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Defect calculations in silicates: olivine

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Abstract

The evaluation of the energy of formation of point defects in silicates is developed using solid-state theory. The calculations require a proper treatment of the polarization effects in the crystal as well as the usual Coulomb and repulsion energy terms. The theory is applied to the calculation of point defects in forsterite. The Mg–O and O–O repulsion potential calculation uses the recent electron gas theory of Gordon and Kim (1972). The partly covalent Si–O bond is treated semi-empirically. The relative importance of the various energy terms in the overall energy of formation is evaluated. The results show a marked difference between defects on the M1 and M2 octahedral sites, and among the three different oxygen sites of olivine. The energy differences are on the order of several electron volts. The implication of the results on the nature of defects and on the diffusion mechanism in olivines is then treated.

Introduction

In the past decade the solid-state theory of defects in ionic crystals has been generally refined (Barr and Lidiard, 1971). Most research has focused on the alkali halides, since rather extensive and precise data on defect concentrations, electrolytic conductivity, and diffusion phenomena exist for these compounds. However, some preliminary data on geochemically interesting solids (*e.g.* silicates) are available, and it is important to develop the necessary models to digest and interpret the experimental data as well as to extend the data to predict other useful quantities within a sound chemical and physical basis.

The structure and energetics of defects in crystalline materials are central to the understanding of solid-state transport processes. A quantity of paramount importance in the applications of kinetics to geochemistry (*e.g.* isotope dating, geothermometry, geospeedometers, alteration of minerals) is the diffusion coefficient of an element in a particular crystal. Some diffusion coefficients are rather small at low temperatures and hence are sometimes difficult to determine experimentally. Furthermore, when multicomponent diffusion experiments are carried out, their interpretation is not always clear. One possible way of increasing our ability to apply kinetics, therefore, lies in developing a theoretical framework that may allow us to predict some of the microscopic details of the defect structure and diffusion coefficients of minerals. While we are not now in a position to derive absolute diffusion coefficients with reasonable accuracy, we can begin to predict some of the useful terms in the theory. Based on the success of the alkali halide calculations (*e.g.* Barr and Lidiard, 1971), these models will be able to aid considerably in understanding geochemical kinetics.

An important class of defect, which can be significant in the transport theory of silicates, is the so-called point defect class, which includes vacant lattice sites, interstitial atoms, and impurities. This paper will focus on the physical chemistry used to characterize the energetics of these point defects in silicates.

Energetics of defects—general remarks

There are two approaches to the energetics of point defects. On the one hand, one may write different "defect reactions" which describe the formation of vacancies, interstitials, electron holes, or conduction electrons. With this approach one writes expressions for the chemical equilibrium constants of these reactions, assuming thermodynamic equilibrium for all the defects possible in the structure. This leads to an interrelationship between the concentration of the different defects and the fugacities of important species such as O_2 (if multivalent ions are involved) or the concentration of foreign ions. If used in conjunction with experimental data, this simple

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approach enables us to reduce the number of possible dominant transport mechanisms under the specified experimental conditions (*e.g.* Kroger, 1971, 1974; Smyth and Stocker, 1975; Stocker, 1978a; Buening and Buseck, 1973).

The second approach focuses on the microscopic details of these defects, *i.e.* it tries to relate the energies of formation and migration of the defects to the electronic, optical, and elastic properties, as well as the crystal structure of each mineral. (For a review, see Barr and Lidiard, 1971; Lidiard, 1972.) This approach opens up new avenues of research as well as a deeper understanding of the details of the transport processes.

Of course, both approaches are complementary and should be used together in the analysis of experimental data and in predicting new transport phenomena. For example, suppose we were interested in the formation of Mg^{2+} and O^{2-} vacancies in a forsterite crystal. We could then write the defect reaction as

$$\mathrm{Mg(M1)_{Mg(M1)} + O(3)_{O(3)} \rightarrow V^{\cdot\cdot}_{Mg(M1)} + V''_{O(3)} + MgO\ (surface)} \quad (1)$$

Equation 1 states that an Mg^{2+} ion on a magnesium M1 octahedral site in forsterite (Mg_{Mg}) and an O^{2-} ion on an O(3) oxygen site (O_O) are removed to new sites on the surface of the crystal, leaving behind a magnesium site vacancy ($V^{\cdot\cdot}_{Mg}$) and an oxygen site vacancy (V''_O). Note that we must also distinguish among the different crystal sites in the reaction. The notation, at first a bit cumbersome, is the one generally used and introduced by Kroger (1971). The $\cdot\cdot$ in V_{Mg} indicates a loss of +2 charge at the site—or equivalently a gain of −2—and the ″ in V_O indicates a loss of −2 charge.

The first approach to the treatment of defects would introduce an equilibrium constant for reaction 1:

$$(X_{Mg,v}\, X_{O,v})/(X_{Mg,Mg}\, X_{O,O}) = K_{eq} \quad (2)$$

where $X_{Mg,v}$ is the fraction of Mg-M1 sites which are vacant, $X_{Mg,Mg}$ is the fraction of Mg sites which are occupied by Mg and similarly for oxygen. Obviously it is usually a very good approximation to set $X_{Mg,Mg}$ and $X_{O,O}$ equal to 1. In this case, equation 2 simplifies to

$$X_{Mg,v}\, X_{O,v} = K_{eq} = \exp(-\Delta G_s/RT) \quad (3)$$

where ΔG_s is the free energy of formation for the pair of vacancies (generally called Schottky defects in simple crystals). Equation 3 is always true at equilibrium and shows that the defect concentrations will depend exponentially on temperature. The first method proceeds along similar lines to obtain many relations such as equation 3 for the possible different defect reactions. In the true thermodynamic tradition, this enables us to derive relationships between the various defect concentrations and/or the external variables.

The second approach, in this example, obtains the size of the critical energy term, ΔG_s. Obviously the first method cannot predict this term, but merely states its existence. It will be concerned with the current status of the theory for estimating ΔG_s and with its geochemical significance.

One important function of point defects, of course, is enabling diffusion to take place in a crystal. Therefore the diffusion coefficient (as well as the conductivity) depends on the type and the energetics of point defects. In fact, the number of atoms jumping from their sites into adjacent vacancies will depend on (1) the fraction of sites which are vacant and (2) the fraction of atoms which, being next to a vacancy, have sufficient thermal energy to go over the migration activation barrier and into the vacancy. Under general conditions the diffusion coefficient is given by an equation of the form

$$D = \frac{d^2\nu}{3} X_v \exp(-U/RT) \quad (4)$$

(Jost, 1960, p. 137) where d is the interatomic distance traveled in a jump, X_v is the site fraction of vacancies, and U is the energy barrier to go from a filled site to a neighboring vacant site. ν is a vibrational frequency which sometimes is set to the Einstein frequency of a crystal or some fraction of the Debye frequency (see Flynn, 1972, p. 330). Of course, the pre-exponential factor in equation 4 is quite approximate and gives only a rough idea of the magnitude of D. More detailed treatments involve a sophisticated account of the atomic dynamics in a crystal (Flynn, 1972, Ch. 7). A similar equation would follow if the diffusion mechanism involved interstitial sites (Jost, 1960). Both X_v and the term exp $(-U/RT)$ are very sensitive to temperature variations (the fundamental reason for their importance as geospeedometers!) and X_v is possibly sensitive to the impurity content and/or oxidation state of the crystal. These terms are therefore critical in the evaluation of diffusion coefficients.

Equation 4 is usually multiplied by the so-called correlation factor, f (Barr and Lidiard, 1971; LeClaire, 1971). This factor corrects for the fact that once an atom jumps into a vacancy, it has a higher than random probability of jumping back. However, this factor is usually between 1 and 0.5 and is useful in correlating isotopic data (which may be useful in determining the diffusion mechanism) and not in understanding the overall size of the diffusion coefficient, D.

In elucidating the variation with temperature of the term X_v in equation 4 (or similarly the term X_i if an interstitial mechanism is involved) we must make the important distinction between an extrinsic diffusion mechanism and an intrinsic diffusion mechanism. At high temperatures the size of X_v is determined from the energy needed to form the vacancy, E_f, *i.e.*

$$X_v \propto \exp(-E_f/RT) \qquad (5)$$

where we have a simple Boltzmann term. This exponential dependence on temperature in equation 5 will contribute to the overall exponential dependence of D in equation 4. This overal activation energy is then the value obtained from the temperature dependence of the diffusion coefficient in the intrinsic region. However, as the temperature is dropped, we reach a point where the number of vacancies induced by the impurities (*e.g.* aliovalent ions) is much bigger than the number of vacancies generated intrinsically (*i.e.* by thermal equilibrium). Below this temperature, X_v is then fixed by the concentration of impurities and is therefore independent of temperature. As a result, an exponential term from equation 4 is lost and the activation energy for diffusion decreases drastically. Below this temperature is the extrinsic region. This variation of the activation energy with temperature manifests itself as a kink in the ln D *vs.* $1/T$ curve. A well-documented example of this behavior is seen in the experimental data for the self-diffusion of Na^+ ions in NaCl (Jost, 1960) or in the self-diffusion of Br^- in KBr doped with $CaBr_2$ (Barr and Lidiard, 1971). Clearly a prediction of where these temperature regions lie necessarily depends on the energetics of the point defects. It is also important to understand where these changes in slope occur, since they will seriously affect the validity of any extrapolation of experimental data.

The treatment of the energetics of point defects (vacancies or interstitials) in ionic crystals dates back to the classic paper by Mott and Littleton (1938). Most current theories still employ the same approach as Mott and Littleton, although the treatment of the various terms in the original theory has been refined. The energy needed to move ions in an ionic lattice or to create vacancies and interstitials can be attributed essentially to three terms: (1) the Madelung energy, (2) the short-range energy (mainly repulsion) due to ionic overlap, and (3) the polarization energy. The physical property which distinguishes ionic crystals and creates problems in theoretical calculations is the presence of a large polarization energy. I will comment on the evaluation of each and apply the theory to an important silicate, forsterite.

Madelung energy

The evaluation of the Madelung energy is perhaps the most well-established and oldest of the procedures. The Coulomb energy at a site with position vector $\mathbf{r}_i$ of an ion with charge z_i is given by the series:

$$V_{Coul} = \sum_j \frac{z_i z_j e^2}{|\mathbf{r}_j - \mathbf{r}_i|} \qquad (6)$$

where the sum in equation 6 is over all the ions in the lattice. The direct summation of the Coulomb potential, equation 6, converges very slowly. This slow convergence is a result of the long-range interactions due to the 1/r form of Coulomb's law. Fortunately, this slowly-convergent series can be profitably rewritten using Fourier transforms. A standard result derived by Ewald (1921) (see also Kittel, 1956, p. 574) and using the reciprocal lattice is

$$V_{Coul} = \frac{4\pi}{V_{cell}} \sum_{G\neq 0} S(G) \frac{\exp[-(G^2/4\eta)]}{G^2} - 2 z_i (\eta/\pi)^{1/2} + \sum_l \frac{z_l}{r_l} \operatorname{erfc}(\eta^{1/2} r_l) \qquad (7)$$

In equation 7 the first term is a sum over all reciprocal lattice vectors, $\mathbf{G} = 2\pi(h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^*)$, where $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ are the reciprocal basis vectors, h, k, l are any integers, and S(G) is the structure factor defined by

$$S(G) = \sum_t z_t \exp(-i\,\mathbf{G}\cdot\mathbf{r}_t) \qquad (8)$$

The sum in equation 8 is over all ions in a unit cell (which, of course, can be arbitrarily chosen). V_{cell} is the volume of the unit cell. The third sum is a direct sum over all the ions in the crystal. η is an adjustable parameter and V_{Coul} should be independent of the value chosen for η. An interesting result is that if η is small enough so that $\exp(-G^2/4\eta)$ is negligible even for the smallest non-zero G vector, the sum in equation 7 reduces to only the last two terms. Therefore the Ewald method essentially multiplies the direct series in equation 6 by an error function term, erfc, (which makes the series converge very fast) and then corrects for the erfc term by the simple second term in equation 7. Of course, as $\eta \rightarrow 0$ equation 7 approaches equation 6. There have been some recent papers on the optimization of the Madelung calcuation (*e.g.* Catti, 1978; Tupizin and Abarenkov, 1977) and a recent application to the spinel structure (Thompson and Grimes, 1977). For a useful review see Sherman (1932). Some workers have analyzed the stability of minerals based solely on Madelung calculations (*e.g.* Appelo, 1979; Giese, 1975; Ohashi and Burnham, 1972; van Gool and Piken, 1969a,b; see however, Urusov, 1965). Unfortunately, the evaluation of the Madelung term by itself is not sufficient for our purposes, as we shall see below.

Short-range potential

While the method of evaluation of the long-range summations needed to obtain the Madelung potential is well developed, the description of the repulsive forces between ions is not completely developed. This results, in part, from the necessity to include quantum mechanical effects and the possibility of many-body forces in evaluating the ion–ion short-range potentials. Even though some workers have approximated the repulsive potential by a term of the form $1/r^n$ ($n > 8$), by far the most common treatment uses the empirical Born-Mayer repulsive potential

$$V_{Born} = A \exp(-r/\rho) \qquad (10)$$

which is a pairwise potential between two ions at a distance r (A and ρ are constants). There is some validity to the exponential form of the potential used in equation 10. The rationale rests upon the well-known fact that the electron density in atomic orbitals decays predominantly as $e^{-\alpha r}$ (*e.g.* hydrogen orbitals), where r is the distance from the nucleus. In fact, exponential decay is a general property of all 1/r type potentials.

The parameters A and ρ in equation 10 are usually obtained for simple cubic crystals not from quantum mechanical calculations but from the equilibrium cation–anion nearest bond distance and the compressibility of the crystal. Sometimes the Born-Mayer potential between ions i and j is written as

$$V_{Born} = A \exp[-(r_i + r_j - r)/\rho] \qquad (11)$$

where r_i and r_j are the ionic radii; but clearly equations 10 and 11 have the same form.

An important problem with the Born-Mayer potential is that, although the hydrogenic type potential is reasonable at intermediate distances, this form is not correct at very close separations and in fact underestimates the actual interionic repulsion for small r (*i.e.* for r smaller than the equilibrium distance r_0—see Kim and Gordon, 1974b). This is a consequence of the fact that the Born potential approaches a constant value as $r \rightarrow 0$, while the Coulomb term approaches infinity. This problem leads to the so-called "polarization catastrophe."

It is also usual to add small attractive Van der Waal's terms to the Born potential in order to better describe the long-range part of the interionic potential. The form of this term is

$$V_{V.d.W.} = -C/r^6 \qquad (12)$$

However, the choice and size of the parameter C is not well-established for the common ions.

In this paper, I use a more recent method, hitherto not widely used in defect calculations, for evaluating the short range potential; this is the so-called electron gas model of Gordon and Kim (1972). The basic assumption of the model is to treat ions as spherically symmetric charge distributions of known electron density (*e.g.* analogous to the densities that X-ray crystallographers use) and then evaluate the interionic interaction by using the well-known electron theory, which relates the energy of an electron gas to its electron density (Fetter and Walecka, 1971, p. 29). The electron density at any one point is given by the sum of the electron densities of each ion separately at that point. This model works very well in predicting the positions (r_{eq}) and depths of potential minima for the intermolecular potentials of the rare gases (which are isoelectronic with many of the common ions) and of closed shell ions (Gordon and Kim, 1972; Kim and Gordon, 1974a,b). In particular, it predicts very well the important potential wall for distances closer than the internuclear equilibrium distance, r_{eq}. The theory is slightly off in predicting the long-range part of the potential, since some of the dispersion energy is not incorporated into the simple theory (more recent versions can include some polarization terms and correct for this).

Calculation of elastic properties, their pressure derivatives, and the equilibrium distances in alkali halides and alkaline-earth dihalides using the electron gas theory have been very successful (*e.g.* Kim and Gordon, 1974a). This has also been extended to alkaline earth oxides (Cohen and Gordon, 1975, 1976). One important problem, which arises when oxides are considered, is the choice of electron density for the O^{2-} ion. Since O^{2-} is an unstable ion in vacuum (*i.e.* the reaction $O^{2-} \rightarrow O^{-} + e^{-}$ would occur spontaneously) calculations of the electron density of the oxygen anion must involve some sort of stabilizing "fictitious" positive charges, such as do occur in real crystals (*e.g.* six +1 charges arranged in an octahedral arrangement about the oxygen anion). This problem leads to some ambiguity in the electron density. The two widely used electron densities for O^{2-} obtained in this fashion are those of Watson (1958) and of Yamashita and Asano (1970). Both electron densities will be used in our calculations of the short-range interionic potentials.

The other problem arises from the use of an ionic model in the electron gas. This model will be debatable especially if Si–O bonds are involved, as they are in silicates. Our group is currently working on a scheme which combines the covalent bonds (treated by molecular orbital methods) with ionic interactions (treated by the electron gas). At this stage, however, the Si–O potentials will be approximated using empirical Born type terms (see below). In later papers, this treatment will be refined.

Polarization energy

A very important term in the energetics of point defects is the polarization energy. The sign of the polarization energy is the opposite of that of the Coulomb energy term. Therefore, the polarization term reduces significantly the energy needed to remove an ion from a lattice. It is the importance of this term, its long-range nature, and the difficulty of evaluating it that makes the treatment of defects in ionic lattices much harder than that needed in metals.

The macroscopic polarization induced in a crystal lattice at a position r from a defect with an effective charge q is given by the expression

$$\mathbf{P} = \frac{1}{4\pi}\left(1 - \frac{1}{\epsilon_0}\right)\frac{q\,\mathbf{r}}{\mathrm{r}^3} \qquad (13)$$

where the polarization, **P**, is defined as the induced dipole moment per unit volume of crystal and ϵ_0 is the static dielectric constant of the lattice. Equation 13 is the point of departure for all evaluations of the polarization energy, including the classic work by Mott and Littleton (1938). However, a simple treatment due to Jost (1960) readily shows the importance of the polarization energy. The polarization energy of a charged sphere of radius r and charge q embedded in a dielectric continuum with dielectric constant ϵ_0 is given by

$$E_{\mathrm{polar.}} = -1/2\,\frac{q^2}{r}\left(1 - \frac{1}{\epsilon_0}\right) \qquad (14)$$

(*e.g.* see Jost, 1960, p. 105, or Jackson, 1962, p. 115). In this case r would be the size of the cation or anion hole and is comparable to an ionic radius. Compare equation 14 to the Coulomb potential in an NaCl lattice at a lattice site:

$$E_{\mathrm{Coul}} = 1/2\,\frac{1.746\,q^2}{a} \qquad (15)$$

where a is the cation–anion distance and 1.746 is the usual Madelung constant. Since the hole size, r, in equation 14 is nearly equal to a/2 and ϵ_0 is approximately 5, the magnitudes of the terms in equations 14 and 15 are similar. Since the polarization term has the opposite sign to the Coulomb term, it cannot, therefore, be ignored in evaluating the overall energetics of the defects.

In a more correct treatment (see next section), equation 13 is used to compute the total electric field at any point in the lattice (which includes a contribution from the induced dipole moments) and then the induced dipole moment is calculated at that point (self-consistently). This induced dipole moment will then yield a potential energy at the defect site. Summation of all the potentials yields the polarization energy.

Application to defects in forsterite

Forsterite is a relatively simple orthorhombic orthosilicate with a reported space group of *Pbnm* (Hazen, 1976). The structure consists basically of an almost ideal hexagonal close-packing of oxygen atoms with Mg filling 1/2 of the octahedral sites and Si filling 1/8 of the tetrahedral sites. There are two crystallographically distinct octahedral sites, M1 and M2, one tetrahedral site, and three crystallographically distinct oxygen sites, O1, O2, and O3. The M1 site is a center of symmetry for the structure and the M2 site lies on a mirror plane (Fig. 1).

To convert the structure to a cartesian coordinate representation we have used the fractional cartesian coordinates (of Mg-M1, Mg-M2, Si, O1, O2, and O3 in one unit cell) given by Hazen (1976) for forsterite at 1 atm and 1000°C. (The unit cell contains 4 Mg_2SiO_4 molecules.) The Madelung energy term at each site in forsterite is calculated using equation 7. The results, which are given in Table 1, are verified

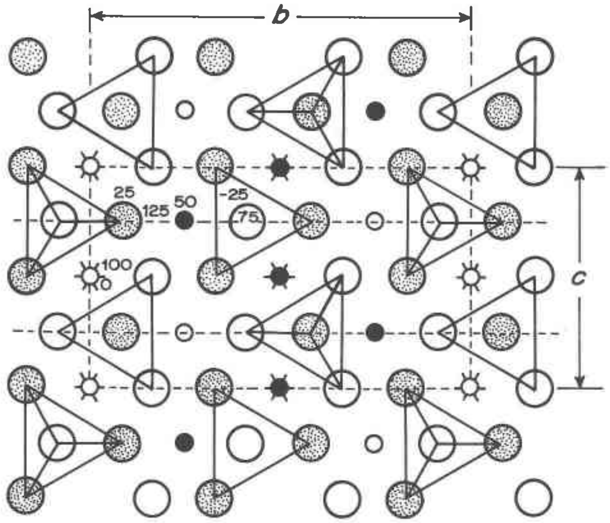

Fig. 1. Olivine structure parallel to (100) plane. Small open circles Mg atoms at x = zero; small solid circles Mg atoms at x = $\frac{1}{2}$. Radial lines on small circles designate the M1 octahedral sites. Big circles are oxygens. Si atoms, at centers of tetrahedra, are not shown. (Redrawn from Deer *et al.*, 1962.)

to be independent of η as a check on the calculations. The numbers given are the Coulomb potentials at the particular site in units of $e^2/1$ Å. Thus, the Coulomb energy of a Mg^{2+} ion at an M1 octahedral site is $(+2)(-1.590556) = -3.1811$ $e^2/\text{Å}$. Since $e^2/\text{Å} = 14.3990$ ev, the energy is V_{coul} (Mg-M1) = 45.8048 ev. Using the potentials ψ_s from Table 1, we easily obtain the lattice Coulomb energy of the crystal from the equation:

$$\begin{aligned}E_{\text{lattice}} &= -\frac{e^2}{1\,\text{Å}}\,1/2\,\sum_s z_s\psi_s\\ &= (-14.3990\text{ ev})\,1/2\,[2(-1.590556)\\ &\quad + 2(-1.712426) + 4(-3.273312)\\ &\quad + (-2)(1.908726) + (-2)(1.901546)\\ &\quad + 2(-2)(1.826216)] = 249.280\text{ ev}\\ &= 5758\text{ kcal/mole}\end{aligned}$$

This calculation shows that the Coulomb lattice energy is in reasonable agreement and indeed makes up a major portion of the whole lattice energy extrapolated from experiments: 4927 kcal/mole (Urusov, 1965). The Coulomb energy is higher since we must subtract the repulsion energy. Note that we multiplied the O3 potential energy by two since there are two O3 oxygen atoms in one formula unit of Mg_2SiO_4.

Polarization energy

Removing an ion from a crystal lattice site is "coulombically" equivalent to adding a charge of opposite sign to the site, that is removing a Mg^{2+} ion is the same as inserting a -2 charge in an Mg site. If we place a charge Q on a given site (or on an interstitial site), we will obtain first of all an energy due to the Coulomb interactions of the charge with all of the other ions in the crystal. The calculations of this energy follow directly from the data in Table 1. However, the extra charge Q also induces a dipole moment on all the ions in the crystal. This effect arises since the symmetry of the crystal is broken by the charge, leading to the existence of a net electric field at each ionic lattice site. The electric field, **E**, in a continuum of static dielectric constant, ϵ_0, at a distance r from the charge Q is given by $(Q/\epsilon_0 r^2)\ \hat{r}$ (where $\hat{r}$ is a unit vector pointing from the charge Q to the position in question at a distance r). The macroscopic polarization in the medium, **P**, is therefore given by (Jackson, 1962, p. 109):

$$\begin{aligned}\mathbf{P} &= \frac{\epsilon_0 - 1}{4\pi}\,\mathbf{E}\\ \mathbf{P} &= \frac{Q}{r^2}\,\frac{1}{4\pi}\left(1 - \frac{1}{\epsilon_0}\right)\hat{r}\end{aligned} \tag{16}$$

We must use the static dielectric constant in equation 16 since the electric field is static. This means that the induced dipoles in the lattice are the net result of both electronic dipole moments and dipole moments resulting from the induced ionic displacements. We treat ϵ_0 as a scalar in this paper; in a refinement, we would have to take into account slight variations of ϵ_0 with crystallographic direction due to the tensorial nature of the dielectric constant.

The quantity needed to obtain the polarization energy is the actual induced dipole on each ion, μ_{ion}, as a result of the introduction of the defect charge, Q. The induced dipole on an ion is given by the usual

Table 1. Coulomb potentials—forsterite (units of e^2/Å)

Ion	ψ_s
Mg-M1	- 1.590556
Mg-M2	- 1.712426
Si	- 3.273312
O1	1.908726
O2	1.901546
O3	1.826216

formula involving the total ionic polarizabilities and the total electric field:

$$\mu_{\text{ion}} = \alpha_i \mathbf{E}_{\text{tot}} \tag{17}$$

(We will also treat the polarizabilities as scalars.) $\mathbf{E}_{\text{tot}}$ in equation 17 is the total electric field at the site of the ion; it is the sum of the electric field from the charge Q and the electric field from the induced dipoles themselves. If N is the number of formula units per unit volume, then the polarization of forsterite (dipole moment per unit volume) is simply:

$$\mathbf{P} = N(2\mu_{\text{Mg}} + \mu_{\text{Si}} + 4\mu_{\text{O}}) \tag{18}$$

Since there are 4 formula units of forsterite in the primitive unit cell, N = 4/(abc). Therefore, using equations 17 and 18:

$$\mathbf{P} = \frac{4}{\text{abc}}(2\,\alpha_{\text{Mg}} + \alpha_{\text{Si}} + 4\,\alpha_{\text{O}})\,\mathbf{E}_{\text{tot}} \tag{19}$$

Solving for $\mathbf{E}_{\text{tot}}$ from equation 19 and inserting into equation 17:

$$\mu_i = \frac{\text{abc}}{4}\,\frac{\alpha_1}{(2\,\alpha_{\text{Mg}} + \alpha_{\text{Si}} + 4\,\alpha_{\text{O}})}\,\frac{Q}{4\,\pi r_i^2}\left(1 - \frac{1}{\epsilon_0}\right)\hat{r} \tag{20}$$

We have replaced **P** in equation 20 by the expression in equation 16.

Equation 20 gives the induced dipole on ion i at each lattice site. From a knowledge of the dipole moments, μ_i, the calculation of the polarization energy is straightforward; we simply add all the potential energies at the position of the charge Q due to the existence of the induced dipole moments. The potential of a dipole μ a distance r away from the dipole is given by the formula

$$V_{\text{dipole}} = \mu \cos\theta / r^2 \tag{21}$$

where θ is the angle between the vector μ and the vector **r** (Karplus and Porter, 1970, p. 251). Since all the dipoles point towards Q in this approximation (use of scalars), the vectors μ and **r** are parallel and thus $\theta = \pi$. Therefore equation 21 reduces to $V_{\text{dipole}} = -\mu/r^2$. The total polarization energy is obtained by summing over all the ions:

$$V^{\text{tot}}_{\text{dipole}} = -\sum_i \frac{\mu_i}{r_i^2}$$

Inserting equation 20,

$$V^{\text{total}}_{\text{polar.}} = -Q\,\frac{\text{abc}}{4}\sum_i \frac{\alpha_i}{(2\alpha_{\text{Mg}} + \alpha_{\text{Si}} + 4\alpha_{\text{O}})}\,\frac{1}{4\pi}\left(1 - \frac{1}{\epsilon_0}\right)\frac{1}{r_i^4}$$

which we can rewrite (using Mott and Littleton's notation) as:

$$V_{\text{polar.}} = -Q\,\frac{\text{abc}}{4} \cdot \left[M_{\text{Mg}} \sum_{\text{Mg}} \frac{1}{r^4} + M_{\text{Si}} \sum_{\text{Si}} \frac{1}{r^4} + M_{\text{O}} \sum_{\text{O}} \frac{1}{r^4}\right] \tag{22}$$

where

$$M_i \equiv \frac{\alpha_i}{(2\alpha_{\text{Mg}} + \alpha_{\text{Si}} + 4\alpha_{\text{O}})}\,\frac{1}{4\pi}\left(1 - \frac{1}{\epsilon_0}\right) \tag{23}$$

The sums in equation 22 are over the distances from Q to all the ions of the particular type (*e.g.* in the first sum all Mg ions). The evaluation of the $\Sigma(1/r^4)$ terms by direct summation is not as hard as evaluating the Coulombic term. Hence we have carried out a direct summation in our calculations of the dipole sums. The results are shown in Table 2.

Before proceeding, we should mention a few of the important expressions relevant to the terms used in the final polarization equation 22. There is an important relation between the ion polarizabilities, α_i, and the crystal dielectric constant, ϵ_0, which for crystals of high symmetry is termed the Clausius-Mosotti relation. In the presence of high-frequency electric fields (*e.g.* visible light) the net induced dipole moment of the crystal per unit volume (polarization) only arises from the induced electronic dipoles on each ion. This gives rise to the high frequency dielectric constant, ϵ_∞ [*e.g.* see Kittel (1956, Ch. 7) for a detailed account]. The polarizabilities involved are the electronic polarizabilities of the ions, α_e. The relationship between ϵ_∞ and α_e is derived in several standard texts (for a good exposition see Karplus and Porter, 1970, p. 250). The result, in the case of forsterite, is

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3\bar{V}}\,\alpha^e_{\text{forsterite}} \tag{24}$$

where $\bar{V}$ is the molecular volume of forsterite and $\alpha^e_{\text{Mg}_2\text{SiO}_4}$ is the electronic polarizability of one forsterite formula unit and is given by

$$\alpha^e_{\text{Mg}_2\text{SiO}_4} = 2\,\alpha^e_{\text{Mg}} + \alpha^e_{\text{Si}} + 4\,\alpha^e_{\text{O}} \tag{25}$$

Table 2. Dipole sums—forsterite [$\Sigma(1/r^4)$ in Å^{-4}]

Site of defect	Mg-M1	Mg-M2	Si	O1	O2	O3
Mg-M1	0.06180	0.07345	0.09120	0.14487	0.15001	0.20323
Mg-M2	0.07345	0.05254	0.08317	0.10009	0.10748	0.27503
Si	0.09120	0.08317	0.05141	0.20521	0.19359	0.39565
O1	0.14487	0.10009	0.20521	0.04942	0.09222	0.17905
O2	0.15001	0.10748	0.19359	0.09222	0.05174	0.17989
O3	0.10162	0.13752	0.19782	0.08952	0.08995	0.14103

This relationship (equation 24) and the assumption of universality for polarizabilities allows us to obtain the electronic polarizabilities from the high frequency dielectric constants, which are known for most crystals (*e.g.* from the index of refraction). In turn, the electronic polarizabilities of the ions (equation 25) are also reasonably well known (see Tessman *et al.*, 1953). We should note that the polarizability of oxygen in particular seems to vary depending on the crystal structures. This effect may be partly due to covalency effects.

However, we do not have an oscillating electric field but a static field due to the presence of a charged point defect. In this case, the atomic displacements of the ions due to the presence of the charge become important. (For fast frequency fields the net force on an ion over a vibrational period is zero!) This adds a new component to the net dipole moment, namely the dipole due to ionic displacement. Thus the correct polarizability, α^T, is the sum of the electronic and displacement terms

$$\alpha^T = \alpha^e + \alpha^d \qquad (26)$$

The new bigger polarizabilities lead to a new and higher dielectric constant, the static dielectric constant, ϵ_0. Analogous to equation 24:

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{4\pi}{3V}(2\alpha^T_{Mg} + \alpha^T_{Si} + 4\alpha^T_O) \qquad (27)$$

Unfortunately, there is a gap in knowledge of the static dielectric constant. Thus, the value is not known very well even for forsterite. We are in the process of carrying out detailed measurements of ϵ_0 as a function of temperature and pressure for a variety of important silicates. However, based on similar compounds, the static dielectric constant is expected to be in the range 6–8 (Cygan and Lasaga, 1979). More work needs to be done to measure and characterize ϵ_0 as well as to evaluate the systematics of the α^T (*e.g.* Roberts, 1949; Agrawal *et al.*, 1977; Shanker *et al.*, 1977, 1978). Without proper data on the dielectric constants of various silicates, it is hard to narrow down the values of the total polarizabilities of the individual ions, α^T_i, which are needed in equations 19, 20, and 23. We must, in fact, test the additivity and universality assumption, which is used in equation 27.

We can, however, make a good start by using values for the α^T's obtained from other ionic crystals. Some preliminary work by Cygan and Lasaga (1979) gives credence to the additivity rule and supports the general range of values used for the polarizability. In this paper, we will furthermore vary the value of the various polarizabilities to investigate the possible effect that this uncertainty has on the calculated energetics of point defects. We will also give the resulting dielectric constant, ϵ_0, computed from the polarizabilities and equation 27.

Short-range potential

To calculate the short-range part of the potentials for the O–O and Mg–O interactions in forsterite, we have used the electron gas approximation, including both the Yamashita–Asano (1970) and the Watson (1958) models for the oxygen anion. Although some covalency is present even in the Mg–O bond (for a recent discussion of bonding in MgO see Bukowinski, 1980), we expect these interactions to be largely ionic.

The problem arises with the treatment of the much more covalent Si–O bond. We did not use an electron gas model for this interaction; instead, we chose a Born-Mayer type potential

$$V_{Si-O} = A\exp[-(r_{SiO}/\rho)] \qquad (28)$$

where A and ρ are constants, which must be determined. At this stage the simplest path is to at least choose the repulsive potential in such a way that within the electrostatic model we reproduce some of the most important features of the Si–O bond. Within this scheme, the entire potential describing the Si–O bond in the crystal is given by:

$$V_{tot} = V_{coulomb} + V_{Si-O}$$

$$V_{tot} = -\frac{8e^2}{r} + A\exp[-(r/\rho)] \qquad (29)$$

The first term is the Coulomb attraction of the ions, and the second term is the short-range repulsion.

Two important physical properties of the Si–O bond are the equilibrium distance, obtained from X-ray measurements, and the stretching force constant, obtained from infrared and Raman spectroscopy. The A and ρ parameters in equation 29 are then chosen to ensure that the potential satisfies these crystal data, *i.e.*

$$\frac{dV}{dr} = \frac{8e^2}{r^2} - \frac{A}{\rho}\exp[-(r/\rho)]$$

$$= 0 \quad \text{when } r = r_0 = 1.62\text{Å}$$

$$\frac{d^2V}{dr^2} = -\frac{16e^2}{r^3} + \frac{A}{\rho^2}e\exp[-(r/\rho)]$$

$$= F = \text{Force constant}$$

~ 4.4 mdyne/Å (see Basile *et al.*, 1973; Devarajan and Funck, 1975). With these two conditions, the Si–O repulsion is given by

$$V^{\text{rep}}_{\text{Si–O}} = 474 \exp\left[-(r/.53)\right] \text{ ev} \tag{30}$$

Note that in computing the repulsive potential, we now include only Si–O pairs which are directly bonded. The summation is not limited in this way for the electron gas Mg–O or O–O interactions, although the most dominant contributions are from nearest neighbors. In the calculations any possible repulsion between the silicon and magnesium ion has been neglected.

Results

We can combine the various terms derived in the previous sections for forsterite and compute the overall energy needed to remove the ions from the various lattice sites in forsterite. For an ion of charge z_i, the Coulomb potential at the ion's site would be $z_i\Psi_i$, where Ψ_i is given by equation 7 and shown in Table 1. This quantity is the Coulomb energy needed to take the ion out of its structural site and remove it to infinity. However, this is not the Coulomb energy needed to form the vacancy, since in this case the ion is on the surface of the crystal. At the surface, we now regain half of the Coulomb energy since the ion is surrounded by ½ of its usual neighbors. Therefore, the net Coulomb energy needed to form the vacancy is $\frac{1}{2} z_i\Psi_i$. The same reasoning applies to the polarization and short-range energy terms. Hence the net energy needed to form the vacancy of ion i is given by

$$E_i = \tfrac{1}{2}[z_iV_{\text{coul}}(i) + z_iV_{\text{polar}}(i) - V_{\text{rep}}(i)] \tag{31}$$

where $V_{\text{polar}}(i)$ is given by equation 22, $Q = -z_i$, and $V_{\text{rep}}(i)$ is the repulsion energy of ion i with all its nearest neighbors. Table 3 shows the size of each term in equation 31 for each type of Mg and O ion in forsterite as well as the overall energy, E_i. We have chosen a particular set of ionic total polarizabilities, α_i^T, for Table 3, which gives a static dielectric constant, ϵ_0, of 6.44 from equation 27. The Yamashita–Asano O^{2-} potential was also used in the electron gas calculations.

Table 3. Defect energies in forsterite[a]

Site	V_{coul}(ev)	V_{pol}(ev)	V_{rep}(ev)	V_{tot}[b]
Mg-M1	45.8049	33.5103	4.5872	7.7074
Mg-M2	49.3143	32.3256	4.1799	12.8088
O-1	54.9676	25.9265	26.2177	2.8234
O-2	54.7608	26.3449	25.5061	2.9098
O-3	52.5915	25.7443	25.6634	1.1838

[a] α_{Mg}=0.91, α_{Si}=0.20, α_O=2.39, ϵ_o=6.44. Yamashita-Asano O^{2-} used in the calculations.

[b] The actual energy needed to remove the ion is half this amount as explained in the text.

Table 3 points out explicitly some of our earlier comments. First, the repulsion energy for the magnesium ions is only 10% of the Coulomb energy. This is a typical result. On the other hand, the polarization energy is a significant fraction of the Coulomb energy. We have already commented on the necessity to include this term. An important point is that the energy differences between the sites (*e.g.* M1 and M2 sites) depend on differences in all three energy contributions. The repulsion energy for oxygen is a much bigger fraction of the Coulomb energy than in the case of magnesium. The reason is that the Si–O bond is partly covalent and was modeled by fitting the Born-Mayer potential to the bond properties. In fact, it is surprising and encouraging that the absolute size of the energies needed to form oxygen vacancies is so close to what is expected! (Remember we did not parameterize the size of $V_{\text{Si–O}}$ in equation 28.)

Clearly magnesium vacancies alone or oxygen vacancies alone cannot exist in the crystal, since this would result in a net macroscopic build-up of charge. Hence, in ionic crystals the effective charge of a newly-formed vacancy must be balanced by forming other vacancies (Schottky defects) or by the formation of interstitials (Frenkel defects). We ignore here the formation of electron holes or particles. An important type of defect in forsterite, therefore, is the formation of "MgO" Schottky vacancies, that is the simultaneous formation of a magnesium and an oxygen vacancy. The overall energy needed to form the various MgO Schottky defects in forsterite ($E_{Mg} + E_O$) is also included in Table 3. The types of energies obtained in the table are in the right range for the energies expected. For example, the Schottky formation energies for periclase, MgO, have been estimated at 5±1 ev (Yamashita and Kurosawa, 1954) and at 6.6 ev (Barr and Lidiard, 1971).

Table 4 gives the overall energy for the MgO defect formation under various total polarizabilities, α's, and various O^{2-} potentials. Note that the oxygen anion has the largest total polarizability, as expected from its large size. It also largely controls the size of the dielectric constant and the polarization term for the same reason. While Si^{4+} would have a negligible electronic polarizability (see Tessman *et al.*, 1953), it does have a small total polarizability due to the ionic displacement contribution.

Table 4. Energies needed to remove ions in forsterite

O^{2-} model	α_{Mg}	α_{Si}	α_0	ε_o	1/2 V^{tot}(ev)				
					Mg-M1	Mg-M2	O1	O2	O3
Yamashita	0.91	0.10	2.39	6.31	3.89	6.43	1.61	1.64	0.78
Watson	0.91	0.10	2.39	6.31	1.25	3.94	0.62	0.58	0
Yamashita	0.91	0.05	2.39	6.25	3.90	6.44	1.71	1.73	0.87
Watson	0.91	0.05	2.39	6.25	1.27	3.96	0.72	0.67	0.05
Yamashita	0.91	0.20	2.39	6.44	3.85	6.41	1.41	1.45	0.59
Watson	0.91	0.20	2.39	6.44	1.22	3.92	0.43	0.40	0
Yamashita	0.80	0.10	2.39	6.04	3.90	6.43	1.81	1.86	0.98
Yamashita	0.91	0.10	2.10	5.05	4.82	7.34	2.09	2.11	1.26

Note that the two different oxygen potentials (Yamashita–Asano and Watson) yield different sizes for the total potential. The Watson O^{2-} density always gives much lower energies for vacancy formation and in some cases gives unreasonable numbers for the O3 vacancy formation energy. On the other hand, Cohen and Gordon (1976) obtain somewhat better equations of state with the Watson charge density.

There are some important results from the numbers in Tables 3 and 4. Table 4 shows that the differences in the energies needed to form the different vacancies (*i.e.* between M1 and M2 or O1 and O3) are significant. Thus the most stable MgO vacancy pair would be an Mg(M1)–O3 vacancy pair. The most unstable vacancy would be an Mg(M2)–O1 Schottky defect. In fact, the stability of the possible vacancies decreases in the order:

$$\mathrm{Mg(M1)–O3} > \mathrm{Mg(M1)–O2} > \mathrm{Mg(M1)–O1}$$

$$> \mathrm{Mg(M2)–O3} > \mathrm{Mg(M2)–O2} > \mathrm{Mg(M2)–O1} \quad (32)$$

Table 4 shows that the sequence in equation 32 is not altered by reasonable variations in ϵ_0 and in the ionic α_i^T's, although the actual energy differences between the defects do vary. Defects involving Mg-M2 tend to require 2 to 3 electron volts more energy to form than defects involving Mg-M1. Thus the predominant Mg vacancy should be Mg-M1 and the predominant O vacancy should be O3.

If the "MgO" defect formation energies are indeed around 6 ev's, then it suggests that cation diffusion will be largely controlled by impurity-induced vacancies (*i.e.* extrinsic diffusion). In the case of olivine these impurities are most likely Fe^{3+} ions and the diffusion will be dependent on f_{O_2}, which is indeed the case (Buening and Buseck, 1973; Stocker, 1978b). Even in the case of pure forsterite, we expect minor impurities to limit the cation diffusion to the extrinsic region. This has been shown to be true in periclase (Wuensch *et al.,* 1973). However, we can predict that the cation vacancies formed (either thermally or due to a charge imbalance such as with Fe^{3+}) will probably be in the M1 octahedral sites.

Note that the predominance of M1 vacancies expected from the calculations has direct bearing on the diffusion behavior in forsterite. Since the M1 sites line up in a row along the *c* direction (see Fig. 1), M1 vacancies should facilitate diffusion along the *c* axis. On the other hand, for an Mg atom to move along the *a* or *b* direction, it would have to hop alternately from an M1 to an M2 site. Since there are much fewer M2 vacancies, diffusion along the *a* or *b* direction should be harder. In fact, experiments have shown this marked diffusion anisotropy in olivine with the energy of activation for D_c, E_c, being much less than E_a or E_b (see Buening and Buseck, 1973; Misener, 1974). Hence the calculations yield an understanding of the observed diffusion anisotropy.

The reasonable results obtained here suggest that the migration energies may also be obtained by the model. Obviously, in this case the repulsion potential will play a bigger role, since the ions will come into closer contact. We are now carrying out such calculations. The migration energy will be directly related to the observed diffusion activation energy for olivine in the case of extrinsic diffusion. This will therefore be an important use of this model in geochemical kinetics.

The energy differences obtained here between the M1 and M2 sites are also directly related to cation exchange calculations. Obviously in this case we would have to compute the energies needed to take out a second type of ion (*e.g.* Fe^{2+}) from the M1 or M2 sites and then take the appropriate differences. The total polarizability of the different ions in minerals becomes, of course, a very important parameter to evaluate for these calculations. For transition metal ions, though, crystal field energies may have to be added besides the polarization and repulsion terms developed here. There are now methods using approximate *ab initio* molecular orbital theories, which can be used to obtain these crystal fields (Ballhausen, 1977).

Finally, the oxygen vacancies are important in the oxygen diffusion. Reddy *et al.* (1980), using proton activation techniques, found an energy of activation for oxygen diffusion in forsterite of 89±3 kcal/mole or 3.9 ev. Anion diffusion in this case may be controlled by both the formation and the migration energies of the vacancy. Since the relation

$$X_{v,O}X_{v,Mg} = \exp[-(E_s/RT)]$$

must always be satisfied, the presence of an impurity controlled (and therefore constant) $X_{v,Mg}$ leads to a simple dependence of $X_{v,O}$ on temperature. E_s is the Schottky formation energy, *i.e.* the energy given in Table 4. Therefore the energy of activation for oxygen diffusion must include both E_s and the migration energy, if the diffusion is intrinsic, and must also be greater than E_s. If the values for the oxygen migration energy are low, the experimental value of 3.9 ev is in reasonable agreement (although somewhat lower) with the values obtained in this paper for the "MgO" Schottky formation energies, E_s. However, if, as is more likely, the migration energy is at least 1–2 ev, the experimental value is substantially less than expected. We expect the migration energy to be at least 1–2 ev, since Misener (1974) obtained an activation energy for magnesium diffusion of 2.64 ev (for T greater than 1125°C) and 1.36 ev (T less than 1125°C) along the *c* axis of forsterite. Since magnesium diffusion is expected to be extrinsic, these values reflect the migration energy for magnesium diffusion. Hence we expect the oxygen migration energies to be at least in the same range. We therefore suggest that the oxygen diffusion measured is extrinsically controlled or is occurring along dislocations.

Summary

We have developed the basic theory needed to understand the formation and migration of defects in "ionic" silicates. Although more work needs to be done in refining the model and in particular the treatment of the silicon–oxygen bonds, the results obtained are encouraging. The computed absolute values of the energies of formation are quite reasonable when compared to results from similar crystals. The ordering of site vacancies in forsterite according to predicted stability (M1 > M2; O3 > O1 or O2) should be important in understanding the atomistic dynamics (*e.g.* diffusion) in olivines. For example, the results obtained here are in complete agreement with the observed diffusion anisotropy in olivines. The type of model developed here will also be used in carrying out molecular dynamical calculations in olivines and in obtaining migration energies for ions in the crystal (and hence activation energies). Extensions of the model to the understanding of site preferences in a crystal should be important, although ligand field calculations must also be performed if transition metal ions are involved.

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