

A computer simulation study of point defects in diopside and the self-diffusion of Mg and Ca by a vacancy mechanism

FERIDOON AZOUGH¹, ROBERT FREER¹, KATE WRIGHT² AND ROBERT JACKSON³

¹ Materials Science Centre, University of Manchester/UMIST, Grosvenor Street, Manchester M1 7HS, UK

² Department of Earth Sciences, University of Manchester, Oxford Road, Manchester M13 9PL, UK

³ Department of Chemistry, University of Keele, Keele, Staffordshire, ST5 5BG, UK

ABSTRACT

Computer simulation techniques have been used to investigate defect formation and the diffusion of Ca and Mg in diopside. It was found that isolated, non-interacting CaO and MgO Schottky defects had the lowest formation energies (3.66 and 3.97 eV respectively); oxygen Frenkel defects are the most favourable oxygen defects (formation energies 3.93 eV). Magnesium and calcium self-diffusion in the *c*-direction of diopside is easiest by a vacancy mechanism involving either direct jumps along the *c*-direction, or double jumps in the *b-c* plane. In the extrinsic regime, diffusion activation energies for Mg are predicted to be 9.82 eV (direct route) and 1.97 eV (double jump route); for Ca diffusion, activation energies are predicted to be 6.62 eV (direct route) and 5.63 eV (double jump route). If additional vacancies (oxygen or magnesium) are present in the vicinity of the diffusion path, Ca migration energies fall to 1.97–2.59 eV. At elevated temperatures in the intrinsic regime, diffusion activation energies of ≥ 5.95 eV are predicted for Mg self-diffusion and 9.29–10.28 eV for Ca self-diffusion. The values for Ca diffusion are comparable with published experimental data. It is inferred that a di-vacancy mechanism may operate in diopside crystals.

KEYWORDS: computer-simulation, point defects, diopside, vacancy mechanism, self-diffusion.

Introduction

THE importance of diffusion data to the understanding of kinetic processes and interpretation of the thermal history of the host rock has long been recognised for pyroxenes (e.g. Buseck *et al.*, 1980). For example, the calibration of mineral thermometers and barometers based on cation exchange depends critically on the availability of appropriate diffusion coefficients. Such systems include the garnet–clinopyroxene Al barometer, the two-pyroxene solvus thermometer (Ca–Mg exchange) and the garnet–clinopyroxene Fe–Mg exchange thermometer (e.g. Essene, 1989; Pattison and Tracy, 1991). It has become apparent that cation diffusion rates in pyroxene minerals are comparatively slow. Indeed, many of the early experimental studies yielded ‘null results’, which placed only upper bounds on individual diffusion

coefficients (Freer *et al.*, 1982). The subsequent availability of instruments such as the ion microprobe and α -particle Rutherford Backscattering facilities have enabled investigation of short, sub-micron diffusion profiles. In spite of these developments, there is still a paucity of directly determined, experimental diffusion data for diopside. The more recent studies include strontium and samarium diffusion (Sneeringer *et al.*, 1984), Al diffusion in diopside at 1180°C (Sautter *et al.*, 1988) and Ca diffusion at 1000–1380°C (Dimanov and Ingrin, 1995). The final investigation in this group also addressed premelting phenomena.

Within the last decade, computer simulation procedures based upon atomistic techniques have emerged as powerful and reliable methods to investigate the structures and dynamical properties of complex silicate minerals. Such methods

can have advantages over experimental studies where environments of very high temperature and pressure are of interest, or where processes are exceptionally sluggish (as in the case of diffusion in pyroxenes). Previous simulation studies of diopside have concentrated on the structure and thermodynamic behaviour (Patel *et al.*, 1991). In order to contribute to the understanding of diffusion processes in diopside, we have employed atomistic simulation techniques to examine point defects in diopside and the transport of Ca and Mg along the *c*-direction.

We begin by outlining the atomistic model used in our study, present results for a variety of Schottky and Frenkel defects and migration energies for the diffusion of major host cations by a vacancy mechanism. Comparison is made with the limited data from experimental studies.

Methodology

Computer simulation techniques have been successfully used to model the perfect and defective lattice properties of a wide range of geologically important materials (Catlow and Price, 1990), including magnetite (Lewis *et al.*, 1985), quartz (Leslie, 1989), Mg₂SiO₄ polymorphs (Price *et al.*, 1987), feldspar (Purton and Catlow, 1990; Patel *et al.*, 1991), perovskite (Wright and Price, 1993), OH defects in olivine (Wright and Catlow, 1994), and oxygen diffusion in grossular (Wright *et al.*, 1995). These methods employ an atomistic approach in which an interatomic potential function is defined to describe the energy of the system in terms of atomic positions. The lattice energy includes contributions from ionic, covalent, and van der Waals type bonding, but for ionic or semi-ionic solids the dominant component of the cohesive

energy, U_T , is the electrostatic or Coulombic term, U_c . Since the ions are not simple point charges, it is necessary to take into account the short range repulsive interactions, U_{ij} , produced by the overlap of nearest neighbour electron clouds. This latter component may be conveniently modelled by the pair potentials of the Buckingham form:

$$U_{ij} = \sum_{ij} A_{ij} \exp \left(-\frac{r_{ij}}{\rho_{ij}} \right) - C_{ij} r_{ij}^{-6} \quad (1)$$

where the parameters A , ρ and C may be determined by empirical fitting procedures or by theoretical methods using calculated energy surfaces. The shell model of Dick and Overhauser (1958) was used to simulate oxygen polarizability and a three-body term added to describe the directionality of O-Si-O bonds. The short range parameters for Ca-O and Mg-O (Lewis and Catlow, 1985) are based upon the empirical fitting of experimental data. The potential parameters used in the study are presented in Table 1.

The defect energy calculations were performed using the generalised Mott-Littleton approach (Mott and Littleton, 1938) available in the computer code CASCADE (Leslie, 1981). In this procedure, the crystal is divided into two concentric spherical regions. The inner region (1) contains the defect of interest at its centre; an explicit simulation is performed to adjust the co-ordinates of all ions within the region until they are at positions where no net forces act on them, i.e. they are relaxed around the defect. In the outer region (2), the effects of the defect are relatively weak and the relaxation is calculated essentially as the polarization response to the effective charge of the defect; a quasi-continuum approach is adopted

TABLE 1. Potential parameters used to simulate defects in diopside

Interaction	Buckingham potential			Ref.
	A (eV)	ρ (Å)	C (eV Å ⁶)	
Si ⁴⁺ -O ²⁻	1283.907	0.32052	10.66158	1
O ²⁻ -O ²⁻	22764.0	0.149	27.88	2
Ca ²⁺ -O ²⁻	1090.4	0.3437	0.0	2
Mg ²⁺ -O ²⁻	1428.50	0.29453	0.0	2

The short range potential cut-off was set to 9.75 Å

1. Sanders *et al.* (1984).
2. Lewis and Catlow (1985).

for calculations. An additional interface region (2A) is also employed in practice. The resulting defect energy is a measure of the perturbation by the defect of the static lattice energy of the crystal. It should be noted that in this approach no account is taken of zero-point energy, or indeed entropic effects. Further details of the methodology are given in Catlow (1986) and Lidiard (1989). In this study we mainly used a region 1 size of 8 Å, containing approximately 280 ions to evaluate the various defect configurations.

Results and discussion

Defects in diopside

At any temperature above 0 K, all crystals contain an equilibrium number of point defects (vacancies and interstitials) in the lattice. Such defects may be generated thermally (intrinsic) or in response to impurity species (extrinsic). For intrinsic defects, vacancies are charge-balanced by the formation of interstitials (of the same charge) or by equal and oppositely charged vacancies. The former case is termed Frenkel disorder; the formation energy of Frenkel defects is the sum of the individual vacancy and interstitial energies:

$$E_{\text{fr}} = V_n + n_i \quad (2)$$

where V denotes a vacancy of species n , and the subscript i denotes an interstitial of species n . The alternative arrangement in which there is the generation of charge-balanced vacancy defects is known as Schottky disorder. A 'genuine' stoichiometric Schottky defect in diopside would comprise one Ca vacancy, one Mg vacancy, two Si vacancies and six oxygen vacancies (one formula unit of diopside). However, forming one Ca vacancy and one O vacancy maintains charge neutrality but results in a local change in composition. Here the ions removed are assumed to form another phase on the surface. These nonstoichiometric defects therefore maintain the bulk stoichiometry of the system. The formation energy of a pseudo-Schottky defect (E_{ps}) is defined as the energy of the composite vacancy plus the lattice energy (U) of the phase removed to the crystal surface

$$E_{\text{ps}} = \sum_{j=1} N V_j + U \quad (3)$$

The intrinsic pseudo-Schottky and Frenkel defect formation energies are given in Table 2. In general they were calculated on the assumption that individual vacancies and interstitials were isolated and non-interacting. However, we have

TABLE 2. Defect formation energies in diopside (the numbers in brackets represent the energy per defect)

Defect	ΔE (eV)
V_{Ca}	20.41
V_{Mg}	26.31
V_{Si}	101.88
$V_{\text{O1}}, V_{\text{O2}}$	22.93
V_{O3}	25.27
Unbound pseudo-Schottky defects	
$\text{MgO}_1, \text{MgO}_2$	7.95 (3.97)
MgO_3	10.25 (5.13)
$\text{CaO}_1, \text{CaO}_2$	7.32 (3.66)
CaO_3	9.62 (4.81)
$\text{CaMgSi}_2\text{O}_6$	55.36 (5.536)
Unbound Frenkel defects	
$\text{Mg}_i + \text{Mg}_v$	10.71 (5.35)
$\text{Ca}_i + \text{Ca}_v$	12.00 (6.00)
$\text{O}_{1,2i} + \text{O}_{1,2v}$	7.85 (3.93)
$\text{O}_{3i} + \text{O}_{3v}$	10.17 (5.09)
Lattice energies	
CaO	-36.07
MgO	-41.33
SiO_2	-128.75
$\text{CaMgSi}_2\text{O}_6$	-337.56

Subscripts 1,2,3 refer to oxygen sites

i = interstitial

v = vacancy

also determined binding energies for CaO and MgO pseudo-Schottky defects. It is more helpful to compare the energy per defect, rather than the total balanced formation energies. It should also be noted that there are three inequivalent oxygen sites (O_1 , O_2 and O_3) in diopside; defects involving oxygen have been calculated for each of the three sites. Table 2 shows that the most favourable unbound pseudo-Schottky defect, with the lowest energy per point defect (3.66 eV), is predicted to be the CaO vacancy pair (involving O_1 or O_2), where the formation of a Ca vacancy is charge balanced by an accompanying O vacancy, and a unit of CaO is formed at the surface. The unbound pseudo-Schottky defects for Mg- O_1 and Mg- O_2 are only marginally more expensive in energy terms. The lowest energy interstitial defect is the oxygen Frenkel (3.93 eV). We have also determined the binding energy (ΔE_{B}) associated with the pseudo Schottky defects. For V_{CaO} , ΔE_{B}

$= -1.12$ eV for $\text{CaO}_{1,2}$ and $\Delta E_B = -2.44$ eV for CaO_3 , whilst for $\text{MgO}_{1,2}$ $\Delta E_B = -1.81$ eV. Thus the energy for both defects is less when they are bound.

Cation diffusion in diopside

Pyroxene minerals are densely packed structures. This fact and the calculated defect formation energies (Table 2) suggest that cation diffusion may operate by a vacancy mechanism, by which ions migrate by moving to successive vacant sites. To simulate diffusion of the primary cations Ca and Mg in diopside by this mechanism, two adjacent Ca vacancies (or Mg vacancies) were created in the lattice to represent the initial and final sites of the migrating ion; a Ca ion (or Mg ion) was then placed at fixed points between the two sites. At each point, the defect energy was calculated, and by repeating the processes it was possible to build a potential energy surface, enabling the saddle point for the jump to be determined.

Diopside has a well defined chain structure in which Mg and Ca ions are located in planes perpendicular to the a -axis (Fig. 1). It can be seen that the c -direction is the most favourable for the migration of both Mg and Ca. In the b -direction,

rows of Mg ions exist in the pathway of migrating Ca ions, and *vice versa* (Fig. 1). Similarly, diffusion of Ca and Mg in the a -direction is difficult since the ions would need to pass very close to, or through, SiO_4 tetrahedra. In this study we focus on cation diffusion in the more favourable c -direction. Figure 2 shows the structure of diopside normal to (100). The rows of Ca and Mg atoms parallel to the c -direction are clearly visible. For Ca or Mg to move along the c -direction, two alternative routes are available: either a direct single jump between successive sites (S) or a double jump between sites in adjacent rows (D1-D2) as shown in Fig. 2. The value of the migration energy (ΔE_m) for a particular route is found by subtracting the energy of the initial state (i.e. with one Ca or Mg vacancy present) from that of the activated state with the migrating ion at the saddle point. Plots of energy as a function of distance for Mg ions migrating via routes D1-D2 and S are shown in Fig. 3. It should be noted that the double jump is symmetrical, and only half the route is shown in Fig. 3. The values of ΔE_m for Ca migration are presented in Table 3. Both the direct route and double jump routes are associated with high migration energies (≥ 5.63 eV). Only when additional vacancies are introduced in the

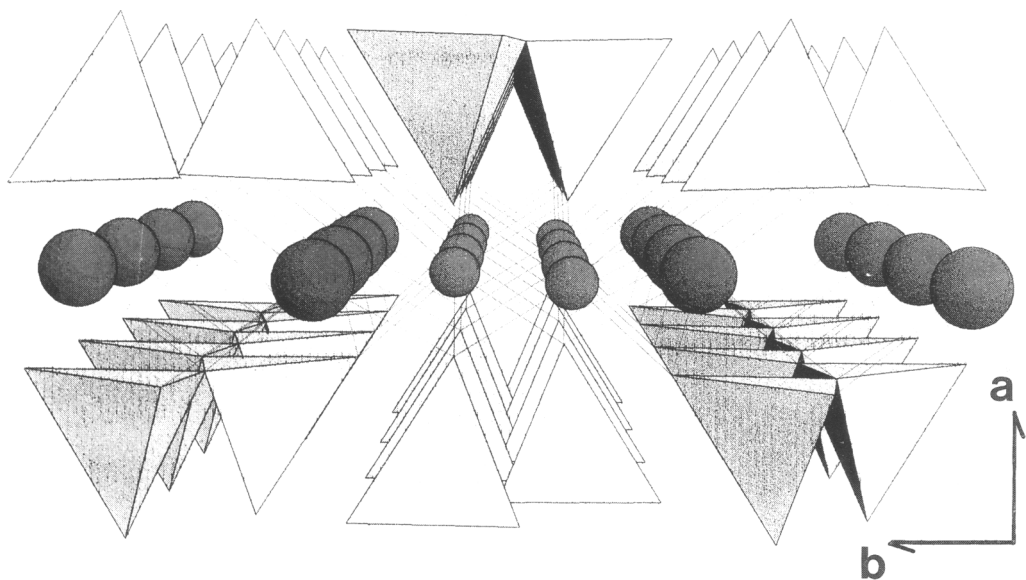


FIG. 1. The structure of diopside viewed along a direction normal to (001). The large circles represent Ca atoms and the small circles Mg atoms.

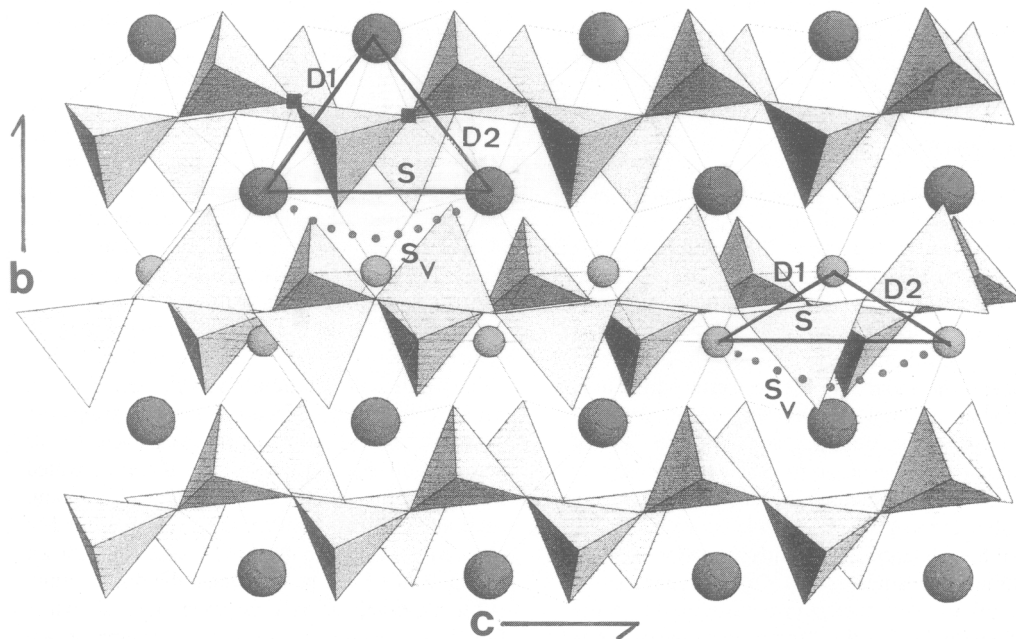


FIG. 2. The structure of diopside viewed along a direction normal to (100). The large circles represent Ca atoms and the small circles Mg atoms. The direct diffusion routes for Mg or Ca cations along the c -direction are indicated by S; the direct route with a Mg or Ca vacancy in the vicinity is denoted by S_v . The indirect double jump route is shown by D1-D2. The location of selected oxygen vacancies are shown by squares.

neighbourhood, e.g. Mg vacancy near the direct route or an oxygen vacancy in the layer which lies directly above the cation layers (marked by squares in Fig. 2), does the migration energy fall significantly (~ 1.97 – 2.59 eV). The introduction of a Mg vacancy near the direct route shifts the saddle point towards the vacant site (route S_v in Fig. 2). The introduction of an oxygen vacancy (shown by squares in Fig. 2) near to the double jump (D1-D2) route, shifts the saddle point by approximately 0.9 Å towards the oxygen layer immediately above the cation layer. The values of ΔE_m for Mg migration are presented in Table 4. Again, the direct route is particularly unfavourable, ($\Delta E_m = 9.82$ eV) but the double jump route is more likely (1.97 eV). The introduction of additional Ca vacancy near the direct route lowers ΔE_m to ~ 2.28 eV. In contrast to the case for Ca migration, the creation of oxygen vacancies near to the diffusion route does not reduce the migration energy for Mg via either the single or double jump route.

These minimum values for ΔE_m (~ 1.97 eV)

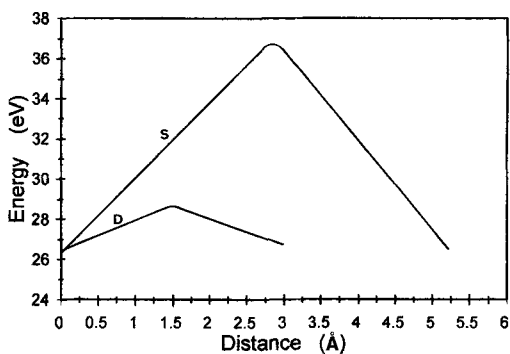


FIG. 3. Plots of energy as a function of distance for Mg diffusion in the c -direction: direct route involving only a single jump, (S); indirect, double jump route, (D), but note that the figure shows only the D1 jumps in the b - c plane; the second jump is identical to the first in energy terms and the length of the D1-D2 jump is twice as long as that shown in the figure.

TABLE 3. Migration energies for Ca self-diffusion in the c-direction of diopside

Type of jump	Type of excess vacancy	Migration energy (eV)
Single	None	6.62
Single	Mg vacancy	1.97
Single	Oxygen vacancy	4.60
Double	None	5.63
Double	Oxygen vacancy	2.59

should correspond to the extrinsic diffusional activation energy, where all vacant sites are formed by extrinsic processes. However, at high temperatures the majority of defects may be thermally generated, provided the formation energies are sufficiently low. To calculate the activation energy for diffusion under intrinsic conditions, it is necessary to add a fraction of the defect formation energy to the migration energy. If we assume that the Mg vacancy is part of an unbound defect (Table 2), then the activation energy for intrinsic diffusion (ΔE_D) is given by

$$\Delta E_D = \Delta E_M + \left(\frac{\Delta E_{def}}{2} \right) \quad (4)$$

where E_{def} is the defect formation energy. Using the E_{def} value for MgO (O_1 and O_2) from Table 2 (7.95 eV) and ΔE_m values from Table 4 (9.82 eV for the direct route and 1.97 eV for the double route) yields ΔE_D values of 13.79 eV and 5.95 eV for intrinsic diffusion of Mg via single or double jump routes respectively. For extrinsic diffusion of Mg via a vacancy mechanism (double route) ΔE_D would fall to 1.97 eV.

Similarly, for Ca diffusion in diopside the activation energy for intrinsic diffusion (ΔE_D) is equal to ($\Delta E_{def}/2$) 3.66 eV (based on CaO_1 and

CaO_2) plus (ΔE_m) 6.62 eV for a single jump or 5.63 eV for the double jump, i.e. ΔE_D values of 10.28 eV and 9.29 eV respectively. If we consider transport mechanisms involving extra vacancies, e.g. Ca diffusion via the direct route with an additional Mg vacancy in the neighbourhood of the migration route, then ΔE_m falls to 2.29 eV (from 9.82 eV), but in calculating the intrinsic diffusional activation energy, it is necessary to add $\Delta E_{def}/2$ for the Ca vacancy *and* $\Delta E_{def}/2$ for the Mg vacancy, i.e. $2.29 + 3.66 + 3.97 = 9.92$ eV. This value is not significantly different from those determined for Ca diffusion via the single or double routes without additional vacancies. However, the interactions between multiple vacancies can be complex and therefore this study concentrates primarily on isolated, non-interacting defects. Depending upon whether magnesium vacancies or oxygen vacancies assist the Ca diffusion, the activation energy for extrinsic diffusion is predicted to be 1.97 or 2.59 eV respectively.

Three experimental studies have examined Ca diffusion in single crystal pyroxene. Brady and McCallister (1983) obtained (Ca-Mg,Fe) interdiffusion data from lamellar homogenisation

TABLE 4. Migration energies for Mg self-diffusion in the c-direction of diopside

Type of jump	Type of excess vacancy (eV)	Migration energy
Single	None	9.82
Single	One Ca vacancy	2.29
Single	One oxygen vacancy	10.71
Double	None	1.97
Double	One oxygen vacancy	2.79
Double	Two oxygen vacancies	5.93

experiments (1150–1250°C); the activation energy was 3.73 ± 1.97 eV. Dimanov (1995) and Dimanov and Ingrin (1995) obtained Ca self-diffusion activation energies of 2.90 eV for natural and synthetic diopside in the low temperature regime. Above 1242°C, Dimanov and Ingrin found a higher activation energy of 9.87 eV for diffusion in the *b*-direction.

The present simulation data are for Ca diffusion in the *c*-direction of diopside and therefore not directly comparable with the experimental results of Dimanov and Ingrin who examined diffusion in the *b*-direction of diopside. Furthermore, the calculations assume ideal, homogeneous materials, containing only the specified defects while the experimental data depends critically on both the experimental set up and the quality of the samples; the latter may contain a variety of defects and impurities. In spite of these restrictions it is of interest to note that the calculated migration energies of 1.97–2.59 eV (Table 3) are comparable with experimental data obtained in low temperature extrinsic regime. The calculated intrinsic activation energies 9.29–10.28 eV for Ca diffusion are compatible with the high temperature experimental data of Dimanov and Ingrin (9.87 ± 0.90 eV).

On the basis of calorimetric measurements, Dimanov and Ingrin (1995) estimated the formation energy for Frenkel defects in diopside to be 15.81 ± 2.76 eV. It was inferred that the premelting behaviour in diopside was due to Ca-Frenkel defects. The calculated value for Ca-Frenkel defects from atomistic simulation was 12.00 eV (Table 2). This is only marginally outside the range of values obtained from the experimental studies. A separate study, examining interstitial diffusion processes, will be reported elsewhere.

Conclusions

The results of atomistic simulation of diopside indicate that defect formation energies are generally high. Consequently, diffusion processes are likely to be dominated by extrinsic effects, except at the highest temperatures in the premelting region. The most favourable defects, with the lowest defect formation energies, are CaO and MgO Schottky defects (3.66 eV and 3.97 eV per defect respectively), and oxygen Frenkel defects (3.93 eV).

The diffusion of Ca and Mg in diopside is easiest in the *c*-direction and can take place by a

vacancy migration mechanism. Two alternative routes were identified for cation self-diffusion: direct jumps along the *c*-direction and double jumps between adjacent sites in the *b-c* plane. The double jump routes are associated with lower energies than the direct route for Mg and Ca. The migration energies can be reduced considerably if additional oxygen or cation vacancies are created near to the diffusion route. Therefore diffusion in real diopside crystals may operate via a divacancy mechanism. Calculated diffusion activation energies (fraction of defect formation plus cation migration energy) are comparable with published experimental data for Ca diffusion in the extrinsic and intrinsic regimes.

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