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Ab initio investigation of the melting line of nitrogen at high pressure

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Understanding the behavior of molecular systems under pressure is a fundamental problem in condensed-matter physics. In the case of nitrogen, the determination of the phase diagram and, in particular, of the melting line, are largely open problems. Two independent experiments have reported the presence of a maximum in the nitrogen melting curve, below 90 GPa, however the position and the interpretation of the origin of such maximum differ. By means of *ab initio* molecular-dynamics simulations based on density-functional theory and thermodynamic integration techniques, we have determined the phase diagram of nitrogen in the range between 20 and 100 GPa. We find a maximum in the melting line, related to a transformation in the liquid, from molecular N_2 to polymeric nitrogen accompanied by an insulator-to-metal transition.

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The properties of elemental materials under pressure attract considerable attention in condensed-matter physics, geophysics, and planetary science.[1,2] In particular, nitrogen, with its intricate phase diagram, and its potential applications as an energetic material, has been widely studied in recent years; however its phase diagram, including its melting line as a function of pressure, is still the subject of heated debate.

In its solid form nitrogen remains molecular up to relatively high pressure ($P \sim 100$ GPa) and its phase diagram exhibits a variety of competing crystalline phases.[3] At low P, N_2 molecules interact via weak dispersion forces, while N atoms are held together by a triple bond, which is the strongest chemical bond in nature. The ability of transforming the triple bonds of molecular nitrogen into single bonds would open the way to storing energy at very high density.[4] This is, in principle, possible: by pressurizing nitrogen to about 110 GPa, nonmolecular crystalline and/or amorphous phases are formed,[3,5] as predicted by pioneering theoretical works.[6,7] A crystalline covalent form, dubbed "cubic gauche (CG)" and proposed theoretically,[8] was obtained and fully characterized[9] in diamond-anvil cell experiments. In this insulating phase every N atom forms three single covalent bonds with its neighbors arranged in a cubic lattice. Further covalent crystalline forms have been predicted to occur at even higher P,[10,11] but are yet to be found in experiments.

By analogy with high-pressure solid phases, the existence of nonmolecular, liquid nitrogen was suggested as well,[12] and very recently a first-order liquid-liquid (LL) phase transition has been proposed,[13] between a low-density liquid (LDL) molecular phase and a high-density liquid (HDL) polymeric phase, located between 2000 and 6000 K at ~80 GPa. Such structural transformation is accompanied by metallization of fluid nitrogen, as observed in shock reverberation experiments.[14] Though uncommon in elemental liquids, a first-order LL phase transition, from a molecular to an atomic phase, has been observed in phosphorus,[15] which is isovalent to nitrogen. Support in favor of a LL phase transition in nitrogen comes from the observation of a maximum in the melting curve,[16,17] whose presence may be an indication of a change in the liquid properties.[15,18,19] A negative slope of the melting line may also be associated with the presence of open crystalline structures, as, e.g., in carbon and water, or with changes in the electronic structure of the system, for example, a metal-insulator transition[19] or promotions of valence electrons to electronic orbitals higher in energies than those occupied at low P, as found, e.g., in cesium.

The position and the character of the maximum in the melting curve of nitrogen are still matter of debate[16,17,20,21] According to Ref. 16 the maximum is sharp and located at 50 GPa, and may possibly be the signature of a triple point associated to a first order LL phase transition. Goncharov *et al.*[17,20] measured instead a slight change in the melting line slope near 70 GPa. In addition, by performing *in situ* Raman scattering, they found no evidence of a LL phase transition, and related the maximum in the melting curve to polymor-

phic transitions between crystalline molecular phases.

In this Rapid Communication, we report the theoretical melting line of nitrogen between 20 and 100 GPa as obtained from first-principles molecular-dynamics (MD) simulations. We predict that the melting temperature reaches a maximum between 80 and 90 GPa, in correspondence to a transition in the liquid phase involving both a structural modification from a molecular to a polymeric fluid, and a semiconductor to metal transition. We show that close to the maximum, the liquid polymerizes and becomes denser than the corresponding molecular solid, thus giving rise to a negative slope in the *PT* melting curve.

Calculations of melting lines can be obtained either by the two-phase simulation method[18,22,23] or by thermodynamic integration (TI). The two approaches are, in principle, equivalent[24] but the two-phase method may require larger simulation cells and longer runs to achieve accuracy comparable to TI. We therefore determined the melting temperature of nitrogen at several different P by computing free-energy differences between liquid and crystalline phases by TI, in a manner similar to the C and Si melting line studies reported in Refs. 25 and 26. Our computational framework relies upon Born-Oppenheimer MD simulations,[27,28] where the electronic structure is solved within density-functional theory (DFT). We used the generalized gradient approximation by Perdew, Burke and Ernzerhof (PBE),[29] for the exchange and correlation functional, norm-conserving pseudopotentials, and a plane-wave expansion of the electronic orbitals with a kinetic-energy cutoff of 60 Ry. We simulated nitrogen in supercells containing 128 atoms with Γ-point sampling of the supercell Brillouin zone. The MD equations of motion are integrated with a time step of 20 a.u., the temperature is controlled by stochastic velocity rescaling,[30] and the pressure is kept constant by first-order cell dynamics. This scheme yields good agreement with the $P(V)$ curve of liquid N at 2000 K reported in Ref. 13.

The use of TI requires the availability of a potential to describe a reference system, for which we have chosen a classical force field that provides a good description of molecular nitrogen at low P.[31,38] Our TI protocol consists of three steps: (i) we compute the melting temperature of the reference system (T_m^{ref}) at a given pressure P by a two-phase simulation, using a supercell with 3400 molecules and a simulation time of 100 ps. We note that the melting line of the classical system is monotonic as a function of P and does not exhibit any maximum. (ii) The (Gibbs) free-energy differences (ΔG) of the reference and the DFT/PBE systems are computed both for the solid and the liquid phase by adiabatic switch[32] (AS) in 2 ps runs. The convergence of ΔG as a function of switching time has been tested by performing longer AS runs at 40 GPa and error bars on ΔG are obtained as the standard deviation of four independent runs. Longer AS runs, up to 10 ps have been performed to obtain an accurate evaluation of the free energy of the liquid at 90 GPa, given the inability of the classical model used as reference system to describe the dissociated liquid. The free-energy differences between solid and liquid at different volumes need to be corrected because of the finite plane-wave cutoff used in our simulations.[25] A correction term is computed by performing single-point calculations for selected MD snapshots with a plane-wave cutoff of 160 Ry, that is sufficient to yield well-converged values of P at all volumes considered here. (iii) The melting temperature (T_m) of nitrogen at the PBE level is finally computed by reversible scaling:[33,34,39] T_m is located at the intersection of the Gibbs free-energy curves $[G(T)]$ of the liquid and the solid phases with an initial offset determined by ΔG at T_m^{ref}, obtained in step (ii). In addition, we have computed the slope of the melting curve at 65, 80.5, and 90 GPa using the Clausius-Clapeyron equation,[35] evaluating the differences in density and enthalpy over 5 ps long independent *ab initio* MD runs, carried out in the canonical ensemble at constant pressure (NPT).

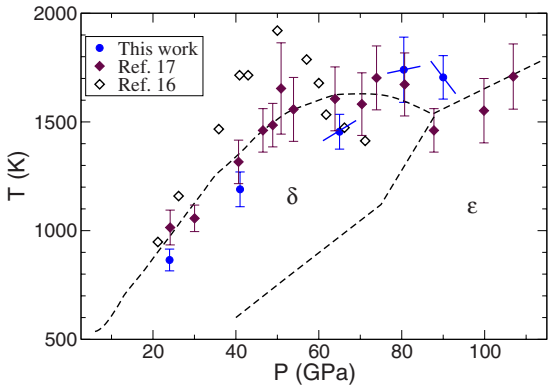

FIG. 1. (Color online) Proposed phase diagram of nitrogen. The computed points on the melting line are indicated with blue circles and the slopes obtained from the Clausius-Clapeyron equation with blue straight lines. The experimental points from Goncharov *et al.* (Ref. 17) are shown as solid diamonds and those measured by Mukherjee and Boehler (Ref. 16) as empty diamonds.

Using the procedure discussed above, we have computed the melting temperature at five different values of P: the results are reported in Fig. 1 and compared with the experiments from Refs. 16 and 17. Our results agree within one error bar with the melting points measured by Goncharov *et al.*,[17] while they are not compatible with the presence of a cusp at 50 GPa, as in Ref. 16. Our computed melting curve displays a maximum between 80.5 and 90 GPa; the presence of a maximum is further supported by the opposite signs of the slope of the curve, computed at 80.5 and 90 GPa. The position of the maximum in the melting line is shifted toward higher pressure with respect to the measurements of Ref. 17 by about 10 GPa.

Our simulations show that the thermodynamically stable crystalline phase between 80 and 90 GPa is molecular, even at T close to the melting point, in agreement with the experimental observations reported in Refs. 3 and 17. Yet, at variance with Ref. 17, we could not locate a polymorphic phase transition between the δ and the ε phase within this pressure range. By direct *ab initio* MD simulations in the NPT ensemble we observe that at 1500 K and 90 GPa phase ε transform rapidly into δ and we estimate the δ/ε phase boundary at P above 120 GPa at 1500 K. Experiments confirm that solid nitrogen is molecular in the (P,T) range of interest (80–90 GPa, ~1750 K), however the presence of several competing metastable structures and strong hysteresis effects make the determination of the stable crystalline phase

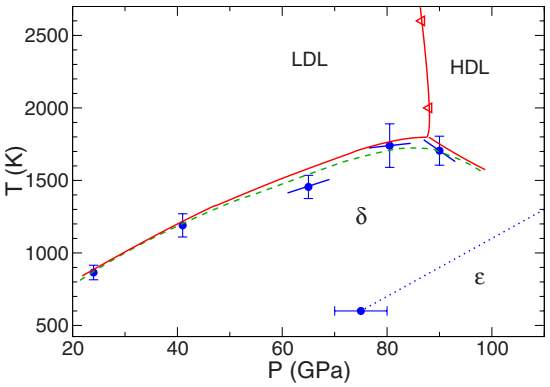

FIG. 2. (Color online) Computed melting line of nitrogen (see Fig. 1) and liquid-liquid phase boundary. The red solid line (guide to the eye) indicates the presence of a triple point occurring in the case of a first-order LL phase transition. Instead, the green dotted line (guide to the eye) does not show any triple point corresponding to a second-order LDL-HDL transition.

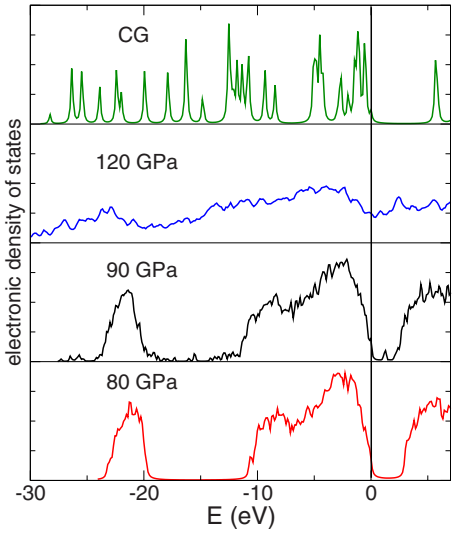

FIG. 3. (Color online) Computed electronic density of states for the liquid phase at 80, 90, and 120 GPa and for the CG crystalline phase.

uncertain.[36] Nevertheless the density differences between the various molecular solids observed at this P are small, compared to the density difference between the liquid and the solid phase; thus uncertainties in the relative stability of the molecular polymorphs may only result in small quantitative variations in the melting line predicted by our simulations.

Therefore we conclude that the presence of a maximum in the melting line stems from structural and electronic transformations occurring in the liquid, rather than in the solid phase. As observed in Ref. 13, and confirmed by our simulations, liquid nitrogen undergoes a transition from a molecular to a polymeric phase, which at 2000 K occurs at ~88 GPa. The analysis of our liquid sample at 90 GPa shows the coexistence of molecular N_2 and chains of N atoms where triple bonds give way to longer single bonds, whose signature appears as a second peak in the radial distribution function (not shown) at ~1.3 Å, while the triple bond yields a peak at 1.1 Å. The distribution of the bond angles around the tetrahedral value (109.3) and the observed tendency to form pentagonal rings are signatures of sp^3 hybridization of the atomic orbitals, analogous to the one observed in covalent crystalline phases[9,10] of nitrogen. The formation of covalent chains causes a drop in the volume of the liquid, which becomes denser than its crystalline counterpart. At 90 GPa and at the predicted melting temperature of 1705 K, liquid N is 1% denser than the solid. Such density difference results in a negative slope of the melting line.

If the molecular to polymeric LL transition was first order, as suggested in Ref. 13, then the maximum in the melting curve predicted by our simulations would coincide with a triple point, and it would be a cusp (i.e., the melting line would have discontinuous derivatives at the maximum), as in Ref. 16. However the location of the maximum found here is different from the one found in Ref. 16 (at about 50 GPa). If the LL transition was instead second order, then the derivative of the melting line would be a continuous function, similar to what observed, for example, in liquid carbon.[22,26] The two possible scenarios are illustrated in Fig. 2. We note that the characterization of the LL phase transition as first order[13] is plausible but not definitive: the use of small periodic simulation cells may make a second-order phase transition resemble a first-order one and a statistically significant size scaling analysis was not performed.[13] Unfortunately such analysis would likely require cells with at least 500 molecules and, most importantly, simulation times on the order of several nanoseconds, that are outside the reach of current *ab initio* simulation techniques.

As a consequence of the structural changes occurring upon compression, the electronic structure of the liquid undergoes major modifications (Fig. 3). Up to 80 GPa liquid nitrogen is an insulator with a DFT/PBE gap of 3.1 eV. At 90 GPa, the formation of chains and pentagonal rings give rise to the appearance of defectlike states in the middle of the electronic gap. These states have antibonding π^* character and are delocalized over the polymeric chains (Fig. 4). As P is further increased, the liquid loses its molecular character, an increasing number of polymeric chains are formed, and

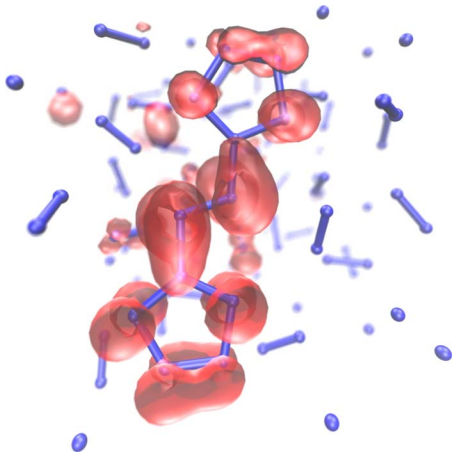

FIG. 4. (Color online) Isosurface of the square modulus of the wave function of a single-particle state with energy inside the electronic gap of liquid nitrogen at 90 GPa.

eventually metallization occurs. The electronic density of states of liquid nitrogen at 120 GPa shows indeed no gap. The observed metallization is consistent with an increase in electrical conductivity measured in shock reverberation experiments.[14] The density of states of the CG phase at 120 GPa is shown in the upper panel of Fig. 3: it is remarkable that the stable crystalline covalent polymorphs of nitrogen are semiconducting (or insulating) up to a pressure as high as 240 GPa.[3] However a chainlike metallic crystalline polymorph was predicted to have an enthalpy close to that of the CG phase.[37]

In summary, by means of *ab initio* MD simulations and thermodynamic integration we have determined the melting line $[T_m(P)]$ of nitrogen up to 90 GPa. We have found that $T_m(P)$ exhibits a maximum between 80 and 90 GPa which is related to a structural transformation in the liquid from a molecular to a polymeric phase. This transformation is accompanied by an insulator-to-metal transition. Our computed melting temperatures are in fair agreement with those determined in recent diamond-anvil cell experiments,[17] and not compatible with the data of Ref. 16, where melting was established by visual inspection. If the transformation observed in the liquid corresponds to a first-order phase transition, as suggested in Ref. 13, then the maximum found here will coincide with a triple point and thus a cusp in the melting line, as proposed by Ref. 16. However, the shift in the transition of the electronic properties of the liquid, which undergoes metallization at high pressure, with respect to its structural transition is an indication against a first-order transition in the liquid phase. Work is in progress to compute spectroscopic observables capable of unequivocally identifying different liquid phases.

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[38] This potential is made of an intramolecular Morse term and an intermolecular Lennard-Jones (LJ) term. We have rescaled the LJ parameters, so as to bring the melting temperature of the reference system closer to the experimental one.
[39] The force rescaling factor is varied linearly between 1 and 0.7 over 4 ps long MD simulations.