \tag{5}$$

where $\nu_{\rm D}$ denotes the Debye frequency of the host material, $m_{\rm m}$ and $m_{\rm i}$ represent the masses of the matrix and the diffusant, respectively. Henceforward, the resulting values of $c^{\rm act}$ and D can only be correctly calculated from Eqs. (3) and (4) through employing the appropriate ν determined from Eq. (5).

The accuracy of the calculated value of $c^{\rm act}$ relies on lots of parameters, such as diffusion data D_1 at T_1 and elastic properties (f, a, ν, B, and Ω). Among them, appropriate D_1 and T_1 are crucial for the accurate determination of $c^{\rm act}$ in Eq. (4). Several approaches have been proposed to obtain them, including the lowest[34,36,41–44] or highest[54] experimental temperature and an improved approach based on the compensation effect.[50–52] However, in this work, the most important constant $c^{\rm act}$ can be directly estimated by using the mean value method.[28–30] Another source of error is the determination of the Debye frequency. From a physical point of view, there are two kinds of Debye frequencies, one is the optic Debye frequency, the other refers to the acoustic one. Although these two frequencies are not equal to each other for most silicate minerals, the recent studies[28,30] have verified that the value of $c^{\rm act}$ merely yields a small change and the resultant refined diffusivities remain within the experimental uncertainties even if the optic Debye frequency was replaced by the acoustic one in Eqs. (4) and (5). A major challenge in the precise refinement of diffusion coefficients arises from the errors associated with the experimental elastic and expansivity data (especially B and Ω) of minerals. The bulk properties of minerals, such as compressibility and expansivity, are frequently determined by experimental studies in quite limited temperature and pressure ranges, and thus the extrapolation of these available bulk properties to relative higher or lower temperatures of geological interest is required in practical application. Unfortunately, such an extrapolation can easily introduce additional uncertainty in the framework of the $cB\Omega$ model, because the bulk properties of minerals (especially volume V and isothermal bulk modulus B) often vary with the temperature and pressure in a nonlinear manner at relatively lower temperatures and near the melting point.[26,30,36,50]

3. Results and discussion

In order to check the validity of the $cB\Omega$ model for aluminum diffusion in MgO, we will reproduce both temperature and pressure dependences of diffusion coefficient reported by Van Orman *et al.*[21,26] in periclase at 1577–2273 K and from 1 atm to 25 GPa. First of all, we have to determine the value of $c^{\rm act}$ in Eq. (4). For the reason of brevity, ambient pressure data[26] are taken as an example to show how the value of $c^{\rm act}$ can be calculated. At isobaric conditions of $P = 1$ atm, each experimental temperature (see Table 1 of Ref. [26]) is used to calculate the corresponding expansivity and elastic data (a, B, and Ω) based on the equation of state (EOS) of MgO.[8,9,55] The frequency ν is estimated from Eq. (5) in terms of the experimental Debye temperature.[11] By inserting all elastic properties and the known diffusion data (listed in Table 1) into Eq. (4) for each T with $f = 0.75$,[36] we finally get a mean value $c^{\rm act}_{\rm mean} = 0.3281(\pm 0.0080)$. The same procedures can also be applied to calculate the mean value of $c^{\rm act}$ at other confined pressures (for instance 15 GPa and 25 GPa) provided that the necessary bulk elastic and experimental diffusion data are available.

Table 1. Elastic data, experimental ($D_{\rm exp}$) and calculated ($D_{\rm calc}$) diffusion coefficients of Al in MgO at atmospheric pressure along with their errors for different temperatures.

T/K	a[8]/Å	B[55]/GPa	Ω[9]/Å^3	$D_{\rm exp}$[26]/m$^2\cdot$s^{-1}	$D_{\rm calc}$/m$^2\cdot$s^{-1}
1577	4.2629	122.7920	9.7819	$5.52^{+1.07}_{-1.07}\times10^{-14}$	$3.98^{+2.43}_{-1.21}\times10^{-14}$
1578	4.2630	122.7616	9.7823	$6.78^{+3.47}_{-3.47}\times10^{-14}$	$4.04^{+3.36}_{-2.54}\times10^{-14}$
1670	4.2658	119.9657	9.8146	$1.46^{+0.37}_{-0.37}\times10^{-13}$	$1.52^{+1.97}_{-0.83}\times10^{-13}$
1673	4.2659	119.8745	9.8156	$1.81^{+1.19}_{-1.19}\times10^{-13}$	$1.58^{+2.01}_{-1.32}\times10^{-13}$
1674	4.2660	119.8441	9.8159	$2.02^{+0.58}_{-0.58}\times10^{-13}$	$1.60^{+2.47}_{-1.02}\times10^{-13}$
1767	4.2689	117.0179	9.8486	$3.11^{+1.80}_{-1.80}\times10^{-13}$	$5.27^{+4.69}_{-2.62}\times10^{-13}$
1768	4.2689	116.9875	9.8498	$3.23^{+0.64}_{-0.64}\times10^{-13}$	$5.34^{+4.51}_{-2.71}\times10^{-13}$

Once $c^{\rm act}$ is known, we can proceed to calculate the diffusion coefficient $D_{\rm calc}$ from Eq. (3) using the approximate elastic and expansivity data listed in Table 1 for each temperature. The resulting values of $D_{\rm calc}$ are presented in Table 1 along with their errors arising from the uncertainties of B, Ω, ν, and $c^{\rm act}$.

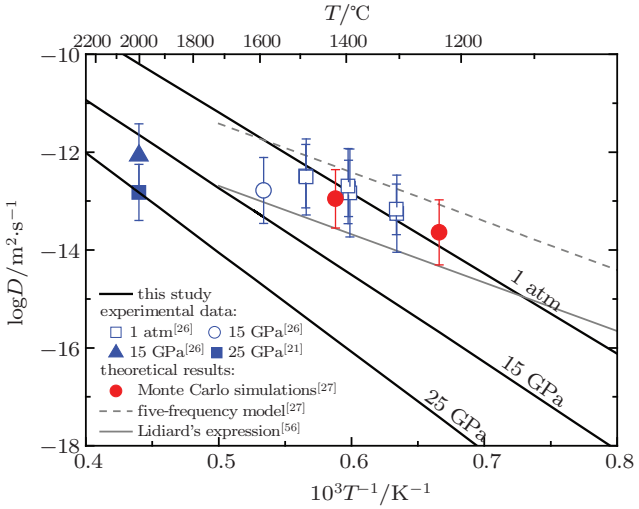


Fig. 1. (color online) Comparison of the calculated temperature dependence of Al diffusion in MgO via the $cB\Omega$ model with the experimental and theoretical data.

Figure 1 shows a comparison of the present calculations with the available data for the temperature dependence of Al diffusion in periclase. It is evident that not only the experimental results at ambient and high pressures (15 GPa and 25 GPa)[21,26] but also the theoretical calculations[27] are in good agreement with our predictions. However, we note that the theoretically computed diffusion coefficients of Al at ambient pressure using the five-frequency model[27] (the gray dashed line in Fig. 1) and the Lidiard's expression[56] (the gray line in Fig. 1) are by one order higher or lower than our thermodynamic calculations, respectively, as well as the experimental reports.[21,26] This discrepancy may be caused by the complicated diffusion mechanisms of Al and Al-vacancy association in periclase (for details see Refs. [26] and [27]). In particular, the theoretical investigations[27,56] have demonstrated that the diffusion coefficient of Al has a complicated dependence on the Al concentration. Unfortunately, the $cB\Omega$ model cannot give any direct explanation for the aforementioned phenomena (i.e., diffusion mechanism and concentration dependence).[29,50,51]

We proceed to calculate the pressure dependence of D. As an example, the elastic data (a, B, and Ω) and the experimental values of $D_{\rm exp}$ along with their errors for various pressures at $T = 2273$ K are given in Table 2. We apply Eq. (4) for all data at 15 GPa and 25 GPa, leading to a mean value $c^{\rm act}_{\rm mean} = 0.2984(\pm0.0134)$. By employing a similar procedure for other temperatures, we can obtain the corresponding values of $c^{\rm act}$. As a result, the satisfactory agreement between our predictions and the experimental/theoretical investigations implies that the present thermodynamic model is successful for calculating the pressure variation of D, as shown in Fig. 2 and Table 2. In addition, if differentiating Eq. (1) with respect to pressure and considering the definition of activation volume $\upsilon^{\rm act} = -(\partial g^{\rm act}/\partial P)_T$, we can write the activation volume as $\upsilon^{\rm act}(P,T) = -k_{\rm B}T(\partial \ln D/\partial P)_T$. Here, $(\partial \ln D/\partial P)_T$ is directly determined through the slop of $\ln D$ versus P plot (for additional details see p. 126 of Ref. [36] and our previous discussion[29,30,51]). Consequently, our calculated $\upsilon^{\rm act}$ at 2273 K is 3.53 ± 0.05 cm^3/mol, which is fairly comparable to that estimated experimentally (3.22 ± 0.25 cm^3/mol).[21,26]

We now turn to the estimation of the activation enthalpy for Al diffusion in periclase based on the $cB\Omega$ model. Note that, when $c^{\rm act}$ is known, the activation enthalpy can be directly calculated at any temperature from the relation[57,58]

$$h^{\rm act} = c^{\rm act}\Omega\left(B - T\beta B - T\left.\frac{{\rm d}B}{{\rm d}T}\right|_P\right), \qquad (6)$$

which immediately results from the definition of the defect enthalpy ($h^{\rm act} = g^{\rm act} - T({\rm d}g^{\rm act}/{\rm d}T)|_P$) by introducing Eq. (1), where β is the thermal (volume) expansion coefficient. For example, at $T = 2273$ K and $P = 1$ atm, by inserting $c^{\rm act} = 0.3281$, $\Omega = 10.026\times10^{-24}$ cm^3,[9] $\beta = 3.16\times10^{-5}$ K^{-1},[55] $B = 101.641$ GPa,[55] and $(\partial B/\partial T)_P = -0.023$ GPa/K[14] into Eq. (5), we find $h^{\rm act} = 2.91$ eV. This value is higher than the experimental value 2.21 eV reported by Van Orman *et al.*[26] and the first-principles calculation result 2.56 eV,[27] but close to the theoretical value 2.71 eV.[19] The difference in the activation enthalpy $h^{\rm act}$ (the activation volume $\upsilon^{\rm act}$) between our calculation and the experimental/theoretical works might be arisen from the anharmonic effects.[4,30,36,54] Especially, at relatively lower temperatures and near the melting point, this

phenomenon becomes clear and more important, because the bulk properties of minerals (volume V and isothermal bulk modulus B) often change with temperature and pressure in a nonlinear manner.[36] As a consequence, such anharmonic properties would introduce additional uncertainties into the present calculations, as our calculated results of T and P dependences of $D_{\rm calc}$, $h^{\rm act}$, and $\upsilon^{\rm act}$ in the framework of the $cB\Omega$ model do not consider anharmonicities which may be present.

Table 2. Elastic data, experimental ($D_{\rm exp}$), calculated ($D_{\rm calc}$), and theoretical ($D_{\rm theor}$) diffusion coefficients of Al in MgO for different pressures at $T = 2273$ K along with their errors.

P/GPa	a[8]/Å	B[55]/GPa	Ω[9]/Å^3	$D_{\rm exp}$[21]/m$^2\cdot$s^{-1}	$D_{\rm calc}$/m$^2\cdot$s^{-1}	$D_{\rm theor}$[27]/m$^2\cdot$s^{-1}
0	4.2847	102.6262	10.2152	–	$1.26^{+1.37}_{-0.84}\times10^{-10}$	–
15	4.1852	165.1814	9.2133	$0.85^{+0.10}_{-0.10}\times10^{-12}$	$1.34^{+2.36}_{-1.51}\times10^{-12}$	$2.36^{+2.51}_{-1.48}\times10^{-12}$
25	4.1189	206.8823	8.7285	$1.50^{+0.13}_{-0.13}\times10^{-13}$	$0.87^{+0.67}_{-0.36}\times10^{-13}$	$1.25^{+2.42}_{-1.35}\times10^{-13}$
40	4.0194	269.4336	8.2471	–	$1.58^{+2.47}_{-1.24}\times10^{-15}$	–
60	3.8867	352.8354	8.0750	–	$3.81^{+2.59}_{-1.27}\times10^{-18}$	–

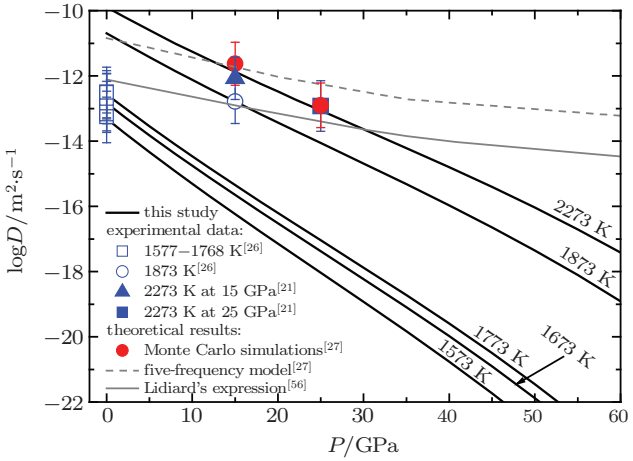


Fig. 2. (color online) Comparison of the calculated pressure dependence of Al diffusion in MgO via the $cB\Omega$ model with the experimental and theoretical data.

4. Summary

The thermodynamic calculated diffusion coefficient of aluminum in periclase is presented as a function of temperature and pressure. The quantitative agreements between our predictions and the experimental/theoretical data show that such a model is capable of adequately describing the aluminum diffusion in periclase over a wide range of temperature and pressure (up to 60 GPa). We also show that, despite a small difference, the estimated activation volume and enthalpy are comparable to the known ones when errors are taken into account.

The major difficulty associated with the meaningful calculation of the diffusivity of impurity-Al in the MgO host crystal is that the diffusion of cations has a strong dependence on the Al concentration.[21,26] Unlike the case of self-diffusion, within the framework of the $cB\Omega$ thermodynamic model, it is not possible to account for this dependence, because the mechanism of Al-vacancy association in periclase is quite complicated.[19,26,27] On the other hand, as stated previously,[29,30,36,51] the validity of the $cB\Omega$ model largely depends on the estimation of uncertainties including the bulk elastic and expansivity data, the Debye frequency, and the accuracy of the calculated value of $c^{\rm act}$. In addition, the effect of anharmonicities on the bulk properties may induce potential uncertainties for the present thermodynamic calculation. This needs further investigation.

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