UDC 533.9.004.14; 621.039.6

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Phase diagram of polymerizing nitrogen – a theoretical prediction

Polymerization of nitrogen molecules in both solid and liquid phases, which was discovered in dynamic and static experiments, and predicted in ab initio simulations, stimulated discussion on a new configuration of phase diagram of nitrogen at high pressures. We consider the high-pressure phase diagram of solid nitrogen, which has long been discussed in theoretical studies, and only in the last decade began to investigate experimentally.

Key words: Nitrogen, the phase diagram, the pressure polymerization.

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Диаграмма полимеризации азота – теоретическое предсказание

Полимеризация молекул азота, как в твердых, так и жидких фазах, которая была обнаружена в динамических и статических экспериментах, и предсказана в неэмпирических моделированиях, стимулирована обсуждением новой конфигурации фазовой диаграммы азота при высоких давлениях. Рассмотрим фазовую диаграмму высокого давления твердого азота, который уже давно обсуждается в теоретических исследованиях, и только в последнее десятилетие начали исследовать экспериментально.

Ключевые слова: азот, фазовая диаграмма, давление, полимеризация.

Л.Н. Якуб

Азоттың полимеризациясының диаграммасы – теориялық болжам

Динамикалық және статикалық тәжірибелерде анықталған және эмпирикалық емес модельдеуде болжамдалған азот молекулаларының қатты, сонымен қатар сұйық фазалардағы полимерленуі жоғары қысымдағы азоттың фазалық диаграммасының жаңа конфигурациясының талқылануымен негізделген. Қатты азоттың жоғары қысымдағы бұрыннан теориялық зерттеулерде талқыланған және тек соңғы онжылдықта тәжірибе жүзінде зерттеліп басталған фазалық диаграммасын қарастырайық.

Түйін сөздер: азот, фазалық диаграмма, қысым, полимерлену.

Polymerization of nitrogen molecules in both solid and liquid phases, which was discovered in dynamic and static experiments, and predicted in ab initio simulations, stimulated discussion on a new configuration of phase diagram of nitrogen at high pressures. We consider the high-pressure phase diagram of solid nitrogen, which has long been discussed in theoretical studies, and only in the last decade began to investigate experimentally. The aim of this work is to demonstrate the possibility of predicting the phase diagram of polymeric nitrogen based on a combination of computer Monte Carlo simulations and theoretical equations of state describing thermodynamic properties of the polymer and molecular nitrogen at high pressures and temperatures.

Location of the molecular crystal – polymeric crystal transition line, for polymer having cubic gauche (CG) structure, on the phase diagram of nitrogen is predicted. Parameters of the phase transition line were determined by the conventional double-tangent procedure. Canonical equations of state of the molecular high-pressure nitrogen phase and polymeric CG-crystalline phase (modified Mie-Grueneisen equation), were calibrated on available ab initio data. The proposed modification of the Mie-

Grüneisen equation for solid polymeric nitrogen [1] based on the Monte Carlo computer simulation data describes negative thermal expansion and significant deviations of heat capacity from the Dulong-Petit law in CG-phase.

The generality of idea, which explains the phenomenon of polymerization in liquid and solid phases and use of canonical equations of state for both phases, allows also predicting the melting line of polymeric nitrogen [2]. In this work we applied the new equation of state of high-pressure polymeric liquid, also calibrated on *ab initio* simulations [3].

We analyzed the predicted P-T-relation, calculated volumes of the coexisting phases and the entropy jump on the melting line of polymeric nitrogen. The predicted P-T dependencies of two phase transition lines: (1) molecular solid into the hypothetical A7-polymeric structure, having positive slope, and (2) the same transition into CG-polymeric solid, demonstrating the negative slope, were compared.

The role of structure in the location and slope of the molecular-to-polymeric solid phase transition line on the nitrogen phase diagram was investigated. It was found that this qualitative difference is closely related to the negative thermal expansion of CG-polymeric solid. Both P-T dependences of transition of molecular solid into polymeric CG-phase and on the melting line of CG-solid have negative slopes due to its negative thermal expansion.

The predicted volume jump on the transition from the molecular to the polymeric phase is in good agreement with experimental data of. The predicted location of the triple point of polymeric nitrogen in the pressure range of 80-100 GPa, is also consistent with available experimental data.

References

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