



# The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics

Series 8

ISSN: 0031-8086 (Print) (Online) Journal homepage: <https://www.tandfonline.com/loi/tphm19>

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J. Rungis & A. J. Mortlock

To cite this article: J. Rungis & A. J. Mortlock (1966) The diffusion of calcium in magnesium oxide, The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics, 14:130, 821-827, DOI: [10.1080/14786436608211974](https://doi.org/10.1080/14786436608211974)

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Published online: 02 Sep 2006.



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## The Diffusion of Calcium in Magnesium Oxide

By J. RUNGIS† and A. J. MORTLOCK

Physics Department, Australian National University, Canberra

[Received 1 June 1966]

### ABSTRACT

The diffusion of  $\text{Ca}^{2+}$  at tracer concentrations in 99.99% pure single crystal MgO has been measured over the temperature range 900°C to 1700°C. It was found that the diffusion coefficient,  $D$ , could be expressed in the form :

$$D = (2.95 \pm 2.6) \times 10^{-5} \exp [-(2.13 \pm 0.1)/kT] \text{ cm}^2/\text{sec},$$

where  $k$  is Boltzmann's constant in  $\text{ev}/\text{K}^\circ$  and  $T$  is the absolute temperature.

The observed activation energy can be correlated with the corresponding data for other divalent ions diffusing in MgO through the equation :

$$Q = k_1 \left( \frac{r}{\alpha} \right) + k_2,$$

where  $r$  is the ionic radius in centimetres ;  $\alpha$  is the ionic electronic polarizability in cubic centimetres and  $k_1$  and  $k_2$  are equal to  $0.37 \times 10^{-16} \text{ ev cm}^2$  and 1.20 ev respectively.

### § 1. INTRODUCTION

FROM a consideration of measurements of the diffusion of the divalent metal ions  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  in single crystal magnesium oxide Wuensch and Vasilos (1962) proposed that a correlation existed between the logarithm of the observed activation energy and the ratio of the radius of the diffusing ion to its electronic polarizability. By applying a least-squares analysis to the above experimental data it is possible to express this correlation more simply by the linear relationship :

$$Q = k_1 \left( \frac{r}{\alpha} \right) + k_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $Q$  is the activation energy in electron volts ;  $r$  is the ionic radius in centimetres ;  $\alpha$  is the ionic electronic polarizability in cubic centimetres, and the constants  $k_1$  and  $k_2$  are equal to  $0.40 \times 10^{-16} \text{ ev cm}^2$  and 1.08 ev respectively.

It is of interest to see if this correlation can be extended to include other metal ions. This is so because, unlike the case of impurity diffusion in metals (Le Claire 1962), there are no correlations between observed diffusion parameters and atomic properties of the diffusing species in

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† Now at Department of Physics, University of Western Australia, Nedlands, Western Australia.

oxides which could form a basis for an improved understanding of the diffusion process. For this reason a series of measurements of impurity diffusion in MgO are being made with the intention of checking the general validity of eqn. (1). The first impurity to be studied in this regard is the non-transition metal ion  $\text{Ca}^{2+}$ , and the results obtained are reported in this paper.

## § 2. MATERIALS

The single crystals of MgO used were supplied by Monocrystals Co. of Cleveland, Ohio, in the form of right cylinders,  $\frac{1}{4}$  in. diameter by  $\frac{1}{4}$  in. long with a stated purity of 99.99%. The manufacturer's typical quantitative analysis of these crystals showed that the major impurities were Fe, Al and In, being present in concentrations of 25, 25, and 15 p.p.m. respectively. Other impurities listed were never present in concentrations in excess of 10 p.p.m. A separate qualitative spectrographic analysis of these crystals by the Defense Standards Laboratories, Melbourne, did not show any impurities to be present which were not already listed by the manufacturer.

## § 3. METHOD

In diffusion experiments of the type described here it is usual to deposit a thin layer of radioactive solute on the end face of the specimen, anneal for a fixed time,  $t$ , at a high temperature, and then determine the resulting concentration,  $C$ , versus penetration distance,  $x$ , profile by using one of the standard tracer techniques. Providing the surface concentration,  $C_s$ , of solute falls below the solubility limit and to a relatively low level in a time which is short compared to the total annealing time, then  $C$  and  $x$  are related by:

$$C = C_s \exp(-x^2/4Dt), \quad . . . . . (2)$$

and the diffusion coefficient  $D$  is easily found from a plot of  $\ln(C/C_s)$  versus  $x^2$ .

If the surface concentration does not fall below the solubility limit  $C_0$  throughout the entire annealing period then the penetration profile is defined by:

$$C = C_0 \operatorname{erfc}[x/2\sqrt{(Dt)}], \quad . . . . . (3)$$

This enables  $D$  to be found from a plot of  $\operatorname{erfc}^{-1}(C/C_0)$  versus  $x$  providing  $C_0$  can be found by backward extrapolation of the  $C$  versus  $x$  data to zero penetration. Should the experimental data be such that  $C_0$  is not easily calculable in this way then an alternative equation which is independent of  $C_0$  may be used. It is obtained by differentiating eqn. (3) to give:

$$\ln(-\partial C/\partial x) = -(x^2/4Dt) + \text{constant}. \quad . . . . . (4)$$

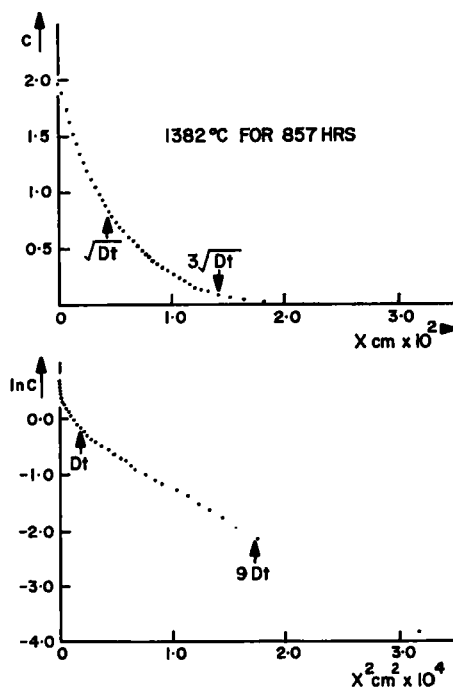
Unfortunately, unless the experimental data are sufficiently smooth the calculated values of the differential coefficient on the left-hand side may be subject to such a large scatter that this equation represents no real advantage in the analysis of the data.

Faced with these problems in the present case due to the low solubility of CaO in MgO (Doman *et al.* 1963) use was made of an analysis due to Mortlock (1964). Briefly, if the experimental data do in fact follow eqn. (3) then a plot of  $\ln(C/C_0)$  versus  $x^2$  will be curved. If a straight line is fitted to this curve over a limited range of  $x^2$  and an apparent diffusion coefficient  $D_a$  found from its slope as if eqn. (2) applied, then  $D_a$  is related to the correct value of  $D$ ,  $D_c$ , which operates in eqn. (3) by:

$$\frac{D_c}{D_a} = \sqrt{\left(\frac{D_c t}{\pi}\right)} \cdot \frac{2 \exp(-x^2/4D_c t)}{x \operatorname{erfc}[x/2\sqrt{(D_c t)}]} \quad (5)$$

This indicates that  $(D_c/D_a)$  is constant providing  $D_a$  is evaluated at the same effective value of  $x^2/D_c t$  in each experiment. In practice the range of  $x^2$  used in the least-squares calculation of  $D_a$  was kept fixed at from  $D_a t$  to  $9D_a t$  and the corresponding  $D_c$  values found by multiplying by the factor 1.64. This factor was found empirically by comparing the values of  $D_a$  and  $D_c$  calculated separately in a number of runs which, by virtue of the smoothness of the data, allowed eqn. (4) to be used as well as eqn. (2). A typical penetration profile which could be treated in this way is shown in fig. 1.

Fig. 1



Concentration versus penetration distance profile for the diffusion of  $\text{Ca}^{2+}$  in MgO at  $1382^\circ\text{C}$  plotted as  $C$  versus  $x$  and as  $\ln C$  versus  $x^2$ .

## § 4. EXPERIMENTAL DETAILS

The radioactive tracer employed in this work was  $^{45}\text{Ca}$  which decays with the emission of a 0.25 mev beta particle. Because of the low energy of this radiation quantitative autoradiography represented a convenient and accurate method of following the diffusion penetration.

The MgO crystals were cleaved parallel to their end faces to form two approximately equal-sized cylinders. An end face of each of these was lapped with diamond paste and onto one a few drops of radioactive  $^{45}\text{CaCl}_2$  solution was deposited. After drying the two polished faces were butted together to form a diffusion couple and held in this position by a loop of Pt/Rh alloy wire.

The diffusion annealings were carried out in air. After this heat treatment a flat face was either ground at right angles to the diffusion interface or cut with a diamond slitting wheel at a small angle  $\theta$  to the interface. This latter treatment was reserved for those cases where the diffusion penetration was small as the value of  $Dt$  apparent on the inclined face is increased by a factor of  $[\sin^2 \theta]^{-1}$  relative to that for a surface parallel to the specimen axis. This simple relationship derives from the geometry of the situation neglecting the small contribution to total film blackening due to radioactivity below the surface. After careful polishing of these faces the distribution of  $^{45}\text{Ca}$  on them was determined by standard autoradiographic procedures: see, for example, Mortlock and Tomlin (1959).

As in all such experiments some correction had to be made for the imperfect resolution of the technique due to the fact that even an undiffused couple will yield an autoradiographic image of finite breadth. In the present case the correction itself was represented by an effective value of the product  $Dt$ ,  $(Dt)_{\text{res}}$ , determined from the autoradiograph of an undiffused couple assuming an effective penetration profile following eqn. (2). This was subtracted in each case from the apparent  $Dt$  value found for the diffused couple. This technique is an extension of an idea due to Brown and Blackburn (1963).

Due to the fact that the undiffused profile was in fact only approximately represented by eqn. (2) this procedure yielded only a first approximation to the actual correction required. Also, the manner in which  $(Dt)_{\text{res}}$  is used here to represent the entire result of a simulated further annealing period is strictly only valid for gaussian penetration profiles described by eqn. (2). This is because further diffusion following eqn. (3) is influenced not only by gaussian spreading-out but by a flux of new material from the constant surface source which operates in this case.

Because of these uncertainties in this correction it was applied as described only in those cases where  $(Dt)_{\text{res}}$  did not exceed 10% of the observed value of  $Dt$ . In those cases where  $(Dt)_{\text{res}}$  exceeded this arbitrary limit the specimens were angle cut as described above to reduce this correction to below 10%. This was possible due to the short range of the beta radiation of  $^{45}\text{Ca}$ , which makes  $(Dt)_{\text{res}}$  effectively a measure of the

diffuseness of the autoradiographic image of a very narrow and thin strip source of radioactivity located at the specimen surface.  $(Dt)_{\text{res}}$  is therefore virtually independent of the actual distribution of radioactivity along the surface as any such distribution which varies in one dimension only can be thought of as broken up into parallel strips of this sort. Thus,  $(Dt)_{\text{res}}$  is independent of the angle of the inclined face yet the value of  $Dt$  apparent on this face is increased by a factor of  $[\sin^2 \theta]^{-1}$ : it follows that the corresponding percentage resolution correction is reduced on the inclined face by a factor of  $\sin^2 \theta$ . The general consistency of the calculated diffusion coefficients with each other in spite of quite large variations in the magnitude of the initial percentage resolution correction confirmed that the above procedure was a valid one.

### § 5. RESULTS

The table lists the diffusion coefficients obtained for Ca diffusing in MgO. Each of these coefficients is the mean of eight to ten results obtained from a series of transversely separated but parallel microphotometer scans of a single autoradiograph. A careful consideration of all sources of error, such as temperature measurement, angle of autoradiographed face, and assigned autoradiographic background level, indicated that each of these mean diffusion coefficients was subject to absolute error limits of approximately  $\pm 20\%$ .

Diffusion of Ca in MgO

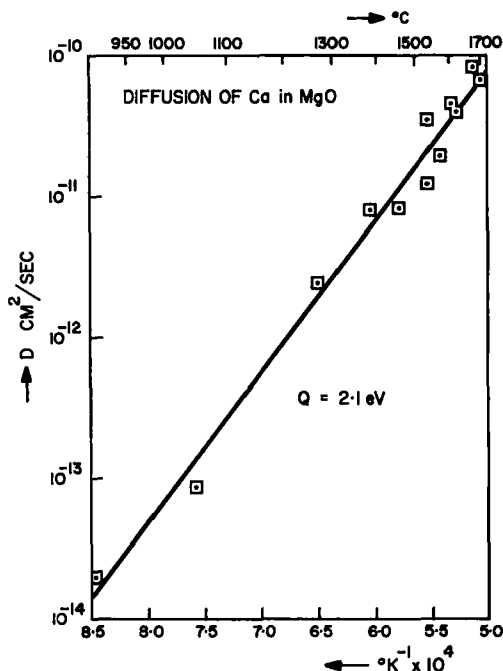
Temperature (°C)	Time (h)	Diffusion coefficient ( $D_0$ ) (cm <sup>2</sup> /sec)
910	3,168.0	$3.38 \times 10^{-14}$
1051	2,184.0	$1.44 \times 10^{-13}$
1270	754.0	$3.80 \times 10^{-12}$
1382	857.0	$1.30 \times 10^{-11}$
1458	738.0	1.35
1537	691.5	1.97
1544	426.0	5.63
1571	347.7	3.00
1604	192.0	7.23
1617	157.5	6.28
1676	169.0	$1.29 \times 10^{-10}$
1700	35.8	1.07

In fig. 2 these data are plotted as a graph of  $\log D_a$  versus  $(1/T)$ ,  $T$  being the absolute temperature. Fitting a straight line to the data on this basis yields the following equation expressing the temperature dependence

of  $D_c$  with the errors shown being standard errors based on the scatter of the tabulated coefficients:

$$D = D_c = (2.95^{+2.6}_{-1.5}) \times 10^{-5} \exp [-(2.13 \pm 0.1)/kT] \text{ cm}^2/\text{sec.} \quad (6)$$

Fig. 2



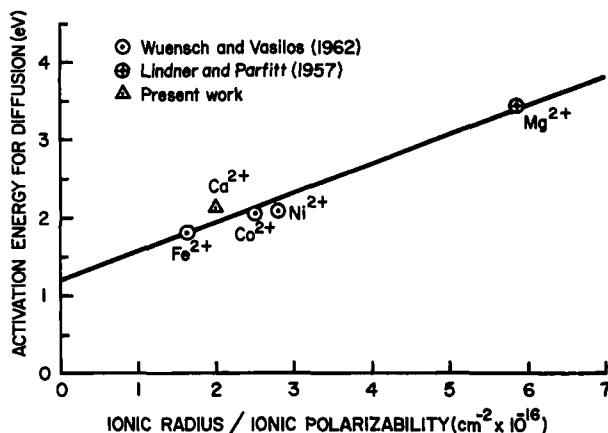
Arrhenius plot of experimental diffusion coefficients,  $D_a$ , for the diffusion of  $\text{Ca}^{2+}$  in  $\text{MgO}$ .

## § 6. DISCUSSION

Using available data for the ionic radius ( $1 \times 10^{-8} \text{ cm}$ ; Pauling 1960) and ionic electronic polarizability ( $0.5 \times 10^{-24} \text{ cm}^3$ ; Mott and Gurney 1940) of  $\text{Ca}^{2+}$ , the activation energy predicted by eqn. (1) for this ion is 1.9 eV, which is not inconsistent with the experimental result. If the present result is used with the earlier data as a basis for a re-calculation of eqn. (1) it is found that the new values for  $k_1$  and  $k_2$  are  $0.374 \times 10^{-16} \text{ eV cm}^2$  and 1.200 eV respectively. Figure 3 illustrates the satisfactory fit of the experimental data to the new straight line, but also points the need for additional experiments with other divalent ions to test the correlation further.

The question of the details of the diffusion mechanism which operates in the case of the divalent ions so far studied in  $\text{MgO}$  is still an open one. However, the fact that they exhibit activation energies consistent with each other suggests that they all diffuse by the same process. In this

Fig. 3



Correlation of activation energies for the diffusion of divalent ions in MgO with the parameter : ionic radius divided by ionic electronic polarizability.

connection it is of interest to note that Mitoff (1964) reports that MgO is predominantly an electronic conductor at temperatures  $\sim 1500^\circ\text{C}$  and predominantly an ionic conductor at temperatures  $\sim 1000^\circ\text{C}$ . It is to be expected therefore that there would be a change in the mechanism for cation diffusion with temperature. However, this is not reflected in the observed activation energy, which is constant over the temperature range  $900^\circ\text{C}$  to  $1700^\circ\text{C}$ .

#### ACKNOWLEDGMENTS

Thanks are due to Professor L. Slifkin of the University of North Carolina and Professor D. N. F. Dunbar of this University for useful comments. The investigation was supported by funds provided by The Australian Atomic Energy Commission.

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