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## Mechanical and thermal properties of methane clathrate hydrates as an alternative energy resource

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Mechanical, acoustic and thermal properties for three common hydrates structures sI, sII, and sH were investigated using first-principles methods. Elastic constants were estimated by fitting strain energy versus Lagrangian strain. Bulk modulus, shear modulus, Young's modulus and Poisson's ratio deduced from elastic constants are in reasonable agreement to experimental values. The longitude and transverse velocity compare reasonably with the experimental results with systematical overestimation. Using the quasi-harmonic approximation and Debye model, some thermal properties including heat capacity, linear thermal expansion, Grüneisen parameter, and Debye temperature for structure sI and sII were estimated and compared with available experiments. © 2011 American Institute of Physics. [doi:10.1063/1.3670410]

### I. INTRODUCTION

Clathrate hydrates<sup>1</sup> are ice-like compounds of which guest molecules are encapsulated in hydrogen-bond cages by water molecules. There are three common crystal structures of clathrate hydrates, i.e., type sI,<sup>2</sup> type sII,<sup>3</sup> and type sH.<sup>4</sup> The cubic hydrate structure of type sI is composed of two pentagonal dodecahedra ( $5^{12}$ ) with 20 water molecules and six tetrakaidecahedra ( $5^{12}6^2$ ) with 24 water molecules. Type sII hydrate with cubic structure consists of eight hexakaidecahedra ( $5^{12}6^4$ ) with 28 water molecules and sixteen pentagonal dodecahedra ( $5^{12}$ ) with 20 water molecules. Hexagonal hydrate structure sH is made up of three pentagonal dodecahedra ( $5^{12}$ ), two irregular dodecahedra ( $4^35^66^3$ ) with 20 water molecules, and one large icosahedron ( $5^{12}6^8$ ) with 36 water molecules. The structure type of clathrate hydrates mainly depends on the size of guest molecules and external temperature-pressure condition.

Among the gas hydrates, methane hydrates play a predominant role because of its wide-spread impact on many aspects, especially the fields related to energy and environment. According to the U.S. Geological Survey,<sup>5</sup> in the permafrost and neritic floor there are a huge amount of natural gas hydrates, in which the carbon contained is more abundant than all other fossil fuel together. With appropriate exploitation, clathrate hydrates of natural gases could act as alternative energy resource issues for a quite long period.<sup>6,7</sup> On the other hand, hydrogen hydrate as a potential hydrogen storage material has attracted increasing attention, because of excellent capacity as well as cleanness with regard to the other hydrogen storage materials.<sup>8,9</sup> In addition, since the greenhouse effect of methane is about 20 times more than CO<sub>2</sub>,<sup>10</sup> large-scale decomposition of the methane hydrate deposits would lead to serious environmental problems. At the same time, the geology of sea floor might become unstable after extraction of methane clathrates, some geological disasters would be induced. Therefore, clathrate hydrates of natural gases, especially methane, have been focus of intensive research from many different fields.

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Up to now, there were many both experimental and theoretical works on the fundamental properties as well as formation mechanism of clathrate hydrates. Raman, NMR, and other spectroscopy means are the frequently used methods to identify the type of crystal structure and to determine the cage occupancy of clathrate hydrates.<sup>11,12</sup> Currently, significant attentions have been paid to the formation mechanism of clathrate hydrates using molecular dynamics (MD) simulation with empirical potentials.<sup>13–15</sup> In contrast, much less is known about the basic physical (mechanical, acoustic, and thermal) properties of clathrate hydrates, which not only can help us thoroughly understand hydrates, but also can facilitate the exploitation of gas hydrates in future. Previously, the elastic properties for methane hydrates of type sI and sII have been measured in laboratory,<sup>16–18</sup> and the elastic properties for methane hydrates of type sI were calculated by Shpakov *et al.*<sup>19</sup> and Miranda *et al.*<sup>20</sup> using empirical potential and first-principles method, respectively. Longitude and transverse wave velocities for cubic structure sI were also measured by Brillouin spectroscopy technique.<sup>21</sup> However, within the best of our knowledge, the elastic properties of sH methane hydrate have not been explored both experimentally and theoretically. Moreover, it would be valuable to conduct a comparative study on the three phases of clathrate hydrates.

For further exploiting and utilizing the enormous energy resources contained in clathrate hydrates, it is of importance to understand the fundamental properties of the clathrate hydrates. In this work, we systematically calculated the elastic constants and some other mechanical, acoustic, and thermal properties of these three types of methane clathrate crystals using first-principles approaches. In particular, the fully elastic moduli of the cubic sII and the hexagonal sH phases of methane hydrates have been obtained. These theoretical results, with some acceptable systematic error, constitute a useful database for the fundamental properties of clathrate hydrates.

## II. THEORETICAL METHODS

Here, we calculated three conventional clathrate hydrates, i.e., cubic structure sI and sII, and hexagonal structure sH, which are shown in Figs. 1(a)–1(c), respectively. For structure sI, one methane molecule is encapsulated within each cage. In type sII, eight propane molecules and sixteen methane molecules are filled into the cavities of  $5^{12}6^4$  and  $5^{12}$  cages, respectively. The largest cage is occupied by one propane molecule and other kinds of cages are occupied by methane molecules in hexagonal structure sH.

Our first-principles computations are based on the generalized gradient approximation<sup>22</sup> with the revised Perdew-Burke-Ernzerh (revPBE) parametrization<sup>23,24</sup> for the exchange-correlation functional within the framework of density functional theory,<sup>25,26</sup> as implemented in the Quantum-Espresso Package. We employed Andrea Dal Corso (rrkj3) ultrasoft pseudopotentials<sup>27</sup> to describe the ion-electron interactions. A kinetic energy cutoff of 62 Ry was adopted for plane-wave basis. Due to the reasonably large size of unit cell and weak dispersion of electronic bands, Brillouin zone for all three type of structures, i.e., sI, sII, and sH, was sampled by  $\Gamma$  point. The geometry optimization was conducted with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm.

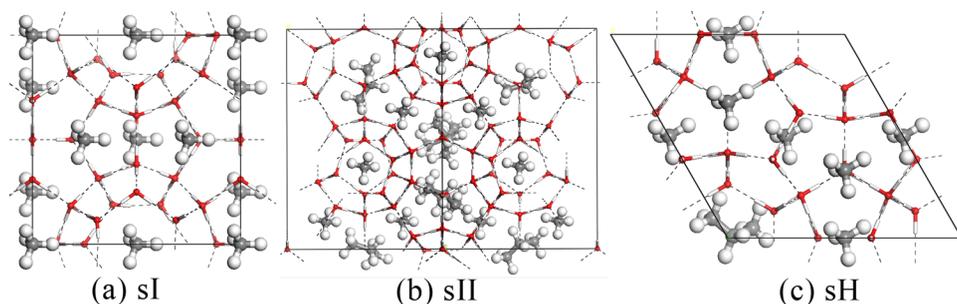


FIG. 1. Crystal structures for type sI (a), sII (b), and sH (c) clathrate hydrates. Color scheme: red for oxygen, white for hydrogen, grey for carbon, black dashed lines for hydrogen bonds. For the guide of eyes, the hydrogen atoms in methane molecules are shown in larger balls while those on water molecules are in sticks.

In the work, we first determined the equilibrium cell parameters for the stress-free states. Starting from the equilibrium unit cells, full sets of second order elastic constants (SOECs) were calculated using the homogeneous finite strain method incorporated with first-principle total energy method. The detailed description of this method can be found in the early publication by one of us.<sup>28</sup> In short, elastic constants are defined by expanding the Gibbs free energy as a Taylor series versus Lagrangian strains. The second-order Taylor expansion coefficients  $A_2$  as combinations of SOECs of the crystal are obtained from a polynomial fit to the calculated energy-strain relation. The relationship between the expansion coefficient  $A_2$  and the SOECs for cubic and hexagonal crystals are given in Table I.

For cubic structure (sI and sII), there are three independent constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ , which can be determined from the three Lagrangian strains  $S_1$ ,  $S_2$ , and  $S_3$ . Meanwhile, five independent constants are needed to describe the elastic properties of hexagonal crystals, and we used strain tensors  $S_3$ ,  $S_4$ ,  $S_5$ ,  $S_6$ , and  $S_7$  to compute these five elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ , and  $C_{44}$  of hexagonal structure sH. Using the SOECs, the bulk modulus (B) and shear modulus (G) of the clathrate hydrate crystals are calculated via the Voigt-Reuss-Hill averaging scheme.<sup>29</sup> Afterwards, (E) and Poisson's ratio ( $\nu$ ) can be calculated from B and G.

The thermodynamics properties were further calculated using the Gibbs program<sup>30</sup> based on the quasi-harmonic approximation and the Debye model. For the sI and sII hydrates of cubic phase, the total energies were calculated for a series of cell volume (including both positive-pressure and negative pressure ranges). At each volume, the ionic positions were fully optimized using the first-principles methods described above. The energy-volume data were then used to extract some thermal properties (heat capacity, thermal expansion coefficient, Grüneisen parameter, and Debye temperature) approximately using the Gibbs program.

### III. RESULTS AND DISCUSSION

The equilibrium unit cell parameters for these three types of clathrate hydrate crystals from the present first-principles calculations are summarized in Table II. Our theoretical results agree satisfactorily with experimental values.<sup>1</sup> Within the current theoretical scheme, the lattice parameters are systematically overestimated by 0.83% for structure sI, 2.4% for sII, and 2.4% or 2.2% for sH, respectively, with regard to experiment. Accordingly, the deviations of unit cell volume from experiments are 2.6% for sI, 7.4% for sII, and 7.1% for sH. We all know that the hydrogen bonding interactions between water molecules and the van der Waals (vdW) interactions between guest molecules and host cages play a key role in clathrate hydrates. However, the GGA-revPBE functional used here is unable to accurately describe the vdW interactions. This may account for the overestimation of lattice constants. On the other hand, the reasonable agreement between experiments and theoretical calculations indicates that the present theoretical scheme is able to reproduce the hydrogen-bond in certain extent.

The elastic constants are important parameters for characterizing the mechanical properties of a crystal, and many other physical properties like bulk modulus, longitude wave velocity can be calculated from them. The computed elastic constants of the clathrate hydrates are given in

TABLE I. The second-order coefficient  $A_2$  as combinations of second order elastic constants for cubic and hexagonal crystals. The strains tensors are defined in Appendix.

	Strain	Second order coefficient $A_2$
Cubic crystal	S1	$C_{11}$
	S2	$2C_{11} + 2C_{12}$
	S3	$12C_{44}$
Hexagonal crystal	S3	$2C_{11} - 2C_{12} + 8C_{44}$
	S4	$C_{11}$
	S5	$C_{33}$
	S6	$C_{11} + 2C_{13} + C_{33}$
	S7	$2C_{11} - 2C_{12}$

TABLE II. Lattice parameter ( $a$ ) and unit cell volume ( $V$ ) for three types of clathrate hydrate crystals compared with experimental data (Ref. 1) and previous calculations (Ref. 17).

Structures		This work	Ref. 17	Expt. (Ref. 1)	Deviation
sI	$V (\text{\AA}^3)$	1786.45	1775.96	1741.00	2.6%
	$a (\text{\AA})$	12.13	12.11	12.03	0.83%
sII	$V (\text{\AA}^3)$	5561.38	–	5177.72	7.4%
	$a (\text{\AA})$	17.72	–	17.30	2.4%
sH	$V (\text{\AA}^3)$	1394.46	–	1301.88	7.1%
	$a (\text{\AA})$	12.49	–	12.20	2.4%
	$c (\text{\AA})$	10.32	–	10.10	2.2%

Table III, along with experimental values<sup>1</sup> and previous theoretical results<sup>20</sup> for comparison. Generally speaking, our calculations systematically overestimate the elastic constants of sI clathrate by 1.9–2.6 GPa. In addition to the known deficiency of our computational method within DFT framework, such discrepancy can be attributed to two factors: temperature effect and partial cage occupancy. The experimental data on clathrate hydrate were usually measured at a high-pressure of about 200 atm and room temperature of 296 K.<sup>21</sup> Compared with the zero temperature data from first-principles calculation, temperature effect can soften the elastic constants. Besides, our calculations assumed that all water cages are fully occupied by guest molecules, whereas experiments show partial cage occupancy in the realistic clathrate hydrate samples.<sup>31,32</sup> It is also noteworthy that previous first-principles results seem to be closer to experimental data but their deviations are not systematical.

In the natural-gas hydrates reservoirs discovered so far, the type sI methane hydrate is dominant. However, Chou *et al.* indicated sI methane hydrate would transform to type sII at 100 MPa and to sH phase at 600 MPa.<sup>33</sup> Therefore, the methane hydrates may largely exist in the form of sII phase or even sH phase in the greater depth of permafrost areas. But much less experimental data are available for the latter two types. Especially, there were no measured elastic constants for hydrates of type sII and sH. Indeed, the mechanical strengths for hydrates of different structural phases buried in sediments determine the stability of sediments in the ocean floor, which are further related to the optimal exploiting sites and schemes. Therefore, our present data of SOECs provide useful database for these materials, even though there is some systematical error due to the limitation of theoretical method.

Using the theoretical elastic constants and mass density (cell volume), we further compute some key parameters for mechanical and acoustic properties calculated for these three types of crystals. These results are listed in Table IV and compared with the available experimental data<sup>1,34</sup> and previous calculations<sup>20</sup> for type sI and sII. Again, our theoretical calculations systematically overestimate the moduli ( $B$ ,  $G$ ,  $E$ ) of both type sI and sII hydrates; but the overall agreement is still satisfactory. Similar to the discussion of elastic constants, such deviation can also be partially explained by the temperature effect as well as the incomplete cage occupancy. Previous first-principles results<sup>20</sup> are closer to experiment but the deviation shows no systematical trend (i.e.,  $B$  is smaller than experiment but  $G$  and  $E$  are larger).

TABLE III. Elastic constants for the three types of clathrate hydrate crystals compared with experimental data (Ref. 1) and previous calculations (Ref. 17).

		$C_{11}$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)	$C_{13}$ (GPa)	$C_{33}$ (GPa)
sI	This work	14.2	6.0	7.9	–	–
	Ref. 17	15.1	3.8	4.9	–	–
	Expt. (Ref. 1)	11.9	3.4	6.0	–	–
sII	This work	15.3	7.0	4.6	–	–
sH	This work	15.9	5.7	4.8	4.5	17.3

TABLE IV. Bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio ( $\nu$ ), longitudinal and transverse sound velocities ( $v_L$  and  $v_T$ ), and mass density ( $\rho$ ) for methane hydrates with structures sI, sII, and sH.

		B (GPa)	G (GPa)	E (GPa)	$\nu$	$v_L$ (km/s)	$v_T$ (km/s)	$\rho$ (g/cm <sup>-3</sup> )
sI	This work	9.98	4.62	12.01	0.299	4.205	2.250	0.91
	Ref. 17	8.3	4.3	11.07	0.278	3.981	2.209	0.89
	Expt. (Refs. 1 and 32)	8.76	3.57	8.4	0.314	3.778	1.964	0.91
sII	This work	9.76	4.43	11.55	0.303	4.141	2.203	0.91
	Expt. (Refs. 1 and 32)	8.48	3.67	8.2	0.311	3.822	2.001	0.94
sH	This work	8.74	5.40	13.43	0.244	4.262	2.481	0.88

Poisson's ratio is a characteristic quantity of a material that reflects its ductility, while the sound velocities of clathrate hydrates are of geologic importance. These properties were also computed and compared with experimental data in Table IV. One can see that the Poisson's ratios for both sI and sII hydrates from our calculations are very close to experimental values with maximum deviation of only 0.015. The predicted Poisson's ratios for type sH clathrate is 0.244, much lower than the experimental and theoretical values for type sI and sII (around 0.3). In other words, our theoretical calculations predict that the sH clathrate is more ductile than the sI and sII counterparts.

As for the sound speeds, our theoretical longitudinal wave velocity is larger than experimental value by 11.3%, and the transverse wave velocity is larger by 14.6%. Such overestimation can be related to the higher theoretical elastic moduli from our calculations. In addition, compared with the clathrate hydrate systems considered in our calculations, the hydrate samples in the experimental measurements may contain different kinds of guest molecules and the specific occupancy of the water cages could also be different. Note that the sound velocities of these three types of clathrate hydrates are different (see Table IV). Among them, sI and sII are relatively closer, while the sound speeds of sH (especially the transverse one) are considerably larger. These theoretical results may help us differentiating the structural type of the hydrate deposits under ocean or permafrost.

In addition to mechanical properties, some key thermal properties of the type sI and sII clathrate hydrates, such as heat capacity, thermal expansion coefficient, Grüneisen parameter, and Debye temperature, were also calculated using the Gibbs program and summarized in Table V. In Fig. 2, we display the energy-volume relationships for type sI and sII hydrates with cubic crystalline structures from first-principles calculations. The temperature-dependent heat capacities at zero pressure are shown in Fig. 3.

Experimental measurement for the heat capacity of structure sI and sII were performed under ambient pressure and temperature of about 240 K.<sup>34</sup> At  $T=240$  K, our theoretical calculations yield a heat capacity of 4369 J/Kg·K for sI hydrate and 4488 J/Kg·K for sII one. Compared with the experimental data, the values are overestimated by 32.4% for sI hydrate and 24.7% for type sII (see Table V). That is partially due to the difference of cage occupancy between our structure model and experimental samples. The linear thermal expansion obtained by our calculation is  $94 \times 10^{-6} \text{ K}^{-1}$  at 200 K for structure sI, while the experimental value is  $77 \times 10^{-6} \text{ K}^{-1}$  at

TABLE V. Heat capacity ( $C_v$ ), thermal expansion coefficient ( $\alpha$ ), Debye temperature ( $\theta_D$ ), and Grüneisen parameter ( $\gamma$ ) for structure sI and sII at selected temperatures.

		$C_v$ (J/Kg·K) (240 K)	$\alpha$ (K <sup>-1</sup> ) (200 K)	$\theta_D$ (K) (0 K)	$\gamma$ (0K)
sI	This work	4369	$94 \times 10^{-6}$	166.7	3.68
	Expt. (Ref. 32)	3300	$77 \times 10^{-6}$	–	–
sII	This work	4488	$45 \times 10^{-6}$	238.8	1.43
	Expt. (Ref. 32)	3600	$52 \times 10^{-6}$	–	–

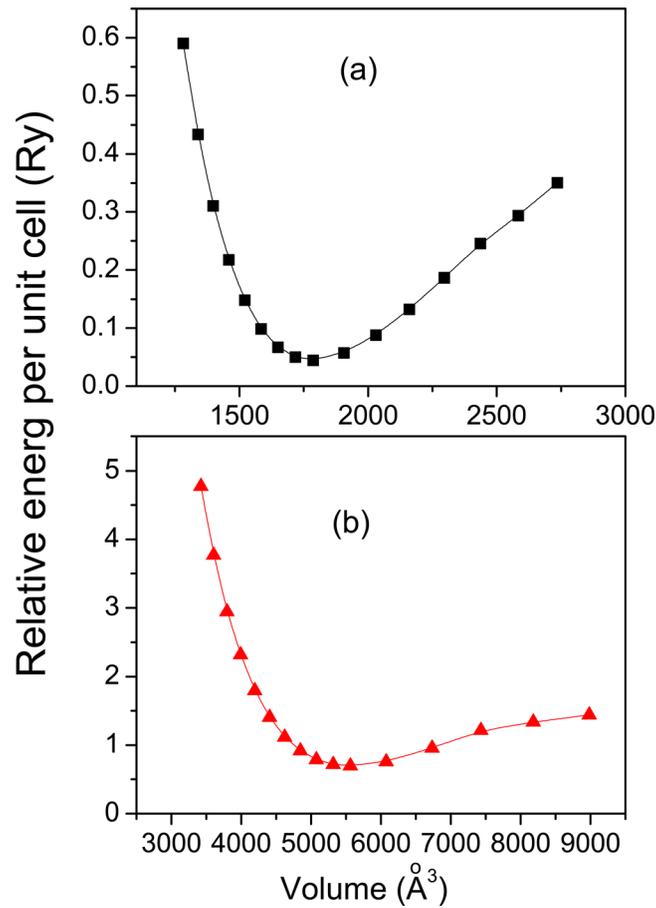


FIG. 2. Relative energy versus unit cell volume for type sI (a) and sII (b) hydrates.

the same temperature. For structure sII, the calculated linear thermal expansion of  $45 \times 10^{-6} \text{ K}^{-1}$  is very close to the experimental data of  $52 \times 10^{-6} \text{ K}^{-1}$ . The Grüneisen parameter and Debye temperature were also obtained for type sI and sII hydrates (see Table V). We anticipate future experiments to validate our theoretical predictions.

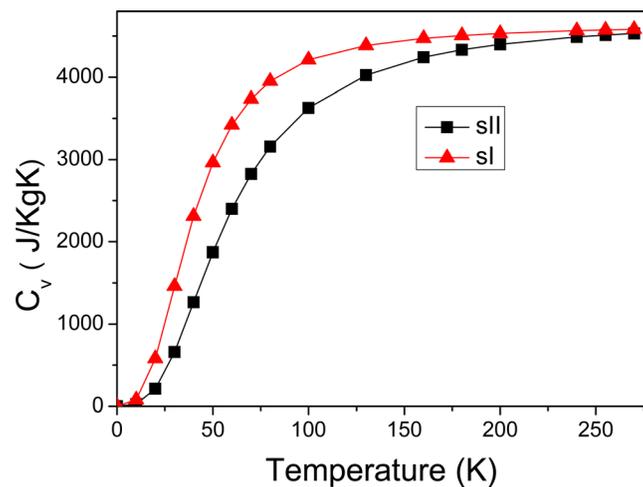


FIG. 3. Heat capacity as function of temperature for type sI (filled triangles) and sII (filled squares) clathrate hydrates.

#### IV. CONCLUSION

In this work, we investigated mechanical, acoustic, and thermal properties of three well-known clathrate hydrates of type sI, sII, and sH with first-principles calculations. The theoretical structural parameters are in well accordance with experiments with largest deviation of about 2%. Compared with experiments, the elastic parameters and sound speed are systematically overestimated. The mechanical and acoustic properties of structure sH are predicted. The heat capacity as function of temperature and linear thermal expansion were estimated by Gibbs based on Debye model for cubic structure sI and sII. In addition, two thermal parameters, i.e., Grüneisen parameter and Debye temperature are predicted for structure sI and sII. These theoretical results provide useful database for further understanding the fundamental properties of the methane clathrate hydrates of different structural phases, and also present reference data for further exploiting and utilizing the enormous energy resources contained in clathrate hydrates.

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#### APPENDIX: LAGRANGIAN STRAIN TENSORS

Here we list the Lagrangian strain tensors  $\eta_{ij}$  used in this work. For cubic crystals, the strain tensors (S1)-(S3) were used, while the strains (S3)-(S7) were used for hexagonal crystals,

$$\begin{array}{cccc}
 \begin{pmatrix} \zeta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} S_1 & \begin{pmatrix} \zeta & 0 & 0 \\ 0 & \zeta & 0 \\ 0 & 0 & 0 \end{pmatrix} S_2 & \begin{pmatrix} 0 & \zeta & \zeta \\ \zeta & 0 & \zeta \\ \zeta & \zeta & 0 \end{pmatrix} S_3 & \begin{pmatrix} 0 & 0 & 0 \\ 0 & \zeta & 0 \\ 0 & 0 & 0 \end{pmatrix} S_4 \\
 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \zeta \end{pmatrix} S_5 & \begin{pmatrix} 0 & 0 & 0 \\ 0 & \zeta & 0 \\ 0 & 0 & \zeta \end{pmatrix} S_6 & \begin{pmatrix} 0 & \zeta & 0 \\ \zeta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} S_7 & 
 \end{array}$$

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