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First-principles calculations of high-pressure physical properties anisotropy for magnesite

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ABSTRACT

The first-principles calculations based on density functional theory with projector-augmented wave are used to study the anisotropy of elastic modulus, mechanical hardness, minimum thermal conductivity, acoustic velocity and thermal expansion of magnesite(MgCO_3) under deep mantle pressure. The calculation results of the phase transition pressure, equation of state, elastic constants, elastic moduli, elastic wave velocities and thermal expansion coefficient are consistent with those determined experimentally. The research results show that the elastic moduli have strong anisotropy, the mechanical hardness gradually softens with increasing pressure, the conduction velocity of heat in the [100] direction is faster than that in the [001] direction, the plane wave velocity anisotropy

first increases and then gradually decreases with increasing pressure, and the shear wave velocity anisotropy increases with the increase of pressure, the thermal expansion in the [100] direction is greater than that in the [001] direction. The research results are of great significance to people's understanding of the high-pressure physical properties of carbonates in the deep mantle.

Introduction

Magnesite is a likely main host of carbonates in the mantle and plays an important role in the transport and storage of carbon in the Earth's mantle. Its high-pressure physical properties are crucial for understanding the deep carbon cycle¹. However, the structure of its high-pressure phase and its phase transition boundary are controversial. The experiment shows that the phase transition pressure range from magnesite(space group $R\bar{3}c$) to magnesite-II(space group $C2/m$) is 75-115 GPa²⁻⁶, while the theoretical result is 75-101 GPa⁷⁻¹³.

The elastic properties of minerals control the stress-strain relationship under elastic loading and are related to understanding strength, hardness, brittle/ductile behavior, damage tolerance, and mechanical stability. The elastic modulus controls the propagation of elastic waves, including the seismic anisotropy of the crust and mantle, so it is very important for the interpretation of seismic data. As derivatives of the free energy, they are

also related to the thermodynamic properties of minerals and are important for understanding the equation of state, phase stability and phase transition mechanism¹⁴. However, it is very difficult to measure the elastic constant under high temperature and high pressure. Recently, the elastic constants of magnesite are measured only up to 13.7 GPa¹⁵. The available results of the elastic properties are mainly limited to first-principles calculations^{1, 9, 11, 16}, these studies mainly discuss the elastic properties and the elastic wave velocity of magnesite. The thermal expansion coefficient of magnesite is mainly measured at low pressure, while the results under high pressure and high temperature are extrapolated¹⁷⁻¹⁹, and the result is also obtained by theoretical calculation^{1, 20}. So far, the thermal expansion anisotropy of magnesite has not been reported. In addition, its hardness and minimum thermal conductivity anisotropy have not been studied.

In present work, the elastic properties, hardness, thermal conductivity, elastic wave velocity and thermodynamic properties of magnesite under high pressure are investigated using the first-principles calculations based on density functional theory with generalized gradient approximation (GGA) combined with the quasi-harmonic approximate Debye model, and compared the calculated results with the existing experimental data, the anisotropy of the elastic modulus, mechanical hardness, minimum thermal conductivity, sound velocity and thermal expansion of magnesite are obtained.

Results and discussion

Phase transition, structural parameters and equation of state. The crystal structures of magnesite with space groups $R\bar{3}c$ ($Z=6$ formula units) and magnesite-II with space group $C2/m$ ($Z=12$ formula units) are shown in Figure 1, respectively. The calculated phase transition pressure from magnesite to magnesite-II is 72 GPa by using gibbs2 program²¹. This result is consistent with the recent experimental⁶ and theoretical¹¹ results of 75 GPa. Therefore, the present work only studies the anisotropy of the physical properties for magnesite when the pressure rises to 80 GPa.

As seen in Figure 1, Magnesite has a hexagonal crystal system with rhombohedral symmetry and space group $R\bar{3}c$. The structural parameters, isothermal bulk modulus and equation of state for magnesite are determined from a third order Birch-Murnaghan equation of state²². Table 1 shows the present calculated structural parameters and isothermal bulk modulus of magnesite, along with the experimental data^{19, 23, 24}. It is found that the present calculated results are in good agreement with previously reported values. The equation of state provides important information about minerals, which helps to model the composition of the deep layers of the earth. From Figure 2, the present calculated equation of state from 0 GPa to 80 GPa agrees well with the previous experimental data^{17, 19, 23-25}. The agreement of present calculated structural parameters and equation of state with the experiment indicates the feasibility and reliability of the

computational method.

Single-crystal elastic constants. The elastic properties of the earth's minerals are crucial to understanding their internal properties, especially in terms of their chemical composition and the propagation of seismic acoustic waves. Magnesite has six(c_{11} , c_{12} , c_{13} , c_{14} , c_{33} , c_{44}) independent elastic constants since $c_{66} = (c_{11} - c_{12})/2$. In order to confirm its mechanical stability, the following mechanical stability criteria are checked²⁶:

$$c_{11} > |c_{12}|, c_{44} > 0, 2c_{13}^2 < c_{33}(c_{11} + c_{12}), 2c_{14}^2 < c_{44}(c_{11} - c_{12}). \quad (1)$$

In this work, all the calculated elastic stiffness constants c_{ij} satisfy the mechanical stability criteria, so it may be said that magnesite is mechanically stable.

The calculated elastic constants of magnesite from 0 to 80 GPa are plotted in Figure 3, along with the previous experimental¹⁵ and theoretical^{11, 16} results. It can be clearly seen from Figure 3 that the present calculated elastic constants of magnesite are in excellent agreement with the available experimental and theoretical results, and gradually increase with the pressure.

Anisotropy of elastic modulus. The polycrystalline elastic moduli, such as bulk modulus B , shear modulus G and Young's modulus E , can be evaluated by Voigt-Reuss-Hill scheme²⁷⁻²⁹. For rhombohedral magnesite, bulk modulus B , shear modulus G can be calculated from the Voigt bounds(B_V and G_V) and Reuss bounds(B_R and G_R) from the following

expressions:

$$B_V = \frac{2c_{11} + c_{33} + 2c_{12} + 4c_{13}}{9} \quad (2)$$

$$G_V = \frac{(2c_{11} + c_{33}) - (c_{12} + 2c_{13}) + 3(2c_{44} + (c_{11} - c_{12})/2)}{5} \quad (3)$$

$$B_R = \frac{1}{(2s_{11} + s_{33}) + 2(s_{12} + 2s_{13})} \quad (4)$$

$$G_R = \frac{15}{4(2s_{11} + s_{33}) - 4(s_{12} + 2s_{13}) + 3(2s_{44} + s_{66})} \quad (5)$$

$$B = \frac{B_V + B_R}{2}, \quad G = \frac{G_V + G_R}{2} \quad (6)$$

According to the bulk modulus B and shear modulus G , Young's modulus E is defined as $E = 9BG/(3B + G)$.

Figure 4 presents the changes of bulk modulus B , shear modulus G , and Young's modulus E of magnesite along with the previous experimental¹⁵ and theoretical^{11, 16} results with pressure. As shown in figures, the present calculated elastic moduli increase smoothly and monotonically with increasing pressure, which agree well with the experimental and theoretical data.

The elastic anisotropy in mineral is of great significance due to its implication in geoscience as well as in crystal physics. In order to evaluate the elastic anisotropy of magnesite, Ranganathan and Ostoja-Starzewski universal anisotropy index³⁰, Kube's log-Euclidean anisotropy index³¹, and Chung and Buessem percent elastic anisotropy³² are used. The A^U , A^L , A_B , and A_G are given by the following relations:

$$A^U = \frac{B_V}{B_R} + 5 \frac{G_V}{G_R} - 6 \quad (7)$$

$$A^L = \sqrt{\left[\ln\left(\frac{B_V}{B_R}\right) \right]^2 + 5 \left[\ln\left(\frac{G_V}{G_R}\right) \right]^2} \quad (8)$$

$$A_B = \frac{B_V - B_R}{B_V + B_R}, \quad A_G = \frac{G_V - G_R}{G_V + G_R} \quad (9)$$

For an elastically isotropic crystal, $A^U = A^L = A_B = A_G = 0$, while the larger values of A^U , A^L , A_B and A_G represent a more elastic anisotropy. The universal anisotropy, log-Euclidean anisotropy, and percentage of bulk and shear anisotropies for magnesite are plotted in Figure 5. From Figure 5(a) may be observed that A^U and A^L increase with the increase of pressure, and the change trend is basically the same. It is found in Figure 5(b) that the percentage of shear anisotropy increases with the increase of pressure, and the percentage of bulk anisotropy decreases, and the increase in the percentage of shear anisotropy is much greater than the decrease in the percentage of bulk anisotropy, this means that the contribution of shear anisotropy in the elastic anisotropy of magnesite is greater than that of bulk anisotropy.

In order to furthermore elucidate this anisotropic behavior, the most straightforward method is to plot the three-dimensional contours of mechanical moduli. The ElasticPOST program^{33, 34} is used to obtain the 3D spatial distribution and their projection of shear modulus and Young's modulus for magnesite at various pressures, and the results are displayed in Figure 6 and Figure 7, respectively. As can be seen, the 3D figures of

shear modulus and Young's modulus reveals a large degree of deviation in shape from the sphere. This means that magnesite has a strong anisotropy, which also confirms the calculation results in Figure 5. The comparative analysis of shear modulus and Young's modulus for different directions as seen from the planar projections also indicates the anisotropy level.

Anisotropy of mechanical hardness. Vickers hardness is a fundamental property that is essential to describe the mechanical behavior of mineral, various semi-empirical relations have been proposed to estimate hardness using the elastic moduli. Vickers hardness is predicted using two theoretical models of hardness:

Chen's model³⁵:

$$H_V^{Chen} = 2(k^2 G)^{0.585} - 3, \quad (k = G/B) \quad (10)$$

Tian's model³⁶:

$$H_V^{Tian} = 0.92 \left(\frac{G}{B} \right)^{1.137} G^{0.708} \quad (11)$$

The calculated Vickers hardness of magnesite are depicted in Figure 8 from 0 to 80 GPa. As illustrated in Figure 8, the Vickers hardness decrease with increasing pressure, indicating magnesite becomes softer under high pressure, the Vickers hardness predicted by the Chen's model is smaller than that Tian's of the model in the entire pressure range. In order to evaluate the anisotropy of Vickers hardness of magnesite. The 3D spatial distribution and its projection of Vickers hardness for magnesite at various pressures are presented in Figure 9. The Vickers hardness exhibit strong

direction-dependent changes, resulting in large anisotropy, The 2D representations planar projection in different directions also show this result.

Anisotropy of acoustic velocity. The velocities of plane and shear modes of minerals can be calculated from the single crystal elastic constants. The plane wave velocity (v_P) and shear wave velocity(v_S) are calculated using³⁷:

$$v_P = \sqrt{\frac{3B + 4G}{3\rho}}, v_S = \sqrt{\frac{G}{\rho}} \quad (12)$$

The elastic wave velocities of magnesite are shown in figure 8 from 0 to 80 GPa. Figure 10 show that the calculated elastic wave velocity is in good agreement with the previous experimental results¹⁵ within the studied pressure range, the plane wave velocity v_P propagate more speedily than the shear wave velocity v_S . The consistency between the calculated elastic wave velocity and the experimental results provides reliability for further research on elastic wave velocities anisotropy.

Directional elastic wave velocities are computed by solving Christoffel's equation $\det|C_{ijkl}n_jn_l - \rho v^2\delta_{ik}| = 0$ ³⁸, where C_{ijkl} are the elastic stiffnesses, the n_j are unit vectors of the wave propagation direction, v is the acoustic velocity, and δ_{ik} is the Kronecker δ . Using AWESoMe program^{39, 40} with quadruple precision, the elastic wave velocities of P-mode and S-mode and the shear wave splitting of S-mode for magnesite in different propagation directions under various pressures are obtained, 3D

representation of the elastic wave velocity and the shear wave splitting of magnesite are plotted in Figure 11. It is observed from Figure 11(left) that the elastic wave velocities of P-mode have minimum values along the z direction, firstly decreasing with the increase of pressure, and then gradually increasing. For the two S-modes(fast and slow), the minimum values of the two wave velocities are shifted from the z direction yet they are still allocated around the z direction, but the magnitude of the shift gradually increases with the increase of pressure, especially the fast S-mode, the results of shear wave splitting in Figure 11 (right) also further verify this result.

Anisotropy of plane and shear wave velocity can be defined as $A_P = (v_{P,\max} - v_{P,\min}) / v_P \times 100\%$ and $A_S = (v_{S,\max} - v_{S,\min}) / v_S \times 100\%$, respectively. The calculated elastic wave velocities anisotropy of magnesite is presented in figure 12, along with the previous experimental^{15, 41, 42} and theoretical¹¹ results. At 0 GPa, the maximum error between the calculated plane wave velocity anisotropy and the experimental¹⁵ value is about 2.5%, and the maximum error between the shear wave velocity anisotropy and the experimental value⁴² is about 2.75%, indicating that the calculated data are in agreement with available experimental data. At low pressure, the plane wave velocity anisotropy increases with the increase in pressure, but gradually decreases at high pressure. Since the experimental results of Yang's¹⁵ are at low pressure, the conclusion that the anisotropy increases

with increasing pressure is obtained. The shear wave velocity anisotropy increases with increasing pressure, this result is consistent with the experimental¹⁵ and theoretical¹ results. Especially at 75 GPa, the present calculated results are consistent with the theoretical results of Li and Stackhouse¹¹.

Anisotropy of minimum thermal conductivity. The thermal conductivity is a measure of material's heat conduction ability. Therefore, the research on it of magnesite is significant. The minimum thermal conductivity of magnesite is calculated on the basis of Clark's model⁴³ and Cahill's model⁴⁴:

Clark's Model:

$$k_{min} = 0.87k_B M_a^{-2/3} E^{1/2} \rho^{1/6}, \quad M_a = M / (n \cdot N_A) \quad (13)$$

Cahill's Model:

$$K_{min} = (k_B / 2.48) n^{2/3} (v_p + 2v_s) \quad (14)$$

where M_a is the average mass per atom, E is Young's modulus, ρ is the density, M is the molar mass, n is the number of density of atoms per volume, k_B is Boltzmann's constant, N_A is Avogadro's number, respectively. Based on the two theoretical model, the calculated minimum thermal conductivity of magnesite from 0 to 80 GPa is shown in figure 13. It is seen that the minimum thermal conductivity of magnesite increases with the increase of the external pressure, the calculated results using the Cahill's model is greater than that computed by the Clark's model. This is

due to the atom number density and phonon spectrum are both considered in Cahill's model, whereas the Clark's model does not. Thus, the Clark's model underestimates the thermal conductivity. That is, the data obtained by Cahill's model should be closer to the real values than Clarke's model. To investigate the anisotropy of thermal conductivity, which can be summed from three acoustic branches such as one longitudinal branch (v_p) and two transverse branches (v_{s1} and v_{s2}). Therefore, the expression of Cahill's model can be changed in form as follows:

$$K_{min} = (k_B/2.48)n^{2/3}(v_p + v_{s1} + v_{s2}) \quad (15)$$

The calculated minimum thermal conductivities of magnesite in principal directions are also presented in figure 13, indicating the anisotropic characteristic of the minimum thermal conductivities. It can be observed that the $k_{min}[100]$ values are always higher than the $k_{min}[001]$ values within the pressure range of the study. It indicates that the conduction velocity of heat in the [100] direction is faster than that in the [001] direction. As can be seen from the crystallographic structures of rhombohedral magnesite, Mg, C and O atoms mainly align along the [100] direction. This atomic alignment means that the phonon mean free path in the [100] direction will be smaller than that in the [001] direction due to the high phonon collision probability in the [100] direction, therefore, $k_{min}[100]$ is higher than $k_{min}[001]$.

Anisotropy of thermal expansion. The thermal expansion coefficients

α_V) can be obtained by the following expressions:

$$\alpha_V = \frac{\gamma C_V}{B_T V}, \gamma = -\frac{d \ln \theta_D}{d \ln V} \quad (16)$$

where γ , C_V , B_T , V and θ_D represent the thermal Grüneisen parameter, the heat capacities, the isothermal bulk modulus, the volume and the Debye temperature, respectively. The volume thermal expansion coefficient of magnesite at 300 K and 0 GPa is $3.376 \times 10^{-5}/\text{K}$, in good agreement with the present calculated value of $3.688 \times 10^{-5}/\text{K}$. Having obtained the volumetric thermal expansion at different temperatures and pressures, the thermal expansion along different directions can be calculated from the linear compressibility. For rhombohedral crystal, The expressions are as follows⁴⁶:

$$\alpha_V = 2\alpha_{[100]} + \alpha_{[001]}, \quad \alpha_{[100]}/\alpha_{[001]} = K_{[100]}/K_{[001]} \quad (17)$$

where $K_{[100]}$ and $K_{[001]}$ are the linear elastic compressibility in the [100] and [001] directions, respectively. it is obtained by⁴⁷:

$$K_{[100]} = s_{11} + s_{12} + s_{13}, K_{[001]} = s_{33} + 2s_{13} \quad (18)$$

The anisotropic linear thermal expansion coefficients of magnesite at various pressures are calculated and are depicted in Figure 14. As can be seen, the thermal expansion in the [100] direction is the largest relative to

the [001] directions in magnesite, and it decrease with increasing pressure. Unfortunately, there is no experimental data or theoretical calculation results to compare with the linear thermal expansion coefficient of magnesite. Thus, the present work is beneficial for future research on the thermal properties of minerals.

Conclusions

The anisotropy of elastic modulus, mechanical hardness, minimum thermal conductivity, acoustic velocity and thermal expansion of magnesite under high pressure are investigated using the first-principles calculations within the density functional theory. The calculated phase transition pressure, equation of state, elastic constants, elastic moduli, elastic wave velocities and thermal expansion coefficient of magnesite are in excellent agreement with the previous experimental and theoretical results. It provides reliability for further research on the anisotropy of elastic modulus, mechanical hardness, minimum thermal conductivity, acoustic velocity and thermal expansion. The results of shear modulus and Young's modulus show that magnesite has strong anisotropy. The Vickers hardness changes strongly in different directions, leading to large anisotropy and softening under high pressure. Due to the higher probability of phonon collision in the [100] direction, the minimum thermal conductivity in the [100] direction is higher than that in the [001] direction and increases with the increase of pressure. The propagation of the plane wave along the z

direction has a minimum value, which decreases first and then gradually increases as the pressure increases. The minimum value of the two shear wave velocities shifts from the z direction, and the magnitude of the shift gradually increases with the increase of pressure, especially in the fast S-mode. The plane wave velocity anisotropy first increases and then gradually decreases with increasing pressure, and the shear wave velocity anisotropy increases with the increase of pressure. As discussed in literature¹, the elastic anisotropy of magnesite is much greater than that of the main minerals in the mantle, and its local enrichment provides a new explanation for the large local anisotropy in the transition zone. Finally, the anisotropy of thermal expansion is studied using the Debye quasi-harmonic approximation and elastic constants. It is found that the anisotropic linear thermal expansion coefficients in the [100] direction is the largest relative to the [001] directions and decrease with increasing pressure. The present work helps people to further understand the high-pressure physical properties of magnesite under deep mantle conditions, and also has important geophysical significance.

Methods

First-principles calculations based on density functional theory^{48, 49} are performed by using a Vienna Ab Initio Simulation Package (VASP)^{50, 51} with the projector-augmented wave method (PAW)⁵². The Perdew-Burke-Ernzerhof revised for solids(PBEsol) in GGA⁵³ is used to expound the

$\sqrt{3}c$ and $C2/m$ structures for $MgCO_3$ are set to 850 eV and 880 eV, and the Brillouin zone of Monkhorst-Pack grid sampling⁵⁴ is $9 \times 9 \times 2$ and $4 \times 5 \times 5$, respectively. The convergence threshold for electronic self-consistent field and forces acting on the atoms are 1.0×10^{-8} eV and 0.02 eV/Å, respectively. The elastic constant is obtained using the stress-strain method^{55, 56}. The thermodynamic properties are calculated by the quasi-harmonic approximation Debye (QHA) approach⁴⁵.

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Author contributions

Z. J. designed the calculations and wrote the manuscript. X. W. and C. R. analyzed the results, S. J. wrote the code, Z. R. and N. Z. performed partial calculations. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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Figure 1. Crystal structures of magnesite(a) and magnesite-II(b)

Figure 2. Equation of state for magnesite from 0 to 80 GPa.

Figure 3. Elastic constants of magnesite from 0 to 80 GPa.

Figure 4. bulk modulus B , shear modulus G (a) and Young's modulus E (b) of magnesite from 0 to 80 GPa.

Figure 5. Universal anisotropy A^U , log-Euclidean anisotropy A^L (a), and percentage of bulk(A_B) and shear(A_G) anisotropies(b) for magnesite from 0 to 80 GPa.

Figure 6. 3D spatial distribution and its projection of shear modulus for magnesite at various pressures.

Figure 7. 3D spatial distribution and its projection of Young's modulus for magnesite at various pressures.

Figure 8. Vickers hardness of magnesite from 0 to 80 GPa.

Figure 9. 3D spatial distribution and its projection of hardness for magnesite at various pressures.

Figure 10. Elastic wave velocities of magnesite from 0 to 80 GPa.

Figure 11. 3D representation of the elastic wave velocities of the P-modes and S-modes (left) and the shear wave splitting and polarization vectors of the S-modes(right) for magnesite in different propagation directions at various pressures.

Figure 12. Anisotropy of plane(a) and shear(b) wave velocity of magnesite from 0 to 80 GPa.

Figure 13. Minimum thermal conductivity of magnesite from 0 to 80 GPa.

Figure 14. Linear thermal expansion coefficients α_a (a) and α_c (b) along the $[100]=[010]$ and $[001]$ directions of magnesite at various pressures.

	a (Å)	c (Å)	V(Å ³)	K ₀	K ₀ '
Present work	4.649	14.906	279.23	108.27	4.58
Experimental results					
Fiquet and Reynard ²³	4.628	15.055	279.14	108	4.6
Ross ²⁴	4.634	15.018	279.28	111	4(fixed)
Zhang et al ¹⁹	4.635	15.013	279.32	103	4(fixed)

Table 1. Calculated structural parameters of magnesite along with the experimental data.