

# Estimation of diffusion coefficients of $\text{Cr}^{3+}$ and $\text{Ga}^{3+}$ in $\text{MgO}$ at temperatures of the Earth's lower mantle.

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**Abstract-** Here, we show that the diffusion coefficients of trivalent cations  $\text{Cr}^{3+}$  and  $\text{Ga}^{3+}$  in periclase can be theoretically predicted by means of a thermodynamic model, in a temperature range representative of the Earth's lower mantle conditions. Although severe discrepancies are reported between theoretical and experimental results, due to the complicated behaviour of trivalent ions, our theoretically calculated diffusion coefficients are compatible with recent experimental ones, in a range of values of almost four orders of magnitude.

**Index Terms-** Diffusion,  $\text{Cr}^{3+}$ ,  $\text{Ga}^{3+}$ , periclase, lower mantle,  $\text{MgO}$

## 1 INTRODUCTION

RHEOLOGY of the lower mantle characterizes the dynamics of the earth's interior and it is often controlled by diffusion processes in constituting minerals such as periclase ( $\text{MgO}$ ) which is a significant and the second in abundance component of the lower mantle. To gain a better understanding of kinetic mechanisms of underlying solid-state transport, diffusivity in  $\text{MgO}$ , plays an important role and contributes to clarify the physics, chemistry and geodynamics of the lower mantle of the Earth. Various experiments of self and hetero diffusion in  $\text{MgO}$  have been performed under temperature and pressure conditions dominating in the lower mantle [1], [2], [3], [4], [5], [6], [7]. Although simple vacancy diffusion studies in  $\text{MgO}$  showed a good agreement between

positively charged dopants block the availability of host vacancies and build pair vacancies which control diffusion process.

In this work, we investigate the temperature dependence of diffusivity of the trivalent cations  $\text{Cr}^{3+}$  and  $\text{Ga}^{3+}$  in  $\text{MgO}$  with the aid of a thermodynamic model and we compare our theoretical results to recent experimental ones.

## 2 THE THERMODYNAMICAL MODEL AND ITS APPLICATIONS

The model which interrelates point defect parameters to bulk elastic and expansivity data, termed as  $cB\Omega$ , gives the Gibbs energy  $g$  according to the formula [8], [9], [10], [11]:

$$g = c B \Omega \quad (1)$$

where 'i' stands for different process mechanisms (activation, formation, migration),  $B$  is the isothermal bulk modulus,  $\Omega$  the mean volume per atom and  $c$  a dimensionless constant, practically independent of temperature and pressure. This model has various successful applications such as in lead fluorides [12], in diamond [13] in metals [14], as well in the case of seismic electric signals preceding large earthquakes [15], [16], [17].

For a single operating mechanism the diffusion relation is given by

$$D = f a^2 v \exp(-g/k_B T) \quad (2)$$

where  $f$  is a numerical constant depending on the diffusion mechanism and the structure,  $a$  the lattice

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experimental and theoretical results, severe disagreement appears in the case of trivalent ions. The behaviour of trivalent ions is more complicated since Coulomb interactions between the magnesium vacancies and the

constant and  $\nu$  is the attempt frequency. For the latter quantity we consider that for a given matrix and mechanism it depends roughly on the mass of the diffusant. As an approximation, we accept the usual relation [10], [8], [18]

$$\nu / \nu_D = (m_m / m_j)^{1/2} \quad (3)$$

where  $m_m$  and  $m_j$  denote the mass of the matrix (m) and of the diffusant (j), respectively, and  $\nu_D$  is the Debye frequency. We note that the Debye frequency  $\nu_D$  can substitute the attempt frequency  $\nu$  in (2) without considerable changes in the values of diffusion coefficients, since both are of the same order of magnitude.

Thus, introducing (1) into (2) we can write :

$$D = f a^2 \nu \exp(-c^i B \Omega / k_B T) \quad (4)$$

The constant  $c^i$  is calculated from (4) if for a given temperature  $T$  the diffusion coefficient  $D$  is known, as :

$$c^i = - \frac{kT}{B \Omega} \ln \frac{D}{f a^2 \nu} \quad (5)$$

Since  $c^i$  is computed, we can estimate the diffusion coefficients  $D$  at any temperature  $T$  from (4) when the relevant values  $a$ ,  $B$  and  $\Omega$  at each temperature  $T$  are known.

### 3 DIFFUSIVITY OF $Cr^{3+}$

Using elastic and expansivity data for MgO reported by Sushil [19] we first calculate the diffusion coefficients of  $Cr^{3+}$  at temperature range  $T=(1573-2273)$  K and at pressure  $P=2$ GPa. We consider that at room conditions of pressure and temperature the lattice constant is  $a_0=4.20 \times 10^{-8}$ cm [20] and hence the atomic volume is  $\Omega_0= a_0^3/8=9.261 \times 10^{-24}$ cm<sup>3</sup>. The numerical constant is  $f=0.78$  and the attempt frequency is estimated from the Debye temperature  $\Theta_D=927.4$  [21] as  $\nu_D=19,315 \times 10^{12} \text{ s}^{-1} = 19,31 \text{ THz}$ . From (3) we find for Cr that  $\nu_{Cr}=13.65 \text{ THz}$ .

The values of  $\Omega(T,P)$  at the temperature range  $T= (1573-2273)$ K and at  $P=2$ GPa are calculated by multiple interpolations to the elastic and expansivity data of Sushil [19] and the results are listed in Table 1.

TABLE 1  
THE VALUES  $\Omega$ ,  $B$ , CALCULATED ( $D_{CAL}$ )  
AND EXPERIMENTAL ( $D_{EXP}$ )  
DIFFUSION COEFFICIENTS AT  $P=2$ GPa FOR  $Cr^{3+}$   
ALONG WITH THEIR ERRORS

T K	$\Omega(10^{-24}\text{cm}^3)$	B (GPa)	$D_{cal} (\text{m}^2/\text{s})$	$D_{exp} (\text{m}^2/\text{s})$
1573	9.6552	134.7	$1.20_{-0.07}^{+0.07} \times 10^{-13}$	$6.1_{-0.1}^{+0.1} \times 10^{-13}$
1873	9.7952	126.5	$0.84_{-0.04}^{+0.04} \times 10^{-13}$	$1.66_{-0.02}^{+0.02} \times 10^{-13}$
2073	9.8919	120.6	$7.26_{-0.37}^{+0.37} \times 10^{-13}$	$3.65_{-0.44}^{+0.44} \times 10^{-13}$
2273	9.9945	115.2	$4.53_{-0.40}^{+0.40} \times 10^{-13}$	$1.91_{-0.07}^{+0.07} \times 10^{-13}$

For example, the value  $\Omega(1573,2)$  is obtained as follows; first, from Table 3 of Sushil [19] for  $P=0$ , the quantity  $V(T,0)/V(300,0) = \Omega(T,0)/\Omega(300,0)$  for  $T=1500$ K leads to  $\Omega(1500,0) = 1.0527 \times 9.261 \times 10^{-24} \text{cm}^3 = 9.7490547 \times 10^{-24} \text{cm}^3$  and in analogy for  $T=2000$ K to  $\Omega(2000,0) = 10.0000278 \times 10^{-24} \text{cm}^3$ . Second, from Table 4 of Sushil [19] and for  $V(1500,9.21)/V(1500,0) = 0.9396$ , we get  $\Omega(1500,9.21) = 9.160211796 \times 10^{-24} \text{cm}^3$  and in a similar way  $\Omega(2000,9.21) = 9.33002593 \times 10^{-24} \text{cm}^3$ . Then from another interpolation to the above values in the pressure range (0-9.21) GPa we easily have  $\Omega(1500,2) = 9.621184363 \times 10^{-24} \text{cm}^3$  and  $\Omega(2000,2) = 9.854533367 \times 10^{-24} \text{cm}^3$ . Finally an interpolation between these two last values results to  $\Omega(1573, 2) = 9.6552 \times 10^{-24} \text{cm}^3$  (see Table 1).

Concerning now the isothermal  $B$  values we used the data of Table 6 of Sushil [19] for the pressure and temperature range (0-56.6) GPa and (1500-2500)K respectively. From interpolations to these data we first get the  $B$  values at temperatures (1573, 1873, 2073, 2273)K relevant to those of experimental diffusion data (Table 1 of Crispin and Orman [6]) in the pressure range (0-56.6) GPa. Then from plots of  $B$  versus pressure for each of the above temperatures, we estimate the value of the  $B$  at the corresponding temperature and at  $P=2$ GPa. The derived values are shown in Table1.

For the determination of the constant  $c^i$ , we can apply (5) for all temperatures and associated data listed in Table 1 for which experimental diffusion coefficients  $D_{exp}$  are available at  $P=2$ GPa (Table 1 of Crispin and Orman [6]) and we get (for  $D_{exp}= 1.66 \times 10^{-13} \text{m}^2/\text{s}$  at  $T=1873$ K) the mean value of  $c_{mean Cr}^i = 0.35392$ . We note that the other two experimental diffusion values  $D_{exp}$  at  $T=1873$ K lead to slightly different  $c_{mean Cr}^i$  and do not affect considerably the calculated  $D_{cal}$  diffusion coefficients, (see Fig. 1a,b and c).

Once  $c^i$  is computed, by inserting in (4) all the relevant values of  $a$ ,  $\Omega$  and  $B$  for each temperature, we calculate the diffusion coefficients  $D_{cal}$  for  $P=2$ GPa. The derived values  $D_{cal}$  along with their errors due to uncertainties  $\pm 3\%$ , in the estimation of  $B$ , as well as the experimental diffusion coefficients  $D_{exp}$ , are given in Table 1. Plots of  $\log D_{cal}$  versus  $1/T$  for the three different

$D_{exp}$  values at  $T=1873$  K (i.e.  $D_1=1.01 \times 10^{-13}$  m<sup>2</sup>/s,  $D_2=1.36 \times 10^{-13}$  m<sup>2</sup>/s and  $D_3=1.66 \times 10^{-13}$  m<sup>2</sup>/s) are shown in Fig.1a,b,c respectively. Red triangles denote calculated data while blue dots the experimental ones.

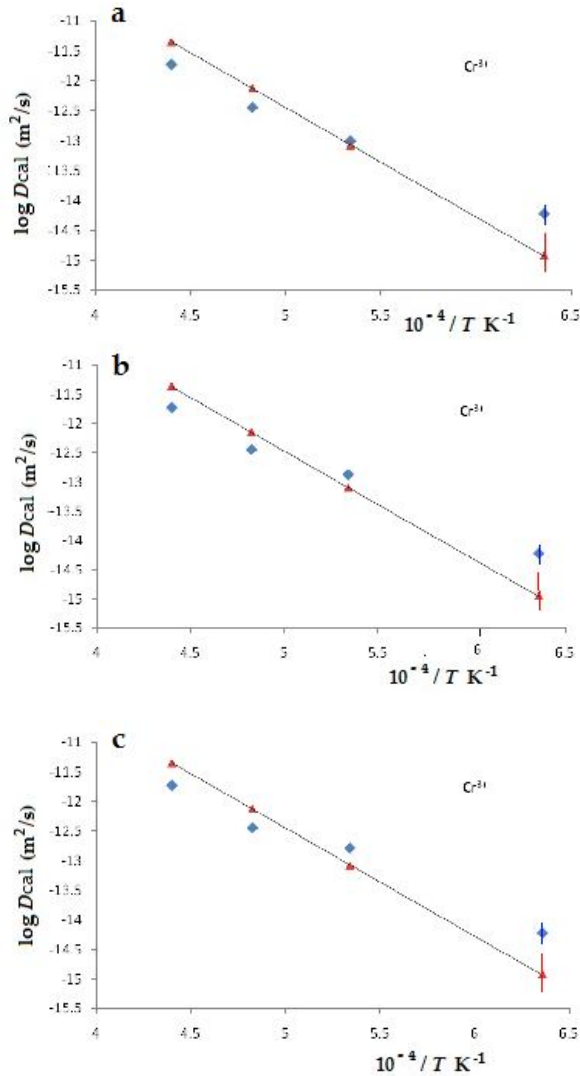


Fig.1 Temperature dependence of the diffusion coefficient of  $Cr^{3+}$  in MgO. Red triangles denote the calculated data and blue dots the experimental ones. **a.** for experimental  $D_1=1.01 \times 10^{-13}$  m<sup>2</sup>/s **b.** for experimental  $D_2=1.36 \times 10^{-13}$  m<sup>2</sup>/s and **c.** for experimental  $D_3=1.66 \times 10^{-13}$  m<sup>2</sup>/s. Vertical bars (red and blue) show the errors for  $D_{calc}$  and  $D_{exp}$  respectively, at the lowest temperature.

#### 4 DIFFUSIVITY OF $Ga^{3+}$

In the case of  $Ga^{3+}$  we calculate diffusion coefficients at room pressure and temperature range (1563-1783)K for which experimental diffusion data  $D_{exp}$  are available (Table 2 of Crispin and Orman [6]). The values of  $\alpha$  and  $\Omega$  at different temperatures and  $P=0$  GPa are again obtained by interpolation to the data of Table 3 of

Sushil [19] while the isothermal bulk modulus  $B$  by interpolation to the data of Table 6 of Sushil [19] in the temperature range (300-2500)K and at  $P=0$  GPa. All derived values are listed in Table 2.

TABLE 2  
THE VALUES  $\Omega$ ,  $B$ , CALCULATED ( $D_{CAL}$ ) AND EXPERIMENTAL ( $D_{EXP}$ ) DIFFUSION COEFFICIENTS FOR  $Ga^{3+}$  ALONG WITH THEIR ERRORS

T K	$\Omega(10^{-24}cm^3)$	B (GPa)	$D_{cal}(m^2/s)$	$D_{exp}(m^2/s)$
1563	9.7806	124.0	$0.25_{-0.11}^{+0.15} \times 10^{-13}$	$0.53_{-0.15}^{+0.13} \times 10^{-13}$
1678	9.8384	120.6	$1.25_{-0.37}^{+0.41} \times 10^{-13}$	$1.32_{-0.28}^{+0.24} \times 10^{-13}$
1777	9.8881	117.6	$4.26_{-1.55}^{+2.45} \times 10^{-13}$	$3.19_{-0.45}^{+0.42} \times 10^{-13}$
1782	9.8906	117.5	$4.49_{-1.44}^{+2.59} \times 10^{-13}$	$3.50_{-0.37}^{+0.37} \times 10^{-13}$
1783	9.8911	117.4	$4.59_{-1.44}^{+2.54} \times 10^{-13}$	$4.00_{-0.37}^{+0.35} \times 10^{-13}$

Following a similar procedure, and considering that  $\nu_{Ga}=12.01$  THz, we find for  $Ga^{3+}$  the value  $C_{mean Ga}=0.32096$  and through (4) we calculate the values  $D_{cal}$  which are shown in Table 2. A plot of  $\log D_{cal}$  versus  $1/T$  is presented in Fig.2 where red triangles denote the calculated data and blue dots the experimental ones while relevant errors are given by vertical bars.

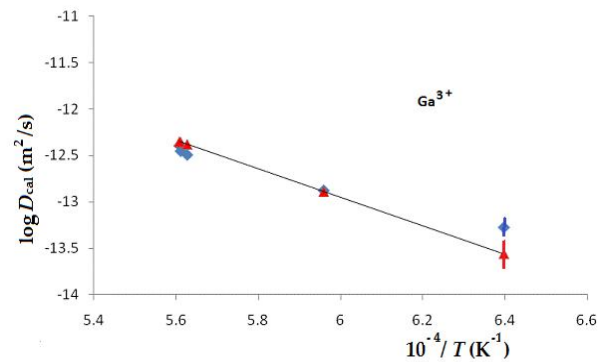


Fig.2 Temperature dependence of the diffusion coefficient of  $Ga^{3+}$  in MgO. Red triangles denote the calculated data and blue dots the experimental ones. Vertical bars (red and blue) show the errors for  $D_{calc}$  and  $D_{exp}$  respectively at the lowest temperature.

#### 5 DISCUSSION

The behaviour of trivalent ions, such as  $Cr^{3+}$  and  $Ga^{3+}$  is complicated compared to divalent impurities, due to interactions between the positively charged dopants and the magnesium vacancies, and thus leading to significant disagreement between theoretical and experimental results. Although, this study reveals from an inspection in Table 1, that despite of this

complexity, our predicted diffusion values  $D_{cal}$  for  $Cr^{3+}$  by means of the thermodynamic cBQ-model, are in reasonable agreement with the experimental ones  $D_{exp}$ , (Table 1 of Crispin and Orman [6]), when errors are included. It is worth to note that  $D_{exp}$  span a range of values of almost four orders of magnitude and deviations of the  $D_{cal}$  values for the middle temperatures are within the error limits and only for the edge temperatures lie just outside of the error margins. The origin of the discrepancies between theoretical and experimental diffusivity may be attributed to the fact that in theory the thermodynamic model has a simplistic approach and does not consider the full complexity of the problem.

On the other hand in the case of  $Ga^{3+}$  the results are significantly improved as it is obvious from

Table 2 and Fig. 2. There is a good agreement between calculated  $D_{cal}$  and experimental  $D_{exp}$  coefficients and all values are within error limits.

## 6 CONCLUSIONS

In this work, we show that the diffusion coefficients of trivalent cations  $Cr^{3+}$  and  $Ga^{3+}$  in MgO can be predicted theoretically by means of a thermodynamic model which interrelates point defect parameters and bulk properties, in a temperature range representative of the Earth's lower mantle conditions. Although the behaviour of trivalent ions is complicated, in the case of  $Cr^{3+}$  our theoretical diffusion results reasonably compare with recent experimental ones, in a range of values of almost four orders of magnitude, when errors are considered. The source of these differences may arise from the fact that in theory the thermodynamic model has a simplistic approach since it refers to a single operating mechanism and does not consider the full complexity of the problem. In contrast, in the case of  $Ga^{3+}$  there is a good agreement between our theoretically calculated and recent experimental diffusion coefficients and all values are within error limits.

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