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March 10, 2010

Physical Review B

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Pressure-induced isostructural transition in PdN₂

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(Dated: March 9, 2010)

We show that a synthesized Pd-N compound crystallize into the pyrite structure by comparison of experimental and calculated Raman intensities. The decreasing Raman intensities with decreasing pressure is explained by a closing of the fundamental band gap. We further discuss the experimental decomposition of this compound at 11 GPa in terms of an isostructural transition within the pyrite structure.

Several solid compounds of the platinum group metals and nitrogen have recently been synthesized (Pt, Ir, Os, Pd, Rh) [1–6]. These compounds are of fundamental and possibly technological importance due to their unusual or extreme properties. IrN₂, for example, has a bulk modulus of 428 GPa and is conceivably superhard [3]. PtN₂, IrN₂ and OsN₂ are recoverable to standard conditions after synthesis at high pressure and temperature. Their behaviour under pressure is uncomplicated; their bonding characteristics and optical properties remain qualitatively unchanged. In stark contrast, the nominal PdN₂ exhibits strongly temperature dependent Raman activity. It decomposes at low pressure shortly after the disappearance of all Raman modes. In this paper, we describe the unusual behavior of the electronic structure of PdN₂ under pressure. We show that this is responsible for the pyrite-to-pyrite (isostructural) phase transformation that leads to the decomposition of this compound at low pressures. We describe how during the course of this transformation the band gap first closes and then reopens while the hybridization between the Pd and N electrons is dramatically reduced leading to the N–N pairs in the structure forming triple bonds. Finally, we argue the necessity of the existence of a critical point for the isostructural transition. We predict massive fluctuations in the electronic structure at the critical point due to very strong electron-phonon coupling in the vicinity of the isostructural transition.

Experimental and theoretical results [2, 7–9] indicate that the crystal structures of PM-nitrides depend on the group number of the parent metal. Specifically, it has been proposed that the nitrides of Os and Ru crystallize in the marcasite structure [8], Rh [8] and Ir [4, 8, 9], in the marcasite and baddeleyite structures respectively, and Pt [2, 7, 10, 11] and Pd [4, 9], in the pyrite structure. The experimental investigations of these materials have been made using x-ray diffraction, which because of the low atomic number of nitrogen implies that only the metallic sublattice is actually directly observable. In the case of the Pd compound, diffraction measurements reveal a face centered cubic metal lattice which is consistent with the pyrite structure. As the composition is still unknown and

electronic structure calculations have revealed new low-enthalpy crystal structures of these nitrides [9, 12–14] we have revisited this issue, by comparing *in-situ* Raman measurements with first-principles calculations.

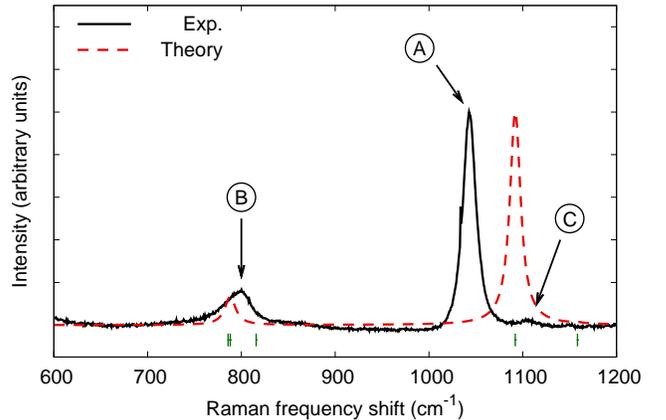


FIG. 1: (Color online) Experimental and calculated Raman spectrum recorded at 58 GPa. The bars below the spectra indicate theoretical peak positions. The peaks identified by A, B, and C are the E_g, A_g and T_g modes, respectively.

Figure 1 shows the experimental as well as the calculated Raman spectra of PdN₂ at 58 GPa [15]. Experimentally, two relatively intense peaks (A and B in Fig. 1) together with a third weak feature (C) at high frequencies are observed. According to group theoretical arguments, the Raman active modes of the pyrite structure at Γ decompose into three modes as A_g, E_g, and T_g. Previously it has been conjectured that unpolarized spectra of materials in the pyrite structure may be dominated by the A_g and E_g modes which can mask the less intense T_g modes [2, 7, 16]. In order to verify this conjecture, we have carried out calculations of the Raman susceptibility tensors of PdN₂ at 58 GPa from first principles. For this purpose, we performed density functional perturbation theory calculations of the mixed third derivatives of the total energy with respect to the electric field and phonon displacements using the ABINIT

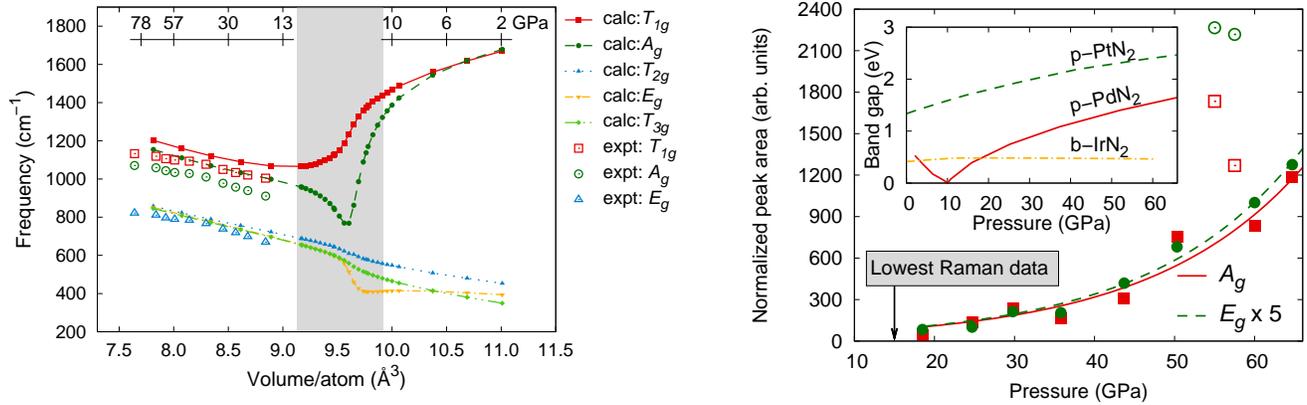


FIG. 2: (Color online) Left panel; Experimental and theoretical Raman frequencies as a function of volume. The corresponding pressures as obtained from the EOS are shown in the scale at top part of the figure. Right panel; Experimental Raman intensities of the A_g and E_g modes as a function of pressure. The solid lines are fitted to filled data-points only. The arrow marks the lowest pressure at which we were able to obtain reliable low temperature spectra. The inset shows the band gaps of pyrite-PdN₂(HSE06), pyrite-PtN₂(GGA), and baddelyite-IrN₂(GGA). We note that the band gaps of PtN₂ and IrN₂ are underestimated as they are obtained from the GGA exchange-correlation functional.

software package. To sample the Brillouin zone we used a $10 \times 10 \times 10$ Monkhorst-Pack grid. Norm conserving Troullier-Martin pseudopotentials within the local density approximation were employed. Since the experimental spectra are unpolarized, we averaged the theoretical intensities over the individual polarizations and crystal directions. Fig. 1 shows that the calculated Raman spectrum in good agreement with the experiment, confirming the dominance of the A_g and the E_g modes in pyrite-PdN₂. We thus conclude that the Pd-N compound crystallizes in the pyrite structure. In what follows, we describe an extensive theoretical and experimental study of the pressure dependence of the electronic structure, Raman spectra, as well as the crystal structure of the PdN₂ compound. All first principles calculations presented below use the projector augmented wave method [17] as implemented in the Vienna ab-initio simulation package (VASP) [18] and the exchange-correlation functional of Heyd-Scuseria-Erzenhof (HSE06) [19]. Comparisons are also made with the generalized gradient approximation (GGA) within the PBE scheme [20, 21]. The Brillouin zone integrations were performed using 8^3 and 6^3 Monkhorst-Pack k -point grids [22] for structural relaxations and calculation of Raman spectra, respectively.

Figure 2, left panel, shows the calculated Raman frequencies for the pyrite-PdN₂ together with the measured ones as a function of pressure. As mentioned above, experimentally only three modes are discernible. Nevertheless, the overall agreement between theory and experiment is quite good. While the PtN₂ and IrN₂ compounds in our earlier experiments exhibited Raman spectra whose intensities were insensitive to pressure, the relatively intense room temperature Raman spectrum of PdN₂ obtained at 58 GPa weakens significantly as pres-

sure is lowered. Eventually at ~ 18 GPa no convincing spectra could be obtained at room temperature. We attempted to quantify this positive pressure dependence in PdN₂ by keeping the laser power reaching the DAC constant at 20 mW and by trying to return to the same point on the sample after each pressure measurement. The resulting pressure dependence of the normalized spectral intensities, i.e. the Lorentzian areas for the A_g and E_g modes normalized by acquisition time is displayed in Fig. 2, right panel. It is quite well described by an exponential function. This behavior is telltale of a significant increase in the electromagnetic screening of the incident laser beam by the crystal as the pressure is reduced. In the inset of Fig. 2, right panel, we show the band gap of PdN₂ as a function of pressure. It clearly narrows as the pressure is reduced, leading to a dramatic increase in the number of carriers excited across the gap, which in turn diminishes the volume penetrated by the laser light. The theoretical 0K gap vanishes at about 11 GPa, leading to metal-like optical response of the material. It is worth noting here that while at room temperature, the Raman signal was observed to vanish below 18 GPa, low temperature measurements could obtain convincing spectra down to 15 GPa. The inset in Fig. 2, right panel, also shows the pressure dependence of the GGA band gaps of the two other insulating PM-nitrides synthesized to date: PtN₂ and IrN₂. The band gap of pyrite-PtN₂ exhibits the same positive pressure dependence as PdN₂. Its magnitude is however much larger and thus never closes in the pressure regime accessible in experiments. In contrast, the band gap of IrN₂, which crystallizes in the Baddeleyite structure does not show any significant temperature dependence. These results are consistent with the fact that there have been no reports of vanishing Raman

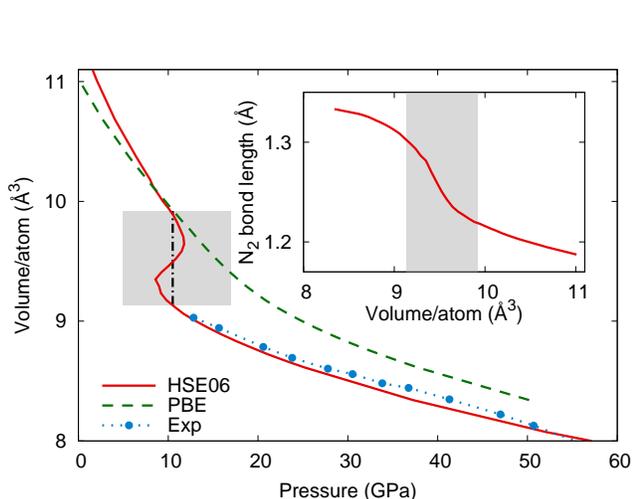
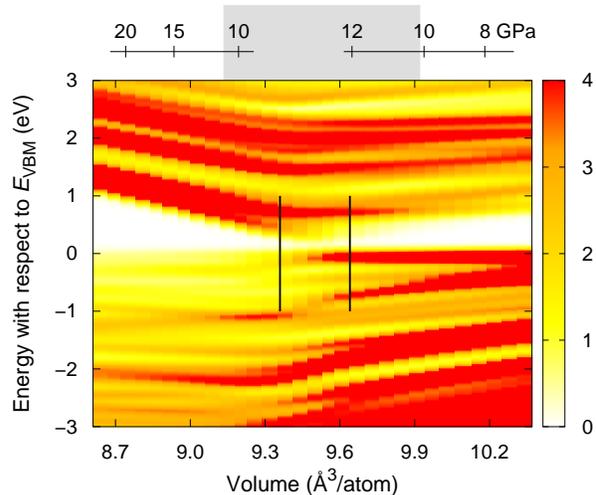


FIG. 3: Theoretical HSE06 (red solid), PBE (green dashed) and experimental (blue dotted) equations of state. The dashed-dotted line indicates the transition pressure for the predicted isostructural transition. The inset nitrogen bond length as a function of atomic volume.

signals as a function of pressure in either IrN₂ or PtN₂.

To summarize, we have explained above the disappearance of Raman signals in PdN₂ by an insulator-to-metal transition in this system. This is however, not a Mott transition. For one, as we will discuss in greater detail below, no real metallic phase ever forms. As can be seen in Fig. 2, right panel inset, the band gap as a function of volume is V-shaped: it closes with increasing volume but reopens upon further expansion. There is an apparent singular point in the band gap vs. volume curve. Does then the electronic structure in PdN₂ undergo a phase transition at this point? If so, a number of other physical properties must exhibit unusual behavior. For example, the Raman frequencies change very rapidly in the region close to the gap closure, marked by gray in Fig. 2, left panel. In particular the A_g mode, which signifies the breathing mode of the N₂ dimers in the pyrite lattice, sharply drops and then rises. More dramatic effects are observed in the acoustic phonons, in particular the longitudinal branch related to the bulk modulus. This is shown in the left panel of Fig. 3, where experimental equation-of-state (EOS) as obtained from XRD-measurements are displayed together with *ab initio* HSE06 as well as GGA calculations of ditto for pyrite-PdN₂. Note the good agreement between HSE06 calculations and experiment above 11 GPa. Below this pressure, no XRD pattern can be obtained implying decomposition of the compound. The HSE06 calculations show a two-phase region where the EOS becomes multivalued. This in turn implies an isostructural transition within the pyrite structure and corresponds to an inflexion point in the energy vs. volume curve. This is an important finding since it provides an explicit microscopic mechanism for the apparent phase decomposition observed at



11 GPa in the experiments. It is interesting to note the much poorer agreement between GGA and experimental EOS above 11 GPa. Neither does any structural instability appear in the EOS according to GGA. This implies that quite subtle electronic exchange and correlations are at play for the isostructural transformation in PdN₂ to occur.

The electronic phase transition accompanying the isostructural transformation of pyrite-PdN₂ is illustrated in Fig. 3, right panel. Here we show the density of *d*-electrons projected onto spheres of radius 1.4 Å around Pd atoms as a function of band energy and volume. Due to the approximately cubic site symmetry of the Pd atoms the five Pd *d*- orbitals are split up into two e_g-like and three t_{2g}-like orbitals, the latter lying at ≈ 5 and 3 eV below the Fermi energy in the high (HD) and low density (LD) phase, respectively. The white segments in this plot depicts the V-shaped band gap as a function of volume with a singular point at V_S = 9.5 Å³/atom. At this volume a massive transition in the character of the electrons takes place as the e_g-states migrate across the band gap. This is further demonstrated Fig. 4 where we show the Pd-*d* and N-*p* projected band-structures. In the HD phase the conduction band edge is dominated by the e_g-states and the valence band edge by N₂ - 2pπ* antibonding states. The situation is reversed in the LD phase without any significant rearrangement of the energy levels. As the states associated with the band edges belong to the same irreducible representation, band anti-crossings (BAC) are observed both as a function of reciprocal lattice vectors and volume. This explains two things: firstly the closing and re-opening of the band gap. Secondly, since the BAC:s are also associated with an exchange of eigenvector components we

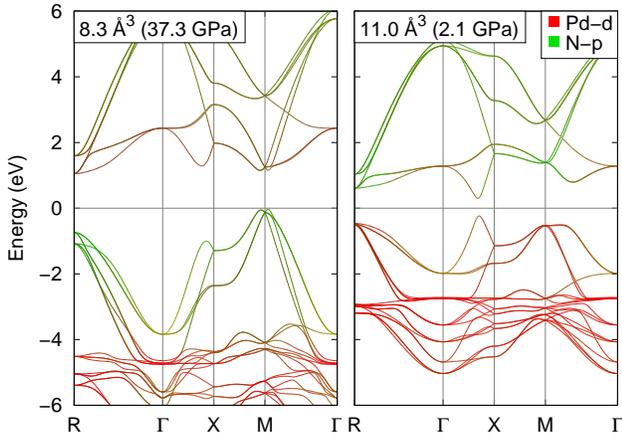


FIG. 4: Orbital-projected Band structures of PdN₂ at four different pressures. The line color indicates the degree of Pd-*d* (red) and N-*p* and Pd-*d* (green) character, respectively.

obtain a migration of e_g and $N_2 - 2p\pi^*$ states across the gap as a function of volume. The weak Pd-N bonding in the LD phase then manifests itself by a transition to triply bonded nitrogen dimers from single bonds in the HD phase. Hence, the bulk of the occupied manifold of electrons undergo a discontinuous transition at V_S .

Finally, let us discuss the order of the isostructural transition. We have above discussed this transition in terms of an Z-shaped 0K EOS (see Fig. 3, left panel, gray zone). This implies a first order transition with hysteresis as the pressure is reduced below 11 GPa. However, due to symmetry conservation of the isostructural transition, one would expect a critical point at a finite temperature. At the critical point the phase boundaries disappear and the correlation length of the fluctuations in the order parameter diverge. Hence it is important to discuss what the real order parameter for this transition is. Up to now, we have discussed the isostructural transition with volume/pressure as order parameter, which was necessary in order to compare with experimental observation. However, the isostructural transition in the pyrite lattice is driven by a hidden order parameter that we have not yet touched upon. The pyrite-PdN₂ structure is described by two independent parameters: (i) the lattice constant of the fcc metal cage, and (ii) the nitrogen dimer bond length. The inset in Fig. 3, left panel, illustrates the N-N bond length as a function of volume in the region around the isostructural transition. It shows that the isostructural transition results in a sharp decrease in the nitrogen dimer bond lengths. This is in fact the origin of the sharp transition in the electronic structure as a function of volume displayed in Fig. 3, right panel. In the HD phase the N-N bond length is on the order of 1.3 Å corresponding to single bonded nitrogen dimers, while in the LD phase it is reduced down to 1.2 Å, corresponding to triple bonded nitrogen dimers. The almost discontin-

uous behavior of the N-N bond length with volume in the transition region is consistent with the sharp drop in the A_g Raman mode frequency, depicted in Fig. 2, left panel. Hence at the signature of the critical point of the isostructural transition is divergent fluctuations of the nitrogen dimer bond lengths accompanied by massive fluctuations in the electronic degrees of freedom. In order to explore the physics of this phase transition, extensive experiments on pure bulk samples of pyrite PdN₂ crystals close to the critical necessary.

In summary, we have shown that the synthesised Pt-N compound crystallize into the pyrite structure, as well as discussed the exponential increase in Raman intensities. We have also assigned the experimental observation of decomposition to an isostructural transformation derived from forming Pd-N bonds from the Pd-*d* orbitals. The possibility of recovering PdN₂ to ambient conditions is an intriguing prospect but probably requires low temperature XRD and Raman measurements. As the Raman stretch modes of triply bonded N₂ are very distinguishable from the single bonded modes we conjecture that their appearance together with an fcc XRD pattern would serve as evidence. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory in part under Contract DE-AC52-07NA27344.

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