

Solid atomic nitrogen structures

A new method for the theoretical search of new solid atomic structures. New solid atomic phases of nitrogen.

We have developed a new method for the theoretical search of new solid atomic all-nitrogen structures. This method is based on physical principles: at high pressures, the molecular phase transition into a solid atomic state. Therefore, we carried out simulations of the adiabatic compression of various molecular nitrogen crystals formed by stable nitrogen clusters (see Fig. 1). Using this method, we theoretically obtained 3 new solid nitrogen atomic phases that are dynamically stable over a wide pressure range. The phase with $P2_1$ lattice symmetry is dynamically stable up to normal pressure (see Fig. 2). The phase with $P-1$ lattice symmetry is dynamically stable up to 20 Gpa. The phase with $R-3c$ lattice symmetry is dynamically stable up to 30 Gpa.

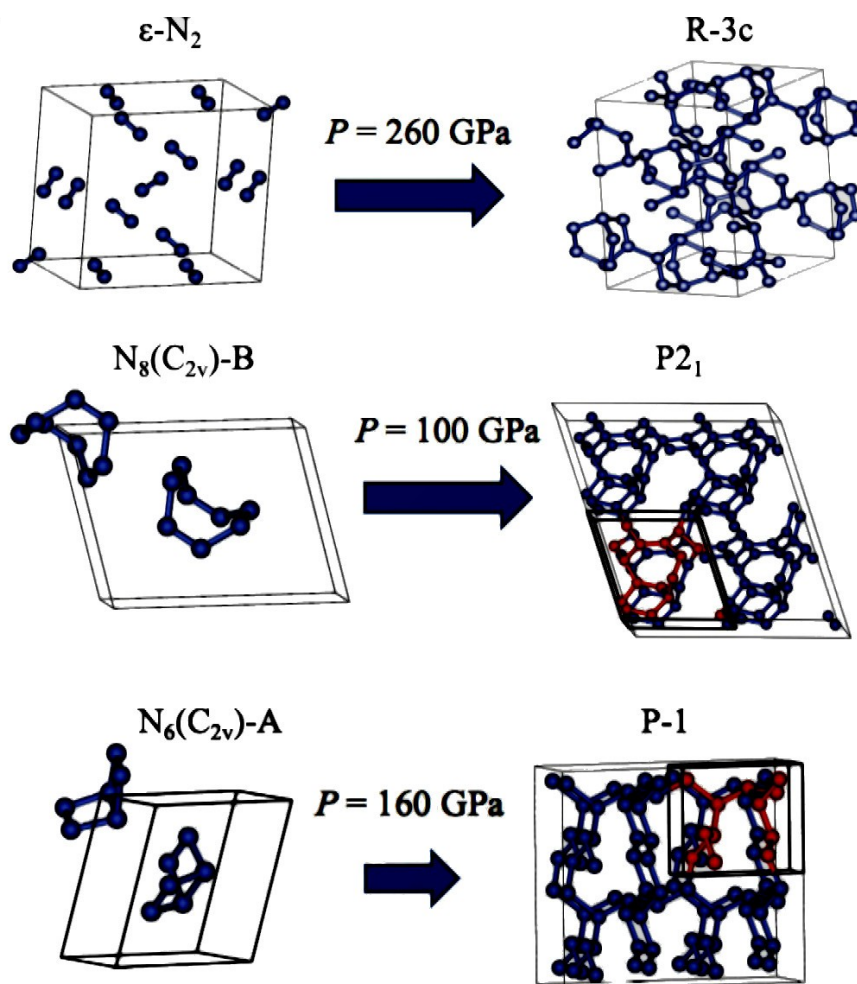


Fig. 1. Transformation of various molecular nitrogen crystals into solid atomic phases under pressure.

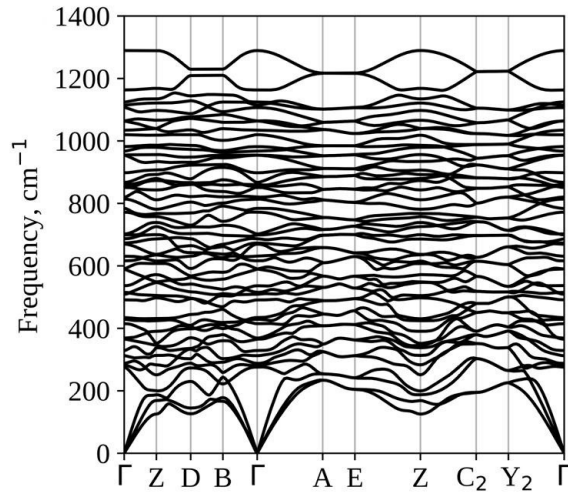


Fig. 2. Phonon spectrum for $P2_1$ solid atomic phase of nitrogen at normal pressure.

The solid atomic phases of nitrogen are semiconductors or dielectrics in the pressure range from 0 to 200 GPa. The theoretically predicted $P-1$ phase has semimetallic electronic properties that are unique for such structures.

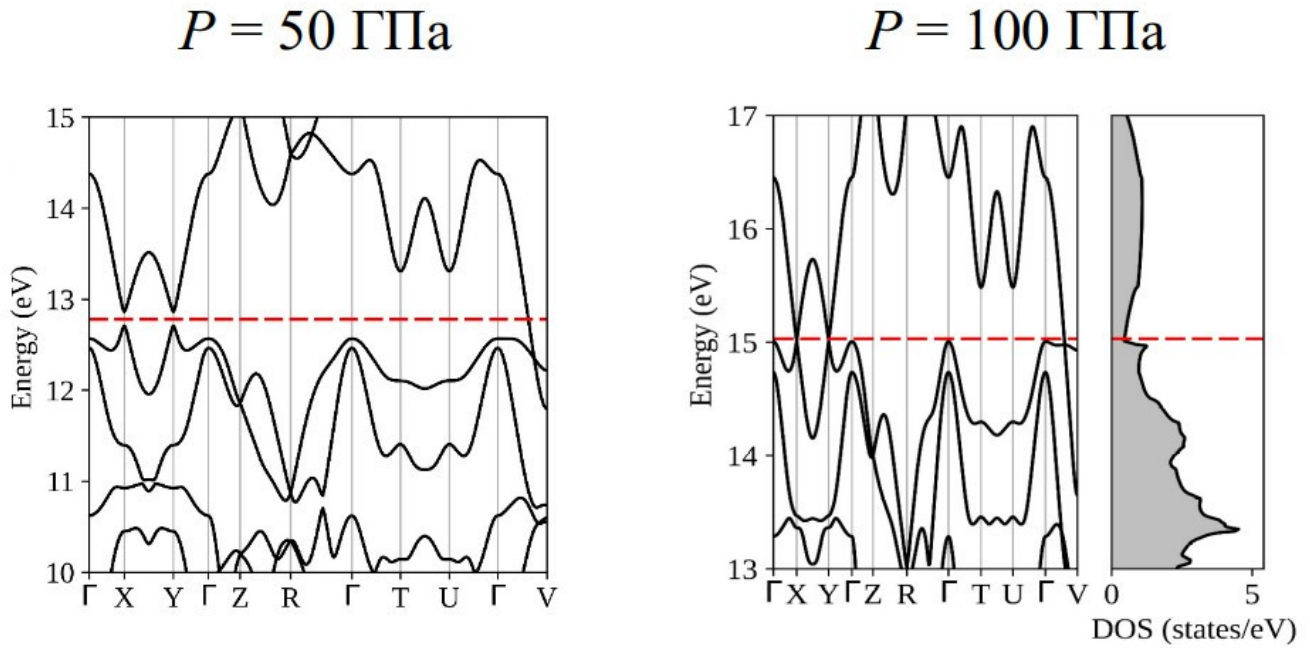


Fig. 3 Electronic band structure and electronic density of states (DOS) of $P-1$ solid atomic phase of nitrogen at different pressures.

Stability of solid atomic phases of nitrogen at normal pressure.

We have studied the stability under normal pressure of metastable atomic crystal structures with single bonds between atoms to various structural defects that violate the ideal periodicity, such as vacancies and surfaces.

We considered structures with $I2_13$, $Pccn$, $R-3$, $P-62c$ and $P2_1$ lattice symmetries, since in previous works it was shown that they are dynamically stable at normal pressure. The formation of vacancies (concentration less than 0.3%) in the $Pccn$ solid atomic phase leads to destroy the metastable state.

For the $P-62c$ phase at normal pressure, there are positions of vacancies for which the enthalpy of formation turns out to be negative. This indicates the energetic advantage of the formation of vacancies in these positions. The concentration of such vacancies exceeds 10%, which is considered sufficient for the destruction of the material. Thus, the local minima on the potential energy surface corresponding to the metastable states of the $Pccn$ and $P-62c$ phases are shallow and the system can be easily derived from them by small structural perturbations even at low temperatures.

The $I2_13$, $R-3$, and $P2_1$ solid atomic phases of nitrogen are resistant to the formation of vacancies, and the corresponding values of the enthalpy of formation are quite large. An estimate of the defect concentration in the model of independent random vacancies shows that the formation of vacancies in such crystals at room temperature has a low probability (see Fig. 4).

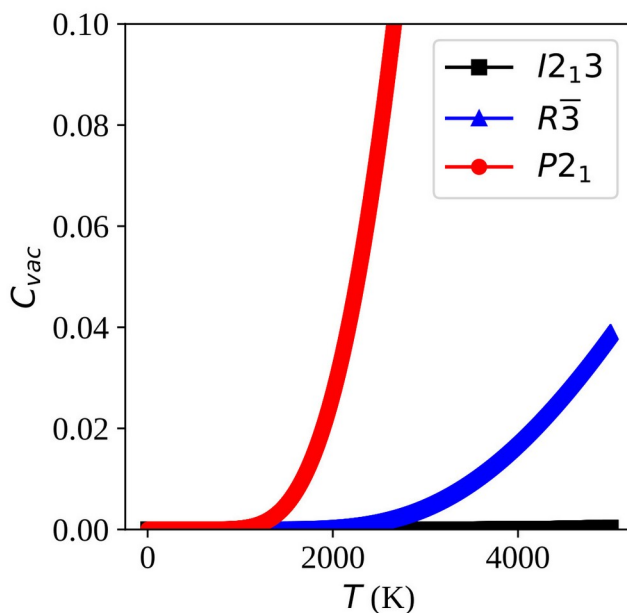


Fig. 4. Vacancy concentration as a function of temperature for various solid atomic phases of nitrogen at normal pressure.

For nitrogen structures resistant to the formation of vacancies, surface models were constructed. The issues of optimization of the geometry of the surface, as well as the

elementary process of detachment of two neighboring atoms from the surface into a vacuum with the formation of an N_2 molecule are considered.

For the $R-3$ and $P2_1$ phases, the surface is unstable (see Fig. 5). The only structure that is not removed from the metastable state by structural perturbations is the gauche phase of nitrogen with $I2_13$ lattice symmetry.

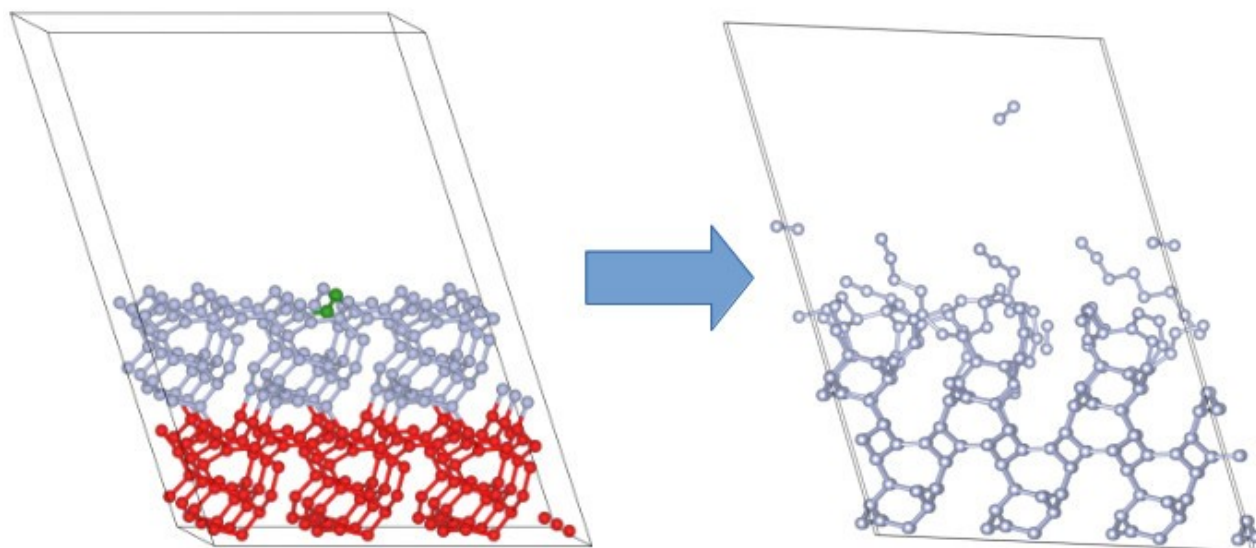


Fig. 5. Demonstration of the instability of the surface model for the solid atomic phase of nitrogen at normal pressure.

Azidofullerene $C_{60}N_{60}$

We have theoretically proposed a new high-energy molecule of azidofullerene $C_{60}N_{60}$. The frequency spectrum of this molecule does not contain imaginary frequencies. The estimate of stored energy for azidofullerene $C_{60}N_{60}$ is 6 kJ/g. Azidofullerene $C_{60}N_{60}$ has a highly deformed carbon cage structure, high chemical reactivity, and is also capable of storing a large amount of energy, comparable to the best high-energy molecules known to date.

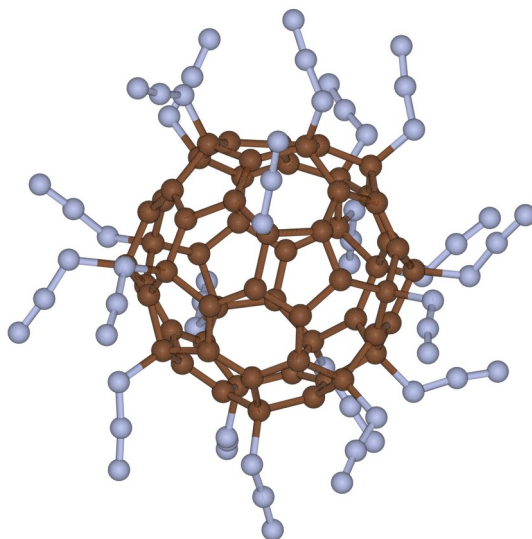


Fig. 6 Geometry of azidofullerene $C_{60}N_{60}$.

Publications

For detailed information, see the following publications:

1. Grishakov K.S., Degtyarenko N.N. // *Phys. Chem. Chem. Phys.*, 2022, V. 24, P. 8351.
DOI: 10.1039/d2cp00620k
2. Grishakov K.S., Degtyarenko N.N. // *Jetp Lett.*, 2022, V. 115, P. 422–427.
DOI: 10.1134/S0021364022100289
3. Grishakov K.S., Degtyarenko N.N. // *Jetp Lett.*, 2023, V. 119, P. 676.
DOI: 10.31857/S1234567823090069

Conferences

1. International Conference «PHYSICS AND TECHNOLOGY OF ADVANCED MATERIALS-2021» October 5-8, 2021 Ufa, Republic of Bashkortostan, Russia. Oral presentation “NEW PHASES OF POLYMER NITROGEN, STABLE IN THE LOW PRESSURE REGION”.
2. The VIII International Conference LaPlas-2022 March 22-25, 2022 Moscow, Russia. Oral presentation “NEW METASTABLE SOLID ATOMIC PHASES OF NITROGEN”.
3. The 10th International Symposium on Nonequilibrium Processes, Plasma, Combustion and Atmospheric Phenomena October 3-7, 2022 Sochi, Russia. Oral presentation “New low-pressure metastable solid atomic nitrogen phases“.

4. The IX International Conference LaPlas-2023 March 28-31, 2023 Moscow, Russia.. Oral presentation “STABILITY OF SOLID ATOMIC NITROGEN STRUCTURES IN THE ABSENCE OF PRESSURE”.

Acknowledgments

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