Supplementary Information:
Magnetic-Collapse Driven Mott Transition in MnO

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I. SUPPLEMENTARY METHODS

Here we describe the computational method used in the paper and present some numerical details. The single particle part of the Hamiltonian was obtained by a Wannier function projection method [1], which amounts to a unitary transformation in the Hilbert space containing Mn $3d$, O $2p$ bands and the next lowest empty (polarization) conduction band. The site energy of the Mn $3d$ orbitals was corrected for double counting of the $d-d$ interaction by subtracting a Hartree like term $(N-1)\bar{U}n_{LDA}$, where $N=10$ is the total number of orbitals per Mn site, $\bar{U}$ is the average Coulomb repulsion and n_{LDA} is the average occupancy per d-orbital. The DMFT equations were solved numerically on a Matsubara contour (using asymptotic expansions for frequencies $\omega_n > 500$ eV), and the k-space integrals were performed by summation over 3375 k-points in the first Brillouin zone. The chemical potential was adjusted in each DMFT iteration to guarantee the total electron count of 11 ± 10^{-6}. The impurity problem was solved using the Hirsch-Fye QMC algorithm modified for multiple orbitals.

The key innovation in this application to MnO in the transition regime was introduction of global Monte-Carlo moves in addition to the usual single-flips of the Hubbard-Stratonovich fields. These moves allow for fluctuations between HS- and LS-like configurations, which are otherwise practically unreachable with the standard single-Hubbard-Stratonovich-field-flip moves. The acceptance rate of the global moves was found to be non-negligible only in the transition regime, which had been characterized by unusually slow convergence of the DMFT cycle. We checked for the possibility of multiple solutions, but found none at the temperature of these simulations. The numerical value of the total energy, limited by the stochastic error of the E_{DMFT} term, was converged to the accuracy of 0.06 eV in the transition regime and 0.02 eV anywhere else. The spectral densities were calculated by the maximum entropy analytic continuation technique[2] applied to the imaginary-time Green functions from $4\times10^7 - 6\times10^7$ QMC-simulation sweeps collected into 2000-20000 bins.

II. SUPPLEMENTARY BACKGROUND

The first experimental indication of a transition in the range of the Mott transition in MnO (in the vicinity of one Megabar [100 GPa]) was obtained in 1996 from shock compres-

sion experiments (both single stage and two-stage) reported by Noguchi *et al.*[3] The onset, obtained from Hugoniot data, was recorded at $v \equiv V/V_0 \approx 0.72$, with quoted pressure of 90 GPa. A volume collapse of 8% was reported.

In 2000 Kondo used a diamond anvil cell (DAC) for static pressure x-ray studies to 137 GPa at room temperature. They confirmed the transition to rhombohedral symmetry at 30 GPa (associated with magnetic ordering) that had been reported earlier. A structure change was clearly seen around 90 GPa, but the structure in the 90-120 GPa region was not deduced. A change in reflectivity strongly suggested metallization occurred around 90 GPa. The phase above 120 GPa was determined to be the B8 (NiAs) structure.

In a Raman and optical study at static pressure in 2001 by Mita and collaborators[4, 8] a change in the Raman peak at 30 GPa and room temperature was seen, reaffirming the magnetic ordering transition. The vanishing of the Raman signal at 89 GPa was interpreted as due to metallization.

In 2004 Patterson *et al.* performed electrical conductivity measurements in a DAC, in two runs up to 90 GP and 106 GPa. A drop in resistivity of 4-5 orders of magnitude occurred between 90 GPa and 103 GPa. With no data points between these two pressures, it was unknown just where, or how abruptly, the metallization transition occurred. At 106 GPa, the resistivity had a temperature dependence of a metal.

X-ray emission spectroscopy was used by Rueff *et al.*[6] in 2005 to monitor the magnetic moment (via the exchange splitting of core levels). A LS moment was found at 80 GPa. A more recent interpretation by this group[7] is that the high spin (HS) state moment decreases smoothly, reaching the low spin (LS) value around 100 GPa.

Yoo and collaborators[9] in 2005 obtained x-ray diffraction and x-ray emission data up to 132 GPa. 90 GPa marks the onset of a sluggish B1 (NaCl) to B8 (NiAs) structural transition, and the Mott transition occurs around 105 GPa, in a first-order transition within the NiAs phase that involves a simultaneous volume collapse (6.6%), moment collapse (consistent with $S = \frac{1}{2}$ or less), and metallization (from the above experiments). Unlike the data of Rueff *et al.*, Yoo *et al.* observed no change in the XES spectrum (and hence in the magnetic moment) in the 40-98 GPa range, then an abrupt change to the LS state. (The disagreement between the actual XES data obtained by Yoo *et al.* and Rueff *et al.* is minor, emphasizing the need for a clean and precise interpretation of the spectrum.)

Although all of these data (rather, analysis and inferences from the data) are not fully

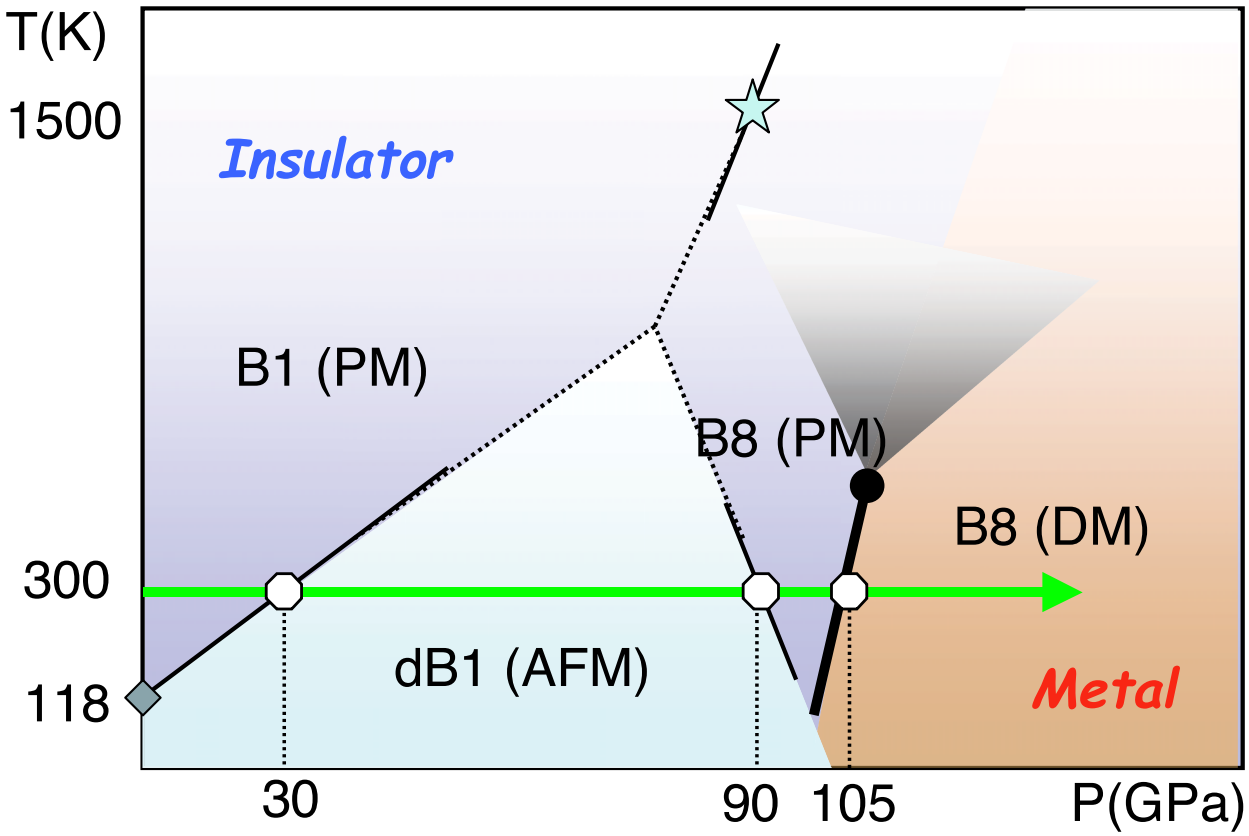

FIG. 1: The conceptual phase diagram constructed by Yoo *et al.* from the data discussed here. The Mott transition occurs, at room temperature, in the NiAs (B8) crystal structure, and is comprised of a 6.6% volume collapse, HS→LS moment collapse, and insulator-to-metal transition. Our calculated transition at 1100 K and 120 GPa lies very near an extrapolation of the heavy black line beyond the critical point (black dot) in the "crossover" region (gray fan area). here).

consistent, a reasonably clear picture of the experimental situation has emerged. The Mott transition occurs within the NiAs structure, very close to 105 GPa at room temperature. The data up to 2005 were gathered by Yoo *et al.* into the conceptual phase diagram displayed in the Figure. It is gratifying to note that the Mott transition obtained from our calculations are fully consistent with the current understanding of the phase diagram (see the Figure caption).

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