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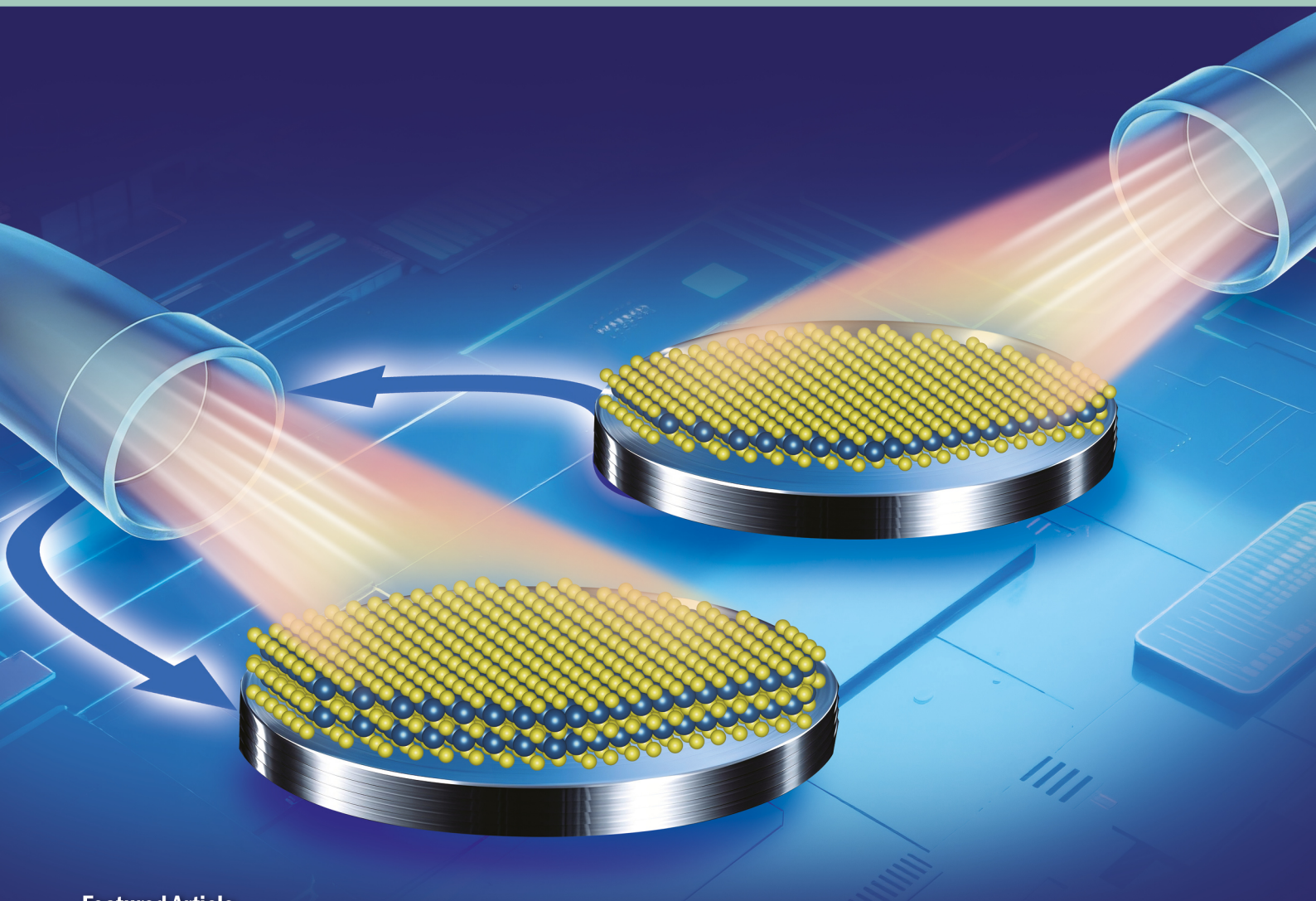

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TOPICAL REVIEW — Structures and properties of materials under high pressure

Bulk modulus of molecular crystals

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Bulk modulus is a constant that measures the incompressibility of materials, which can be obtained in high pressure experiment by fitting the equations of state (EOS), like third-order Birch–Murnaghan EOS (BM EOS) and Vinet EOS. Bulk modulus reflects the intermolecular interaction inside molecular crystals, making it useful for researchers to design novel high pressure materials. This review systematically examines bulk moduli of various molecular crystals, including rare-gas solids, di-atom and triplet-atom molecules, saturated organic molecules, and aromatic organic crystals. Comparisons with ionic crystals are presented, along with an analysis of connections between bulk modulus and crystal structures.

Keywords: high pressure, bulk modulus, molecular crystal, intermolecular interaction

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1. Introduction

1.1. Molecular crystals at high pressure

Molecular crystals are primarily composed of small molecules interconnected through intermolecular interactions such as van der Waals interactions, which exhibit lower binding strength compared with covalent or ionic interactions. These weak intermolecular interactions result in enhanced compressibility under pressure. Such high compressibility gives rise to a greater variety of distinct high-pressure structures and generates more materials with new properties under high pressure.[1] High pressure enables to reduce the intermolecular distances,[2,3] increase the density of electron,[4,5] or change the energetic ordering of the outer atomic orbitals of molecules.[6,7] In term of the different compressibility of molecular crystals, applying pressure could produce interesting phenomena, like pressure-induced polymerization,[8–10] pressure-driven phase transition,[11–13] and even molecule dissociations.[14,15]

In recent decades, high-pressure responses of molecular crystals have been widely investigated across chemistry, physics, biology, geoscience, and materials science. For instances, the water-ice system has been found to have a very rich phase diagram with about twenty stable and metastable phases, which is of crucial importance for understanding the entire diversity of nature.[16] Unsaturated molecular crystals like nitrogen,[17–19] carbon monoxide,[20,21] nitriles,[22] alkene,[23–25] alkyne,[26–28] and aromatic compounds[29–33] tend to polymerize under high pressure, providing a new method to develop novel materials.

1.2. Bulk modulus and the equations of state

Bulk modulus (B) quantifies the degree of deformation,[34–36] and can be used to probe the phase transition[37–39] and reaction[40] of molecular crystals in high pressure experiment, making it significant to characterize the physical property of a material system.[41–45] The bulk modulus is defined as

$$B = -\frac{\mathrm{d}P}{\mathrm{d}V/V} = -\frac{\mathrm{d}P}{\mathrm{d}\ln V}, \tag{1}$$

where P is pressure, and V is volume. A reduced bulk modulus in materials directly correlates with enhanced compressibility, demonstrating weakened intermolecular bonding forces between constituent atoms/molecules.[46]

High pressure bulk modulus is normally obtained by fitting the equations of state (EOS), the formula that describes the equilibrium state by a series of thermodynamic variables like pressure, volume, and temperature.

If we assume that bulk modulus is a linear function of pressure as

$$B = B_0 + B_0' P, \tag{2}$$

$$B_0' = \partial B/\partial P, \tag{3}$$

where B_0 is the bulk modulus at $P = 0$ GPa and B_0' is the first derivative of the bulk modulus. Then we can derive the Murnaghan EOS (MU) by integrating formula (1) and substituting it into the boundary condition of $P = 0$ GPa.[44,47] It can be represented as

$$P = \frac{B_0}{B_0'}\left[\left(\frac{V}{V_0}\right)^{-B_0'} - 1\right], \tag{4}$$

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where B_0 is the bulk modulus at $P = 0$ GPa, B_0' is the first derivative of the bulk modulus, and V_0 is the cell volume at $P = 0$ GPa. Murnaghan EOS is widely used for calculating metamorphic phase equilibria because it provides a simple algebraic resolution of P in terms of V, but it is considered only suitable for low pressure[48] (4 GPa suggested by Kumar)[49] or compressions up to about 10% ($V/V_0 > 0.9$).[41] The most popular EOS is the Birch–Murnaghan EOS (BM EOS).[50,51] BM EOS is based on Murnaghan's theory of finite deformations to describe the effect of hydrostatic pressure upon the elastic coefficients of an isotropic body.[50] It defines the Eulerian finite strain of uniformly compressed cubic as

$$f = -\varepsilon_E = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right]. \tag{5}$$

Then substitute formula (5) into the third-order expansion of Helmholtz free energy by Eulerian finite strain[44]

$$\Delta F \cong af^2 + bf^3, \tag{6}$$

where F is the Helmholtz free energy, a and b are two elastic constants. Combining with the definition of B and B', the third-order Birch–Murnaghan EOS that contains both bulk modulus and its first derivative is represented as

$$P = \frac{3}{2}B_0\left[\left(\frac{V}{V_0}\right)^{\frac{-7}{3}} - \left(\frac{V}{V_0}\right)^{\frac{-5}{3}}\right] \times \left\{1 + \frac{3}{4}\left(B_0' - 4\right)\left[\left(\frac{V}{V_0}\right)^{\frac{-2}{3}} - 1\right]\right\}, \tag{7}$$

where B_0 is the bulk modulus at $P = 0$ GPa, B_0' is the first derivative of the bulk modulus, and V_0 is the cell volume at $P = 0$ GPa. BM EOS was developed for isotropic materials and was commonly applied to all solids, especially metals. Fitting accuracy may decrease under non-hydrostatic pressure conditions or deviations from isotropic compression criteria.

Another conventional EOS is Vinet EOS, which is also called the "universal" EOS.[52–54] Vinet EOS is based on a semi-universal relationship for interatomic potentials, assuming wave-function-overlap interactions dominate during compression for all solids. This approach simplifies treatment of diverse bonding types, enabling formulation of a unified EOS framework.[52]

The Vinet EOS can be derived from the relation[55] between energy and the interatomic separation distance as

$$E(r) = E(r)_0\left(1 + \frac{r - r_0}{l}\right) \times \exp\left(-\frac{r - r_0}{l}\right), \tag{8}$$

where $E(r)$ is the total energy, r is the interatomic separation distance, and l is a scaling length. Considering the relation of P and $E(r)$, we will get

$$P = -\frac{\partial E(r)}{\partial V} = \frac{E(r)_0}{3l^2}V^{-\frac{2}{3}}(-V^{-\frac{1}{3}} + V_0^{\frac{1}{3}}) \times \exp\left(\frac{-V^{-\frac{1}{3}} + V_0^{\frac{1}{3}}}{l}\right). \tag{9}$$

Combining formula (9) with formulas (1) and (3), the Vinet EOS can be represented as

$$P = 3B_0\left(\frac{V}{V_0}\right)^{\frac{-2}{3}}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right] \times \exp\left\{\frac{3}{2}\left(B_0' - 1\right)\left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\right\}, \tag{10}$$

where B_0 is the bulk modulus at $P = 0$ GPa, B_0' is the first derivative of the bulk modulus, and V_0 is the cell volume at $P = 0$ GPa. Vinet EOS has a better performance in organic crystals, but has a larger error when considering the influence of temperature.[54] Besides, Vinet EOS requires modifications for strong compression to remain "universal" for different systems.[56]

As shown in Table 1, Holzapfel summarized other common equations of states,[48] like the EOS form of the generalized strain expansion (GS2),[48] the linearization form EOS that represents the Hugoniot curves related to linear u_s–u_p relations (MS2),[57] the EOS based on an effective Lennard–Jones potential used by Grüneisen (MG3),[58] the EOS based on a generalized Born–Mayer type effective potential (GBM),[48] the EOS based on the effective Morse potential (Emo),[48] the Vinet EOS modified by replacing the Born type exponential repulsion with an effective Thomas–Fermi type potential (HO_2),[59] the EOS that can perfectly match with the free electron Fermi-gas limit ($B_\infty' = 5/3$) which can't be approached for other EOS under high pressure (H12).[59]

Table 1. Commonly used equations of states forms with their parameter relations. B_0 is the bulk modulus at $P = 0$ GPa, B_0' is the first derivative of the bulk modulus, V_0 is the cell volume at $P = 0$ GPa, and $x = (V/V_0)^{1/3}$.

Name	Equations of states	B_0'
MU[47]	$P = \frac{3}{c}B_0 \cdot x^{-c} \cdot (1 - x^c)$	$\frac{c}{3}$
BM[50]	$P = \frac{3}{2}B_0 \cdot x^{-7} \cdot (1 - x^2) \cdot (1 + c(x^{-2} - 1))$	$4 + \frac{4}{3}c$
GS2[48]	$P = \frac{3}{n}B_0 \cdot x^{-2n-3} \cdot (1 - x^n) \cdot (1 + c(x^{-n} - 1))$	$n + 2 + \frac{2n}{3}c$
MS2[57]	$P = B_0(1 - x^3) \cdot (1 + c(1 - x^3))$	$4c - 1$
MG3[58]	$P = \frac{3}{n}B_0 \cdot x^{-m} \cdot (1 - x^n)$	$\frac{2m-n}{3}$
GBM[48]	$P = \frac{3B_0}{c-n-1} \cdot x^{-2} \cdot (1 - x^{-n-1} \cdot \mathrm{e}^{-c(1-x)}) \cdot e^{c(1-x)}$	$\frac{4}{3} + \frac{c^2 - c - (n+1)^2}{3(c-n-1)}$
Emo[48]	$P = \frac{6}{c}B_0 \cdot x^{-2} \cdot (1 - e^{-(c/2)(1-x)}) \cdot \mathrm{e}^{c(1-x)}$	$1 + \frac{1}{2}c$
Vinet[52]	$P = 3B_0 \cdot x^{-2} \cdot (1 - x) \cdot \mathrm{e}^{c(1-x)}$	$1 + \frac{2}{3}c$
HO2[59]	$P = 3B_0 \cdot x^{-5} \cdot (1 - x) \cdot \mathrm{e}^{c(1-x)}$	$3 + \frac{2}{3}c$
H12[59]	$P = 3B_0 \cdot x^{-5} \cdot (1 - x) \cdot \mathrm{e}^{cx(1-x)} \cdot \mathrm{e}^{c_0(1-x)}$	$3 + \frac{2}{3}(c + c_0)$

Researchers need to understand the applicable pressure range and assumptions of the EOSs to avoid over-fitting. Both Murnaghan EOS, BM EOS and Vinet EOS are semi-empirical equations, because their assumptions like isotropic compression or energy relation have not been strictly expanded to other fields, although they have shown good fitting ability for different systems. As comparisons, Vinet EOS normally has a

better result for strong compression due to its strong exponential term, which represents the ability for materials to store energy by deformation under strong compression. Third-order BM EOS also has a good fitting result for strong compression, while Murnaghan EOS was considered not suitable for compression of process greater than 4 GPa because its low exponent term.[49]

However, there are also some cases in which Murnaghan EOS has the best fitting result, or these three EOSs have similar results. For example, Pravica *et al*. found that Murnaghan EOS had the lowest relative error for the compression of cyclohexane up to 40 GPa,[60] though the Murnaghan EOS was suggested to be accurate up to 4 GPa.[49] Vlasic *et al*. found that there is almost no difference for Vinet EOS, BM EOS and a four-parameter EOS[61] when considering the structure II gas hydrate system.[62]

1.3. High pressure device

The EOS is normally measured by shock-wave and static high-pressure experiments with crystallographic techniques. There are two types of conventional static high-pressure devices, Paris–Edinburgh cell (PE cell)[63,64] and diamond anvil cell (DAC)[65] for *in situ* neutron and synchrotron or lab x-ray diffraction measurements, respectively. DAC is the most popular device that can produce a super high pressure up to 1 TPa.[66] Paris–Edinburgh cell is suitable for mg-scale experiments, which can reach pressure up to 40 GPa.[67–69] Researchers can obtain the cell parameters at different pressures and then obtain the bulk modulus by fitting the equations of state.[70]

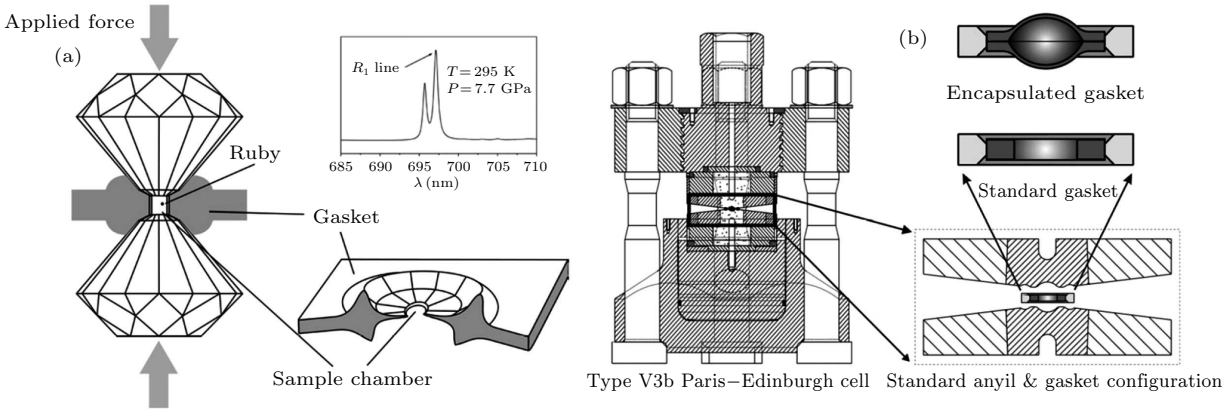

Fig. 1. The structure of (a) diamond anvil cell[71] and (b) Paris–Edinburgh cell.[71]

2. Bulk modulus of different molecular crystals

2.1. Rare-gas solids

The bulk modulus of monoatomic molecules is important for the investigation of giant planet, and also for high pressure experiment, because rare gases are commonly used as pressure transmitting media (PTM) in DAC.[72] Generally, the high-pressure structure of rare gases is hexagonal close packed (hcp), which is different from the cubic close packed (fcc) low pressure phase. It is interesting that neon remains a fcc phase up to 208 GPa without evidence of the formation of hcp phase,[73] indicating weaker three-body-exchange interactions which cause phase transitions of other rare gases.[74]

The bulk moduli of rare gases are assorting in Table 2. Helium has the smallest bulk modulus of 0.65 GPa for fcc phase and 3 GPa for hcp phase.[75] Neon has a larger bulk modulus, with the reported data from 1.07 GPa,[73] 0.74 GPa,[76,77] to 12 GPa[75] for fcc phase. Argon's bulk modulus ranges from 2.4 GPa[76,78] to 6 GPa[75] for fcc phase, and has a bulk modulus of 13 GPa for hcp phase,[75] and a value of 3 GPa was reported for the mixed phase of fcc and hcp.[79] Krypton has bulk modulus of 1.6 GPa[80] or 3.3 GPa[79] for mixed phase even under a pressure of 140 GPa,[80] and has a bulk modulus of 5.5 GPa for fcc phase and 23 GPa for hcp phase.[75] Xenon has the largest bulk modulus in rare-gas solids of 3.6 GPa,[81] 4.5 GPa[82] or 7 GPa[75] for fcc phase, while having the bulk modulus of 4.3 GPa[81] or 22 GPa[75] for hcp phase and 4.3 GPa[79] for the mixed phase.

Considering the similar crystal structures for rare gases, we can generally find that atomic radius has the major influence on bulk modulus. The larger atom radius leads to a stronger dispersion interaction,[83] which will induce a larger bulk modulus. Besides, the hcp phase usually has a larger bulk modulus than the fcc phase, indicating a more compact packing structure under high pressure. The deduction about the relationship between bulk modulus and atomic radius can be extended to more complex molecular crystals. The difference between the reported data reflects the error of the experimental data and the fitting processes. Due to the deviation of experiment and EOS, it is difficult to determine the accuracy of bulk modulus only by the fitting results. DFT calculation[84] and acoustic techniques such as Brillouin scattering or ultrasonic interferometry[85,86] may be needed for auxiliary judgment.

Table 2. Bulk modulus of rare-gas solids.

Name	Structure	Pressure range (GPa)	EOS & Model	B_0 (GPa)	B_0'
Helium[75]	fcc	1–10	BM	0.65	2
Helium[75]	hcp	1–80	BM	3	12
Neon[76,77]	fcc	4.7–14.4	Murnaghan	0.74	7.1
Neon[73]	fcc	1–208	Vinet	1.07	8.4
Neon[75]	fcc	1–110	Murnaghan	12	4.2
Argon[76,78]	fcc	1.2–8.2	Murnaghan	2.4	7
Argon[79]	fcc+hcp	1–128	Mie–Grüneisen	3	7.2
Argon[75]	fcc	1–20	BM	6	4
Argon[75]	hcp	20–114	BM	13	3.5
Krypton[80]	fcc+hcp	1–140	BM	1.6	7.1
Krypton[79]	fcc+hcp	1–128	Mie–Grüneisen	3.3	7.2
Krypton[75]	fcc	1–20	Murnaghan	5.5	3.8
Krypton[75]	hcp	20–140	Murnaghan	23	3.5
Xenon[81]	fcc	3.7–70	BM	3.6	5.5
Xenon[81]	hcp	70–127	BM	4.3	4.9
Xenon[79]	fcc+hcp	1–128	Mie–Grüneisen	4.3	6.5
Xenon[82]	fcc	1–60	BM	4.5	5.6
Xenon[75]	fcc	1–20	Vinet	7	5.8
Xenon[75]	hcp	20–175	Vinet	22	3

2.2. Di-atom and triplet-atom molecules

The bulk modulus of diatoms molecules (H_2 and N_2) listed in Table 3 are both small but the latter (2.69 GPa)[87] is larger than the former (0.162 GPa),[88] which agrees with the above result that the bulk modulus is dependent on the molecular size. Ice under high pressure exhibits a larger bulk modulus (12–260 GPa),[89–93] which arises from the hydrogen-bonding interactions within the crystalline lattice. For comparison, the low pressure phase carbon dioxide has a bulk modulus of 2.93 GPa[94] or 6 GPa,[95] representing the enhancement effect of hydrogen bond on bulk modulus. The unusual high bulk modulus (87 GPa, 131 GPa, and 365 GPa)[95] of high pressure phase carbon dioxide was explained by the transformation from molecular crystal to covalent crystal,[95–97] the different fitting pressure range,[98] or the inaccuracy of the experiment caused by the hysteresis of phase transition.[99] The enhancement effect of hydrogen bond was also observed in complex systems. For example, Dreger *et al.*[100] found that 5,5′-bistetrazole-1,1′-diolate has a negative linear compressibility of the *a* axis caused by the strong hydrogen bonding interaction along the *a* axis.

Table 3. Bulk modulus of di-atom and triplet-atom molecules.

Name	Pressure range (GPa)	EOS & Model	B_0 (GPa)	B_0'
Hydrogen[88]	10–109	Vinet	0.162	6.813
Hydrogen[88] (Cal)	120–350	Mie–Grüneisen	0.999	5.799
δ phase nitrogen[87]	5.7–43.9	Olinger & Halleck[89]	2.69	3.93
ε phase nitrogen[87]	5.7–43.9	Olinger & Halleck[89]	2.98	3.78
Ice VII[89]	3.0–8.0	Olinger & Halleck[89]	12.54	5.56
Ice VII[90]	0–13	Vinet	27.8	2.8
Ice VII[90]	13–66	Vinet	97	3
Ice VII[90]	66–106	Vinet	260	7.3
Ice VII[91]	2–13.7	BM	13.8	5.9
Ice VII[91]	2–13.7	Vinet	13.6	6.2
Ice VII[91]	2–13.7	H12	13.7	6.0
mixed phase ice[92]	2.2–170	Vinet	4.26	7.75
Ice VIII[93] (300 K)	2.2–18	BM	20.4	4.7
Ice VIII[91] (93 K)	2–13.7	BM	18.7	5.7
Ice VIII[91] (93 K)	2–13.7	Vinet	18.5	6.0
Ice VIII[91] (93 K)	2–13.7	H12	18.6	5.9
Ice VIII[91] (196 K)	2–13.7	BM	15.6	6.2
Ice VIII[91] (196 K)	2–13.7	Vinet	15.4	6.4
Ice VIII[91] (196 K)	2–13.7	H12	15.6	6.2
Mixed phase CO_2[94]	1–51.4	BM	2.93	7.8
Phase I CO_2[95]	1–11	BM	6	6.1
Phase III CO_2[95]	11–50	BM	87	3.3
Phase II CO_2[95] ($>$ 500 K)	20–50	BM	131	2.1
Phase V CO_2[95] ($>$ 1600 K)	40–50	BM	365	0.8

2.3. Saturated organic molecules

The bulk moduli of saturated organic molecules are listed in Table 4. Generally, we can find that the larger molecules have a larger bulk modulus. For example, ethane (25.9 GPa or 71.1 GPa),[101] heptane (14.5 GPa),[102] cyclohexane (12 GPa)[60] and cubane (14.5 GPa)[103] have a larger bulk modulus than methane. However, the data of ethane is a little surprising. Normally, the bulk modulus of small molecular crystals with van der Waals interactions only is smaller than 15 GPa and the bulk modulus of ionic crystals is larger than 20 GPa.

Besides, what we need to note is that researchers propend to fix the B_0' at 4 when having too limited data to fit the EOS. This means ignoring the influence of B_0',[104] $B_0' \approx 4$ is actually a common value for ionic crystals and metals, but fixing it at 4 will likely result in a larger B_0, especially for molecular crystals.[48,105] For example, Lin *et al.*[106] found that the fitted B_0 of ammonia borane will increase from 4.8 GPa to 9.8 GPa if the fixed B_0' decreases from 10 to 6.4, and Fan *et al.*[107] found that the calcium-lead fluorapatite solid solution will have a B_0 smaller by about 10–20 GPa if not fixed the B_0' at 4. As shown in Table 3, Hazen *et al.*[108] and Sun *et al.*[109] fixed B_0' at 4 for methane and obtained a series of bulk moduli for different phases, such as 4.9 GPa for fcc phase,[108] or 7.9 GPa for rhombohedral phase,[110] 23.7 GPa[109] or 23.1 GPa for simple cubic phase,[111] and 28.5 GPa for a high-pressure phase,[109] which will mathematically make B_0 larger. In comparison, when B_0' is not fixed, the bulk modulus of $C(CN)_4$[112] and $C[Si(CH_3)_3]_4$[113] is 4.4 and 5.4, respectively. It is reasonable to infer that the bulk modulus of methane should be smaller than $C(CN)_4$ and $C[Si(CH_3)_3]_4$ without B_0' fixed. Therefore, in consideration of the increasing size of substituent group, we probably could find a positive relation between the bulk modulus and molecular volume, in consistent with the previous conclusion.

Table 4. Bulk modulus of saturated organic molecules.

Name	Pressure range (GPa)	EOS & Model	B_0 (GPa)	B_0'
$C(CN)_4$[112]	0.1–14.7	BM	4.4	18
[121]Tetramantane[114]	1–13	BM	5.4	18.75
$C[Si(CH_3)_3]_4$[113]	1–5	BM	5.5	15
Fcc CH_4[108]	1.6–5.2	Murnaghan	4.9	4 (fixed)
Rhombohedral CH_4[109]	11–27	BM	7.8	4 (fixed)
Rhombohedral CH_4[110]	7–13	BM	7.9	4 (fixed)
Simple cubic CH_4[109]	19–69	BM	23.7	4 (fixed)
Simple cubic CH_4[111]	17–85	BM	23.1	4 (fixed)
High-pressure phase CH_4[109]	94–202	BM	28.5	4 (fixed)
C_2H_6[101]	2.7–13.4	BM	25.9	9.2
C_2H_6[101]	13.4–110	BM	71.1	3.5
Heptane[102]	1.7–10	BM	14.5	4 (fixed)
NH_3BH_3[106]	1.6–5	BM	8	6.4 (Cal)
1,1-diamino-2,2-dinitroethene[115]	1–4.5	BM	10.1	14.3
ε-CL-20[116]	1–12	BM	11.5	11.2
Cubane[103]	1–60	BM	14.5	6.2
α-glycine[117]	0.2–6.4	Vinet	19.5	6.5
l-cystine[118]	0–6.4	BM	29.1	4 (fixed)
Cyclohexane[60]	1–40	BM	12	14.5
Cyclohexane[60]	1–40	Vinet	9.9	8.1
Cyclohexane[60]	1–40	Murnaghan	22.9	4.8

2.4. Aromatic organic molecules

Aromatic organic molecules are always hot spots in the research on high-pressure chemistry. The pressure-induced polymerization of aromatic compounds enables the production of novel extended carbon materials, for example, the one-dimension diamondoid nanothreads with high strength and stiffness.[119] In the studies of aromatics under high pressure, scientists found that the structures of polymerized samples are highly related to the high-pressure molecular structures before reaction. Therefore, the comprehensive studies of the crystalline structures and phase transitions under high pressure are greatly helpful for understanding the interactions between aromatic molecules.[120] The details of aromatic organic crystals are assorting in Table 5, arranging in an ascending order of bulk modulus.

Generally, aromatic molecular crystals have a small bulk modulus, normally ranging from 2 GPa to 10 GPa, as shown in Table 5. Benzene as the typical model of aromatics was proven to have two high pressure phases, the phase I with *Pbca* space group[121] and the phase II with $P2_1/c$ space group[122] in a herringbone packing structure. It has a bulk modulus of 7.8 GPa for phase I[123] and 13.9 GPa for phase II at room temperature.[123] Aniline (5.4 GPa)[124] and deuterated phenol (5.8 GPa)[125] have a similar bulk modulus and packing structure to benzene due to the similar size.

With the increasing size of the conjugated coplanar structure, the bulk modulus correspondingly increased. For example, the bulk modulus of naphthalene,[126] anthracene,[127,128] tetracene[128] and pentacene[128] is 7.9 GPa, 8.4–8.8 GPa, 9 GPa and 9.6 GPa, respectively. There is a similar situation for phenylenes, biphenyl (4.3 GPa),[105] *para*-terphenyl (7.2 GPa),[105] *para*-quaterphenyl (8.3 GPa),[105] *para*-quinquephenyl (9.3 GPa)[105] and *para*-sexiphenyl (10 GPa),[105] with the increasing number of benzene rings. In addition, comparing the two types of aromatic molecules, the biphenyl structure linked by the rotatable σ bond has a relatively smaller bulk modulus, which means the biphenyl compounds are more easily compressed under high pressure.

The size of molecules also makes a contribution to the bulk modulus of other aromatic crystals. The *s*-triazine (6.3 GPa)[139] and pyridine (6.2 GPa or 6.4 GPa)[140] have a similar bulk modulus compared with benzene because of the similar molecules, while 1,3,5-triethynylbenzene (10 GPa)[137] has a larger bulk modulus and a larger volume. Besides, the strong hydrogen bonds in the crystal structure of 3,3′-diamino-4,4′-azoxyfurazan (9.1 GPa),[141] melamine (12 GPa),[142] 1H-tetrazole (13.6 GPa),[144] 2,5-furandicarboxylic acid (21 GPa),[145] and 1,5-diamino-1H-tetrazole (23 GPa),[146] make them have a larger bulk modulus than similar volume molecules, such as bibenzyl (4.9 GPa),[131] benzene (7.8 GPa),[123,132] and naphthalene (7.9 GPa).[126] Azulene has a much larger bulk modulus of 18.1 GPa[138] than its tautomer naphthalene, which can be explained by its differential charge distribution and large dipole moment (1.08 D).[148]

Table 5. Bulk modulus of aromatic organic crystals.

Name	Pressure range (GPa)	EOS & Model	B_0 (GPa)	B_0'
$C_2H_2{\cdot}C_6H_6$[129]	1–20	BM	2	17
para-xylene[130]	0.1–4.7	BM	3.5	14
Biphenyl[105]	1–6	Murnaghan	4.3	8.4
Bibenzyl[131]	1–20	Vinet	4.9	9.3
Aniline[124]	1.6–7.3	Vinet	5.4	9.9
Phase I benzene[123]	0.9–2.2	BM	7.8	4.7
Phase II benzene[132] (540 K)	1–26	Vinet	5.5	8.5
Phase II benzene[123]	2.5–24.1	BM	13.9	4
Full deuterated phenol[125]	1~20	Vinet	5.8	8.6
Azobenzene[133]	1–9.5	Vinet	5.8	9.5
Fluorene[134]	1–14	Murnaghan	6.2	7.9
Naphthalene·Octafluoronaphthalene[135]	1–20.6	Vinet	7.1	9.2
Anthracene·Octafluoronaphthalene[135]	1–25.5	Vinet	7.2	8.6
1,3,5-triamino-2,4,6-trinitrobenzene[136]	1–10	Vinet	7.2	13.9
para-terphenyl[105]	1–6	Murnaghan	7.2	6.1
Naphthalene[126]	1–5.6	Vinet	7.9	7.5
para-quaterphenyl[105]	1–6	Murnaghan	8.3	6.4
Anthracene[128]	1–9	Murnaghan	8.4	6.3
Anthracene[127]	1–22.6	Murnaghan	8.8	6.0
Tetracene[128]	1–9	Murnaghan	9	7.9
para-quinquephenyl[105]	1–6	Murnaghan	9.3	7.5
Pentacene[128]	1–9	Murnaghan	9.6	6.4
para-sexiphenyl[105]	1–6	Murnaghan	10	5.6
1,3,5-triethynylbenzene[137]	0.1–3.6	BM	10	5
Azulene[138]	2.7–7.7	BM	18.1	3.9
s-triazine[139]	1–7	Vinet	6.3	10.8
Phase II pyridine[140]	0.9–2.5	BM	6.4	8.7
Phase III pyridine[140]	1.2–2.7	BM	6.2	8.1
Thiophene[31]	0–20	BM	8.1	6.7
3,3′-diamino-4,4′-azoxyfurazan[141]	2–12.1	BM	9.1	8.3
Perdeuterated melamine[142]	0–5	BM	12.0	7.8
2,6-diethynylpyridine[143]	0.7–5.4	BM	13	4 (fixed)
1H-tetrazole[144]	0.1–2	BM	13.6	4 (fixed)
2,5-furandicarboxylic acid[145]	0.2–10.8	BM	21	4 (fixed)
1,5-diamino-1H-tetrazole[146]	1–40	BM	23	4 (fixed)
1,4-difluorobenzene[147]	4.3–9.4	BM	27	4 (fixed)

Additionally, we inferred that the π–π stacking interaction of aromatic crystals may make a different influence on bulk modulus. As shown in Table 5, we can find that the bulk modulus of aromatic molecules is smaller than the non-aromatic molecules with similar size, representing that aromaticity makes a smaller bulk modulus. This could be attributed to the weakened repulsion induced by π-orbital interaction.[149–151] Besides, the softening of the repulsive

wall in aromatic species makes the extra stabilization and lower bulk modulus for aromatic molecular crystals.[149,152] It is worth noting that *para*-xylene has a smaller bulk modulus of 3.5 GPa, which may be attributed to the C–H$\cdots\pi$ interaction between methyl and adjacent benzene ring, in addition to π–π stacking interaction of benzene rings.[130,153,154] The different bulk modulus of cocrystals can also illustrate the influence of molecule size and π stacking interaction. For example, naphthalene·octafluoronaphthalene (7.1 GPa)[135] and anthracene·octafluoronaphthalene (7.2 GPa)[135] have the similar bulk modulus with naphthalene but $C_2H_2{\cdot}C_6H_6$ have a small bulk modulus (2 GPa)[129] than benzene. This is because that octafluoronaphthalene has a similar size with naphthalene, anthracene has a larger size and π stacking interaction that almost cancel the influence of each other, and acetylene has a small size than benzene that makes a small bulk modulus.

2.5. Typical ionic crystals

For comparison, we also list some bulk moduli of ionic crystals. Ionic crystals normally consist of Coulomb interaction, which has an inverse-square relationship between the interaction strength and interaction distance. The different degree of strength attenuation with interaction distance between Coulomb interaction and van der Waals interactions[52] makes the different correlation between crystal structure and bulk modulus. For example, the bulk moduli of alkali halides represent a negative correlation with the atomic radius as shown in Table 6,[155] while rare-gases solids represent a positive correlation. We can also find that most of the ionic crystals have a large B_0 with a B_0' between 4 and 6, indicating a dense structure and low compressibility of ionic crystals.

Table 6. Bulk modulus of typical ionic crystals.

Name	Pressure range (GPa)	EOS & Model	B_0 (GPa)	B_0'
LiI[155]	0–40	H11[156]	17.3	5.56
LiBr[155]	0–40	H11	23.5	5.23
LiCl[155]	0–40	H11	29.7	4.59
LiF[155]	0–40	H11	66.5	4.30
NaI[155]	0–40	H11	14.9	5.58
NaBr[155]	0–40	H11	19.5	5.29
NaCl[155]	0–40	H11	23.7	4.81
NaF[155]	0–40	H11	46.5	4.64
KI[155]	0–40	H11	11.5	5.58
KBr[155]	0–40	H11	14.6	5.33
KCl[155]	0–40	H11	17.4	4.93
KF[155]	0–40	H11	30.2	4.82
RbI[155]	0–40	H11	10.5	5.76
RbBr[155]	0–40	H11	13.2	5.57
RbCl[155]	0–40	H11	15.6	5.29
RbF[155]	0–40	H11	26.7	5.27
CsI[155]	0–40	H11	11.9	5.93
CsBr[155]	0–40	H11	14.3	5.80
CsCl[155]	0–40	H11	16.7	5.58
Phase B1 KBr[157]	0–2.3	Vinet	14.2	5.5 (fixed)
Phase B2 KBr[157]	0–227	Vinet	13.8	5.65
Phase B1 KCl[157]	0–2.6	Vinet	17.1	5.5 (fixed)
Phase B2 KCl[157]	0–233	Vinet	17.4	5.63
NH_4I[158]	1.3–68	BM	18.8	4.22
Sb_2S_3[159]	0–10	BM	26.9	7.9
Sb_2S_3[160]	0–5	BM	27.2	6 (fixed)
Sb_2S_3[160]	0–5	BM	65	4 (fixed)
Sb_2Se_3[161]	0–51	BM	30	6.1
Bi_2S_3[162]	0–10	BM	36.6	6.4
Bi_2S_3[163]	0–50	BM	38.9	5.5
β-$Ba(OH)_2$[164]	0–8.1	BM	35	12
MgO[165]	0.8–52.2	BM	160.2	3.99
CeO_2[166]	0–40	Birch	230	4.0
$CaIrO_3$-type Al_2O_3[167]	120–180	BM	249	4 (fixed)

3. Conclusion

Generally, molecular crystals exhibit lower bulk moduli compared to ionic crystals. Rare-gas solids have the similar bulk modulus and compressibility with organic crystals, which should be taken into consideration in the high-pressure experiment of organics when using the rare-gas as pressure

transition medium. Analysis of molecular crystals reveals a correlation between bulk modulus and molecular size, with hydrogen bonding interactions showing measurable influence on bulk modulus. Although dipole moment and stacking interactions also contribute to bulk modulus, these factors appear secondary to molecular size and hydrogen bond in most molecular crystal systems. This review aims to provide foundational insights for establishing the relationship between bulk modulus and crystal structures. The quantitative relation between the bulk modulus and the size of molecules as well as the molecular interactions needs to be investigated in the future.

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