PAPER

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CH_4 Gas Extraction by CO_2: Substitution in Clathrate Hydrate through Bimolecular Iteration *

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Methane clathrate hydrate (MCH) is a promising energy resource, but controllable extraction of CH_4 from MCH remains a challenge. Gradually replacing CH_4 in MCH with CO_2 is an attractive scheme, as it is cost efficient and mitigates the environmentally harmful effects of CO_2 by sequestration. However, the practicable implementation of this method has not yet been achieved. In this study, using in situ *neutron diffraction, we confirm that CH_4 in the $5^{12}6^2$ cages of bulk structure-I (sI) MCH can be substituted by gaseous CO_2 under high pressure and low temperature with a high substitution ratio (~44%) while conserving the structure of the hydrate framework. First-principles calculations indicate that CO_2 binds more strongly to the $5^{12}6^2$ cages than methane does, and that the diffusion barrier for CH_4 is significantly lowered by an intermediate state in which one hydrate cage is doubly occupied by CH_4 and CO_2. Therefore, exchange of CO_2 for CH_4 in MCH is not only energetically favorable but also kinetically feasible. Experimental and theoretical studies of CH_4/CO_2 substitution elucidate a method to harness energy from these combustible ice resources.*

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Methane clathrate hydrate (MCH), or combustible ice, is a potential clean energy solution to the problem of worldwide fossil fuel shortages: the estimated energy contained in the form of methane clathrate hydrate is probably more than twice that of all natural gas, petroleum, and coal deposits combined.[1−3] However, liberating CH_4 from combustible ice is a challenge with the existing technology because at high pressure and low temperature, CH_4 is trapped in delicate hydrate structures that can rapidly decompose into gaseous CH_4 and water under small perturbations, such as depressurization and/or warming. CH_4 released in this explosive fashion is difficult to collect and harmful to environment, as it will exacerbate the greenhouse effect.[4] An attractive alternative is to employ guest molecules to replace CH_4 in MCH without damaging the hydrate lattice. For example, it was determined that another greenhouse gas, CO_2, can occupy both the large ($5^{12}6^2$) and small (5^{12}) cages of structure-I (sI) MCH with even larger binding energies,[5] indicating that substituting CH_4 with CO_2 in MCH is thermodynamically favorable. Thus, if it is kinetically feasible as well, the replacement reaction could allow for the controllable extraction of CH_4 from the clathrate and the reduction of global warming by storing equivalent amounts of CO_2.[6−8]

Since the first report on natural MCH by Ohgaki *et al.*,[6] great efforts have been made to explore the possibility of CH_4/CO_2 substitution in MCH. For example, solid-state nuclear magnetic resonance (NMR) was widely utilized to demonstrate that the replacement of CH_4 by CO_2 in hydrate is favored in both laboratory setting and porous media.[9−11] Park *et al.* employed Raman spectroscopy to reveal that ~64% of CH_4 in the MCH can be replaced by pure CO_2.[12] The studies on the materials in the presence of impurities such as N_2, SO_2, and C_2H_6 indicated that the key factor of gas exchange is the

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chemical equilibrium between hydrate phase and the surrounding phases.[13,14] The CH_4/CO_2 replacement was also proved by the investigation that CO_2 can induce the convention from structure-II (sII) hydrate to the less stable structure-I (sI) hydrate.[15] Based on these observations, some kinetic models have been established.[16,17] It is worth noting that the synthesized MCHs under experimental and natural conditions are always complex mixtures containing different forms of hydrates and large amount of pure ice, thus the poor spatial resolution of NMR and high surface sensitivity of Raman spectrum make the result of CH_4/CO_2 substitution in bulk form quite ambiguous. Furthermore, neither *in situ* detailed structural information of the substituted MCH nor the microscopic substituting mechanism are clearly known from these experiments. Meanwhile, the first principles studies have given opposite conclusions. For example, the density functional theory (DFT) calculations demonstrated that an extremely high diffusion barrier ($>1.0\,\mathrm{eV}$) through the hydrate cages can obstruct CH_4 diffusion in MCH.[18,19] CH_4/CO_2 substitution was also characterized to be infeasible by molecular dynamics (MD) simulations,[20] in which CH_4/CO_2 replacement follows a two-step process: the CH_4 hydrate first melts at the interface, and then an amorphous CO_2 hydrate layer forms, impeding further exchange of guest molecules. Thereby, as the experimental and simulation studies have given contradictory results, to date, the efficiency and microscopic mechanism of CO_2/CH_4 replacement in clathrate hydrates are still under debate.

Due to relatively higher sensitivity to light elements (e.g., C, H(D), and O), neutron diffraction is the most reliable technique to provide both refined structural characteristics in atomic resolution and the statistic information of MCH in centimeter level.[21,22] In the present work, for the first time, we employ the *in situ* neutron diffraction to study the evolution of MCH crystalline structure in the CO_2 atmosphere, which clearly demonstrates that CO_2 can efficiently substitute for CH_4 in large cavities of bulk-sI MCH with a high substitution ratio of $\sim$44%. Based on the first-principles calculations, we reveal that the replacement reaction is not only energetically favorable, but also kinetically feasible. Through a metastable intermediate state in which one $5^{12}6^2$cage is co-occupied by CO_2 and CH_4, the energy barrier for CH_4 diffusion is significantly reduced by $\sim$50%, so that CH_4 passes by CO_2 from the interior to the surface of the MCH without breaking the hydrate framework. Neutron diffraction and first-principles calculations conclusively confirm this proposed mechanism for CH_4/CO_2 substitution in bulk MCH, which is of great importance for using combustible ice resources.

Figure 1 shows the instrumental setup for MCH synthesis. In order to avoid incoherent scattering of H from H_2O, we used deuterated pure water (D_2O) for synthesis. D_2O was frozen for three days to make bulk ice. Bulk ice was then pulverized with a coffee grinder and quenched in liquid nitrogen to obtain fine ice powder (to avoid the preferred orientation present in large pieces of ice) and thereafter formed the clathrate, as shown in Figs. 1(a) and 1(b). Next, fine powder ice was loaded into a vanadium cell cooled in a circulating bath. The sealed cell was flushed with methane gas multiple times before pumping to the desired initial pressure. As shown in Fig. 1(c), after two weeks in the cooling bath, the synthesized MCH was ready for neutron diffraction and CO_2 replacement experiments. Using this method, synthesized MCH was in the form of the loose powder, as shown in Fig. 1(d).

The structure of CH_4/CO_2 clathrate was investigated using high-pressure neutron diffraction at the Los Alamos Neutron Science Center (LANSCE), Los Alamos National Laboratory. Figure 1(e) shows the schematic layout of the high-pressure preferred orientation (HIPPO) time-of-flight neutron diffractometer[23,24] and the setup for hydrate diffraction at low temperature and high pressure. Forward scattering covers large d spacing, ranging from 1.0 to $\sim$10.6 Å, which provides accurate lattice parameters for the clathrate; back scattering gives higher resolution of the d spacing, ranging from 0.5 to 2.0 Å, which allows us to determine the accurate atomic positions. Using the detector geometry and combined refinement of multi-bank data, we were able to obtain reliable and refined structural parameters for MCH, such as cage occupancy and CO_2/CH_4 substitution ratios. D_2O ice was studied in a high-pressure vanadium gas cell, which withstands a maximum pressure of 50 MPa.

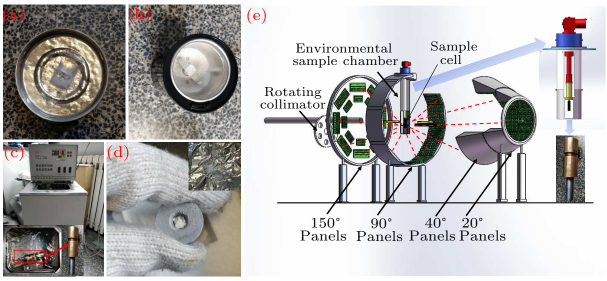

Fig. 1. MCH synthesis in a stainless cell for neutron diffraction measurement: (a) D_2O is frozen in liquid nitrogen; (b) D_2O ice is pulverized with a grinder; (c) D_2O powder is added to a vanadium cell, which is cooled in a circulating bath and flushed with methane gas four times, and then pressurized to 20 MPa; (d) after several days, methane hydrates form; (e) high-pressure preferred orientation (HIPPO) time-of-flight neutron diffraction setup (left panel) with an enlarged view of the sample chamber under vacuum (right upper panel) and the cell used (right lower panel).

Synthesized polycrystalline sample of MCH was characterized by *in situ* high-pressure (20 MPa) and low-temperature (70–270 K) neutron diffractions, and the diffraction patterns were analyzed by the Rietveld method using the General Structure Analysis System (GSAS).[25−27] As shown in Fig. 2(a), the refined data indicate that the sI MCH crystal adopts the $Pm\bar{3}n$ space group with a lattice constant around 11.9 Å for the entire temperature range of 70–270 K. Based on the relationship between the lattice constant and temperature (Fig. S1 in the Supplementary Materials), the thermal expansion coefficient satisfies the equation $a = a_0 \exp \int \alpha(T)dT$, where $\alpha(T) = \beta + \gamma T$. Here we derived $a_0 = 11.783\,Å$, $\beta_a = 5.62 \times 10^{-5}\,\mathrm{K}^{-1}$, and $\gamma_a = 1.39\times 10^{-7}\,\mathrm{K}^{-2}$, consistent with the values previously reported for natural gas clathrate.[28,29] Diffraction patterns were further refined to produce difference Fourier nuclear density maps (without CH_4 in the refined models), which clearly indicate the scattering density with center rotation of CH_4. The refined atomic structure (20 MPa, 270 K) of synthesized sI MCH, as shown in Fig. 2(b) (atomic positions are listed in Table S2 in the Supplementary Materials), indicates that the hydrate framework of the sI clathrate is composed of two kinds of polyhedrons, the 5^{12} (dodecahedron with 12 identical pentagonal faces) and $5^{12}6^2$ (tetradecahedron with 12 pentagonal and 2 hexagonal faces), in a 1 : 3 ratio. The 5^{12} cages share pentagons with the $5^{12}6^2$ cages to form linear chains along the [110] direction, while each $5^{12}6^2$ cage shares two hexagons with neighboring $5^{12}6^2$ cages to form an ice channel along the [100] direction. As shown in Fig. 2(c), the $5^{12}6^2$ hexagonal ring channels run through the whole clathrate, which is essential for the diffusion of guest molecules. CH_4 occupancies for both the $5^{12}6^2$ and 5^{12} cages are ∼1.0, thus the formula for synthesized MCH is $CH_4{\cdot}5.75D_2O$. In addition to coating the clathrate shell on the surface, unreacted D_2O also forms an inner ice core. As a result, the molar ratio between the clathrate and the ice phases from the refinement is approximately 1 : 4.

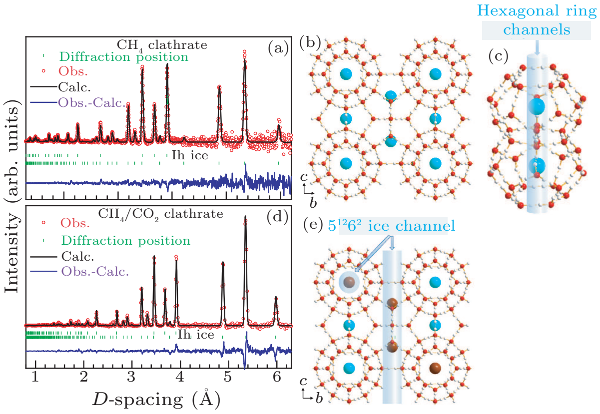

Fig. 2. Characterization of synthesized MCH: (a) time-dependent neutron diffraction patterns for the CH_4 clathrate; (d) neutron diffraction patterns substitution of CH_4 with CO_2 in MCH over 48 h; (b) atomic structure of sI clathrate with CH_4 (balls in cyan); (c) proposed molecular pathway through the hexagonal rings shared by the large $5^{12}6^2$ cages; (e) structure of sI clathrate with partial CO_2 (balls in wine) substitution. Red and white balls represent oxygen and disordered deuterium in the D_2O framework, respectively.

After exposure to CO_2 (35 bar, 270 K) for 48 h, substituted MCH was examined again by high-pressure and low-temperature neutron diffraction. A large CH_4/CO_2 substitution rate of ∼44% was found in the $5^{12}6^2$ cages, while the framework of clathrate was perfectly conserved, as confirmed by identical GSAS diffraction patterns for the unsubstituted and substituted MCHs, as shown in Fig. 2(d) (detailed structural parameters listed in Table S3 in the Supplementary Materials). Refinement data also indicate that CH_4/CO_2 replacement is assisted by the extensive channel network formed by the hexagonal ice rings of the $5^{12}6^2$ large cages, as exhibited in Fig. 2(e). The measured substitution rate in the smaller 5^{12} cages is negligible according to the refinement. Considering the tremendous grain boundaries in the sample and the limited kinetics of gas replacement reactions under high-P/low-T conditions, a substitution rate of ∼44% within finite reaction time is reasonable and consistent with the results of Park *et al.*[12] Furthermore, diffraction data also demonstrate that the ratio of ice phase does not increase in gaseous CO_2; and the unreacted ice core in the original MCH sample is reduced by 25%. This suggests the formation of extra clathrate without melting of the clathrate host lattice during the replacement process. Due to the existence of unreacted ice cores at the end of the synthesis, the system is in a quasi-equilibrium state, where the concentration gradient leads to diffusion of CH_4 towards interior region of synthesized MCH. As the result, the size of ice core is reduced after 48 hours of replacement.

Natural MCH can be porous or confined in pore structures or in bulk and powder forms. Different configurations of natural clathrates and their surrounding hydrogeological conditions can significantly affect their substitution pressures, temperatures, and heat-transfer rates, but do not change the fundamental mechanism for gas exchange at the molecular level. Although neutron diffraction evidence demonstrates that CO_2 can substitute efficiently for CH_4 in the clathrate hydrate without damaging the host framework, experimental investigation of the microscopic substitution process is extremely difficult. Therefore, we employed the first-principles calculations (see the method details in the Supplementary Materials) to evaluate a possible mechanism for the replacement reaction.

The calculated binding energy of CO_2 to the hydrate framework (−0.52 eV) is 0.1 eV larger than that of CH_4 (−0.42 eV), indicating increased stability for the CO_2 clathrate compared to that of guest CH_4, according to the previous reports.[30,31] We also confirmed that the binding energies for CH_4 and CO_2 increase slightly with increasing distance from the air-hydrate interface (0–15 Å), converging at >15 Å. This implies that gas molecules captured in clathrate hydrate are stabilized in the inner bulk phase of the clathrate. The rapidly converging binding energies also suggest that the bulk size of the clathrate affects the substitution process, which further demonstrates that our powder MCH sample is suitable for elucidating the substitution mechanism.

Diffusion of guest molecules in MCH is a key factor determining substitution kinetics. First, we considered the simplest mechanism: CH_4 spreads out through the $5^{12}6^2$ hexagonal ring channels and CO_2 enters the clathrate lattice. According to the DFT calculations, both CO_2 and CH_4 can pass through the large $5^{12}6^2$ cages by slightly stretching the hydrogen bonding network of the hexagonal ring without breaking it (Table S1 in the Supplementary Materials). Although the CO_2 binds more strongly to the clathrate hydrate, its linear geometry allows it to pass through the ice channel more readily than tetrahedral CH_4 molecules. The predicted diffusion barriers for CH_4 and CO_2 are 1.29 and 0.52 eV, respectively (Fig. S2 in the Supplementary Materials), consistent with the values 1.17 and 0.42 eV reported by Román-Pérez *et al.*[18] According to the Arrhenius equation, the barrier difference makes the diffusion rate of CO_2 $\sim 10^{13}$ times larger than that of CH_4, allowing CO_2 to diffuse easily through the sI clathrate lattice, while CH_4 can hardly pass through the water cages. In addition, CH_4 in the deep bulk phase must travel from the interior to the exterior, during which it experiences numerous high diffusion barriers. This reduces the probability of substitution exponentially. Therefore, the model based on the diffusion of freely spreading individual guest molecules is not feasible.

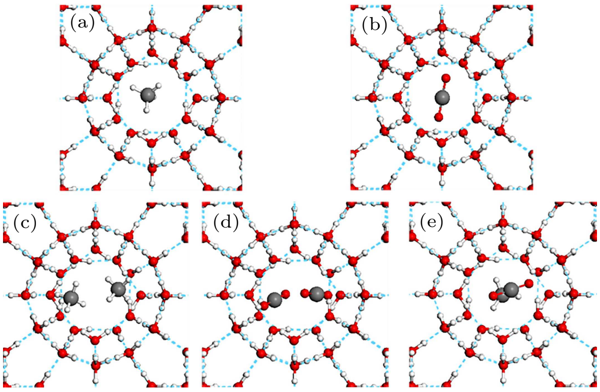

Fig. 3. Optimized structures of $5^{12}6^2$ cages singly occupied by (a) CH_4 and (b) CO_2, as well as the structure of $5^{12}6^2$ cages doubly occupied by (c) CH_4–CH_4, (d) CO_2–CO_2, and (e) CH_4–CO_2, based on the DFT calculations. Detailed parameters can be found in Table S1 for sI.

Since the free-spreading model is kinetically unfeasible, we explored an alternative pathway for the substitution, where CO_2 displaces CH_4 by experiencing a doubly occupied intermediate state. This was also previously observed in molecular dynamics simulations reported by Tung *et al.*[32] We found that the sI clathrate lattice is conserved well when the $5^{12}6^2$ cage is doubly occupied by guest molecules, as shown in Fig. 3. The relative energies of CH_4–CH_4, CH_4–CO_2, and CO_2–CO_2 co-occupation in the $5^{12}6^2$ cage are −0.20, −0.23, and −0.35 eV, respectively, compared to the energy of the empty lattice, illustrating that $5^{12}6^2$ doubly occupied cages (DOC) are less stable than the singly occupied cages, but slightly more stable than empty cages. The order of relative energies confirms our experimental observations that single occupation of clathrate cavities is preferred. In addition, CH_4–CO_2 and CO_2–CO_2 double occupation are more stable than CH_4–CH_4 co-occupation, which illustrates that CH_4 replaced by CO_2 is thermodynamically preferred.

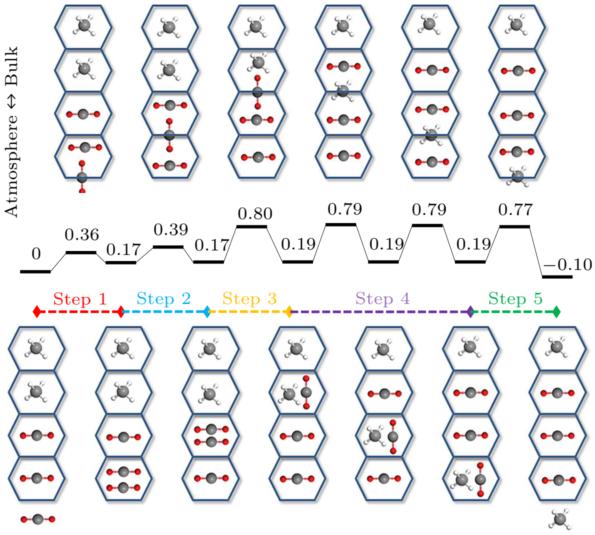

Fig. 4. Schematic representation of the molecular mechanism for iterative exchange of CH_4 in the bulk sI clathrate hydrate with CO_2, and the corresponding potential energy profile for the exchange process (black line).

Additional diffusion barriers for guest molecules were calculated for the DOC. As depicted in Fig. 4, assuming that the $5^{12}6^2$ cages in the outermost shell of the clathrate hydrate are already occupied by CO_2, the generalized exchange procedure, starting from the outer shell to the deep interior, can be divided into 5 steps: Step 1, a gaseous CO_2 molecule penetrates a CO_2 singly occupied cage (SOC) in the outermost layer of the clathrate to form a CO_2-CO_2 DOC. Step 2, the CO_2 molecule from the DOC moves into the clathrate and creates a CO_2 DOC adjacent to a CH_4 SOC. Step 3, one CO_2 molecule in the DOC diffuses to a neighboring CH_4 SOC to form a CH_4-CO_2 DOC. Step 4, the CH_4 molecule moves outward from the doubly occupied cage. Step 5, CH_4 is displaced to a DOC with CO_2 in a $5^{12}6^2$ cage of the outermost clathrate layer, then finally diffuses into the gas phase. Energy barriers for these steps were computed, as shown in Fig. 4. Compared to the extremely unfavorable process (1.29 eV) for diffusion of CH_4 with single occupation, the largest diffusion barrier for CH_4 in the doubly occupied cages is around 0.6 eV, indicating that the diffusion of CH_4 can be significantly enhanced by CO_2. The diffusion barrier for CO_2 in the CO_2 DOC (0.22 eV) is also much lower than that of CO_2 in the SOC (0.52 eV). Therefore, the diffusions of both CH_4 and CO_2 in the clathrate are more favorable with DOCs. Gas phase CO_2 diffusing into a CO_2 SOC also experiences a low energy barrier of 0.36 eV. Furthermore, the process can be accelerated by increasing the partial pressure of CO_2. Therefore, our calculations clearly demonstrate the exchange mechanism is feasible for CH_4/CO_2 replacement without damaging the clathrate hydrate lattice.

Using *in situ* high-pressure and low-temperature neutron diffraction, we have confirmed that CH_4 in bulk sI MCH can be replaced by gaseous CO_2 with a substitution ratio of ∼44% without melting the clathrate lattice. An exchange mechanism for CH_4/CO_2 replacement is proposed, based on first-principles calculations, in which the diffusion barriers of CH_4 and CO_2 through the lattice of clathrate hydrate are reduced by 51% (from 1.29 to 0.63 eV) and 31% (from 0.52 to 0.36 eV), respectively, via doubly occupied $5^{12}6^2$ cages. High CH_4/CO_2 substitution ratios in MCH under moderate conditions (35 bar, 270 K) clearly demonstrate that using CO_2 to gradually substitute for CH_4 in clathrate hydrates presents a safe efficient method to harness these rich combustible ice resources.

References

[1] Claypool G E and Kaplan I R 1974 *Marine Science* (Boston: Springer) vol 3 p 99

[2] Sloan E D 2003 *Nature* **426** 353

[3] Licence P, Sloan E D and Carolyn A K 2007 *Clathrate Hydrates of Natural Gases* (Florida: CRC Press)

[4] Englezos P 2001 *Energy and Environment Technological Challenges for the Future* (Tokyo: Springer) vol 3 p 181

[5] Yezdimer E M, Cummings P T and Chialvo A A 2002 *J. Phys. Chem. A* **106** 7982

[6] Ohgaki K, Takano K, Sangawa H, Matsubara T and Nakano S 1996 *J. Chem. Eng. Jpn.* **29** 478

[7] Jadhawar P, Mohammadi A H, Yang J and Tohidi B 2006 *NATO Science Series* (Dordrecht: Springer) vol 65 p 111

[8] Morohashi K, Abe Y and Watanabe M 2005 *Energy Convers. Manage.* **46** 1680

[9] Lee H, Seo Y, Seo Y T, Moudrakovski I L and Ripmeester J A 2003 *Angew. Chem. Int. Ed.* **42** 5048

[10] Baldwin B A, Stevens J, Howard J J, Graue A, Kvamme B, Aspenes E, Ersland G, Husebø J and Zornes D R 2009 *Magn. Reson. Imaging* **27** 720

[11] Graue A, Kvamme B, Baldwin B A, Stevens J, Howard J, Aspenes E, Ersland G, Husebø J and Zornes D 2008 *SPE J.* **13** 146

[12] Park Y, Kim D Y, Lee J W, Huh D G, Park K P, Lee J and Lee H 2006 *Proc. Natl. Acad. Sci. USA* **103** 12690

[13] Kvamme B 2016 *J. Chem. Eng. Data* **61** 1280

[14] Beeskow-Strauch BandSchicks J M 2012 *Energies* **5** 420

[15] Schicks J M, Luzi M and Beeskow-Strauch B 2011 *J. Phys. Chem. A* **115** 13324

[16] Falenty A, Qin J, Salamatin A N, Yang L and Kuhs W F 2016 *J. Phys. Chem. C* **120** 27159

[17] Salamatin A N, Falenty A and Kuhs W F 2017 *J. Phys. Chem. C* **121** 17603

[18] Romã P G, Moaied M, Soler J M and Yndurain F 2010 *Phys. Rev. Lett.* **105** 145901

[19] Li Q, Kolb B, Román P G, Soler J M, Yndurain F, Kong L Z, Langreth D C and Thonhauser T 2011 *Phys. Rev. B* **84** 153103

[20] Bai D, Zhang X, Chen G and Wang W 2012 *Energy & Environ. Sci.* **5** 7033

[21] Lokshin K A, Zhao Y S, He D W, Mao W L, Mao H K, Hemley R J, Lobanov M V and Greenblatt M 2004 *Phys. Rev. Lett.* **93** 125503

[22] Hester K C, Strobel T A, Sloan E D, Koh C A, Huq A and Schultz A J 2006 *J. Phys. Chem. B* **110** 14024

[23] Li S, Beyerlein I J, Alexander D J and Vogel S C 2005 *Acta Mater.* **53** 2111

[24] Mcdaniel S, Bennett K, Durham W B and Waddington E D 2006 *Rev. Sci. Instrum.* **77** 093902

[25] Larson A C and VonDreele R B 2000 LANL Report (Los Alamos: Los Alamos National Laboratory)

[26] Toby B H 2001 *J. Appl. Crystallogr.* **34** 210

[27] Kotnana G and Jammalamadaka S N 2015 *J. Appl. Phys.* **117** 124101

[28] Shpakov V P, Tse J S, Kvamme B and Belosludov V R 2005 *International Offshore and Polar Engineering Conference* (Honolulu USA, 25–30 May 1997)

[29] Tse J S, Tulk C A, Kvamme B and Belosludov V R 1998 *Chem. Phys. Lett.* **282** 107

[30] Cao X, Su Y, Liu Y, Zhao J and Liu C 2014 *J. Phys. Chem. A* **118** 215

[31] Atilhan M, Pala N and Aparicio S 2014 *J. Mol. Model.* **20** 2182

[32] Tung Y T, Chen L J, Chen Y P and Lin S T 2011 *J. Phys. Chem. B* **115** 15295