

Orientation, location, and total energy of hydration of channel H₂O in cordierite investigated by ab-initio total energy calculations

BJÖRN WINKLER

Mineralogisch-Petrographisches Institut der Christian Albrechts Universität, Olshausenstraße 40, D-24098 Kiel 1, Germany

VICTOR MILMAN

Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6031, U.S.A.

MICHAEL C. PAYNE

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K.

ABSTRACT

Ab initio total energy calculations, based on the local density approximation, have been performed for hydrated Mg end-member cordierite to elucidate the location, orientation, and total energy of hydration in the ground state. In contrast to diffraction studies, but consonant with the interpretation of infrared experiments, the calculations demonstrate that the energetically most stable orientation of the H₂O molecule in alkali-free Mg end-member cordierite is with the proton-proton vector parallel to [001]. The H₂O molecule in cordierite is calculated to be nearly undistorted, and there is only very weak H bonding, again in contrast to the structural studies and a recent interpretation of a calorimetric study, but in agreement with the interpretation of spectroscopic and quasi-elastic neutron scattering experiments. Furthermore, the calculations show that the H₂O molecule is slightly displaced relative to the center of the cavity in (001). The calculated displacement of the O atom in H₂O is 0.04 Å to 0,0,¼, in agreement with results obtained by quasi-elastic incoherent neutron scattering experiments. The total energy of hydration for cordierite with one H₂O molecule per primitive unit cell with fixed unit-cell parameters has been calculated to be ≈0.4 eV. Local distortions in the framework caused by the incorporation of the H₂O molecule are very small, which indicates ideal mixing between H₂O and anhydrous Mg end-member cordierite.

INTRODUCTION

Natural cordierite, (Mg,Fe)₂[Al₄Si₃]O₁₈·nH₂O, has an orthorhombic framework structure (space group *Cccm*) with cavities (approximately 6 Å in diameter) that are linked to form channels parallel to [001] (Gibbs, 1966). A variety of atoms, ions, and molecules can be incorporated into the cavities. In natural cordierite the channels are commonly occupied by H₂O, CO₂, and alkali ions (Armbruster and Bloss, 1982). The channels can be evacuated by heating and refilled under pressure (Johannes and Schreyer, 1981; Armbruster, 1985). Smith and Schreyer (1962) and Langer and Schreyer (1976) deduced from geometric considerations that only one H₂O molecule can be incorporated into a single cavity. There have been suggestions that there might be two adjacent H₂O molecules in a single cavity (Mirwald, 1982). However, no such double occupation has been detected in structural, calorimetric, or spectroscopic studies of either synthetic or natural cordierite. The enthalpy of dehydration of synthetic Mg end-member cordierite has recently been determined by Carey and Navrotsky (1992) to be 41.782 kJ/mol. Carey and Navrotsky (1992) concluded that the mixing between H₂O and cordierite is thermodynamical-

ly ideal. Reviews on the incorporation of molecules into alkali-free and alkali-bearing cordierites have been presented by Schreyer (1985, 1986).

The orientation and the dynamics of the H₂O molecules in cordierite have been the subject of several contradicting spectroscopic and structural studies. Cohen et al. (1977) concluded that in natural Mg-rich samples the H₂O was oriented with its molecular plane parallel to (001) and inferred from their structure refinements that the H₂O molecule was strongly asymmetric [*d*(H1-O) = 1.04 Å, *d*(H2-O) = 0.97 Å] and that the H1-O-H2 angle was compressed to 102.4°. Cohen et al. (1977) assumed disorder over four positions. Hochella et al. (1979) proposed that the O in H₂O was located at ±0.027,0,¼, and that the molecular plane was inclined by ≈29° from (100) with the H-H vector inclined 19° from [001]. Hochella et al. (1979) also concluded that the H₂O molecule was asymmetric.

Based on infrared spectroscopic studies, other workers (Farrel and Newnham, 1967; Goldman et al., 1977; Aines and Rossman, 1984) thought that in ideal alkali-free cordierite the proton-proton vector of the channel H₂O is oriented parallel to [001](H₂O type I), and alkalis in the center of the rings that link the cavities cause a different

orientation (H₂O type II), where the proton-proton vector is lying in (001). With NMR experiments Tsang and Ghose (1972) and Carson et al. (1982) showed that the H₂O molecule was dynamically disordered at room temperature. Carson et al. (1982) inferred from their data that the time scale of the motion was much longer than the typical time scale of the infrared experiment and that the H₂O molecule was tumbling in the cage. However, according to Winkler et al. (in preparation) the dynamics of the H₂O molecule are on the picosecond time scale and have no influence on the orientation of the proton-proton vector, as the H₂O molecule revolves around its center of mass with a fixed orientation of the proton-proton vector.

Quantum mechanical calculations are a unique tool for the investigation of microscopic characteristics of solids. This is especially true for H-containing substances, as these are difficult to model with empirical models based on pair potentials or similar methods. It has recently been shown (Winkler et al., in preparation) that ab initio calculations based on the local density approximation (LDA) can reproduce and predict static and dynamic properties of weak and strong H bonds, including nonlinear bonds. Here we use such quantum mechanical calculations with norm-conserving pseudopotentials to calculate total energies of hydrous and anhydrous Mg end-member cordierite. The present calculations address three questions, namely (1) where is the H₂O located, (2) how is it oriented, and (3) what is the total energy of hydration? Given the different experimental results regarding the orientation of the H₂O molecule above, the value of a theoretical study of a perfect system is obvious. Moreover, there are contradicting views even in the recent literature about the bonding of the H₂O molecule and its effect on the cordierite structure (Stout, 1975, 1976; Langer and Schreyer, 1976; Carey and Navrotsky, 1992), which a computational study can address. Furthermore, because of the close relationship between beryl and cordierite, the results are expected to apply to beryl as well. In the following, we present some technical details regarding the calculations, followed by the results and a discussion.

CALCULATIONS

The software package CASTEP (Cambridge Serial Total Energy Package), which has been described elsewhere (Teter et al., 1989; Payne et al., 1992), and associated programs for symmetry analysis were used for the calculations. CASTEP is a pseudopotential total energy code that employs Perdew and Zunger (1981) parameterization of the exchange-correlation energy, supercells, and special point integration over the Brillouin zone and a plane-wave basis set for the expansion of the wave functions. The calculations were performed using norm-conserving nonlocal pseudopotentials of the form suggested by Kleinman and Bylander (1982), where the pseudopotentials were taken from the CASTEP data base. Because it has been shown by Needs (1992 personal communication) that for H the use of a pseudopotential is not

advantageous compared with the Coulomb (local) potential, the latter was used in the calculations.

To obtain equilibrium structures for a given set of lattice parameters, ionic and electronic relaxations are performed using the adiabatic approximation, where it is assumed that the electronic system is always in equilibrium with the ionic system. Due to the size of the system, it is currently not feasible to relax the unit-cell parameters concomitantly with the atomic positions. It is well known, however, that with the parameters used in the present study LDA calculations give reliable results (De Vita 1992a, 1992b). Fractional coordinates are usually within 1% of the experimental values, whereas absolute distances, cell parameters, and angles may be in error by 2–3%. It should be borne in mind, though, that small differences in otherwise similar systems can be calculated with very high precision. We used experimentally determined unit-cell parameters (Armbruster, 1985), but in the primitive setting (cell volume of 775.7 Å³) and 58 and 61 atoms for the anhydrous and hydrous system, respectively. The cell volume and the constant cutoff for the kinetic energy of 600 eV imply the use of about 25900 plane waves. Because of the size of the system, the sampling of the Brillouin zone had to be restricted to one k point at (0, 0, 0) for all calculations.

Calculations for both anhydrous and H₂O-bearing cordierite have been performed as described above. For the anhydrous cordierite, the structure was relaxed, subject to the experimentally determined symmetry (*Cccm*). This reduced the number of internal degrees of freedom from 171 (number of atoms – 1)·3, to 23. The total energy of anhydrous cordierite was –17344.16 eV for the unrelaxed structure; a relaxation of all of the internal degrees of freedom gave a total energy of –17344.406 eV. The calculated atom positions are given in Table 1, where they are compared with experimental values. The calculated values are in excellent agreement with the experimental data.

For the calculation of the ground state of hydrous cordierite, the atoms of the H₂O molecule have initially been placed so that the O atom in H₂O was located at 0,0,¼ and the O-H distance was slightly more than 1 Å. After a few initial electronic relaxations, all atomic parameters (180 degrees of freedom) were relaxed (Table 1). The total energy after the full relaxation was –17809.411 eV. After the relaxation, the protons were located with the proton-proton vector parallel to [001] within 1°. The O in H₂O was located at 0.0046,0.9978,0.2509. The O-H distances of the H₂O molecule were 0.9813 Å, and the H-O-H angle was 104.9°.

For comparison, the properties of a H₂O molecule have been studied by placing the molecule in a box with periodic boundary conditions shaped like the unit cell of cordierite at 0,0,¼. Again, nearly 25900 plane waves have been used, and the proton positions have been relaxed until all atoms were force free within the limits of the calculation. This led to an O-H distance of 0.977 Å and an H-O-H angle of 103.8°. This is within 2 and 1% of the

TABLE 1. Experimental and calculated atom positions for cordierite

Species	Experimental*			Calc. anhydrous			Calc. hydrous		
	x	y	z	x	y	z	x	y	z
Mg	0.6627	0.6627	0.7500	0.6626	0.6626	0.7500	0.6629	0.6625	0.7500
Al	0.0000	0.5000	0.2501	0.0000	0.5000	0.2500	0.9999	0.5003	0.2499
Al	0.7423	0.3593	0.0000	0.7415	0.3605	0.0000	0.7416	0.3599	0.0005
Si	0.1143	0.2704	0.0000	0.1141	0.2715	0.0000	0.1139	0.2719	0.0000
Si	0.6268	0.1026	0.0000	0.6256	0.1036	0.0000	0.6260	0.1034	0.0003
O	0.3500	0.1442	0.3589	0.3506	0.1456	0.3574	0.3506	0.1452	0.3574
O	0.4787	0.6461	0.3487	0.4800	0.6470	0.3482	0.4799	0.6470	0.3482
O	0.1367	0.5161	0.3584	0.1383	0.5141	0.3570	0.1382	0.5141	0.3571
O	0.2945	0.7927	0.0000	0.2942	0.7914	0.0000	0.2935	0.7924	0.0004
O	0.9370	0.3076	0.0000	0.9360	0.3081	0.0000	0.9362	0.3078	0.9998
O	0.2434	0.0844	0.0000	0.2434	0.0844	0.0000	0.2430	0.0843	0.0003
Ow							0.0046	0.9978	0.2509
H							0.0641	0.0010	0.3339
H							0.0646	0.9986	0.1673

Note: positions are given for the primitive cell, and only positions with at least one degree of freedom are listed. The (random) deviations of atom positions from special points in the calculation for the hydrous cordierite are due to rounding errors. They never exceeded 0.004 Å.

* Armbruster (1985a).

experimental values, respectively. The total energy was -464.604 eV.

The calculations were performed on a Cray Y-MP EL 4-1024 and took >650 h of cpu time in total, using more than 30 million words of core memory.

DISCUSSION

The accuracy of the calculations is obvious from the small differences between the observed and the calculated atom positions. The studies of Gibbs (1966), Armbruster (1985b), and Hochella et al. (1979) showed that the coordination polyhedron of Mg in cordierite is slightly distorted. The observed mean Mg-O distance is 2.107 Å (Armbruster, 1985a). Because of the incorporation of Fe²⁺ into the Mg site in the natural samples used in these studies, this distance is most probably slightly larger than the mean Mg-O distance in a pure orthorhombic Mg end-member cordierite, for which no data are known to us. In the orthorhombic natural sample the deviations of the three pairs of Mg-O bonds from the mean value are -0.35 , ± 0.08 , and $+0.26\%$. The present calculations give a mean of 2.086 and 2.088 Å for the anhydrous and the H₂O-containing cordierite, respectively. This agreement (within 1% of the experimental data) is typical for LDA calculations. Also, the distortion of the Mg coordination polyhedron is reproduced well. Whereas the range of observed O-Mg-O angles is 71.4 – 101.5° , the calculated range is 71.8 – 101.3° for the anhydrous cordierite and 71.7 – 101.3° for the hydrous cordierite. In no case does the calculated angle deviate $>0.5^\circ$ from the observed value. The corresponding deviations of the Mg-O distances from the mean bond length are -0.39 , $+0.19$, and $+0.21\%$. The distortion of the Mg octahedron in anhydrous and H₂O-bearing cordierite is similar. The present study is, therefore, another confirmation of the reliability of pseudopotential LDA calculations.

The present calculations unambiguously demonstrate that the expected location of the O atom in H₂O is not at the center of the cavity. The calculated displacement

along [001] is only about twice as large as the uncertainty of the calculation, and hence may be of little significance, but there is no doubt that there is a distinct displacement of the O atom within the basal (001) plane.

With regard to the orientation of the H₂O molecule, the present calculations agree with the interpretation of infrared spectroscopic results on alkali-free cordierite and beryl, where it is generally thought that the proton-proton vector is aligned parallel to [001] (Farrel and Newnham, 1967; Goldman et al., 1977; Aines and Rossman, 1984). The present results are in contrast to the findings of Hochella et al. (1979) and Cohen et al. (1977). In the work of Cohen et al. (1977), the weaker of the two H bonds between the H₂O molecule and the framework is associated with the longer of the two O-H distances, although increasing H bonding leads to a lengthening of the O-H distance (Nakamoto et al., 1955; Novak, 1974). The spectroscopic experiments support the existence of a symmetric molecule, as obtained in the present calculations. However, the H₂O molecule is dynamically disordered at room temperature (Tsang and Ghose, 1972; Carson et al., 1982; Winkler et al., in preparation); hence it is to be expected that the determination of the probability distribution function of the H₂O molecule is very difficult.

Our results indicate that the H₂O type I orientation is stabilized by weak H bonds that cause a slight lengthening of the O-H distance and that the distortion of the cordierite framework is small. In the hydrated sample there are two cages, one empty and one filled. The distances between the center of the cage and the surrounding O atoms are, within 0.1%, the same for both cages. The present calculations show directly that there are virtually no lattice distortions due to the incorporation of H₂O expected, and hence H bonding between the H₂O molecule and the cordierite framework is negligible. This had previously been inferred from powder infrared spectroscopy (Langer and Schreyer, 1976), which demonstrated that the intermolecular stretching frequency of H₂O in cordierite is nearly the same as for H₂O vapor, whereas

the stretching frequency of liquid H₂O is, because of the presence of H bonds, at significantly lower energies. In contrast, Carey and Navrotsky (1992) claim "that the molecular environment of H₂O in cordierite is similar to that of H₂O in water."

The present calculations show that the most stable position for the O in H₂O does not coincide with the center of the cavity but is slightly displaced within the basal plane. This idea has been advanced on the basis of incoherent quasi-elastic neutron scattering experiments (Winkler et al., in preparation). However, the orientation of the H₂O molecule is not the same. In Winkler et al. (in preparation) the center of mass coincided with the center of the cavity, whereas in the present study it does not. This difference may be due to the neglect of dynamic effects in the present study.

The last aspect to be discussed is the energetics of the incorporation of the H₂O molecule. In the present study, we did not attempt to calculate the lattice parameters but rather used the same set of lattice parameters for both hydrated and anhydrous cordierite. Although the effect of the incorporation of alkalis on the lattice parameters is well known (Schreyer, 1986), to the best of our knowledge there has not yet been a systematic study of the dependence of the lattice parameters on the H₂O content of synthetic Mg end-member cordierite. Most theoretical investigations on thermodynamic properties have therefore assumed that $\Delta V^{\text{mix}} \approx 0$ for the hydration of cordierite. This would imply that the $P\Delta V$ term of the enthalpy of dehydration is small; hence a measured enthalpy can be compared with the calculated energy of hydration. Carey and Navrotsky (1992) measured the enthalpy of dehydration of synthetic Mg end-member cordierite to be 42(2) kJ/mol (0.43 eV) for 1 H₂O molecule pfu. In the present calculations 0.5 H₂O molecules pfu were used, and the calculated energy was 0.4 eV. Carey and Navrotsky (1992) showed that the mixing was ideal; hence the current calculations give an energy too large by a factor of 2. Although the relative difference between observation and calculation is large, we nevertheless judge this as a promising result. The result demonstrates that within this limit it is possible to calculate, with parameter-free predictive models, the energy changes associated with the incorporation of other channel constituents, some of which may occur in nature but are very difficult to introduce experimentally, such as methane. Also, it is well known that LDA calculations give binding energies that are too large, and that they can be improved by so-called gradient corrections (Lee et al., 1993). Such calculations were, however, outside the scope of the present study.

The current calculations could also be improved by relaxing the unit cell and by a better sampling of the Brillouin zone, but that would require significant computing resources. The main shortcoming of the present work is obviously the neglect of the dynamics of the H₂O molecule (Tsang and Ghose, 1972; Carson et al., 1982; Winkler et al., in preparation). Using molecular dynamics with ab initio forces, which are implemented in CASTEP,

it is possible, in principle, to include the effects of temperature and calculate ensemble trajectories (Milman et al., 1993). Unfortunately, for the next few years the computational demand is prohibitive. Nevertheless, some dynamical aspects are currently being investigated using frozen phonon calculations to obtain the frequencies of the rotational motion of the H₂O molecule. This is an important step for the analysis of data recently obtained for synthetic H₂O-bearing cordierite with inelastic neutron scattering experiments using the time-focused crystal analyzer spectrometer at Rutherford Appleton Laboratory (Winkler and Hennion, 1994).

ACKNOWLEDGMENTS

We would like to thank the staff of the Rechenzentrum der Universität Kiel, especially E.-M. Zeidler, for help with the Cray. C.A. Geiger (Kiel) is thanked for proofreading the manuscript. B.W. is grateful to the Deutsche Forschungsgemeinschaft for financial support (grant Wi-1232). The research of V.M. was sponsored by the Division of Material Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Program, administered by the Oak Ridge Institute for Science and Education. Computing resources were provided by the Rechenzentrum der Universität Kiel, Germany, the Gesellschaft für Mathematik und Datenverarbeitung, Bonn, Germany, and by the Deutsche Forschungsgemeinschaft. We also wish to express our thanks to J.A. Tossell and R.N. Abbott for their helpful reviews.

REFERENCES CITED

- Aines, R.D., and Rossman, G.R. (1984) The high temperature behavior of water and carbon dioxide in cordierite and beryl. *American Mineralogist*, 69, 319–327.
- Armbruster, T. (1985a) Ar, N₂, and CO₂ in the structural cavities of cordierite: An optical and single crystal x-ray study. *Physics and Chemistry of Minerals*, 12, 233–245.
- (1985b) Crystal structure refinement, Si,Al-ordering, and twinning in "pseudo-hexagonal" Mg-cordierite. *Neues Jahrbuch für Mineralogie, Monatshefte*, H6, 255–267.
- Armbruster, T., and Bloss, F.D. (1982) Orientation and effects of channel H₂O and CO₂ in cordierite. *American Mineralogist*, 67, 284–291.
- Carey, J.W., and Navrotsky, A. (1992) The molar enthalpy of dehydration of cordierite. *American Mineralogist*, 77, 930–936.
- Carson, D.G., Rossman, G.R., and Vaughan, R.W. (1982) Orientation and motion of water molecules in cordierite: A proton nuclear magnetic resonance study. *Physics and Chemistry of Minerals*, 8, 14–19.
- Cohen, J.P., Ross, F.K., and Gibbs, G.V. (1977) An X-ray and neutron diffraction study of hydrous low cordierite. *American Mineralogist*, 62, 67–78.
- De Vita, A., Manassis, I., Lin, J.S., and Gillan, M.J. (1992a) The energetics of Frenkel defects in Li₂O from first principles. *Europhysics Letters*, 19, 605–610.
- De Vita, A., Gillan, M.J., Lin, J.S., Payne, M.C., Stich, I., and Clarke, L.J. (1992b) Defect energies in oxide materials from first principles. *Physical Review Letters*, 68, 3319–3322.
- Farrel, E.F., and Newnham, R.E. (1967) Electronic and vibrational absorption spectra in cordierite. *American Mineralogist*, 52, 380–388.
- Gibbs, G.V. (1966) The polymorphism of cordierite. I. The crystal structure of low cordierite. *American Mineralogist*, 51, 1068–1087.
- Goldman, D.S., Rossman, G.R., and Dollase, W.A. (1977) Channel constituents in cordierite. *American Mineralogist*, 64, 1144–1157.
- Hochella, M.F., Jr., Brown, G.E., Jr., Ross, F.K., and Gibbs, G.V. (1979) High temperature crystal chemistry of hydrous Mg- and Fe-cordierites. *American Mineralogist*, 64, 337–351.
- Johannes, W., and Schreyer, W. (1981) Experimental introduction of CO₂ and H₂O into Mg-cordierite. *American Journal of Science*, 281, 299–317.

- Kleinman, L., and Bylander, D.M. (1982) Efficacious form for model pseudopotentials. *Physical Review Letters*, 48, 1425–1428.
- Langer, K., and Schreyer, W. (1976) Apparent effects of molecular water on the lattice geometry of cordierite: A discussion. *American Mineralogist*, 61, 1036–1040.
- Lee, C., Vanderbilt, D., Laasonen, K., Car, R., and Parinello, M. (1993) Ab initio studies on the structural and dynamical properties of ice. *Physical Review*, B47, 4863–4872.
- Milman, V., Payne, M.C., Heine, V., Needs, R.J., and Lin, J.S. (1993) Free energy and entropy of diffusion by ab initio molecular dynamics: Alkali ions in silicon. *Physical Review Letters*, 70, 2928–2932.
- Mirwald, P.W. (1982) A high pressure phase transition in cordierite. *American Mineralogist*, 67, 277–283.
- Nakamoto, K., Margoshes, M., and Rundle, R.E. (1955) Stretching frequencies as a function of distances in hydrogen bonds. *Journal of the American Chemical Society*, 77, 6480–6486.
- Novak, A. (1974) Hydrogen bonding in solids: Correlation of spectroscopic and crystallographic data. *Structure and bonding*, 18, 177–216.
- Payne, M.C., Teter, M.P., Allan, D.C., Arias, T.A., and Johannopoulos, J.D. (1992) Iterative minimization techniques for ab initio total energy calculations: Molecular dynamics and conjugate gradients. *Reviews of Modern Physics*, 64, 1045–1097.
- Perdew, J.P., and Zunger, A. (1981) Self-interaction correction to density functional approximations for many-electron systems. *Physical Review*, B23, 5048–5079.
- Schreyer, W. (1985) Experimental studies on cation substitutions and fluid incorporation in cordierite. *Bulletin de Minéralogie*, 108, 273–291.
- (1986) The mineral cordierite: Structure and reactions in the presence of fluid phases. *Berichte der Bunsengesellschaft, physikalische Chemie*, 90, 748–755.
- Smith, J.V., and Schreyer, W. (1962) Location of argon and water in cordierite. *Mineralogical Magazine*, 33, 226–236.
- Stout, J.H. (1975) Apparent effects of molecular water on the lattice geometry of cordierite. *American Mineralogist*, 60, 229–234.
- (1976) Apparent effects of molecular water on the lattice geometry of cordierite: A reply. *American Mineralogist*, 61, 1041–1044.
- Teter, M.P., Payne, M.C., and Allan, D.C. (1989) Solution of Schroedinger equations for large systems. *Physical Review*, B40, 12255–12263.
- Tsang, T., and Ghose, S. (1972) Nuclear magnetic resonance of ¹H and ²⁷Al and the Al-Si order in low cordierite. *Journal of Chemical Physics*, 56, 3329–3332.
- Winkler, B., and Hennion, B. (1994) Dynamics of H₂O in Mg-cordierite. *ISIS annual report 1993*, Rutherford Appleton Laboratory, in press.

MANUSCRIPT RECEIVED OCTOBER 14, 1993

MANUSCRIPT ACCEPTED DECEMBER 2, 1993