UDC 533.9.004.14; 621.039.6

Y. Crespo*, A. Laio, G. E. Santoro, M. Fabrizio,
S. Scandolo, E. Tosatti

International Center for Theoretical Physics, StradaCostiera 1, Trieste, Italy
*E-mail: ycrespo@ictp.it

Unconventional phase transitions on hd and O_2cryocrystals

Both HD and O_2 are molecular solids with an exceedingly well explored phase diagram under pressure. In this talk we focus in two unusual phase transition taking place at high pressures. First we study the unusual reentrant phase transition that the phase diagram of HD exhibits near 50 Gpa where a rotationally ordered ("broken symmetry") crystalline phase (BSP) surprisingly transforms into a rotationally "disordered" high-symmetry phase upon cooling.

Key words: phase diagram, pressure, sample, crystalline phase.

Ю. Креспо, А. Лайо, Г.Е. Санторо, М. Фабрицио, С. Скандоло, Е. Тосатти

Нетрадиционные фазовые переходы в HD и O_2 криокристаллах

Обе молекулы HD и O_2 твердых тел обусловлены хорошо изученной фазовой диаграммой при высоких давлениях. В этом докладе мы фокусируем внимание на двух необычных фазовых переходах, существующих при высоких давлениях. Первоначально мы изучим необычный, возвратный фазовый переход на фазовой диаграмме HD образцов в окрестности 50 ГПа, где вращение обнаруживает «нарушение симметрии» кристаллической фазы, обусловленное превращением в «неупорядоченной» стадии высокой симметрии при охлаждении.

Ключевые слова: фазовая диаграмма, давление, образцы, кристаллическая фаза.

Ю. Креспо, А. Лайо, Г.Е. Санторо, М. Фабрицио, С. Скандоло, Е. Тосатти

HD және O_2 криокристалдарындағы дәстүрлі емес ауысулар

HD және O_2 молекулалары, қатты денелерде жоғарғы қысымда жақсы зерттелінген. Бұл мақалада жоғарғы қысымда бақыланған, ерекше екі фазалық ауысуға зейін салып отырмыз. Ең алғашқыда қайтымды ерекше HD диаграммасындағы үлгілерді зерттедік.

Түйін сөздер: фазалық диаграмма, қысым, үлгілер, кристалдық фаза.

Both HD and O_2 are molecular solids with an exceedingly well explored phase diagram under pressure. In this talk we focus in two unusual phase transition taking place at high pressures. First we study the unusual reentrant phase transition that the phase diagram of HD exhibits near 50 Gpa where a rotationally ordered («broken symmetry») crystalline phase (BSP) surprisingly transforms into a rotationally «disordered» high-symmetry phase upon cooling. While the qualitative reason for reentrance, has been already shown by early mean field studies in this work we aiming at a quantitative understanding of this system. Herein we have applied path integral Monte Carlo (PIMC) within both the constant-volume and constant-pressure ensembles to the reentrant phase diagram of the HD solid at high pressures and low temperatures, considering both hcp (realistic) and fcc (fictitious) lattices. We studied the influence of the potential chosen, the translational degrees of freedom, and the choice of the electronic quadrupolequadrupole (EQQ) interaction potential on the BSP transition line. It was found that while the translational degrees of freedom have a small effect on the transition pressure, the choice of lattice and interaction potential strongly affects the transition pressure. Using a metadynamics based MC scheme, we found that a C_2/c ordered structure, containing 16 molecules per cell is, with the best available potentials, energetically preferred for the classical

BSP phase on an hexagonal closed packed (hcp) lattice.

Successive implementation of quantum molecular rotations by PIMC permitted a full calculation of the reentrant BSP-rotationally symmetric phase line. The transition was identified using two order parameters, one dependent on the new structure and the second related to the total quadrupolar moment of the molecule, particularly sensitive to the rotational state of the molecule. The phase line was calculated for both the hcp and the face centered cubic (fcc) lattices, yielding a realistic reentrant behavior in both cases. The best results are obtained with the Burton potential on the hcp lattice, with features of the BSP-symmetric coexistence line in good agreement with experiment.

The orientationally ordered state edge was found at a minimum pressure Pe≈ 56 GPa for the hcp lattice and the Cui-Burton potential, quite close to the experimental value Pe= 53 GPa and in much better agreement than the previous PIMC calculations, which gave Pe= 10 GPa. The edge point temperature Te= 25K is also in good agreement with the experimental one Te= 30 K. Finally, the entropy jump at the phase transition is found to have a maximum value below but not far from ln[2], in agreement with a Pomeranchuk-like, entropy-driven picture of the reentrant transition.