Polymolecular high-pressure phase of nitrogen

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Recently, a distinct class of molecular phases of solid nitrogen has been discovered at high pressures and temperatures [1]. Optical measurements showed that one of the novel phases (θ) has very strong intermolecular interactions and infrared vibron absorbtion, which are strikingly different from all other known phases of N₂. We have performed x-ray diffraction studies on θ phase of nitrogen which show that intermolecular distances are significantly reduced compared to (epsilon/zeta)N₂ at the same pressures. These findings confirm a charge transfer from intra- to intermolecular bond, as deduced from optical measurements, and provide a microscopic basis for the observed high compressibility. These charge-transfer interactions connect nitrogen molecules in such a way that the chains of rings appear, forming a unit consisting of six nitrogen atoms (e.g. three N₂ molecules). Polynitrogen molecules have been of interest as possible high-energy-density molecules, with heat of formation of the order of few hundreds of kcal per mole [2]. N₆ molecules have been predicted to exist by theoretical investigations [3–5] and two of them, hexaazabicyclopropenyl and in particular hexaazadiazide are close to what we observe in θ phase. Also, solid hydrogen at high pressures pressures might undergo a phase transition to form termolecular complexes such as (H₂)₃ [6], before transition to the atomic or metallic phase at still higher pressures. The identification of this new structure of nitrogen casts new light on the nature of phase III of hydrogen.

- [1] E. Gregoryanz *et al.*, Phys. Rev. B **66**, 224108 (2002).
- [2] R. Engelke, J. Phys. Chem. 96, 10789 (1992).
- [3] W. J. Lauderdale, J. F. Stanton and R. J. Bartlett, J. Chem. Phys. 96, 1173 (1992).
- [4] M. N. Glukhovtsev, and P. v. R. Schleyer, Chem. Phys. Lett. 198, 547 (1992).
- [5] M. Tobita, and R. J. Bartlett, J. Phys. Chem. A 105, 4107 (2001).
- [6] R. LeSar and D. R. Herschbach, J. Phys. Chem. 85, 3787 (1981).

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