



Additional studies on heterodiffusion coefficients in periclase

E. Dologlou

Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, Zografos 157 84 Athens, Greece

Correspondence to: E. Dologlou (edologl@phys.uoa.gr)

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Abstract. By using a thermodynamical model, the activation entropy is extracted from the experimental diffusion data of Al in MgO. Furthermore, we estimate the activation volume. We find a value for the activation entropy of $(4.21 \pm 0.05) \text{ k}$. As for the activation volume, we calculate the value $(3.65 \pm 0.16) \text{ cm}^3 \text{ mol}^{-1}$ which is comparable with the experimental values when errors are considered.

1 Introduction

Periclase (MgO) is of great geophysical interest since it is the second major and abundant mineral of the Earth's mantle. It has been extensively studied (Ita and Cohen, 1997; Yang and Flynn, 1994; Van Orman and al., 2003, 2009; Amman et al., 2012) for a better understanding of chemical exchange mechanism and diffusivity under pressure and temperature conditions prevailing in the lower mantle. A large number of experimental data (Dewaele and Fiquet, 2000; Jacobsen et al., 2008; Hirose et al., 2008) serve to validate various theoretical models (Oganov and Dorogokupets, 2003; Wu et al., 2008) on thermodynamic properties of MgO, but significant discrepancies have been reported between experimental and theoretical findings.

Here we show that a thermodynamical model which interrelates point defect parameters to bulk and elastic properties, allows to extract from experimental diffusion data, the activation entropy and also theoretically estimate the activation volume. As an application we consider the heterodiffusion of Al in MgO, and the resulting activation volume was found to be in agreement with reported ones.

2 Thermodynamical model

According to a thermodynamical model, known as $cB\Omega$, the Gibbs activation energy g^{act} is interconnected to the

isothermal bulk modulus B through the relation (Varotsos, 1976; Varotsos and Alexopoulos, 1977a; 1986; Varotsos et al., 1978)

$$g^{\text{act}} = c^{\text{act}} B \Omega \quad (1)$$

where Ω is the mean atomic volume per atom and c^{act} is a constant considered as independent of pressure and temperature. The above equation also holds for different process mechanisms (e.g. formation and migration) and has been tested in various cases such as in alkali and silver halides (Varotsos and Alexopoulos, 1977b, 1982), in lead fluorides (Varotsos, 2008), in diamonds (Varotsos, 2007a) in metals (Alexopoulos and Varotsos, 1981; Varotsos and Ludwig, 1978) etc. Furthermore, it has been shown to account for the thermodynamic parameters for the defect activation in ionic solids (Varotsos et al., 1999) upon increasing the pressure. This is of profound importance in describing the emission of electric signals before fracture, which explains the electric signals before earthquakes (Varotsos and Alexopoulos, 1984a, b; Varotsos et al., 1986, 1993; Sarlis et al., 2008).

The activation entropy s^{act} is derived when Eq. (1) is introduced to the relation $s^{\text{act}} = -(dg^{\text{act}}/dT)_P$ as

$$s^{\text{act}} = -c^{\text{act}} \Omega \left[\beta B + \frac{\partial B}{\partial T} \Big|_P \right] \quad (2)$$

with β the volume thermal expansion coefficient and T the temperature while the combination of the thermodynamic relation $h^{\text{act}} = g^{\text{act}} - T (dg^{\text{act}}/dT)_P$ and Eq. (1) gives the activation enthalpy h^{act} :

$$h^{\text{act}} = c^{\text{act}} \Omega \left[B - T \beta B - T \frac{\partial B}{\partial T} \Big|_P \right]. \quad (3)$$

Thus, from Eqs. (2) and (3) we can estimate the activation entropy (Varotsos, 2007b, 2008) as

$$s^{\text{act}} = -\frac{\beta B + \frac{\partial B}{\partial T} \big|_P}{B - T\beta B - T\frac{\partial \beta B}{\partial T} \big|_P} h^{\text{act}}. \quad (4)$$

This entropy should not be confused with the entropy defined (Varotsos et al., 2003a) in a new time domain termed natural time (Varotsos et al., 2002, 2003b) which has been shown to be optimal (Abe et al., 2005) in extracting the maximum information possible from an evolving dynamic system.

On the other hand the activation volume v^{act} can be calculated by introducing Eq. (1) to the relation $v^{\text{act}} = dg^{\text{act}}/dP$ which results in

$$v^{\text{act}} = \frac{(\frac{\partial B}{\partial P} - 1)}{B} g^{\text{act}} \quad (5)$$

3 Results and discussion

In order to test the credibility of the above thermodynamical model, we proceed to the estimation of the activation entropy and activation volume, based on experimental diffusion data of Al in MgO. We use the equation reported by Van Orman et al. (2009) activation energy $h^{\text{act}} = 213 \pm 32 \text{ kJ mol}^{-1} = 2.21 \text{ eV}$ which was extracted from experimental diffusion data of Al in MgO. We consider at $T = 2273$ and room pressure, $\beta = 3.16 \times 10^{-5} \text{ K}^{-1}$ (Fabrighnaya et al., 2004). The isothermal $B = 102.6 \text{ GPa}$ and the temperature derivative $(dB/dT)_P = (0.0301 \pm 0.0005) \text{ GPa K}^{-1}$ are obtained from Table 6 of Sushil (2005): the first from interpolation to the data for $P = 0$ and the second from the slope of these data. By inserting all the above relevant values in Eq. (4), we get for the activation entropy $s^{\text{act}} = (4.21 \pm 0.05) \text{ k}$. Concerning now the estimation of the activation volume, we use Eq. (5). The pressure derivative of B at $T = 2273 \text{ K}$ is obtained from Table 6 of Sushil (2005) as follows: first by interpolation to the B-values at 2000 K and 2500 K, we get the B-values at $T = 2273 \text{ K}$ for the pressure range (0–56.6) GPa (see Table 1); then from the slope of these interpolated values versus pressure (Fig. 1), we have $dB/dP = 3.8 \pm 0.1$. At last, considering that $g^{\text{act}} = h^{\text{act}} - T s^{\text{act}}$, we get through Eq. (5) $v^{\text{act}} = (3.65 \pm 0.16) \text{ cm}^3 \text{ mol}^{-1}$. This value, taking into account all uncertainties, is comparable with the reported one $(3.22 \pm 0.25) \text{ cm}^3 \text{ mol}^{-1}$ at $T = 2273 \text{ K}$ by Van Orman et al. (2009) and matches successfully a previously published one of $(3.5 \pm 0.5) \text{ cm}^3 \text{ mol}^{-1}$ (Van Orman et al., 2003), when errors are considered.

4 Conclusions

A thermodynamical model interrelating defect parameters to bulk and elastic expansivity data allows to extract from experimental diffusion data of Al in MgO the activation entropy

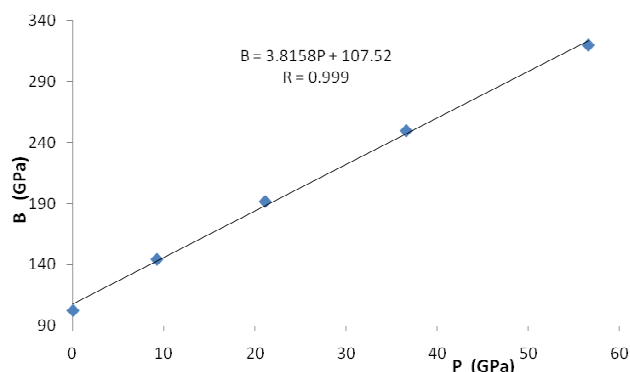


Fig. 1. The pressure dependence of isothermal bulk modulus B at $T = 2273$ for MgO with correlation coefficient $R = 0.999$, based on data listed in Table 1.

Table 1. Values of isothermal bulk modulus B (GPa) for MgO at different temperatures and pressures.

	P (GPa)		B (GPa)	
	2000 K*	2500 K*	2273 K**	
0	111	95.8	102.6	
9.21	151	139	144.5	
21.1	198	187	191.9	
36.6	256	245	249.9	
56.6	325	316	320	

* from Table 6 of Sushil (2005); ** from interpolation to columns 2 and 3.

and estimate the activation volume. We find, for the activation entropy, the value $(4.21 \pm 0.05) \text{ k}$ and, for the activation volume at $T = 2273 \text{ K}$, the value $(3.65 \pm 0.16) \text{ cm}^3 \text{ mol}^{-1}$ which is comparable with the experimental one when errors are considered.

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References

- Abe, S., Sarlis, N. V., Skordas, E. S., Tanaka, H. K., and Varotsos, P. A.: Origin of the usefulness of the natural time representation of complex time series, *Phys. Rev. Lett.*, 94, 170601, doi:10.1103/PhysRevLett.94.170601, 2005.
- Alexopoulos, K. and Varotsos, P.: Calculation of diffusion coefficients at any temperature and pressure from a single measurement, II Heterodiffusion, *Phys. Rev. B*, 24, 3606–3609, 1981.
- Ammann, M. W., Brodholt, J. P., and Dobson, D. P.: Diffusion of aluminium in MgO from first principles, *Phys. Chem. Minerals*, 39, 503–514, doi:10.1007/s00269-012-0506-z, 2012.
- Dewaele, A. and Fiquet, G.: P-V-T equation of state of periclase from synchrotron radiation measurements, *J. Geophys. Res.*, 105, 2869–2879, 2000.

- Fabrichnaya, O., Saxena, S. K., Richet, P., and Westrum, E. F.: Thermodynamic Data, Models, and Phase Diagrams in Multicomponent Oxide Systems, Springer, Berlin, 198 pp., 2004.
- Hirose, K., Sata, N., Komabayashi, T., and Ohishi, Y.: Simultaneous volume measurements of Au and MgO to 140 GPa and thermal equation of state of Au based on the MgO pressure scale, *Phys. Earth Planet. Int.*, 167, 149–154, 2008.
- Ita, J. and Cohen, R. E.: Effects of pressure on diffusion and vacancy formation in MgO from non-empirical free-energy integrations, *Phys. Rev. Lett.*, 79, 3198–3201, 1997.
- Jacobsen, S. D., Holl, C. M., Adams, K. A., Fischer, R. A., Martin, E. S., Bina, C. R., Lin, J. F., Prakapenka, V. B., Kubo, A., and Dera, P.: Compression of single-crystal magnesium oxide to 118 GPa and a ruby pressure gauge for helium pressure media, *American Mineralogist*, 93, 1823–1828, 2008.
- Oganov, A. R. and Dorogokupets, P. I.: All-electron and pseudopotential study of MgO: Equation of state, anharmonicity, and stability, *Phys. Rev. B*, 67, 224110, doi:10.1103/PhysRevB.67.224110, 2003.
- Sarlis, N. V., Skordas, E. S., Lazaridou, M. S., and Varotsos, P. A.: Investigation of the seismicity after the initiation of a Seismic Electric Signal activity until the main shock, *Proceedings of the Japan Academy, Ser. B*, 84, 331–343, 2008.
- Sushil, K.: Volume dependence of isothermal bulk modulus and thermal expansivity of MgO, *Physica B*, 367, 114–123, 2005.
- Van Orman, J. A., Fei, Y., Hauri, E. H., and Wang, J.: Diffusion in MgO at high pressures: constraints on deformation mechanisms and chemical transport at the core-mantle boundary, *Geophys. Res. Lett.*, 30, 1056, doi:10.1029/2002GL016343, 2003.
- Van Orman, J. A., Li, C., and Crispin, K.: Aluminum diffusion and Al-vacancy association in periclase, *Phys. Earth Planet. Int.*, 172, 34–42, doi:10.1016/j.pepi.2008.03.008, 2009.
- Varotsos, P.: Comments on the formation entropy of a Frenkel defect in BaF₂ and CaF₂, *Phys. Rev. B*, 13, 938, doi:10.1103/PhysRevB.13.938, 1976.
- Varotsos, P.: Calculation of point defect parameters in diamond, *Phys. Rev.*, 75, 172107, doi:10.1103/PhysRevB.75.172107, 3 pp., 2007a.
- 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, 2007b.
- Varotsos, P.: Point defect parameters in b-PbF₂ revisited, *Solid State Ionics*, 179, 438–441, 2008.
- Varotsos, P. and Alexopoulos, K.: Calculation of the formation entropy of vacancies due to anharmonic effects, *Phys. Rev. B*, 15, 4111–4114, doi:10.1103/PhysRevB.15.4111, 1977a.
- Varotsos, P. and Alexopoulos, K.: The curvature in conductivity plots of alkali halides as a consequence of anharmonicity, *J. Phys. Chem. Solids*, 38, 997–1001, 1977b.
- Varotsos, P. and Ludwig, W.: On a new analysis of the diffusion experiments under pressure, *J. Phys. C Solid State Phys.*, 11, L305–L309, 1978.
- Varotsos, P. and Alexopoulos, K.: Current methods of lattice defect analysis using dilatometry and self-diffusion. Critical review and proposals, *Phys. Stat. Sol.*, 110, 9–31, 1982.
- 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.: Thermodynamics of Point Defects and Their Relation With the Bulk Properties, North-Holland, Amsterdam, 1986.
- Varotsos, P., Ludwig, W., and Alexopoulos, K.: Calculation of the Formation Volume of Vacancies in Solids, *Phys. Rev. B*, 18, 2683–2691, doi:10.1103/PhysRevB.18.2683, 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., Lazaridou, M., and Nagao, T.: Earthquake predictions issued in Greece by Seismic Electric Signals since February 6, 1990, *Tectonophysics*, 224, 269–288, 1993.
- Varotsos, P., Sarlis, N., and Lazaridou, M.: Interconnection of defect parameters and stress-induced electric signals in ionic crystals, *Phys. Rev. B*, 59, 24–27, doi:10.1103/PhysRevB.59.24, 1999.
- 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, 7 pp., 2002.
- Varotsos, P. A., Sarlis, N. V., and Skordas, E. S.: Attempt to distinguish electric signals of a dichotomous nature, *Phys. Rev. E*, 68, 031106, 311061–311067, 2003a.
- 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, 021109, doi:10.1103/PhysRevE.67.021109, 2003b.
- Wu, Z. Q., Wentzcovitch, R. M., Umamoto, K., Li, B. S., Hirose, K., and Zheng, J. C.: Pressure-volume-temperature relations in MgO: An ultrahigh pressure-temperature scale for planetary sciences applications, *J. Geophys. Res.* 113, B06204, doi:10.1029/2007JB005275, 2008.
- Yang, M. H. and Flynn, C. P.: Intrinsic diffusion properties of an oxide: MgO, *Phys. Rev. Lett.*, 73, 1809–1812, 1994.