Phys Chem Minerals (2006) 33: 484–489
DOI 10.1007/s00269-006-0097-7

ORIGINAL PAPER

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High pressure elasticity and phase transformation in brucite, $Mg(OH)_2$

Received: 19 September 2005 / Accepted: 23 May 2006 / Published online: 8 July 2006
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Abstract The first pressure derivatives of the second-order elastic constants dC'_{IJ}/dp have been calculated for brucite, $Mg(OH)_2$ from the second- and third-order elastic constants. The deformation theory and finite strain elasticity theory have been used to obtain the second- and third-order elastic constants of $Mg(OH)_2$ from the strain energy of the lattice. The strain energy ϕ is calculated by taking into account the interactions up to third nearest neighbors in the $Mg(OH)_2$ lattice. ϕ is then compared with the strain dependent lattice energy from continuum model approximation to obtain the expressions of elastic constants. The complete set of six second-order elastic constants C_{IJ} of brucite exhibits large anisotropy. Since C_{33} (= 21.6 GPa), which corresponds to the strength of the material along the *c*-axis direction, is less than the longitudinal mode C_{11} (= 156.7 GPa), the interlayer binding forces are weaker than the binding forces along the basal plane of $Mg(OH)_2$. The 14 nonvanishing components of the third-order elastic constants, C_{IJK}, of brucite have been obtained. All the C_{IJK} of brucite are negative except the values of C_{114} (= 230.36 GPa), C_{124} (= 75.45 GPa) and C_{134} (= 36.98 GPa). The absolute values of the C_{IJK} are, in general, one order of magnitude greater than the C_{IJ}'s in the $Mg(OH)_2$ system as usually expected for a crystalline material. To our knowledge, no previous data are available to compare the pressure derivatives of brucite. The pressure derivatives of the two components viz., C_{14} and C_{33} become negative ($dC'_{14}/dp = -1.51$ and $dC'_{33}/dp = -1.41$) indicating an elastic instability in brucite while under pressure. This may be related to the phase transition of brucite largely involving rearrangements of H atoms revealed in the Raman spectroscopic, powder neutron diffraction and synchrotron X-ray diffraction studies.

Keywords Brucite · Elastic properties · Phase transition · High pressure

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Introduction

The study of elasticity of Earth materials has become increasingly important over the last decade, as contributions from global seismic tomography, seismological investigations of geographically and radially localized regions, mantle discontinuities, analysis of normal modes of oscillations and other types of studies have revealed the Earth's mantle on unprecedented detail (e.g., Ishii and Tromp 1999). To the extent that the interior of the Earth behaves elastically, the propagation of seismic waves is determined by the elastic constants of the component materials. Magnesium hydroxide, though present in limited amounts in the Earth's crust, is considered to be of great importance as a potential source of water in the mantle, and also as a simple model material for the crystal chemical behavior of complex layered hydrous minerals. The high-pressure behavior of brucite, $Mg(OH)_2$, is of considerable interest for studying such diverse phenomena as dehydration reactions at high pressure, compression-induced amorphization and phase transformation, and the behavior of hydrous minerals in the Earth's upper mantle. Water plays a crucial role in the seismic and rheaological behavior of the Earth's mantle and the reservoirs of water under the high-pressure condition of mantle remain of interest (Kudoh et al. 2004). Since brucite is a typical

mineral having hydroxyl groups on the (0001) cleavage surfaces, it is also most suitable to study water behavior on the surface having hydroxyl groups as well (Sakuma et al. 2003). Because of its chemical and structural simplicity, magnesium hydroxide serves as a useful prototype for hydrous and layered minerals at high pressures. The nature of bonds between layers is relatively complex and depends on the chemistry of layers. These layered materials undergo numerous phase transformations under temperature and pressure. So there is a great deal of interest in understanding the energetics of such structures. The equation of state for brucite, $Mg(OH)_2$ at elevated pressures and temperatures were measured recently by various authors (Fukui et al. 2003; Xia et al. 1998; Fei and Mao 1993). Brucite exhibits considerable elastic anisotropy (Fei and Mao 1993) along and between the layers. Though the thermodynamics of brucite has been studied extensively (Bernal and Megaw 1935; Catti et al. 1995; Duffy et al. 1995a, b; Parise et al. 1994), the nonlinear elasticity is yet to be probed in detail, both theoretically and experimentally. Thus, it is indispensable to have a comprehensive knowledge of the nonlinear elasticity of brucite for the interpretation of material behavior, especially at high pressure, in the relationship between structure and bonding. Further, there is conflicting evidence regarding the nature of the interlayer forces involved in brucite. On the basis of interlayer O distances, Bernal and Megaw (1935) concluded that the layers were held together by weak dipole forces. X-ray emission spectra, however, support the existence of some H bonding between the layers.

The pressure-induced variations in the elastic constants will eventually reflect in the structure and the nature of bonding present in crystalline materials. The discovery of large numbers of magnesium silicates containing structurally bound OH has raised questions concerning the potential role of such phases in the Earth's interior. The crystal structure of brucite is trigonal, space group $P\bar{3}m1$ and is corresponding to that of CdI_2 if OH is treated as a single anion (Bernal and Megaw 1935; Zigan and Rothbauer 1967). Each O atom in the hexagonally close-packed layers is bonded with H such that the O–H bond is perpendicular to the layers, with bond length close to 1 Å, while distance between the layers of octahedral containing Mg is about 2.7 Å (Parise et al. 1994). Brucite has been studied to understand the hydrogen behavior and the nature of hydrogen bonding in solid and to understand the compression behavior of layered dense hydrous magnesium silicates (DHMS) because an $Mg(OH)_6$ unit is regarded as part of a DHMS structure (Kudoh et al. 1993). The objective of this study is to determine the pressure derivatives of the elastic constants and to present the elastic anisotropy as well as the nonlinear elasticity of brucite, $Mg(OH)_2$. To shed further light on the structural transformation in brucite, we discuss it in the backdrop of the pressure derivatives obtained in this study. In this report we have determined the second-order elastic constants, their pressure derivatives and the third-order elastic constants of $Mg(OH)_2$ theoretically. To our knowledge, no data are reported previously on the pressure derivatives of second-order elastic constants as well as third-order elastic constants of $Mg(OH)_2$.

Second- and third-order elastic constants

To obtain the second- and third-order elastic constants we have used a model based on deformation theory. Here we discuss the theory briefly, the details of which are given elsewhere (Jayachandran and Menon 2002). [It should be pointed out that although the symmetry of the material in Jayachandran and Menon (2002) is tetragonal, the treatment of the theory is general until the last part where the symmetrical deduction has been employed. Thus, the methodology described in Jayachandran and Menon (2002) can be applicable to other crystal classes as well.] Elastic constants of all orders can be obtained as algebraic functions of potential parameters. Higher order elastic constants will depend on higher order coordinate derivative of the potential.

The potential energy ϕ of a crystal is expanded in powers of atomic displacements u_j $(L\mu)$ of every atom μ in the cell L using Taylor series as

$$\phi = \phi_0 + \phi_1 + \phi_2 + \phi_3 \tag{1}$$

where ϕ_0 is the static potential energy of the crystal and ϕ_1, ϕ_2 and ϕ_3 are, respectively, the first, second and third coordinate derivative of the potential energy. Here, the contribution to the potential energy from higher than third-order terms is insignificant as they involve fourth and higher powers of strains which are negligibly small (Murnaghan 1951). For example, the normalized elastic constants of $MgSiO_3$ perovskite are found to depend nearly linearly on finite strain over a pressure range 0–140 GPa (Karki et al. 2001). The finite strain expansion truncated at the linear term fits the theoretical elastic constants to within 1%. Normalized elastic constants that vary nearly linearly with finite strains have been found for most of the materials as well, suggesting that third-order equations are in general, sufficient (Karki et al. 2001). The derivatives are to be evaluated in the equilibrium configuration and ϕs are both translationally and rotationally invariant (Born and Huang 1962).

In a homogeneous deformation

$$u_j(L\mu) = \sum_p \in_{jp} R_p(L\mu) + w_i(\mu), \tag{2}$$

where $\in_{js} = (\partial R'_j/\partial R_s - \delta_{js})$ is the deformation parameter and $w_j(\mu)$ is the jth component of the internal

displacement of the sublattice μ. Here R_j is the jth component of the position vector of the atom $(L\mu)$ in the unstrained state and R_j' is the corresponding vector component in the strained state. In order to express the strain energy in a form invariant with respect to rigid rotation, the proper parameters to use are

$$\eta_{ij} = \frac{1}{2}\left(\in_{ij} + \in_{ji} + \sum_p \in_{pi}\in_{pj}\right) \tag{3}$$

$$\bar{w}_j(\mu) = w_j(\mu) + \sum_p \in_{pj} w_p(\mu). \tag{4}$$

The two body potential between a pair of atoms $(L\mu)$ and $(L'\ \mu')$ can be written in powers of $|\ R'\ (L\mu,\ L'\mu'\ )\ |^2\ -\ |\ R\ (L\mu,\ L'\mu'\ )\ |^2$. Therefore, the potential energy in Eq. 1 can be written as (Srinivasan 1966)

$$\begin{aligned}\phi =& \phi_0 + k_2\Big[\mathbf{R}'(L\mu,L'\mu')\cdot\mathbf{R}'(L\mu,L'\mu') \\ &- \mathbf{R}(L\mu,L'\mu')\cdot\mathbf{R}(L\mu,L'\mu')\Big]^2 \\ &+ k_3\Big[\mathbf{R}'(L\mu,L'\mu')\cdot\mathbf{R}'(L\mu,L'\mu') \\ &- \mathbf{R}(L\mu,L'\mu')\cdot\mathbf{R}(L\mu,L'\mu')\Big]^3\end{aligned} \tag{5}$$

where

$$k_2 = \frac{1}{2!}\sum_{L\mu}\sum_{L'\mu'}\sum_{ij}\phi_{ij}(L\mu,L'\mu'), \tag{6}$$

$$k_3 = \frac{1}{3!}\sum_{L\mu}\sum_{L'\mu'}\sum_{L''\mu''}\sum_{ijk}\phi_{ijk}(L\mu,L'\mu',L''\mu'') \tag{7}$$

Here ϕ_{ij} $(L\mu,\ L'\ \mu')$ and ϕ_{ijk} $(L\mu,\ L'\ \mu',\ L''\ \mu'')$ are the second and third coordinate derivatives of ϕ, respectively. Using Eqs. 2, 3 and 4 and neglecting fourth and higher powers, we obtain the strain energy per unit volume $\Phi = \frac{1}{V_z}(\phi - \phi_0)$ (where V_z is the volume of the unit cell) from Eq. 5.

The interlattice displacements $\bar{w}_j(\mu)$ are retained as a power series in the strains from the condition that the strain energy is minimum with respect to these displacements. The lattice sums are taken by making use of the position coordinates of nearest neighbours up to three of each atom in the unit cell of $Mg(OH)_2$ system to obtain Φ in Eq. 5. Comparing the strain energy thus obtained from Eq. 5 with the lattice energy from continuum model approximation (Born and Huang 1962)

$$\phi = \phi_0 + \frac{1}{2!}\sum_{ijkl} C_{ij,kl}\,\eta_{ij}\,\eta_{kl} + \frac{1}{3!}\sum_{ijklmn} C_{ij,kl,mn}\,\eta_{ij}\,\eta_{kl}\,\eta_{mn} + \cdot \tag{8}$$

where $C_{ij,kl}$ and $C_{ij,kl,mn}$ are the second- and third-order elastic constant tensor evaluated at constant entropy and η_{jp} are Lagrangian strains. We get the expressions for the second- and third-order elastic constants of $Mg(OH)_2$ system as

$$\begin{aligned}
&C_{11} = 89.76\left(\frac{a^4k_2}{V_z}\right);\quad C_{12} = 29.40\left(\frac{a^4k_2}{V_z}\right)\\
&C_{13} = 6.08\left(\frac{p^2a^4k_2}{V_z}\right);\quad C_{14} = 3.68\left(\frac{pa^4k_2}{V_z}\right);\\
&\qquad C_{33} = 2.32\left(\frac{p^4a^4k_2}{V_z}\right)\\
&C_{44} = 6.04\left(\frac{p^2a^4k_2}{V_z}\right)
\end{aligned} \tag{9}$$

$$\begin{aligned}
&C_{111} = 9.12\left(\frac{a^4k_2}{V_z}\right) + 459.60\left(\frac{a^6k_3}{V_z}\right);\\
&\qquad C_{112} = 20.72\left(\frac{a^4k_2}{V_z}\right) + 133.60\left(\frac{a^6k_3}{V_z}\right)\\
&C_{113} = 1.04\left(\frac{a^4k_2}{V_z}\right) + 24.60\left(\frac{p^2a^6k_3}{V_z}\right);\\
&\qquad C_{114} = -32.64\left(\frac{pa^6k_3}{V_z}\right)\\
&C_{123} = 1.68\left(\frac{a^4k_2}{V_z}\right) + 9.00\left(\frac{p^2a^6k_3}{V_z}\right);\\
&\qquad C_{124} = -10.69\left(\frac{pa^6k_3}{V_z}\right)\\
&C_{133} = -0.08\left(\frac{a^4k_2}{V_z}\right) + 4.00\left(\frac{p^4a^6k_3}{V_z}\right);\\
&\qquad C_{134} = -2.28\left(\frac{p^3a^6k_3}{V_z}\right)\\
&C_{144} = 8.12\left(\frac{p^2a^6k_3}{V_z}\right);\quad C_{155} = 24.40\left(\frac{p^2a^6k_3}{V_z}\right)\\
&C_{222} = 47.52\left(\frac{a^4k_2}{V_z}\right) + 775.20\left(\frac{a^6k_3}{V_z}\right);\\
&\qquad C_{333} = 1.44\left(\frac{p^6a^6k_3}{V_z}\right)\\
&C_{344} = 3.96\left(\frac{p^3a^6k_3}{V_z}\right);\quad C_{444} = 2.28\left(\frac{p^3a^6k_3}{V_z}\right)
\end{aligned} \tag{10}$$

where a is the lattice parameter, $p = c/a$ the axial ratio and k_2, k_3 and V_z were all defined earlier. Here C_{IJ} and C_{IJK} are, respectively, the second- and third-order elastic constants (evaluated at constant entropy and therefore adiabatic) in Voigt's notation. The adiabatic elastic constants are most relevant to seismology, where the time scale of deformation is much shorter than that of thermal diffusion over relevant length scales.

The second-order parameter of the potential function is fixed by making use of easily and more accurately measurable principal axis C_{IJ}, i.e., C_{11}. The estimation of potential parameter k_2 in comparison with measured value of elastic constant is a common approach in lattice dynamical calculations (e.g., Jayachandran and Liu 2005). Here k_2 has been fixed using the value of C_{11}

measured by Xia et al. (1998) for $Mg(OH)_2$ system in Eq. 9. The parameters used in the calculation of k_2 viz. a (= 3.14 Å), p(= 1.52) and V_z(= 40.8 Å^3) are all taken from Xia et al. (1998).

The third-order anharmonic parameter k_3 is evaluated by assuming a Mie-Grüneisen type of interatomic potential for $Mg(OH)_2$

$$\phi(r) = -A/r^m + B/r^n \tag{11}$$

Here A and B are constants and r refers to the interatomic distance. The value of exponent m which corresponds to the long-range electrostatic (Coulomb) interaction is generally taken as 1 (e.g., Poirier 2000; Stacey 2001). The Born exponent n corresponds to short-range ion-core overlap energy and varies with crystal structure and ion type. We adopt $n = 9$ which has been proved to be a reliable approximation for simple structures (Anderson and Liebermann 1970). k_3 is thus calculated from Eq. 11. The values of k_2 and k_3 thus obtained are substituted in Eqs. 9 and 10 to determine the values of C_{IJ} and C_{IJK} for brucite. The second-order elastic constants thus obtained for $Mg(OH)_2$ are presented in Table 1 along with experimental values and the calculated third-order elastic constants are reported in Table 2.

Pressure derivatives of the second-order elastic constants

We have used the finite strain theory (Murnaghan 1951) to obtain the effective second-order elastic constants of a strained trigonal crystal in terms of the second- and third-order elastic constants. Let a trigonal crystal be subjected to a hydrostatic pressure p. The coordinates of the material particles in the natural state change after applying the pressure. The stress tensor in the final state is given by

$$\tau_{ij} = \frac{\rho}{\rho_0} \sum_{p,q=1}^{3} \left[\frac{\partial x_i}{\partial a_p}\right] \left[\frac{\partial \phi}{\partial \eta_{pq}}\right] \left[\frac{\partial x_j}{\partial a_q}\right] \tag{12}$$

where ρ_0 is the density of the unstrained state and ρ is the deformed state, respectively. x_i is the coordinate of the atoms in a homogeneously deformed state and a_i is the position coordinate of the atoms in the unstrained state of the trigonal crystal.

Comparing this with the expression

$$\tau_{ij} = -p\delta_{ij} + \sum_{kl} C'_{ij,kl}\beta_{kl} \tag{13}$$

Table 1 Second-order elastic constants, C_{IJ} (in GPa), of brucite compared with those obtained by the Brillouin scattering measurements

Reference	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}
This work	156.70	51.30	24.52	9.77	21.6	24.36
Xia et al. (1998)	156.7	44.4	12.0	0.2	46.3	21.7

Table 2 Third-order elastic constants, C_{IJK} (in GPa), of brucite derived in this study

C_{111}	− 2291.28	C_{134}	36.98
C_{112}	− 585.79	C_{144}	− 86.88
C_{113}	− 112.70	C_{155}	− 261.06
C_{114}	230.36	C_{222}	− 3525.89
C_{123}	− 93.36	C_{333}	− 81.38
C_{124}	75.45	C_{344}	− 97.37
C_{133}	− 98.50	C_{444}	− 36.98

where β_{kl} being the infinitesimal strain parameters, which arise out of the superimposition of an infinitesimal strain on the deformed state, the expressions for the effective second-order elastic constants C'_{ijkl} can be obtained to the first order in Lagrangian strains η and ζ

$$\begin{aligned}
C'_{11} &= C_{11} + \eta(4C_{11} + 2C_{12} + C_{111} + C_{112}) \\
&\quad + \zeta(-C_{11} + 2C_{13} + C_{113}) \\
C'_{12} &= C_{12} + \eta(2C_{12} + C_{111} + 2C_{112} - C_{222}) \\
&\quad + \zeta(-C_{12} + C_{123}) \\
C'_{13} &= C_{13} + \eta(C_{113} + C_{123}) + \zeta(C_{13} + C_{133}) \\
C'_{14} &= C_{14} + \eta(C_{14} + C_{114} + C_{124}) + \zeta C_{134} \\
C'_{33} &= C_{33} + \eta(4C_{13} - 2C_{33} + 2C_{133}) + \zeta(5C_{33} + C_{333}) \\
C'_{44} &= C_{44} + \eta(0.5C_{11} + 0.5C_{12} + C_{13} + C_{144} + C_{155}) \\
&\quad + \zeta(0.5C_{13} + 0.5C_{33} + C_{44} + C_{344})
\end{aligned} \tag{14}$$

The pressure derivatives dC'_{IJ}/dp are obtained by taking the derivative of the expressions for the effective second-order elastic constants with respect to pressure p and substituting the values of second- and third-order elastic constants for $Mg(OH)_2$ given in Tables 1 and 2 in the resulting equations. The pressure derivatives thus obtained for $Mg(OH)_2$ are given in Table 3.

Results and discussion

Indeed the response of a material to an applied stress is always determined by the elastic constants and their pressure derivatives. The complete set of six second-order elastic constants C_{IJ} (given in Table 1) of brucite exhibits large anisotropy. Though the results obtained in the present study and the Brillouin spectroscopy study (Xia et al. 1998) falls within the same range, except in the case of off-diagonal elastic constant C_{14}, two elastic constants C_{13} and C_{33} differ from the

Table 3 Pressure derivatives of the second-order elastic constants, dC'_{IJ}/dp, of brucite derived in this study

$\frac{dC'_{11}}{dp}$	$\frac{dC'_{12}}{dp}$	$\frac{dC'_{13}}{dp}$	$\frac{dC'_{14}}{dp}$	$\frac{dC'_{33}}{dp}$	$\frac{dC'_{44}}{dp}$
8.32	7.14	3.39	− 1.51	− 1.41	2.21

corresponding experimental values by a factor of around 2. The value of C_{14} obtained in the Brillouin study (Xia et al. 1998) is negligibly small compared to other C_{IJ} values. The present value of longitudinal elastic constant C_{11} (= 156.7 GPa), which corresponds to the elasticity of brucite along the basal plane is very much greater than the value of C_{33} (= 21.6 GPa). Since C_{33} corresponds to the strength of the material along the *c*-axis direction, this result implies that interlayer binding forces are weaker than the binding forces along the basal plane of $Mg(OH)_2$. This is the characteristic of a layered mineral. We have obtained the value of in-plane shear constant C_{66} (= 57.47 GPa), which was not reported in the Brillouin scattering study (Xia et al. 1998). Indeed a trigonal crystal like brucite possesses seven independent second-order elastic constants including C_{66} (Bhagavantam 1966). The ratio of the elastic constants along the basal plane and the *c*-axis direction, i.e., C_{11}/C_{33} (= 7) obtained in the present study is closer to the value of the ratio of linear compressibilities along the basal plane and the *c*-axis direction of brucite (= 6 and 5), respectively, obtained by Catti et al.(1995) and Fei and Mao (1993). The corresponding value of the ratio C_{11}/C_{33} obtained by Xia et al. (1998) is 3.

For the class of compounds with trigonal $P\bar{3}m1$ symmetry there exist 14 nonvanishing components in the third-order elastic stiffness tensor (Bhagavantam 1966). We have calculated all the 14 independent components of third-order elastic constants C_{IJK} of $Mg(OH)_2$ (Table 2). Higher order elastic constants are basic cohesive properties related inextricably to the cohesive energy and volume. It seems that while the individual velocities at high compressions cannot be probably predicted with confidence if third-order terms are unknown since the wave velocities at elevated pressures are a function of the effective elastic constants (Thurston and Brugger 1964). The effective elastic constants C'_{ijkl} are expressed in terms of third-order elastic constants as shown in Eq. 14 and hence, in turn, the wave velocities at high pressures are inextricably related to third-order elastic constants. In the present work all the third-order elastic constants of brucite are negative except the values of C_{114} (= 230.36 GPa), C_{124} (= 75.45 GPa) and C_{134} (= 36.98 GPa) (Table 2). The magnitudes of third-order elastic constants like C_{144} and C_{155} representing the anisotropy of shear mode have smaller values than C_{111} (= − 2291.28 GPa), which corresponds to longitudinal mode. Hence the effect of pressure is much greater on longitudinal wave velocity than on the shear wave velocity in $Mg(OH)_2$. Also, the effect of pressure on the transverse acoustic modes represented by C_{IJK}s like C_{444} is lesser compared to longitudinal modes. The absolute values of the C_{IJK} are, in general, one order of magnitude greater than the C_{IJ}'s in the $Mg(OH)_2$ system as usually expected of a crystalline material. Moreover, the values of the third-order elastic constants are a measure of the anharmonicity of the lattice vibrations of brucite. The third-order elastic constants could not be compared with other results, as to our knowledge no previous data are available for this.

The pressure derivatives of the second-order elastic constants have been calculated and presented in Table 3 for $Mg(OH)_2$. To our knowledge no previous data are available to compare the pressure derivatives of brucite. Since dC'_{11}/dp(= 8.32) assumes the highest value among the pressure derivatives, the immediate inference is that the elastic stiffness along the basal plane of brucite increases with pressure. This result establishes the characteristic of a layered material that the binding forces in a layer are stronger than the interlayer binding forces. Thus the layers close-up substantially under hydrostatic pressure while change in interatomic distance in a layer is much smaller in $Mg(OH)_2$ system. In most of the materials, elastic constants increase monotonically with increasing pressure. However, in several cases, some elastic constants may decrease with increasing pressure, implying an elastic instability (Karki et al. 2001). The elastic instabilities play an important role in the structural phase transitions (Salje 1990). Nevertheless, it is to be noted that brucite undergoes a structural phase transformation under pressure as revealed in a number of studies (Catti et al. 1995; Duffy et al. 1995a; Duffy et al. 1995b; Shinoda et al. 2002). Moreover, brucite decomposes into periclase (MgO) and H_2O at 3.6 GPa at an elevated temperature (Okada et al. 2002). Hence there are strong indications that brucite undergoes a pressure-driven phase transformation consistent with the findings of the pressure dependencies of the second-order elastic constants in the present study. The pressure derivatives dC'_{IJ}/dp are generally positive for a number of minerals (e.g., Karki et al. 2001; Jayachandran and Liu 2005). The immediate inference once some modes of dC'_{IJ}/dp go negative is that there may be a phase change involving structure. In the present study, we found pressure derivatives of two components viz., C_{14} and C_{33} become negative ($dC'_{14}/dp = -1.51$ and $dC'_{33}/dp = -1.41$) indicating an elastic instability in brucite while under pressure. The pressure dependence of the axial ratio c/a changes dramatically (Duffy et al. 1995a). A large decrease in compressibility is observed along the **c**-axis direction and they conclude that this is due to a structural change in response to compression. Since the layers are closely packed along the **a** direction, brucite is relatively stiff in this direction and hence the c/a anomaly is mainly due to the *c*-axis anomaly (e.g., Duffy et al. 1995a). This corroborates the present anomaly in the corresponding elastic constant C_{33}. When a crystal transforms from a crystal structure to another, the reduction/gain in symmetry leads to several symmetry-related variations and anomalies in the crystal. The anomalous pressure derivatives of C_{33} and C_{14} observed in this study are to be viewed in this perspective. Once the existing symmetry is broken there occurs anomalous softening of some modes of elasticity as is seen in the present case. This may be linked to the pressure induced structural phase transformation of brucite consistent with the Raman spectroscopic (Duffy et al. 1995a), powder neutron

diffraction (Catti et al. 1995), synchrotron X-ray diffraction (Duffy et al. 1995b) and infrared synchrotron radiation (Shinoda et al. 2002) studies. Despite providing clues to the occurrence of a high-pressure phase of brucite, our studies could not capture the structure of the resulting phase of the crystal. Also, it was suggested that (e.g., Duffy et al. 1995a) the transformation in brucite largely involving the rearrangements of the H atoms and X-ray diffraction data (e.g., Fei and Mao 1993; Fukui et al., 2003) are weakly sensitive to the positions of the H atoms. Thus there appears to be no fundamental change to the underlying Mg–O sublattice of brucite.

Acknowledgements One of the authors, KPJ, was supported by a NSC postdoctoral fellowship and the work was supported by the grant (NSC93-2116-M-001-001). KPJ acknowledges discussions with Professor C.S. Menon, Mahatma Gandhi University. Careful review by anonymous reviewer greatly improved the quality of the paper.

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