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LETTER

Hartree-Fock band structure, equation of state, and pressure-induced hydrogen bonding in brucite, $Mg(OH)_2$

DAVID M. SHERMAN
U.S. Geological Survey, Denver, Colorado 80225, U.S.A.

ABSTRACT

The electronic structure and equation of state of brucite has been investigated using the recently developed extension of the Hartree-Fock LCAO formalism to periodic systems. Of primary interest is whether H bonding in brucite can be enhanced at high pressure. Pressure-induced H bonding could stabilize OH-bearing phases in the Earth's interior. It is found, however, that H bonding in brucite is very weak at zero pressure and is not enhanced with high pressure. Pressure-induced H bonding might be more significant in OH-bearing aluminosilicates. The calculated molar volume and equation of state for brucite agree well with experiment as does the calculated Raman-active A_{1g} OH stretch frequency.

INTRODUCTION

A number of dense hydrous phases in the Mg-Si-O-H system have been synthesized at high pressures (up to 22 GPa), and it has been suggested that the Earth's mantle may contain more than five times the H_2O content of the present hydrosphere (Liu, 1987). Knowledge of the pressure dependence of chemical bonding in OH-bearing minerals is needed to understand the stability and crystal chemistry of H_2O in the Earth's mantle. The structures of hydroxides such as brucite $Mg(OH_2)$ involve dipole-dipole forces between opposing OH ions (Fig. 1). In some hydroxides the forces between opposing OH ions are strong enough to cause each H atom to be shared by two O atoms. The usual operational definition of H bonding requires that H atoms are shared by more than one neighboring atom. It has long been argued that H bonding in brucite is either absent or very weak and that the $Mg(OH)_2$ sheets are held together only by the OH-OH dipole-dipole force (e.g., Bragg et al., 1965). On the other hand, one might expect H bonding in brucite to be induced at high pressure by bringing next-nearest-neighbor O atoms in closer proximity. Pressure-induced H bonding could increase the stability of OH-bearing phases under the conditions of the Earth's interior: the limit to the stability of OH-bearing minerals at high temperature is the large entropy gain associated with their dehydration. Strong H bonding might increase the internal energy barrier to dehydration enough to offset the gain in entropy. Moreover, enhanced H bonding may increase the density of the hydrous phase enough to make the work ($P\Delta V$) of dehydration greater than the gain in entropy.

Attempts to understand and predict the stability of minerals using first-principles (ab initio) methods are becoming increasingly common. The most sophisticated approaches are based on solving the Schrodinger equation (approximated using either the Hartree-Fock formalism or the local density approximation) for the system of interest. Until very recently, the applications of quantum mechanics to mineralogy have been limited to molecular orbital calculations on finite clusters. Investigations of bonding and structures of finite clusters have been done using the linear combination of atomic orbital (LCAO) approach and the Hartree-Fock formalism, as coded in the Gaussian series of computer programs (e.g., Hehre et al., 1986). During the 1980s Dovesi, Pisani, and coworkers (Dovesi et al., 1988; Pisani et al., 1988) extended the LCAO method used for molecules to periodic systems (e.g., polymers, slabs, and crystalline solids). This paper presents results on the electronic structure and static equation of state for brucite using the periodic extension of the Hartree-Fock LCAO formalism and the Crystal code.

ATOMIC BASIS SET AND COMPUTATIONAL PARAMETERS

For computational convenience, atomic orbitals are usually expressed in terms of a finite number of Gaussian functions. The quality of the calculation is dependent upon the choice of basis set (Gaussian expansion). The use of such Gaussian expansions of atomic orbitals in solid state problems is new, so one must reoptimize the basis sets for the problem at hand. Preliminary calculations on brucite showed that the Mg-OH bond is quite ionic so that Mg atoms adopt an effective charge near 2.0. For both Mg and O, the basis set used by Causa et al. (1986) in MgO was used. For Mg, this is an 8-61G contraction of a split-valence basis set (i.e., 1s, 2sp, 2sp′ shells), whereas for O an 8-51G contraction of a split-valence basis set (i.e., 1s, 2sp, 2sp′) was used. The exponent for the outer Gaussian on O was reoptimized for brucite but was unchanged from that found in MgO (0.21). For H, a 21G* contraction of a split-valence basis set with polarization

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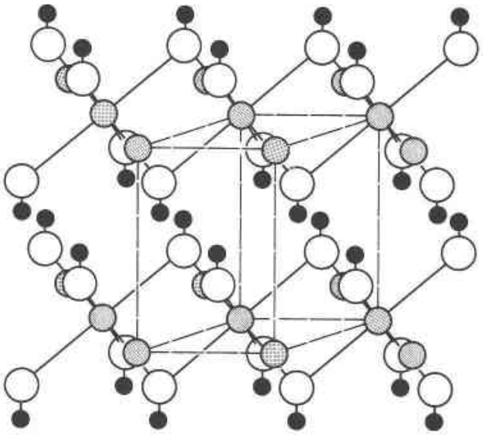


Fig. 1. Structure of brucite, $Mg(OH)_2$. Solid atoms are H, open atoms are O, shaded atoms are Mg. Within each unit cell are two OH groups in opposite orientation to give a dipole-dipole interaction. The dipole-dipole interaction is the only force holding adjacent MgOH sheets together.

functions (i.e., 1s, 1s′, 2p), and the standard polarization function exponent was used (Hehre et al., 1986). Including such polarization functions (2p orbitals) in the atomic basis set for H may be important for an adequate description of H bonding.

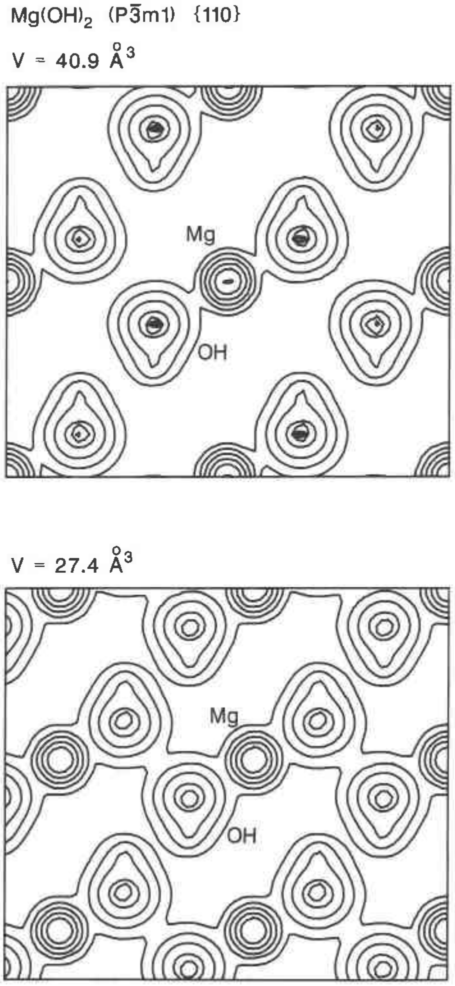
RESULTS AND DISCUSSION

Chemical bonding in $Mg(OH)_2$

The electron density contours for brucite (Fig. 2) show that the Mg-O bond is almost entirely ionic, whereas the O-H bond is very covalent. The OH-OH interaction involves no covalent bonding between the H and next-nearest-neighbor O atom, however. That is, the OH-OH bond in brucite is only a weak dipole-dipole interaction with no delocalization of the H wavefunction onto the next-nearest-neighbor O atoms. Upon compression to $V/V_0 = 0.73$, the bonding remains the same. (As shown below, this compression corresponds to a pressure near 45 GPa.) Hence, in terms of the electron density distribution, there is no pressure-induced H bonding in brucite.

We would expect pressure-induced H bonding to affect the H site potential. The calculated A_{1g} O-H stretch potential (Fig. 3) in brucite, however, does not undergo any significant change upon compression to $V/V_0 = 0.73$. Physically, this means that the next-nearest-neighbor O atoms do not greatly contribute to the H atom site potentials over the volume range explored. The A_{1g} O-H stretch potential was fitted to a Morse function to determine the force constant, vibration frequency (ν), and anharmonicity constant (x_e) in the first-order perturbation expression for the anharmonic energy levels:

$$E_n = \left(n + \frac{1}{2}\right)h\nu + \left(n + \frac{1}{2}\right)^2 x_e h\nu$$



$Mg(OH)_2$ ($P\bar{3}m1$) {110}

V = 40.9 Å^3

V = 27.4 Å^3

Fig. 2. Electron density contours (at 2.43, 0.81, 0.27, 0.09, and 0.03 au) along the (110) plane. There is no bonding between the H atom and the next-nearest-neighbor O atom. Note that the bonding does not change upon compression, although the Mg-O bond becomes slightly covalent.

where h is Planck's constant and n is the vibrational quantum number (n = 0, 1, 2, 3 . . .). The calculated fundamental frequency ($E_1 - E_0$) is 3897 cm^{-1} at zero pressure, and the mode Gruneisen parameter is −3.03. The experimental A_{1g} stretch fundamental is 3653 cm^{-1} (Mitra, 1962). There is a slight increase in the anharmonicity of the A_{1g} mode as the brucite structure is uniformly compressed. This increase in anharmonicity is consistent with the pressure-induced energy decrease of the infrared active A_{2u} hot band observed by Kruger et al. (1989). In contrast to the A_{1g} stretch mode, the A_{2u} stretch mode energy decreases with pressure (Kruger et al., 1989). That the splitting between the Raman-active A_{1g} and the IR-active A_{2u} stretch modes increases with pressure results from the increased coupling (through the dipole-dipole interaction) between the two OH groups in the unit cell. Note that the calculated zero-pressure O-H bond length in brucite (95 pm) is in reasonable agreement

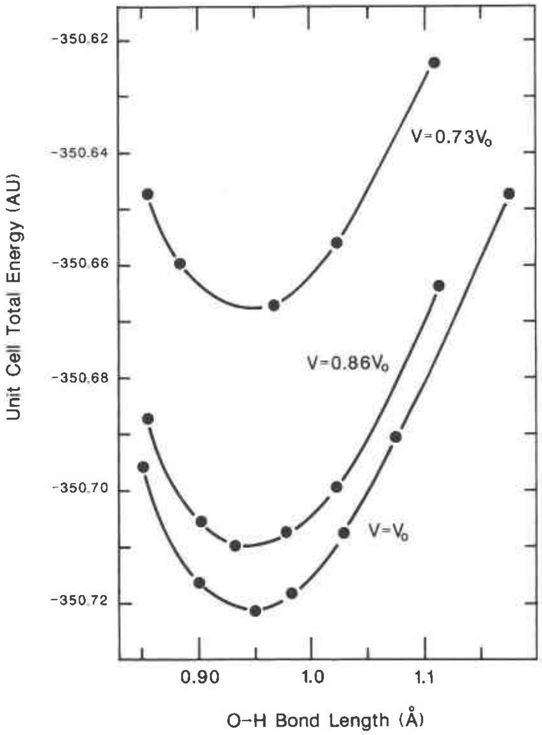


Fig. 3. Total energy vs. O-H bond length at several different volumes (obtained by homogeneous compression and fitted to a Morse potential curve). Note that the lowest energy O-H bond length is fairly insensitive to the bulk volume. The anharmonicity of the O-H bond increases somewhat with homogeneous compression of the brucite structure.

with the experimental value of 98 ± 2 pm obtained by Elleman and Williams (1956). Errors on the order of 3% for bond lengths are expected at the Hartree-Fock level of approximation (i.e., without including electron correlation) (Hehre et al., 1986).

Strong H bonding, which may delocalize the H atom over two or more centers, is associated with phases in which the metal-O bond is more covalent. This lowers the effective charge on the O atom and weakens the O-H bond, which in turn strengthens the O-H···O bond (Fig. 4). It seems unlikely that pressure-induced H bonding can be a significant mechanism for stabilizing OH in the Mg-O-H system. This is because pressure fails to change the nature of the Mg-O bond and, hence, the Bronsted basicity of the OH O atom. A more likely system in which pressure-stabilized H bonding may be important is Al-O-H or Si-O-H since the metal-O bond is more covalent that the Mg-O bond. It may be worthwhile to investigate the existence of possible high-pressure hydrous phases in the Al-Si-O-H system.

Compression mechanism and equation of state for $Mg(OH)_2$

We may calculate the total energy as a function of volume for brucite and fit the results to the integrated third-order Birch-Murnaghan equation of state to get the zero-

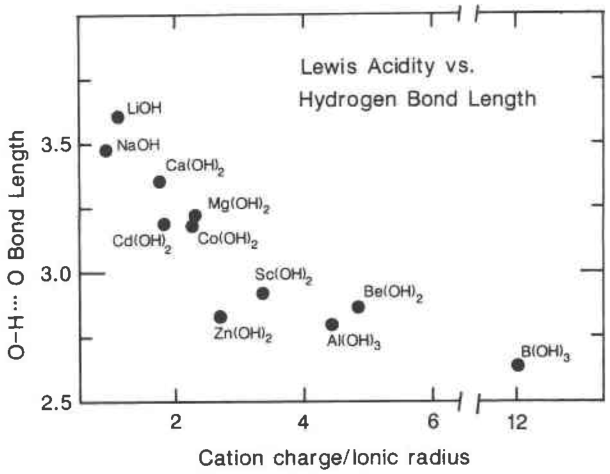


Fig. 4. H bond length in metal hydroxides as a function of cation charge (Z) divided by Shannon and Prewitt (1969) ionic radius (R). Highly polarizing cations (high Z/R) are strong Lewis acids and decrease the Bronsted base character of the O atom. The weaker the Bronsted base character of the O atom, the more readily the H^+ can be shared with its next-nearest-neighbor O atom. Data from Bragg et al. (1965) and Ryskin (1974).

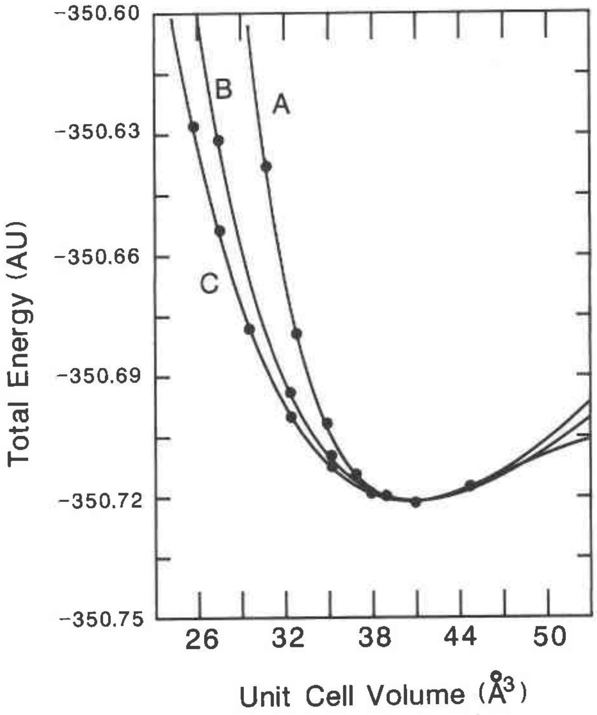


Fig. 5. Total energy vs. volume for brucite along several compressional coordinates fitted to the integrated Birch-Murnaghan equation of state. Curve A is compression along the c axis. Curve B is homogeneous compression but with constant O-H bond length. Curve C is constant c/a ratio and O-H bond length but allowing the O positional parameter to relax. The resulting elastic constants are V_0 = 40.86, K_0 = 68.3 GPa, and K' = 4.0.

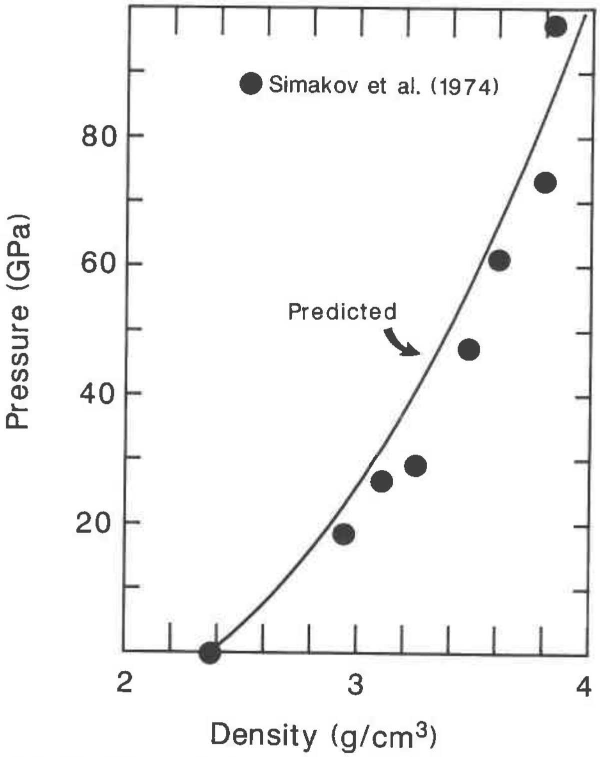


Fig. 6. Calculated Birch-Murnaghan equation of state for brucite (derived from curve C of Fig. 5) compared with the Hugoniot measurements of Simakov et al. (1974). A more precise comparison could be obtained by reducing the Hugoniot data to the isentropic pressure-density curve and correcting for the thermal pressure (thermal expansion). However the Gruneisen parameter and thermal expansivity of brucite are not known.

pressure molar volume (V_0), the zero-pressure bulk modulus (K_0), and the pressure derivative of the bulk modulus $[K'_0 = (dK/dP)_{p=0}]$ at 0 K. For simple oxides such as MgO, this is very simple since there is only one crystallographic parameter. For brucite, there are four crystallographic parameters (a, c, z_O, z_H), and we must search for the configurational coordinate along which the energy is a minimum. This will also be the configurational coordinate with the greatest compressibility. The total energy of brucite as a function of volume along several configurational coordinates is shown in Figure 5. Simple compression along the c axis (curve A) gives $K_0 = 115$ GPa. Homogeneous compression with constant O-H bond length of 95 pm (curve B) is much softer and implies that the c/a ratio does not decrease upon compression. This, in turn, implies a significant repulsive force between the sheets in the brucite structure upon compression. The lowest energy compression curve (curve C) was found by independently optimizing c/a, z_O, and z_H as a function of volume. It was found that the OH-bond length and c/a ratio remain nearly constant but that the O positional parameter increases with decreasing volume. The resulting elastic constants K_0 and K' are 68.3 GPa and 4.0. The zero-pressure volume is estimated to be 40.86 Å³/unit cell (without correcting for anharmonicity or thermal pressure at 298 K), which is in very good agreement with the experimental value of 40.89 Å³. Comparing the theoretical Birch-Murnaghan equation of state with the Hugoniot data of Simakov et al. (1974) shows reasonable agreement with experiment (Fig. 6). The Hugoniot data, however, have not been reduced to the isentrope nor corrected for the thermal pressure. Recent measurements on brucite by Duffy et al. (1991) give elastic constants K_0 and K' of 51 GPa and 5.0, which are quite consistent with the results obtained here. The agreement between theory and experiment suggests that there is no phase transition in brucite in the shock-wave experiment up to 80 GPa.

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REFERENCES CITED

Bragg, L., Claringbull, G.F., and Taylor, W.H. (1965) Crystal structures of minerals, 409 p. Cornell University Press, Ithaca, New York.

Causa, M., Dovesi, R., Pisani, C., and Roetti, C. (1986) Electronic structure and stability of different crystal phases of magnesium oxide. Physical Review B, 33, 1308–1316.

Dovesi, R., Pisani, C., Roetti, C., Causa, M., and Saunders, V.R. (1988) CRYSTAL 88. An ab-initio all-electron LCAO-Hartree-Fock program for periodic systems. Quantum Chemistry Program Exchange no. 577, Indiana University, Bloomington, Indiana.

Duffy, T.S., Arhens, T.J., and Longe, M.A. (1991) Shock-wave equation of state of brucite, $Mg(OH)_2$. Journal of Geophysical Research, in press.

Elleman, D.D., and Williams, D. (1956) Proton positions in brucite crystals. Journal of Chemical Physics, 25, 742–744.

Hehre, W.J., Random, L., Schleyer, P.v.R., and Pople, J.A. (1986) Ab inito molecular orbital theory, 548 p. Wiley-Interscience, New York.

Kruger, M.B., Williams, Q., and Jeanloz, R. (1989) Vibrational spectra of $Mg(OH)_2$ and $Ca(OH)_2$ under pressure. Journal of Chemical Physics, 91, 5910–5915.

Liu, L. (1987) Effects of H_2O on the phase behavior of the forsterite-enstatite system at high pressures and temperatures and implications for the Earth. Physics of the Earth and Planetary Interiors, 49, 12–167.

Mitra, S.S. (1962) Vibration spectra of solids. In F. Seitz and D. Turnball, Eds., Solid state physics, vol. 13, p. 2–80. Academic Press, New York.

Pisani, C., Dovesi, R., and Roetti, C. (1988) Hartree-Fock ab initio treatment of crystalline systems. Lecture notes in chemistry, vol. 48, 193 p. Springer-Verlag, Berlin.

Ryskin, Ya.I. (1974) The vibrations of protons in minerals: Hydroxyl, water and ammonium. In V.C. Farmer, Ed., The infrared spectra of minerals, p. 111–118. Mineralogical Society, London.

Shannon, R.D., and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. Acta Crystallographica, B25, 925–946.

Simakov, G.V., Pavlovskiy, M.N., Kalashnikov, N.G., and Trunin, R.F. (1974) Shock compressiblity of twelve minerals. Izvestiya Physics of the Solid Earth, 448–492.

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