Calculation of the pressure-induced insulator-metal transition of nitrogen

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Abstract. Previous theoretical predictions of metallization below 1000 kbar are in apparent disagreement with the experimental fact that nitrogen is observed to remain a molecular solid up to 1300 kbar. The 0 K transition pressure from molecular to monatomic nitrogen is calculated using simple models and a well tested pair potential. The computed coexistence pressure is found to be 1940 kbar with a volume change of 20 Bohr^3/atom. Although there is some uncertainty (about 18%) in the calculated pressure, it is clear that non-molecular nitrogen could be studied at experimentally accessible pressures.

1. Introduction

Pressure-induced metallization of molecular crystals is one of the interesting physical problems in condensed-matter physics. At very high pressures the effect of compression is an overlapping of the conduction and the valence bands. This is expected as the compressional forces become large enough to disturb the molecular electron charge distribution. Under such circumstances, charge transfer is expected and the intramolecular interaction is drastically different from that in the gas phase. Iodine has been known as a prototype molecular crystal which shows metallization with increasing pressure. The electrical resistance of iodine shows a logarithmic decrease with increasing pressure [1] and the energy gap between the valence and the conduction band decreases with increasing pressure and becomes zero at about 160 kbar [2].

The nitrogen molecule is very stable; it has the largest binding energy of all the elemental diatomic molecules. Also nitrogen has the shortest bond length, apart from hydrogen. Thus at low and moderate pressures it is expected that in solid nitrogen the intermolecular interactions are much weaker than the intramolecular interactions. Solid nitrogen, one of the simplest molecular solids, exists in different crystal forms (see the review article in [3]) depending on pressure and temperature. At low temperatures and at pressures less than about 4 kbar the α-phase exists [4]. This is cubic with space group $Pa3$ (T_h^6). The unit cell contains four molecules, each aligned along a body diagonal. Above 4 kbar and still at low temperatures, a transition to the γ-phase [5] can be induced. This is an ordered tetragonal structure with two molecules per unit cell and space group $P4_2/mnm$ (D_{6h}^{14}). The molecules are arranged in layers with the molecular axes parallel within a layer and perpendicular in adjacent layers. As the temperature is increased, there is a transition to a disordered hexagonal structure, the β-phase [6], with the space group $P6_3/mmc$ (D_{6h}^4) and with a c/a-ratio of 1.62, close to the ideal value of 1.633 for the closest packing of hard spheres on a hexagonal lattice. The β-phase is still present at room temperature and pressures above 24 kbar.

At room temperature and pressures greater than 42 kbar a new phase, the δ-phase [7], is found. This is a disordered cubic structure with space group $Pm3n$ (O_h^3) with eight

molecules per unit cell. Recently [8], at room temperature and pressures around 163 kbar a transition from δ-nitrogen to a new phase ($\epsilon - N_2$) was observed. The ϵ-phase with space group $R3c$ (C_{3v}^6) seems to exist up to 439 kPa. It is observed that, from low pressures to 410 kbar at room temperature, nitrogen remains clear and colourless [9], suggesting that no major changes take place in the nature of the chemical bonding. Kobashi *et al* [10] suggested that at high pressures and low temperatures the $R3m$ (D_{3d}^5) structure might be the structure energetically favoured for nitrogen. This has three molecules in a hexagonal unit cell with all the molecules aligned along the c axis.

Reichlin *et al* [11], using high-resolution Raman spectroscopy, found no evidence for a metallic phase transition in nitrogen up to 1.3 Mbar. They tentatively assigned the low-temperature high-pressure phase to the rhombohedral space group $R3c$ (C_{3v}^6).

To the knowledge of the present author only three previous calculations have been carried out to give a prediction that molecular nitrogen would transfer to a monatomic structure. The transition pressure obtained in these calculations was found to be below 1000 kbar, in apparent disagreement with experiments in which no such transition was found up to a reported pressure of 1300 kbar [11]. The first attempt to calculate the transition pressure was made by Raich [12] using crude models to describe both molecular and non-molecular structures. He estimated the equilibrium pressure to be about 1000 kbar. The theoretical calculations of McMahan and LeSar [13], using linear muffin-tin orbitals to calculate the total energy, indicated that crystal structures composed of N_2 molecules may be less stable than a monatomic simple-cubic structure at 0 K and 770–940 kbar. Martin and Needs [14], using the local-density approximation with an *ab initio* pseudopotential, estimated that the transition occurs at a pressure of approximately 700 kbar.

The purpose of this paper is to estimate the equilibrium pressure for the insulator–metal transition of nitrogen at absolute zero. This is achieved by applying two simple models, which are considerably simpler than using the quantum-mechanical description, to describe the molecular and the atomic phases.

2. Method and interactions

The cohesive energy of the atomic modification of nitrogen was calculated using a free-electron model of metallic binding [15]. According to this model, it is not important to know the crystal structure of the metal in order to calculate the binding energy. The metal is considered as a three-dimensional array of ion cores surrounded by a sea of conduction electrons which cannot penetrate the core but are strongly influenced by the Coulomb field outside the core. The ion core is a sphere of radius a carrying charge Ze. The Z conduction electrons are distributed uniformly in a spherical shell between $r = a$ and $r = r_s$. The energy core relative to the neutral atom is taken as the sum of the ionization energies needed to strip Z electrons from the atom. The energy per atom of the electron gas at a certain volume per atom $\frac{4}{3}\pi r_s^3$ is the sum of the electrostatic potential energy, the kinetic energy and the exchange and correlation energies. The values of the ionization potentials used in the present calculation are [16] 14.53 eV, 29.59 eV, 47.43 eV, 77.45 eV and 97.866 eV for the first to the fifth ionization potentials, respectively. The cohesive energy for the metal relative to the energy of the isolated atom is calculated using the same expressions as in [12]. The free-atom energy was taken to be -108.5114 Ryd/atom [13].

The nitrogen pair potential used in this work was derived by Etters *et al* [17]. These workers modified the *ab initio* potential derived by Berns and van der Avoird [18] which had been used extensively previously [4, 5, 10]. They refitted the *ab initio* data in the potential well and long-range region so that the second virial coefficients and the α-N_2 sublimation energy are in agreement with experiment. At small separations they used the Gordon–Kim electron-gas calculations of LeSar and Gordon [19] and LeSar [20]. In the intermediate
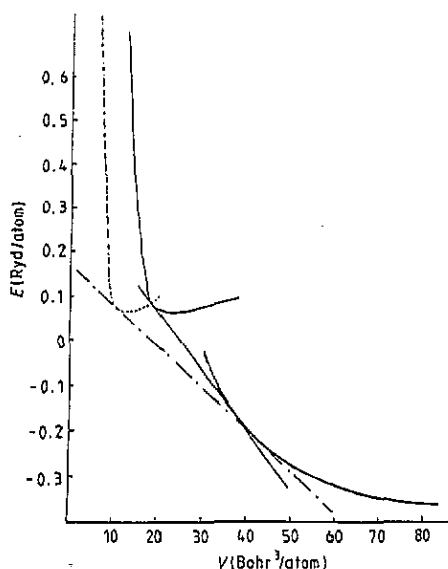
Figure 1. The total energy versus the volume for the molecular and the monatomic crystal of nitrogen at absolute zero. The negative slope of the common tangent gives the equilibrium pressure. The broken curve for the atomic modification of nitrogen differs from the full curve in the way described in the text.

region they joined these two expressions with a quartic spline fit. The force centres for this potential are al the atomic positions which are at ± 0.547 Å with respect to the mass centre. The intramolecular interaction is taken as $V_{\text{intra}} = \frac{1}{2}k(r - h_0)^2$ neglecting cubic and higher-order terms. The values of h_0, the bond length in the gas phase, and the harmonic force constant k are the same as used by Kobashi and Chandrasekharan [22].

Total energy calculations in this paper were carried out using the same method described in [5]. The energy was minimized with respect to the lattice parameters as well as the intramolecular spacing using a multidimensional pattern recognition optimization method described elsewhere [23]. In order to plot the total energy versus volume for the diatomic and monatomic nitrogen, we must subtract the molecular dissociation energy (0.3640 Ryd/atom) [24] from the molecular total energy calculated relative to the ground state of the free molecule and then divide by 2 to obtain the molecular result relative to the atomic ground state. The crystal structure used in this research is $R3m$ [10] (with lattice parameters a and c). Lattice sums were extended to 26 molecular shells, thus ensuring the stability of the calculated energies.

3. Results

Figure 1 shows the cohesive energies of both the molecular and the atomic modifications as functions of the atomic volume. As the zero taken for the energy is arbitrary, both energies are taken relative to the energy of a free atom as mentioned above. The common-tangent construction between the molecular and monatomic curves indicates a zero-temperature transition from solid N_2 to the atomic phase. The equilibrium pressure is the negative slope of the tangent. The value obtained from figure 1 is 1940 kbar, with a volume change of 20 Bohr^3/atom. Here we consider the volume per atom to be $(2r_s)^3$ instead of $\frac{4}{3}\pi r_s^3$, as used in [12]. The broken curve in figure 1 shows the calculated energy for the metallic phase using the volume per atom as in [12]; this gives a transition pressure of 1350 kbar and a larger volume change of 26 Bohr^3/atom; it should be noted that, if we use the above-mentioned method of [12], the transition pressure increases by 27% and the volume change decreases by 20%.

4. Discussion and conclusion

The quality of the results depends on the intermolecular potential. Although the potential used in this research gives excellent calculated results for the second virial coefficients and the zero-pressure molar volume and sublimation energy in solid α-N_2 it also fives excellent P–V results and good agreement with experimental results for the variation in vibron frequencies with pressure; there is no mention that this potential stabilizes the γ-phase at high pressures. The present author thinks that a more accurate quadrupole–quadrupole interaction should be included to take into account the variation in the quadrupole moment with the internuclear separation.

The model for the atomic modification, as opposed to the molecular configuration, is very crude. As in [15] the volume per atom will be the volume of the positively charged core plus the volume of the electron shell around the core. In a realistic model the crystal structure should be taken into consideration and the volume per atom will increase. So we should look at the two different volumes per atom, and thus the two values obtained for the transition pressure as two limiting cases. Thus there exists a large uncertainty, about 18%, in the calculated transition pressure, but the values of the pressure reported are experimentally accessible pressures.

In addition to the predicted molecular-to-non-atomic transition of N_2 it is expected that nitrogen in its monatomic metallic phase may undergo a phase transition. An x-ray diffraction study [25] has revealed that iodine undergoes a phase transition at about 450 kbar from a body-centred orthorhombic to a tetragonal lattice at room temperature.

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