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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 $cB\Omega$ 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:

$$g_i = c_i B\Omega \tag{1}$$

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, Ω 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

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

T K	a 10^{-8} cm	Ω 10^{-24} cm^3	B GPa	D_{calc} cm^2 s^{-1}	D_{exper} cm^2 s^{-1}
1820	4.399	10.641	116.1	$1.00^{+1.91}_{-0.57} \times 10^{-17}$	$1.00^{+0.58}_{-0.37} \times 10^{-17}$
1900	4.409	10.713	114.1	$6.44^{+11.2}_{-4.11} \times 10^{-17}$	$5.01^{+2.93}_{-1.85} \times 10^{-17}$
1950	4.416	10.764	112.2	$2.27^{+3.76}_{-1.41} \times 10^{-16}$	$1.26^{+0.73}_{-0.47} \times 10^{-16}$
2000	4.422	10.808	111.0	$6.34^{+9.96}_{-3.88} \times 10^{-16}$	$3.98^{+2.32}_{-1.47} \times 10^{-16}$
2100	4.435	10.904	108.2	$4.69^{+6.61}_{-2.75} \times 10^{-15}$	$2.51^{+1.07}_{-0.93} \times 10^{-15}$
2350	4.468	11.149	101.0	$3.64^{+4.09}_{-1.93} \times 10^{-13}$	$1.00^{+0.58}_{-0.37} \times 10^{-13}$
2500	4.488	11.299	96.0	$3.95^{+3.87}_{-1.96} \times 10^{-12}$	$1.00^{+0.58}_{-0.37} \times 10^{-12}$

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,

$$D = f \mathrm{a}^2 \nu \exp(-g_{\mathrm{act}}/k_B T) \tag{2}$$

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

$$D = f \mathrm{a}^2 \nu_{\mathrm{D}} \exp(-c_{\mathrm{act}} B \Omega / k_B T). \tag{3}$$

We note that the Debye frequency ν_{D} and the attempt frequency ν are of the same order of magnitude, and thus ν_{D} can be used as an approximation to ν without considerable changes in the values of diffusion coefficients.

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

$$c_{\mathrm{act}} = -\frac{kT_i}{B_i \Omega_i} \ln \frac{D_i}{f \mathrm{a}_i^2 \nu_{\mathrm{D}}}. \tag{4}$$

When c_{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 Ω_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

$$\begin{aligned} C_{ij}(T) = {} & [1 + \alpha_{\mathrm{D}}(T - T_{\mathrm{D}}) + \\ & 1/2\alpha_{\mathrm{D}}^2 \delta_{ij} (T - T_{\mathrm{D}})^2]^{-\delta ij} C_{ij0} \end{aligned} \tag{5}$$

$$\begin{aligned} C_{ij}(T) = {} & [1 + \alpha_{\mathrm{D}}(T - T_{\mathrm{D}}) + 1/2\alpha_{\mathrm{D}}^2 \delta_{ij} (T - T_{\mathrm{D}})^2 \\ & + 1/3\alpha_{\mathrm{D}}^3 \delta_{ij}^2 (T - T_{\mathrm{D}})^3]^{-\delta ij} C_{ij0}]^{-\delta ij} C_{ij0} \end{aligned} \tag{6}$$

where α_{D} is the volume thermal expansion coefficient at initial temperature T_{D} close to Debye temperature and $\delta_{ij} = -\frac{1}{\alpha C_{ij}} (\frac{\partial C_{ij}}{\partial T})\Big|_P$ 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,

$$\begin{aligned} C_{ij}(T) = {} & \\ & \exp\{ - \delta_{ij} [\alpha_{\mathrm{D}}(T - T_{\mathrm{D}})) + 1/2\alpha_{\mathrm{D}}^2 \delta_{ij} (T - T_{\mathrm{D}})^2]\} C_{ij0} \end{aligned} \tag{7}$$

and

$$\begin{aligned} C_{ij}(T) = {} & \exp\{ - \delta_{ij} [\alpha_{\mathrm{D}}(T - T_{\mathrm{D}}) + 1/2\alpha_{\mathrm{D}}^2 \delta_{ij} (T - T_{\mathrm{D}})^2 \\ & + 1/3\alpha_{\mathrm{D}}^3 \delta_{ij}^2 (T - T_{\mathrm{D}})^3]\} C_{ij0}. \end{aligned} \tag{8}$$

In the case of MgO and for the parameter values $T_{\mathrm{D}} = 900\,\mathrm{K}$, $\delta_T^{\mathrm{D}} = 4.86$, $\alpha_{\mathrm{D}} = 4.42 \times 10^{-5}\,\mathrm{K}^{-1}$, $\delta_{11} = 5.38$ and $\delta_{44} = 2.49$, 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 $B = (C11 + 2C12)/3$.

Table 2. The values a, Ω, B, calculated (D_{calc}) and experimental (D_{exper}) diffusion coefficients along with their errors for the temperature range (1820–2500) K and for $c_{\mathrm{act}}^{\mathrm{mean}} = 0.7422$.

T K	a 10^{-8} cm	Ω 10^{-24} cm^3	B GPa	D_{calc} cm^2 s^{-1}	D_{exper} cm^2 s^{-1}
1820	4.399	10.641	116.1	$0.40^{+1.59}_{-0.27} \times 10^{-17}$	$1.00^{+0.58}_{-0.37} \times 10^{-17}$
1900	4.409	10.713	114.1	$2.79^{+5.10}_{-1.80} \times 10^{-17}$	$5.01^{+2.93}_{-1.85} \times 10^{-17}$
1950	4.416	10.764	112.2	$1.02^{+1.75}_{-0.65} \times 10^{-16}$	$1.26^{+0.73}_{-0.47} \times 10^{-16}$
2000	4.422	10.808	111.0	$2.91^{+4.76}_{-1.81} \times 10^{-16}$	$3.98^{+2.32}_{-1.47} \times 10^{-16}$
2100	4.435	10.904	108.2	$2.26^{+3.34}_{-1.36} \times 10^{-15}$	$2.51^{+1.07}_{-0.93} \times 10^{-15}$
2350	4.468	11.149	101.0	$1.95^{+2.28}_{-1.05} \times 10^{-13}$	$1.00^{+0.58}_{-0.37} \times 10^{-13}$
2500	4.488	11.299	96.0	$2.25^{+2.28}_{-1.15} \times 10^{-12}$	$1.00^{+0.58}_{-0.37} \times 10^{-12}$

The lattice constant at ambient conditions is considered as $a_0 = 4.20 \times 10^{-8}$ cm (Geneste et al., 2009), the atomic volume $\Omega_0 = (a_0/2)^3 = 9.261 \times 10^{-24}$ cm^3, the constant $f = 0.78$, while the Debye temperature $\Theta_D = 927.4$ K (Zhao et al., 2007) and consequently $\nu_D = 19.315 \times 10^{12}$ 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): $a_{(1820)} = 4.399 \times 10^{-8}$ cm, $\Omega_{(1820)} = 10.641 \times 10^{-24}$ cm^3, $B_{(1820)} = 116.1$ GPa (Sarkar et al., 2009) and $D_{(1820)} = 1 \times 10^{-17}$ cm^2 s^{-1} (Yang and Flynn, 1994 in their Fig. 1) and we obtained $c_{\mathrm{act}} = 0.7243$. Alternatively, we can apply Eq. (4) for all temperatures and associated data listed in Table 2 and get the mean value of $c_{\mathrm{act}}^{\mathrm{mean}} = 0.7422$. Since c_{act} is known, the diffusion coefficients are calculated from Eq. (3) and the derived values D_{calc} along with their errors (resulting from the uncertainties in the calculation of B and c_{act}) as well the experimental ones D_{exp} (Yang and Flynn, 1994 in their Fig. 1) are shown in Table 1 for $c_{\mathrm{act}} = 0.7243$ and Table 2 for $c_{\mathrm{act}}^{\mathrm{mean}} = 0.7422$. Plots of $\log D$ versus $1/T$, which were obtained either for $c_{\mathrm{act}} = 0.7243$ or for the mean value $c_{\mathrm{act}}^{\mathrm{mean}} = 0.7422$, are presented in Fig. 1a and b, respectively. Our calculated diffusion coefficients D_{calc} reveal a very close accord with experimental ones D_{exp}. The observed slight discrepancy at the highest temperature lies within the errors limits when the mean value $c_{\mathrm{act}}^{\mathrm{mean}}$ 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_{calc} 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 $cB\Omega$ thermodynamic model, which interrelates defect point parameters to bulk properties, the diffusion coefficients can be successfully predicted at mantle's temperature conditions.

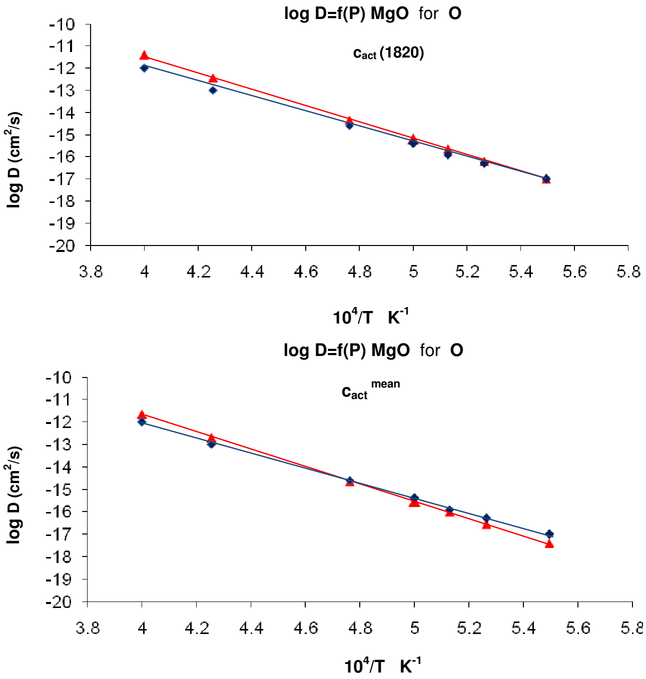

Fig. 1. Temperature dependence of the self diffusion coefficient of O in MgO. Red triangles denote the calculated data and blue dots the experimental ones. **(a)** for $c_{\mathrm{act}} = 0.7243$ at the lowest $T = 1820$ K and **(b)** for the mean value $c_{\mathrm{act}}^{\mathrm{mean}} = 0.7422$.

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

Anderson, O. L.: Equation of State of Solids for Geophysics and Ceramic Science, Oxford University Press, Oxford, 1995.

Anderson, O. L. and Isaak, D. G.: Mineral Physics and Crystallography: A Hand Book of Physical Constants, American Geophysical Union, Washington DC, 2, 64 pp., 1995.

Anderson, O. L. and Zou, K.: Thermodynamic Functions and Properties of MgO at High Compression and High Temperature, J. Phys. Chem. Ref. Data, 19, 69–82, 1990.

Geneste, G., Hayoun, M., Finocchi, F., and Morillo, J.: Competing mechanisms in the atomic diffusion of a MgO admolecule on the MgO(001) surface, J. Phys. Condens. Matter, 21, 315004–315010, 2009.

Murnaghan, F. D.: The Compressibility of Media under Extreme Pressures, Proceedings of the National Academy of Sciences of the United States of America, 30, 224–247, doi:10.1073/pnas.30.9.244, 1944.

Sarkar, B. M., Verma, A. S., and Gupta, R. C.: Temperature dependence of elastic constants for ionic solids, Physica B, 404, 4106–4110, 2009.

Tallon, J. L.: The thermodynamics of elastic deformation – Equation of state for solids, J. Phys. Chem. Solids, 41, 837, doi:10.1016/0022-3697(80)90028-1, 1980.

Varotsos, P.: Comments on the formation entropy of a Frenkel defect in BaF_2 and CaF_2, Phys. Rev. B, 13, 938, doi:10.1103/PhysRevB.13.938, 1976.

Varotsos, P. A.: Temperature and Pressure Dependence of Defect Formation Volume in Ionic Crystals, J. Phys., 38, L455–L458, 1977.

Varotsos, P.: On the Temperature Variation of the Bulk Modulus of Mixed Alkali Halides, Phys. Status Solid. B, 99, K93–K96, 1980.

Varotsos, P.: Comparison of Models that Interconnect Point Defect Parameters in Solids with Bulk Properties, J. Appl. Phys., 101, 123503, doi:10.1063/1.2745359, 2007.

Varotsos, P. and Alexopoulos, K.: Calculation of the formation entropy of vacancies due to anharmonic effects, Phys. Rev. B, 15, 4111–4114, 1977.

Varotsos, P. and Alexopoulos, K.: The Curvature in Conductivity Plots of Silver Halides as a Consequence of Anharmonicity, J. Phys. Chem. Solids, 39, 759–761, 1978.

Varotsos, P. and Alexopoulos, K.: On the possibility of the enthalpy of a Schottky defect decreasing with increasing temperature, J. Phys. C, 12, L761–L764, 1979.

Varotsos, P. and Alexopoulos, K.: Calculation of Diffusion Coefficients at Any Temperature and Pressure from a Single Measurement: I. Self-Diffusion, Phys. Rev. B, 22, 3130–3134, 1980a.

Varotsos, P. and Alexopoulos, K.: Prediction of the Compressibility of Mixed Alkali Halides, J. Phys. Chem. Solids, 41, 1291–1294, 1980b.

Varotsos, P. and Alexopoulos, K.: Physical properties of the variations of the electric field of the earth preceding earthquakes, I, Tectonophysics, 110, 73–98, 1984a.

Varotsos, P. and Alexopoulos, K.: Physical properties of the variations of the electric field of the earth preceding earthquakes, II. Determination of epicentre and magnitude, Tectonophysics, 110, 99–125, 1984b.

Varotsos, P. and Alexopoulos, K.: Connection between the formation volume and formation Gibbs energy in noble gas solids, Phys. Rev. B, 30, 7305–7306, 1984c.

Varotsos, P. and Alexopoulos, K.: Thermodynamics of Point Defects and Their Relation With the Bulk Properties, North-Holland, Amsterdam, 1986.

Varotsos, P. and Lazaridou, M.: Latest aspects of earthquake prediction in Greece based on seismic electric signals, I, Tectonophysics, 188, 321–347, 1991.

Varotsos, P., Ludwig, W., and Alexopoulos, K.: Calculation of the Formation Volume of Vacancies in Solids, Phys. Rev. B, 18, 2683–2691, 1978.

Varotsos, P., Alexopoulos, K., Nomicos, K., and Lazaridou, M.: Earthquake prediction and electric signals, Nature, 322, 120, doi:10.1038/322120a0, 1986.

Varotsos, P., Alexopoulos, K., and Lazaridou M.: Latest aspects of earthquake earthquake prediction in Greece based on Seismic Electric Signals II, Tectonophysics, 224, 1–37, 1993.

Varotsos, P. A., Sarlis, N. V., and Skordas, E. S.: Long-range correlations in the electric signals that precede rupture, Phys. Rev. E, 66, 011902, doi:10.1103/PhysRevE.66.011902, 2002.

Varotsos, P. A., Sarlis, N. V., and Skordas, E. S.: Long-range correlations in the electric signals that precede rupture: further investigations, Phys. Rev. E, 67, 13 pp., 2003a.

Varotsos, P. A., Sarlis, N., and Skordas, E.: Attempt to distinguish electric signals of a dichotomous nature, Phys. Rev. E., 68, 7 pp., 2003b.

Varotsos, P. A., Sarlis, N., Skordas, E., Tanaka, H., and Lazaridou, M.: Entropy of seismic electric signals: analysis in natural time under time reversal, Phys. Rev. E, 73, 031114, doi:10.1103/PhysRevE.73.031114, 2006a.

Varotsos, P. A., Sarlis, N., Skordas, E., Tanaka, H., and Lazaridou, M.: Attempt to distinguish long-range temporal correlations from the statistics of the increments by natural time analysis, Phys. Rev. E, 74, 12 pp., 2006b.

Yang, M. H. and Flynn, C. P.: Intrinsic Diffusion Properties of an Oxide: MgO, Phys. Rev. Lett., 73, 1809–1812, 1994.

Zhao, J. Z., Lu, L. Y, Chen, X. R., and Bai, Y. L.: First-principles calculations for elastic properties of the rocksalt structure MgO, Physica B, 387, 245–249, 2007.