

## **Ionic modeling of mineral structures and energies in the electron gas approximation: TiO<sub>2</sub> polymorphs, quartz, forsterite, diopside**

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### **Abstract**

The modified electron gas (MEG) theory has been used to calculate non-empirical short-range repulsive parameters, which were then employed to calculate minimum-energy structural configurations for quartz, forsterite, diopside and the TiO<sub>2</sub> polymorphs using the ionic model. The structure parameters of the TiO<sub>2</sub> polymorph models match the observed ones to within a few percent, but do not model the slight distortions of TiO<sub>6</sub> octahedra precisely. Calculated structure energies show rutile more stable than anatase by less than 4 kJ/mole and more stable than brookite by about 20 kJ/mole.

The model forsterite structure matches the observed one rather well; the sense of SiO<sub>4</sub> tetrahedral distortions are correct in the model, although the absolute values are not precise. Distortions of model M1 and M2 polyhedra are qualitatively correct but exaggerated in magnitude. Modeling of quartz is less successful; the model structure resembles high quartz closer than low quartz, but the Si-O-Si angle is 163° rather than the observed 145°. Diopside is modeled extremely poorly; some M1-O and M2-O distances are long by up to 130%. Resulting changes in M1 and M2 coordination lead to charge balanced oxygen atoms in the model structure, in contrast to local electrostatic charge imbalances that exist on all oxygens in the observed structure.

### **Introduction**

Structure energy calculations in recent years have provided some important insights into the properties and structural details of a variety of minerals. For example, energy calculations have been used to predict hydroxyl positions in muscovite (Giese, 1971), to determine cation site preferences in pyroxenes (Ohashi and Burnham, 1972) and olivines (Bish and Burnham, 1984), to compare relative stabilities of polymorphs (Catlow et al., 1982), and to interpret positional disorder of alkali cations in amphiboles (Docka et al., 1980) and feldspars (Post and Burnham, 1984). In most of the above studies, a simple ionic model was assumed, and it is perhaps surprising that good results are obtained even for many silicates in which the Si-O bond includes a significant covalent contribution. The successes of these relatively simple calculations provide the incentive to develop more sophisticated and, hopefully, more accurate methods of modeling the bonding forces in structurally complex minerals. This strategy of using the ionic approximation to model entire translationally periodic structures stands in marked contrast with the *ab initio* molecular orbital calculations carried out by Gibbs and others (see, for example, Gibbs, 1982)

on finite molecular clusters. Although the results of cluster calculations are appropriately applied to the behavior of similar fragments in crystals, that applicability is limited by the fact that all aspects of the crystalline environment can not be simulated in the cluster calculations, and cluster size is constrained by computing capacity. In efforts to understand mineral behavior best progress is made when results of both approaches interact and complement each other.

In the ionic approximation the structure energy of a crystal, which is the work required to separate the constituent atoms to infinity, consists of two major components: (1) The long-range or Coulomb interaction energy, and (2) the short-range primarily repulsive energy that results from overlap of electron clouds of neighboring atoms. The Coulomb portion of the structure energy is easily calculated using the Ewald (1921) or Bertaut (1952) summation methods that achieve rapid convergence with Fourier techniques in reciprocal space. In contrast, calculation of the short-range energy is not straightforward, and in fact many previous studies have neglected this contribution altogether. Several functions have been used to represent the short-range interactions; one that has been

widely applied is the Born exponential form (Kittel, 1971, p. 93) given by

$$W_r = \lambda_i e^{-r/\rho_i} \quad (1)$$

where  $W_r$  is the short-range energy for atom pair  $i$  at separation distance  $r$ . The coefficients  $\lambda$  and  $\rho$  are atom-pair dependent and have generally been derived from compressibility data or spectroscopic measurements (see, for example, Bish and Burnham, 1984). One of the drawbacks of this approach is that parameters determined for an atom pair from a single experiment might not be generally applicable to a wide variety of different structures. Also, these methods are severely limited by the shortage of experimental data for many atom pairs. The necessary compressibility data are generally available only for halides and a few simple oxides (e.g., MgO and CaO); they do not exist for mineralogically important pairs such as Na-O, K-O, Al-O, Ti-O, and Si-O. Consequently, several previous studies have approximated the short-range potentials for these metal-oxygen pairs using functions derived for the respective metal halides. Appropriate Born coefficients,  $\lambda$  and  $\rho$ , for cation-anion interactions can be obtained from infrared or Raman spectra only if the force constant for the appropriate polyhedral stretching normal mode can be ascertained.

An alternative, semi-empirical approach for calculating short-range energy terms has been used by Catlow and his coworkers (Catlow, 1977; Catlow et al., 1977; Catlow et al., 1982). The Born coefficients,  $\lambda$  and  $\rho$ , for anion-anion interactions are derived from free-ion Hartree-Fock potentials, while the cation-anion potentials are determined by least-squares fitting to observed interatomic distances in structures similar to those being studied using energy-minimization procedures. Using potentials derived in this manner they have, for example, successfully modeled a number of features of defects in ionic materials (Catlow et al., 1976; Catlow, 1977; Catlow and James, 1982) and have studied structure-composition relationships among pyroxenoids (Catlow et al., 1982). Typically atomic positions and cell parameters are used as observations in the least-squares fitting procedure; because these data are available for most important minerals, it is possible to derive Born coefficients for almost any atom pair. The coefficients are most reliable if derived by fitting to structures that closely resemble the structures being modeled. The general applicability of derived coefficients to a variety of structures must become marginal, or even inappropriate, as the structures increasingly differ from those used for the fittings. Additionally, because  $O^{2-}$  is not a stable species the  $O^{2-}-O^{2-}$  pair potential must be approximated using coefficients calculated for  $O^{1-}-O^{1-}$  interactions.

Obviously, it would be advantageous to be able to calculate all the short-range energy terms by some *ab initio* method, in order to circumvent the limitations posed by a shortage of experimental data and questions that arise as parameters derived by fitting to one set of structures are used to model others. Exact *ab initio* methods, even

at the Hartree-Fock level, however, are ruled out because calculations are complicated even for simple molecules, much less for complex crystals. Thus, some form of approximate nonempirical method is the only alternative at present. The electron gas approach introduced by Gordon and Kim (1972) and subsequently modified by Waldman and Gordon (1979) and Muhlhausen and Gordon (1981a) appears to offer strong promise. The modified electron gas (MEG) theory divides the short-range pair potentials into kinetic, exchange, correlation and nonpoint Coulomb contributions, and each of these terms is written as a functional of the electron densities, using a simple free electron gas approximation. The net electron density of an interacting ion pair is assumed to be a superposition of the individual ionic densities, which are calculated from Hartree-Fock atomic wave functions. For a detailed description of the computational methods used in the MEG procedure, the reader is urged to consult the references to work by Gordon and his coworkers cited above.

The principal advantages of the MEG theory are that no empirical parameters are used in the calculations and that short-range potentials can be easily calculated for a large number of atom pairs important in minerals, including those involving  $O^{2-}$ . Because the MEG approach is based on purely ionic theory, it can provide information about the relative importance of ionic versus covalent interactions in a crystal. Empirically derived short-range potentials on the other hand, describe a mixture of unknown proportions of ionic and covalent contributions, and it is therefore not possible to assess the relative importance of the two effects. Thus, even though empirical methods yield short range parameters that may model a mineral structure reasonably well, such models can provide no real insight into the nature of the bonding in the crystal.

One limitation of the present MEG theory is that short-range energies can be calculated only for pairs involving closed-shell ions (e.g., groups IA-VIIIA), therefore minerals containing Fe, Mn and many of the other transition elements cannot be considered. For minerals involving non closed-shell ions, one approach could be to calculate short-range energies using a combination of MEG potentials and parameters for transition element interactions derived by least-squares fitting to observed structures.

Most energy calculation procedures that assume a crystal's structure energy can be written as the sum of pair interactions between ions ignore many-body contributions to the energy. Such contributions will lead to deviations of the total interaction energy from that calculated by the pair-wise additive approximation. In the context of the MEG theory, many-body contributions cause the charge distributions between atoms to deviate from those of the assumed ideal electron gas. These changes of the electron density are of two forms: (1) isotropic expansion or contraction of the spherical atomic charge densities; and (2) anisotropic distortion or polarization of the electron clouds. A recent modification of the MEG theory (Muhlhausen and Gordon, 1981a) incorporates the first

of these effects, namely isotropic polarization, using anion wave functions that are stabilized by inclusion of a Madelung potential term in the Hamiltonian. Most attempts to model anisotropic polarization in crystals have used some type of shell model (Dick and Overhauser, 1958) in which the anions are divided into a core and moveable shell of electrons. Calculations using simple one-shell models generally yield only slight improvements over the purely ionic case; recent MEG calculations using multiple shells, however, are yielding promising results (Jackson et al., 1985). In the present study we have ignored the effects of anisotropic polarization.

Several workers have demonstrated that structures and cohesive energies of alkali halides and certain simple oxides are modeled well by the MEG procedure despite its limitations (Cohen and Gordon, 1976; Tossell, 1980a,b; Muhlhausen and Gordon, 1981a,b). Tossell (1980a) used the MEG theory to model the structures of low quartz and rutile, and to compare the M1 and M2 site energies in a pyroxene. Currently Jackson and Gordon (pers. commun.) are using the MEG method to model the olivine and spinel forms of  $Mg_2SiO_4$ .

We report here models of the structures of quartz, forsterite, diopside, and the  $TiO_2$  polymorphs—rutile, anatase, and brookite—using MEG-derived short-range energy terms. The primary purpose of this study is to investigate how well the purely ionic MEG theory models a variety of mineral structures. In addition we use our calculated structure energies to compare the relative stabilities of the three  $TiO_2$  polymorphs. Finally we present a table of MEG-derived Born-type short-range energy coefficients for several atom pairs commonly found in minerals.

### Calculations

All structure energy calculations and minimizations in this study were performed using the computer program *WMIN* (Busing, 1981), that we modified to use a Born exponential to calculate the short-range energy terms. The coefficients  $\lambda$  and  $\rho$  (equation 1) for each atom pair were determined by fitting Born exponentials to MEG short-range potential curves that were calculated using the computer program *LEMNPI* (Muhlhausen and Gordon, 1981a). The MEG calculations were carried out with Hartree-Fock self-consistent field (SCF) atomic wave functions calculated by Mark Jackson (Chemistry Department, Harvard University) using computer programs developed by Laws and coworkers (1971), and modified to include potential shells on the anions. The anions are effectively surrounded by charged shells that simulate the potential distribution surrounding an anion in a crystal, and in the case of oxygen serve to stabilize the  $O^{2-}$  wave function, which does not exist as a stable species in the isolated state. The shell radii are adjustable, allowing the anion electron cloud to expand or contract isotropically (i.e., isotropic polarization).

According to Muhlhausen and Gordon (1981a), a simple but physically reasonable method of adjusting an an-

ion shell radius ( $r_i$ ) is to select a value that yields a shell potential,  $V_i = N_i/r_i$  (where  $N_i$  is the shell charge = +2 for O), that is equal to the site potential at the nucleus of the anion in the crystal. An initial calculation is performed using estimated values for anion shell radii, during which the structure parameters are varied to minimize the structure energy. The site potentials are calculated (by *LEMNPI*) for the anions in the minimum energy structure, and new shell stabilized (SS) wave functions are selected that have shell radii consistent with the site potentials (i.e.,  $r_i = N_i/\text{site potential}$ ). Self consistency is achieved when the shell potentials used in the calculation match the respective site potentials in the minimized structure to within  $\sim 1\%$ . In practice, we selected our initial anion wave functions using site potentials calculated for experimentally observed structures of the mineral being modeled. In most cases, we observed only slight ( $<1\%$ ) differences between the anion site potentials in the observed and minimum energy structures. Our calculations show that for structures which the MEG theory models well (halides,  $TiO_2$ , forsterite), the unit-cell volume of the minimum energy configuration best matches the observed value (usually to within a few percent) when the anion shell potentials are equal to the site potentials. The good agreement between calculated and observed cell volumes suggests that the method described above for selecting shell stabilized anion wave functions is probably a valid one.

Although the computer program *LEMNPI* can be used for determining minimum energy structures, *WMIN* is a more flexible and efficient program for that purpose. *LEMNPI* was used only to calculate site potentials and short-range energy coefficients. For each ion pair in a structure, *LEMNPI* calculates the short-range energy for a specified range of separation distances, and for structure energy calculations performed with *LEMNPI*, the short-range energy contribution for each ion pair is derived by cubic spline interpolation. In our calculations, we fit a Born exponential (equation 1) to the short-range potential curve determined by *LEMNPI* for each ion pair. The natural log of the short-range energy ( $\ln W_i$ ) calculated by *LEMNPI* plotted against the ion separation distance,  $r$ , yields a line whose slope is the negative inverse of  $\rho$  in the Born exponential and whose intercept is  $\ln \lambda$ . Least-squares fitting of the line for each ion pair was performed over a range of separation distances that encompassed the nearest neighbor bond lengths observed for the pair in the crystal of interest, or, in the case of anion-anion interactions, next-nearest-neighbor distances. In all cases the correlation coefficients between the parameters of the calculated line and the MEG potentials were greater than 0.9995. It should be pointed out that  $\ln W_i$  vs.  $r$  plots, though nearly linear in the range of nearest-neighbor and next-nearest-neighbor separation distances, may not be strictly linear for larger separations, e.g., those corresponding to third-nearest-neighbor and higher interactions. Thus a more flexible fitting procedure or interpolation scheme might yield slightly improved results. Yet when *WMIN*-based calculated results for the  $TiO_2$  polymorphs and forsterite

Table 1. Born-type repulsive parameters from least-squares fitting to MEG short-range potentials

Ion pair	Anion shell radius(Å)	Fitting range(Å)	$\lambda$ (kJ/mole)	$\rho$ (Å)
Na-O	1.01	2.33 - 2.75	563166	0.2387
Na-F	1.22	2.28 - 2.70	626763	0.2214
Na-Cl	1.64	2.65 - 2.96	433462	0.2727
Mg-O	0.93	1.80 - 2.35	418986	0.2371
	1.01	"	359196	0.2457
	1.03	"	359155	0.2479
	1.05	"	337440	0.2498
	1.08	"	307189	0.2545
	1.11	"	287985	0.2581
Mg-F	1.14	1.80 - 2.35	342335	0.2298
Al-O	1.01	1.48 - 1.91	332419	0.2461
Al-F	1.14	1.48 - 1.91	317775	0.2288
Al-Cl	1.64	2.10 - 3.20	296311	0.2831
Si-O	0.93	1.48 - 1.80	406350	0.2342
	1.01	"	358150	0.2428
	1.03	"	345264	0.2456
	1.05	"	337063	0.2472
	1.08	"	318026	0.2512
	1.11	"	302378	0.2546
Si-F	1.14	1.50 - 1.80	325013	0.2265
Si-Cl	1.64	2.10 - 3.20	287441	0.2853
K-O	1.01	2.70 - 3.10	6297548	0.2134
K-F	1.14	2.60 - 3.01	4433115	0.2078
Ca-O	0.93	2.17 - 2.60	832030	0.2411
	1.01	"	671365	0.2516
	1.11	"	464591	0.2664
Ca-F	1.14	2.10 - 2.60	839394	0.2316
Ca-Cl	1.64	2.65 - 2.95	793872	0.2729
Ti-O	1.08	1.85 - 2.12	440826	0.2607
	1.10	"	430199	0.2620
	1.11	"	416350	0.2639
Sr-O	1.01	2.43 - 2.85	1670546	0.2400
Ba-O	1.01	2.70 - 3.02	2853488	0.2401
O-O	0.93-0.93	2.38 - 2.91	393087	0.2746
	0.93-1.11	"	256772	0.2924
	1.01-1.01	"	290997	0.2876
	1.03-1.03	"	216020	0.2959
	1.03-1.05	"	235476	0.2969
	1.03-1.08	"	221752	0.2995
	1.05-1.05	"	229743	0.2980
	1.05-1.08	"	216857	0.3005
	1.08-1.08	"	205058	0.3029
	1.10-1.10	"	193175	0.3055
	1.10-1.11	"	186146	0.3072
	1.11-1.11	"	180079	0.3086
O-F	1.01-1.14	"	350284	0.2715
O-Cl	1.01-1.64	"	351874	0.2948
F-F	1.14-1.14	"	474968	0.2517
Cl-Cl	1.64-1.64	"	277106	0.3173

obtained using our fitted parameters are compared with results obtained using the interpolation procedures of LEMINPI, no significant differences are apparent. The values of  $\lambda$  and  $\rho$  and separation distances over which equation (1) was fit to the MEG potentials are listed in Table 1 for all of the ion pairs considered in this study, and for several other pairs common in minerals.

The Coulomb energy terms are summed by *wmin* using the method of Ewald (1921) and Bertaut (1952). The summations were carried out within a sphere of radius 6.0 Å in direct space and 0.6 Å in reciprocal space. Formal charges corresponding to conventional valence were assigned to all ions. One of the attractive features of *wmin* is that it offers a choice of three different procedures for calculating minimum energy structures. In mode 1, the minimum energy configuration is obtained by Newton's

method, which calculates first and second derivatives. Mode 2 minimizes energy by the method of steepest descents, which requires that only first derivatives be calculated. In mode 3 the program uses the Rosenbrock search technique which requires no derivatives. Newton's method works very well when the model is close to the minimum energy configuration. In other cases, however, it might locate a saddlepoint or not converge at all, as occurred during our initial energy minimization for the rutile structure. The Rosenbrock search procedure, on the other hand, takes longer to reach a final minimum, but it will always move toward a lower energy, even from a saddlepoint (Busing, 1981). The minerals considered in this study have relatively few variable parameters, and therefore we were able to perform all energy minimizations using the Rosenbrock search method and still obtain convergence within a reasonable amount of computing time. During the energy minimizations, we allowed all of the adjustable structural parameters, including cell parameters, to vary simultaneously.

Modified electron gas calculations indicate that for separation distances normally encountered in crystals, cation-cation short-range interactions are insignificant and can be ignored. Consequently, these terms were not included in any of our models.

The reference state for structure energies obtained directly from the *wmin*-MEG procedure consists of cations and shell-stabilized (SS) anions at infinite separation. Such structure energies cannot be determined empirically because free SS anions do not exist; therefore they are not comparable to any experimental energies, although unfortunately such comparisons have been made in some previous studies. A thermodynamically meaningful quantity is the dissociation energy ( $D_e$ ) of the crystal into free cations and anions. To obtain  $D_e$  from our theoretically calculated structure energy, however, one must know the self-energy difference between the SS and free anions. The self-energy terms can be obtained during the Hartree-Fock SCF calculations (Muhlhausen and Gordon, 1981a);  $D_e$  is then the sum of the structure energy from *wmin* and the self-energy. An additional consideration arises for crystals containing  $O^{2-}$ . The oxide anion is unstable in the gas phase, and consequently its heat of formation is not experimentally known. In the case of oxides, the experimentally obtainable quantity is the dissociation energy into free cations,  $O^{1-}$  ions, and electrons. Thus, to obtain a value comparable with experimental energies, we must add the difference between the self-energies of the gas phase  $O^{1-}$  and SS  $O^{2-}$  anions to the structure energies calculated using SS  $O^{2-}$  wavefunctions. The self-energy differences used in our calculations are listed in Table 2.

Finally, we note that our calculations are for a static lattice at 0 pressure. We assume that temperature and pressure effects on configurations and energies are sufficiently small that—given the level of accuracy of the calculations—our results can be compared directly to experimental observations made under standard conditions. Furthermore because the lattice dynamical behavior of

Table 2. Self energies for  $O_{ss}^{2-} \rightarrow O^{1-} + e^{-}$ 

$O_{ss}^{2-}$ Shell radius(Å)	Self energy (kJ/mole)*
0.93	1225.95
1.01	1113.40
1.03	1078.22
1.05	1061.44
1.08	1026.29
1.10	1015.79
1.11	1001.61

\* Calculated by Mark Jackson, Chemistry Dept., Harvard University.

the three rutile polymorphs must be very similar, the calculated structure energy differences probably outweigh any entropy differences, and hence they approximate free energy differences at low temperature and pressure.

### TiO<sub>2</sub> polymorphs

Three polymorphs of TiO<sub>2</sub>—rutile, anatase and brookite—occur in nature. Of these, rutile is the most abundant and probably the most stable phase, with anatase and brookite being metastable with respect to it (Lindsley, 1976). Although several studies of the relative stabilities of these polymorphs have been made, there is some question as to whether published phase diagrams represent equilibrium conditions (Lindsley, 1976). In each of the three polymorphs, Ti<sup>4+</sup> is in octahedral coordination, but the number of edges shared by the Ti-O octahedra vary from two in rutile to three in brookite and four in anatase. It has been suggested that the relative stabilities of the three phases might be inversely related to the number of shared edges, with rutile more stable than brookite, which would be more stable than anatase (Evans, 1966). Navrotsky and Kleppa (1967) measured a  $\Delta H$  of  $-5.27$  kJ/mole for the reaction anatase  $\rightarrow$  rutile. No experimental data are available for the conversion of brookite to either rutile or anatase.

We calculated structure energies and minimum energy configurations for all three polymorphs. The energy minimizations were carried out in the space groups of the observed structures— $P4/mnm$ ,  $I4_1/amd$ , and  $Pcab$  for rutile, anatase, and brookite, respectively. Observed atom positions and cell parameters were used as initial coordinates for the minimizations. The results of these calculations are summarized in Tables 3 and 4.

Rutile and anatase structures each have three parameters ( $a$ ,  $c$ , and an oxygen positional parameter) that can be adjusted during the energy minimizations. The site potential of the oxygen atom in rutile is 0.95 and in anatase it is 0.97. Using the relationship  $V_i = -2/r_i$  the corresponding shell radii for the SS O<sup>-2</sup> wave functions become 1.11 Å and 1.08 Å, respectively. The cell parameters and volumes for our minimum energy structures of rutile and anatase (Table 3) compare fairly well with observed values, although the calculated  $c$  cell dimension is 3.5% too long in rutile and 6.1% too long in anatase. The observed and calculated mean Ti-O distances for both anatase and rutile compare extremely well, yet the precise distortions

Table 3. MEG-WMIN minimum energy structures of rutile and anatase compared with observed structures

	Rutile (P4/mnm)			Anatase (I4 <sub>1</sub> /amd)		
	Min. energy model	Observed structure	Calc. obs(%)	Min. energy model	Observed structure**	Calc. obs(%)
$a$ (Å)	4.491	4.594	-2.2	3.689	3.776	-2.3
$c$	3.063	2.959	+3.5	10.067	9.486	+6.1
$V$ (Å <sup>3</sup> )	61.78	62.43	-1.0	137.00	135.25	+1.3
Ti-O (x4)	1.961	1.948	+0.7	1.909	1.930	-1.1
Ti-O (x2)	1.935	1.980	-2.3	2.030	1.973	+2.9
<Ti-O>	1.952	1.959	-0.4	1.949	1.944	+0.3
O-O (sh)	2.462	2.536	-2.9	2.405	2.459	-2.2
$D_0$ (kJ/mole)***	-9875.9	-9861.7		-9876.3	-9857.9	
O <sup>2-</sup> shell radius(Å)	1.11			1.08		

\* Abrahams and Bernstein (1971).  
 \*\* Megaw (1973, p. 277).  
 \*\*\* The dissociation energy,  $D_0$ , determined for rutile by a Born-Haber calculation using experimental data is -10385 kJ/mole.

of the Ti-O octahedra are not modeled correctly. In the observed rutile structure the axial Ti-O bonds are 0.032 Å longer than the equatorial bonds, whereas in our model structure the opposite is true by 0.026 Å. The shared edge O-O distance predicted by our calculation for rutile is 0.074 Å less than the observed value. In anatase, the sense of the octahedral distortion is predicted correctly, but the calculated difference between the axial and equatorial Ti-O distance is 0.12 Å compared with 0.043 Å in the observed structure. The O-O shared edge in our minimum energy model of anatase is 0.05 Å too short.

The brookite structure has two oxygen atoms per asymmetric unit and 12 parameters that can vary during the energy minimization. The site potentials for the two oxygen atoms are 0.95 and 0.96, corresponding to SS O<sup>-2</sup> wave functions with shell radii of 1.11 Å and 1.10 Å, respectively. The cell parameters of the model structure compare to within 1.5% of the observed values and the cell volume matches exactly (Table 4). The modeled average Ti-O distance is the same as for the observed structure, however, individual Ti-O distances deviate by as much as 0.065 Å (3.3%). Also, as in the cases of rutile and anatase, the shared edge O-O distances are underestimated in our model structure by about 0.05 Å (2%).

The discrepancies between the minimum energy and observed configurations of rutile, anatase and brookite indicate that although the ionic model describes fairly well the gross aspects of the structures, the precise details of octahedral distortions must result from covalency effects in the bonding. This is consistent with the prediction using Pauling electronegativity tables that the Ti-O bond is 63% ionic, and therefore should contain a significant covalent component. Based on differences between calculated and experimental heats of formation, Tossell (1980a) concluded that covalency contributions are important for stabilizing the rutile structure. In contrast Baur (1961, 1970) concluded that distortions in rutile can be modeled using a simple ionic theory. Baur, however, approximated the short-range energy terms with Leonard-Jones type func-

Table 4. MEG-W<sub>MIN</sub> minimum energy and observed structures of brookite

	Min. energy model*	Observed structure**	CalC-obs(%)
a(Å)	9.171	9.184	-0.1
b	5.373	5.447	-1.4
c	5.224	5.145	+1.5
V(Å <sup>3</sup> )	257.42	257.38	+0.
Ti-O1	1.904	1.865	+2.1
Ti-O1'	1.998	1.992	-0.3
Ti-O1''	1.929	1.994	-3.3
Ti-O2	1.956	1.919	+1.9
Ti-O2'	1.931	1.946	-0.8
Ti-O2''	2.017	2.039	-1.1
<Ti-O>	1.956	1.959	-0.4
O1-O1(sh)	2.434	2.485	-2.1
O2-O2(sh)	2.462	2.514	-2.1
D <sub>e</sub> (kJ/mole)	-9856.7	-9837.0	

\* O<sup>2-</sup> shell radii: 1.11Å for O1; 1.10Å for O2.  
 \*\* Baur (1961).

tions, which incorporate experimentally derived parameters. As mentioned above, such empirical potential functions inherently describe whatever mixture of covalent and ionic bonding exists in the crystal making it impossible to assess quantitatively the relative effects of these two components on the structural configuration.

Calculated dissociation energies for the observed and minimum energy structures of rutile, anatase, and brookite are given in Tables 3 and 4. The experimental dissociation energy for rutile, determined by a Born-Haber calculation, is about 4.9% greater than our calculated value. This difference is less than that reported by Tossell (1980a) for rutile, but still indicates a significant covalent contribution to the structure energy. The necessary thermodynamic data are not available for determining experimental dissociation energies for anatase and brookite.

Our calculated dissociation energies for the observed TiO<sub>2</sub> structures indicate that rutile is the most stable and brookite the least stable of the polymorphs at 0 K and 0 pressure. The difference between the calculated dissociation energies for the observed structures of rutile and anatase is 3.8 kJ/mole, which perhaps coincidentally is close to the  $\Delta H$  of -5.3 kJ/mole measured by Navrotsky and Kleppa (1967) for the reaction of anatase to rutile. We calculate anatase to be more stable than brookite by about 21 kJ/mole. The minimum energy configurations for rutile and anatase have essentially equal dissociation energies (anatase is more stable by ~0.4 kJ/mole), and are more stable than the minimized brookite structure by about 20 kJ/mole. Our indication that anatase is more stable than brookite is contrary to the prediction of Evans (1966) based on the relative number of shared Ti-O octahedral edges in the structures, but is consistent with the greater natural frequency of occurrence of anatase.

All of the dissociation energies reported here include the self-energy terms for O<sup>2-</sup> → O<sup>1-</sup> + e<sup>-</sup>. Because the SS O<sup>2-</sup> wavefunctions used in the three polymorphs are different, it is essential that the appropriate self-energies be included before comparing dissociation energies. It is

Table 5. MEG-W<sub>MIN</sub> minimum energy structures of quartz compared with observed structures

Unit cell	Low quartz observed*	High quartz observed*	Minimum energy structures as function of O <sup>2-</sup> shell radius		
			0.93Å	1.01Å	1.06Å
a, Å	4.91	5.01	4.97	5.05	5.10
c	5.40	5.47	5.52	5.60	5.66
V, Å <sup>3</sup>	112.74	118.90	118.00	123.68	127.33
<u>Interatomic distances</u>					
Si-O, Å		1.594	1.564	1.588	1.603
Si-O'		1.613	1.609	1.588	1.604
<O-O>	2.618	2.626	2.553	2.592	2.618
<u>O-Si-O angles</u>					
Range, °	108.6-111.4	103.0-114.7	104.4-116.3	104.2-116.5	104.2-116.5
Variance, °	1.4	28.6	29.3	30.8	31.5
Si-O-Si, °	144.6	148.7	162.6	162.8	162.9
D <sub>e</sub> (kJ/mole)**			-11079	-11046	-11004

\* Megaw (1973, pp. 263-265).

\*\* Experimental low quartz D<sub>e</sub> from Born-Haber calculation: -11627 kJ/mole.

interesting to note that if the self-energy terms are omitted, the structure energies show anatase more stable than rutile by 46 kJ/mole.

### Quartz, forsterite and diopside

Traditional Pauling electronegativity differences indicate that the Si-O bond has 50% ionic and 50% covalent character; thus, it ought to be questionable whether the purely ionic MEG theory can be used to model silicate structures effectively. In order to investigate the applicability of our MEG-W<sub>MIN</sub> procedure to silicate minerals, we have calculated minimum energy structures for quartz, forsterite, and diopside.

Site potentials for the O anions in both high and low quartz are 1.14, corresponding to SS O<sup>-2</sup> wavefunctions with shell radii of 0.93 Å. The energy minimization calculations were performed in space group P3<sub>2</sub>21 (right-handed low quartz), which allows six variable parameters; initial atom coordinates and cell parameters were those for low quartz given by Megaw (1973, p. 265). Our calculated minimum energy configuration is most similar to that of high quartz (Table 5). The cell volume of the minimized structure is nearly the same as that of high quartz (at ~600°C) but about 5% larger than for room temperature low quartz. Our model yields equal values for the two independent Si-O bond distances, as is the case for high quartz, but they are about 0.05 Å shorter than the observed values. The model Si-O distances are dependent on the O<sup>2-</sup> shell radius used in the calculation; they range from 1.564 to 1.603 Å as the shell radius is increased from 0.93 to 1.06 Å (Table 5). The larger shell radii, even though giving improved Si-O bond distances, yield minimized structures with cell volumes significantly larger (5-10%) than the observed values for high quartz.

Angle variance of the calculated Si tetrahedron (undistorted = 0) is 29.3° compared to 1.4° observed for low quartz and 28.6° observed for high quartz. Framework configuration is modeled poorly: the calculated Si-O-Si angle is 162.6° rather than 144.6° and 148.7° in low and

Table 6. Comparison of observed and minimum energy forsterite structures calculated with MEG repulsions and semi-empirical Born-type repulsions

	Observed structure*	Semi-empirical repulsion model**	MEG potential repulsion model***
<b>Unit cell</b>			
a, Å	4.7535(4)	5.040 (+6.0)	4.874 (+2.5)
b, Å	10.1943(5)	10.187 (-0.1)	10.322 (+1.2)
c, Å	5.9807(4)	6.054 (+1.2)	5.977 (-0.1)
V, Å <sup>3</sup>	289.80(5)	310.71 (+7.2)	300.55 (+3.7)
<b>Si Tetrahedron</b>			
Si-O1, Å	1.615(3)	1.622 (+0.4)	1.560 (-3.4)
Si-O2, Å	1.640(3)	1.683 (+2.6)	1.606 (-2.1)
Si-O3(x2), Å	1.633(2)	1.641 (+0.5)	1.586 (-2.9)
<Si-O>	1.630	1.647 (+1.0)	1.585 (-2.8)
<b>M1 Octahedron</b>			
Mg1-O1(x2), Å	2.083(2)	2.100 (-0.8)	2.076 (-0.3)
Mg1-O2(x2), Å	2.074(2)	2.186 (+4.9)	2.119 (+2.2)
Mg1-O3(x2), Å	2.145(3)	2.230 (+4.0)	2.251 (+4.9)
<Mg1-O>	2.101	2.172 (+3.4)	2.149 (+2.3)
<b>M2 Octahedron</b>			
Mg2-O1, Å	2.166(3)	2.205 (+1.8)	2.332 (+7.7)
Mg2-O2, Å	2.045(5)	2.094 (+2.4)	2.085 (+2.0)
Mg2-O3(x2), Å	2.064(4)	2.087 (+1.1)	2.035 (-1.4)
Mg2-O3'(x2), Å	2.208(4)	2.330 (+5.5)	2.353 (+6.6)
<Mg2-O>	2.126	2.189 (+3.0)	2.199 (+3.4)
O2-O3 (sh)	2.558(5)	2.445 (-4.4)	2.436 (-4.8)
O3-O3' (sh)	2.590	2.578 (-0.5)	2.533 (-2.2)
D <sub>e</sub> (kJ/mole)	-16844.0		-16938.9

\* Hazen (1976); esd's are in parentheses.

\*\* Calculated using WMIN with semi-empirical short-range energy parameters reported by Catlow et al. (1982); % deviations from observed values are in parentheses.

\*\*\* O<sup>2-</sup> shell radii are: O1=1.03Å, O2=1.05Å, O3=1.08Å; % deviations from observed values are in parentheses.

Table 7. Comparison of observed and minimum-energy diopside structures calculated with MEG repulsions and semi-empirical Born-type repulsions

	Observed*	Semi-empirical repulsions**	MEG repulsions***
<b>Unit cell</b>			
a, Å	9.75	10.91 (+12)	11.34 (+16)
b, Å	8.90	8.67 (-2.6)	11.00 (+24)
c, Å	5.25	5.55 (+5.7)	5.41 (+3.0)
β, °	105.6	112.6 (+6.6)	118.7 (+12)
V, Å <sup>3</sup>	438.6	484.9 (+11)	592.3 (+35)
<b>Si Tetrahedron</b>			
Si-O1(C1), Å	1.60	1.63 (+1.9)	1.60 (+0)
Si-O2(C1), Å	1.59	1.64 (+3.1)	1.60 (+0.6)
Si-O3(C1), Å	1.66	1.70 (+2.4)	1.58 (-4.8)
Si-O3(C2), Å	1.69	1.76 (+4.1)	1.59 (-5.9)
<Si-O>	1.63	1.68 (+3.1)	1.59 (-2.5)
<b>Chain angle:</b>			
O3C1-O3C2-O3C1'	166.4°	162.9° (-2.1)	179.5° (+7.9)
<b>Mg (M1) polyhedron</b>			
Mg-O1(A1,B1), Å	2.12	2.17 (+2.4)	4.87 (+130)
Mg-O1(A2,B2), Å	2.06	2.06 (+0)	1.96 (-4.9)
Mg-O2(C1,D1), Å	2.05	2.09 (+2.0)	1.96 (-4.4)
<Mg-O>	2.08	2.11 (+2.9)	2.93 (+41)
Mg-Mg, Å	3.10	3.17 (+2.3)	4.98 (+60)
<b>Ca (M2) polyhedron</b>			
Ca-O1(A1,B1), Å	2.36	2.31 (-2.1)	2.16 (-8.5)
Ca-O2(C2,D2), Å	2.35	2.83 (+2.0)	2.16 (-8.1)
Ca-O3(C1,D1), Å	2.56	2.53 (-1.2)	3.72 (+45)
Ca-O3(C2,D2), Å	2.72	3.45 (+27)	4.50 (+65)
<Ca-O>	2.50	2.78 (+11)	3.14 (+25)

\* Cameron et al. (1973); atom notation from Burnham et al. (1967).

\*\* Calculated using WMIN with semi-empirical short-range energy parameters reported by Catlow et al. (1982); % deviations from observed values are in parentheses.

\*\*\* O<sup>2-</sup> shell radii: O1,2=1.11Å; O3=0.93Å; % deviations from observed values are in parentheses.

high quartz respectively; the calculated angle is furthermore nearly independent of the O<sup>2-</sup> shell radius used. Our calculated Si-O-Si angle does, however, represent an improvement over the value of 180° reported by Tossell (1980a) from MEG calculations on quartz.

The differences between the minimum energy and observed quartz structures point out the mixed ionic and covalent character of the Si-O bond. The fact that our ionic model most closely resembles high quartz indicates that the covalency effects are slightly more pronounced in low quartz. In either case, however, it is obvious that in order to model quartz accurately using structure energy calculations, it is essential to consider both covalent and ionic effects. Recently, Jackson et al. (1985) have developed a greatly improved model for quartz, using a multiple shell approach to represent the anisotropic polarization of the O<sup>2-</sup> electron cloud.

Despite the deviations of our model structure from the observed low quartz configuration, our calculated dissociation energy of 10924 kJ/mole is only about 6% less than the experimental quantity of 11627 kJ/mole. Thus, although covalent interactions significantly affect the geometry of the quartz structure, they apparently contribute only slightly to the total D<sub>e</sub>. This observation is consistent with Gibbs' (1982) molecular orbital results for the energy of Si-O as a function of distance and angle that show an extensive minimum energy trough extending over a rather large range of Si-O-Si angles within a restricted range of Si-O distances.

Minimum energy structures for forsterite and diopside are summarized in Tables 6 and 7. Different SS O<sup>2-</sup> wavefunctions were used for each of the three crystallographically distinct O atoms in forsterite, and two SS O<sup>2-</sup> wavefunctions were used in our model for diopside. The O anion shell radii are included in Tables 6 and 7.

The unit cell parameters for the forsterite minimum energy configuration compare to the observed values within 2.5%, and the cell volume is within 3.7%. The calculated Si-O bond distances are all 0.03 to 0.05 Å too short, as was the case for quartz. The relative distortions in the tetrahedra are, however, modeled generally correctly, indicating that the source of these distortions is at least partly ionic in character and related to the topology of the structure. The shared edge O-O bond distances are 0.06 and 0.11 Å too short in our model structure. The average Mg<sub>1</sub>-O and Mg<sub>2</sub>-O distances are 0.5 and 0.64 Å (2.4 and 3.0%) longer, respectively, than the observed distances, and individual Mg-O distances deviate by a maximum of 0.14 Å (6.6%).

Although we are able to model the forsterite structure reasonably well, we are far less successful with diopside (Table 7). The unit cell parameters for our calculated diopside structure range from 3% (c) to 24% (b) larger than experimental values, and the cell volume is 35% too large. Again, the Si-O predicted bond lengths are too short. The four Si-O distances in our model fall between 1.58 and 1.60 Å, compared with a range of 1.59 to 1.69 Å in the actual structure. The largest deviations between the ob-

served and minimized diopside structures occur in the M-O distances. The average Mg-O and Ca-O distances exceed the observed values by 41% and 25%, respectively. The Mg-O1(A1,B1) bond distances in our minimum energy configuration are 130% too long and the Ca-O3 (C1,D1) and Ca-O3(C2,D2) distances are long by 45% and 65% respectively.

The fact that we model forsterite successfully but fail modeling diopside with the purely ionic MEG/WMIN procedure indicates that the forsterite structure is substantially ionic while that of diopside involves departures from ionicity that are fatal to the specific procedure employed here. In forsterite each O atom has a Pauling bond-strength sum of exactly 2.0, hence the structure fully obeys Pauling's local electrostatic valence rule for ionic materials. The bond strength sums for the three crystallographically distinct O atoms in diopside, however, are 1.91 on O1, 1.58 on O2, and 2.5 on O3 assuming Ca in 8 coordination. In our minimum energy diopside structure the coordinations of Ca and Mg have both been effectively reduced to four (considering only M-O distances less than 3.0 Å), resulting in Pauling bond-strength sums for all three O atoms of 2.0. Our minimum energy configuration thus depicts a hypothetical diopside structure that would obtain if the bonding were purely ionic. Also, this result suggests that the existing local charge imbalances are related to substantial covalent contributions to the bonding.

### Summary

We have calculated minimum energy structure configurations for quartz, forsterite, diopside and the three TiO<sub>2</sub> polymorphs, using short-range potentials derived from the nonempirical MEG theory. Our models for the TiO<sub>2</sub> polymorphs, in general, match the observed structures to within a few percent, although slight distortions in the Ti-O octahedra are not modeled correctly in detail. Our calculated dissociation energies show rutile to be more stable than anatase by 3.8 kJ/mole and more stable than brookite by about 20 kJ/mole. In quartz, forsterite, and diopside our predicted Si-O bond distance are consistently too short by about 0.05 Å. Overall, we model the forsterite structure quite well, but quartz is modeled rather poorly because the model Si-O-Si angle is 16° wider than observed. Diopside is modeled badly, but the poor model does exhibit local electrostatic charge balance on all oxygen atoms, in contrast to the real structure in which no oxygen atoms achieve Pauling charge balance.

The purely ionic MEG-WMIN procedure thus works best for structures that are strongly ionic, such as the TiO<sub>2</sub> polymorphs. In the cases of quartz and the silicate minerals, the deviations between the minimum energy and observed structures can be substantial. We conclude, then, that for the MEG procedure to be useful for modeling many silicates or for predicting mineral structures, the theory must include treatments of anisotropic polarization and other covalency effects. Recently Hemley and Gordon (1985) and Hemley et al. (1985) have demonstrated improved agreement of calculated lattice param-

eters with observation for alkali halides and alkaline-earth oxides using a modified calculation procedure that incorporates the volume dependence of the ion self-energies directly in the minimizations. The multiple shell approach reported by Jackson et al. (1985) models successfully the anisotropic polarization effects in quartz. These and other improvements will continue to enhance the power of the electron gas approximation.

### Acknowledgments

We thank Mark Jackson for discussion and guidance in the use of MEG methods, and especially for providing us with shell stabilized O<sup>2-</sup> self energies. Russ Hemley provided a helpful review. All calculations were carried out on Harvard University geophysics computing facilities. This research was supported by NSF Grant EAR 79-20095 to Charles W. Burnham.

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*Manuscript received, April 23, 1985;  
accepted for publication, September 22, 1985.*