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Melting of cryocrystals at high pressures. Computer simulation

Two types of molecular dynamics simulations: single-phase and two-phase carried out and applied to determine the melting temperatures of highly compressed diatomic cryocrystals: nitrogen and hydrogen, as functions of pressure. Solid hydrogen was modeled by two approximations (1) non-empirical atom-atom potential (AAP) approximation [1], and diatom-diatom (DDP) approximation. Within AAP-model potential energy of hydrogen molecules is represented as a function of interatomic distances between all atoms as a sum of intramolecular (bonding) and intermolecular (non-bonding) parts. Both types of potentials are expressed via known potential energies of two isolated hydrogen atoms in the singlet and triplet states.

Key words: cryogenic, computer simulation, molecular dynamics, the melting point.

Е. Якуб

Плавение криокристаллов при высоких давлениях. Компьютерное моделирование

В данной работе использовались два типа моделирования методом молекулярной динамики: однофазный и двухфазный. Этими методами определялись температуры плавления сильно сжатых диатомных криокристаллов азота и водорода как функций давления. Твердый водород моделировался двумя приближениями – (1) неэмпирическое приближение атом-атомного потенциала (ААП) и (2) диатом-диатомное приближение. Уменьшение температуры плавления при высоком сжатии относится к возросшей роли нецентральных сил и молекулярной жесткости.

Ключевые слова: криокристалл, компьютерное моделирование, молекулярная динамика, температура плавления.

Е. Якуб

Жоғары қысымда криокристалдардың балқуы. Компьютерлік модельдеу

Бұл жұмыста молекулалық динамиканың модельдеуінің екі түрі қолданылды: бірфазалы және екіфазалы. Бұл әдістермен қатты қысылған қысым функциясы ретіндегі сутегінің және азоттың диатомды криокристалдарының балқу температурасы анықталды. Қатты сутегі екі жақындастырылумен (1) эмпирикалық емес атом-атомды потенциалдың (ААП) және (2) диатом-диатомды жақындастырылумен модельдендірілген. Жоғарғы қысыммен қысқанда балқу температурасының кішіреюі центрлік емес күштердің және молекулалық қаттылықтың рөлінің артуына жатады.

Түйін сөздер: криокристалл, компьютерлік модельдеу, молекулалық динамика, балқу температурасы.

Two types of molecular dynamics simulations: single-phase and two-phase carried out and applied to determine the melting temperatures of highly compressed diatomic cryocrystals: nitrogen and hydrogen, as functions of pressure. Solid hydrogen was modeled by two approximations (1)

non-empirical atom-atom potential (AAP) approximation [1], and diatom-diatom (DDP) approximation. Within AAP-model potential energy of hydrogen molecules is represented as a function of interatomic distances between all atoms as a sum of intramolecular (bonding) and intermolecular

(non-bonding) parts. Both types of potentials are expressed via known potential energies of two isolated hydrogen atoms in the singlet and triplet states. In turn, singlet and triplet potential curves are well known from classical *ab initio* variational calculations.

DDP approximation is actually a more general version of AAP-model [2] which takes into account the overlap of electronic shells of two atoms forming a diatomic molecule. Within this approximation non-bonding short-range intermolecular interaction depends on instant distances between bonded atoms. Both AAP- and DDP-models were extended by inclusion of long-ranged quadrupole-quadrupole interaction. Interaction of nitrogen molecules was also described within AAP-model by the sum of semi-empirical atom-atom potentials and quadrupole-quadrupole contribution.

For both diatomic solids, at different sizes of simulation cells, we observed the same non-monotonous dependence of melting temperature: its raise with increasing density becomes more and more smooth and at megabar pressures goes negative. This effect observed in experiments [3] and known as turnover of the melting line, was reproduced first in our recent conventional single-

phase molecular dynamics simulation of molecular hydrogen [4].

The same behavior of nitrogen, when polymerization transition ignored, is reported in this work. We discuss possible explanations of this turnover in absence of changes of interaction and chemical bonding, and analyze its dependence on the rigidity and the length of chemical bonds, structure of the solid phase, and analyze the role of long-range quadrupolar forces.

We conclude that turnover in the melting line observed in diatomic solids has a general reason. It can be explained on the basis of simple molecular models. The decrease of the melting temperature at high compressions is related to the increasing role of non-central forces and molecular rigidity. Energy stored in frustrated chemical bonds is released during melting and this effect becomes more pronounced at higher densities leading to the progressive decrease of the relative crystalline lattice stability, melting temperature and vibronic frequency. Inclusion of quadrupole-quadrupole interactions rises the melting temperature and affects both the nature of the molecular rotation in the solid phase and the type of the most stable crystalline structure.

References

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