Emergence of quantum critical charge and spin-state fluctuations near the pressure-induced Mott transition in MnO, FeO, CoO, and NiO

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We perform a comprehensive theoretical study of the pressure-induced evolution of the electronic structure, magnetic state, and phase stability of the late transition metal monoxides MnO, FeO, CoO, and NiO using a fully charge self-consistent DFT+dynamical mean-field theory method. Our results reveal that the pressure-induced Mott insulator-to-metal phase transition in MnO-NiO is accompanied by a simultaneous collapse of local magnetic moments and lattice volume, implying a complex interplay between chemical bonding and electronic correlations. We compute the pressure-induced evolution of relative weights of the different valence states and spin-state configurations. Employing the concept of fluctuating valence in a correlated solid, we demonstrate that in MnO, FeO, and CoO a Mott insulator-metal transition and collapse of the local moments is accompanied by a sharp crossover of the spin-state and valence configurations. Our microscopic explanation of the magnetic collapse differs from the accepted picture and points out a remarkable dynamical coexistence (frustration) of the high-, intermediate-, and low-spin states. In particular, in MnO, the magnetic collapse is found to be driven by the appearance of the intermediate-spin state (IS), competing with the low-spin (LS) state; in FeO, we observe a conventional high-spin to low-spin (HS-LS) crossover. Most interestingly, in CoO, we obtain a remarkable (dynamical) coexistence of the HS and LS states, i.e., a HS-LS frustration, up to high pressure. Our results demonstrate the importance of quantum fluctuations of the valence and spin states for the understanding of quantum criticality of the Mott transitions.

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I. INTRODUCTION

The Mott metal-insulator transition caused by the mutual interaction between electrons is one of the most fundamental concepts of condensed matter physics [1]. This phenomenon occurs in Mott insulators, e.g., under pressure or doping of charge carries and has attracted much interest in view of its importance for unconventional high-temperature superconductivity in cuprates and iron-based materials, as well as for the understanding of manganites, showing colossal magnetoresistance, and heavy-fermion behavior in the f-electron systems [1,2]. Even today, it remains among the main highly-debated topics of condensed-matter physics [1,3].

The series of transition metal monoxides, MnO, FeO, CoO, and NiO, containing the partially filled 3d shell (with an electronic configuration ranging from 3d^5 to 3d^8, respectively), are perhaps among the most extensively studied examples of a Mott transition. At high temperature, these materials are known to exhibit a pressure-induced Mott transition in their paramagnetic phase with a cubic rocksalt B1 crystal structure [1,4,5]. Below the Néel temperatures, ranging from $T_N \sim 116$ K to $523$ K for MnO to NiO, respectively, these materials undergo a structural phase transition into a distorted rhombohedral phase [5]. The Mott transition is of first-order, often accompanied by a dramatic reduction of the unit-cell volume, implying a coupling between electronic and lattice degrees of freedom. In MnO, FeO, and CoO it is followed by a magnetic collapse – a remarkable reduction of the local magnetic moments of transition metal ions [4,5]. Moreover, MnO, FeO, and CoO exhibit rich allotrop behavior at high-pressures revealing a complex interplay between electron correlation and delocalization (i.e., metallic character) along with changes in crystal structure and transition metal spin-state [5,7]. In spite of intensive research that arguably provided quite complete understanding of the Mott transition [1], there are still many electronic and magnetic phenomena near the Mott insulator-to-metal transition (IMT) which are not fully understood from a theoretical point of view, especially in the high-pressure and high-temperature regime [5]. These are, for example, the nature of quantum criticality of the Mott transition, appearance of strange metal and non-Fermi liquid behaviors in proximity to the Mott IMT, which are actively debated in the literature [8,9].

In practice, many of the electronic, magnetic, and structural properties of real materials can be explained using, e.g., band-structure methods [4,10,12]. While these techniques often provide a quantitative description
of the static electronic properties of correlated systems, such as an energy gap and magnetic moments, band-
structure methods neglect electronic dynamics. As a result, these methods cannot capture all the generic as-
pects of a Mott IMT, such as a formation of the lower-
and upper-Hubbard (incoherent) subbands, to explain coherence-incoherence crossover, quasiparticle behavior and strong renormalization of the electron mass in the vicinity of a Mott IMT, all because of the neglecting of the effect of strong correlations \cite{1}. Here, we overcome this obstacle by using a DFT+DMFT approach \cite{13, 14} (DFT+DMFT: density functional plus dynamical mean-field theory) which merges \textit{ab initio} band-structure methods and dynamical mean-field theory of correlated electrons \cite{15}, providing a good quantitative description of the electronic and structural properties of strongly corre-
lated systems \cite{15, 29}. In particular, this advanced theory makes it possible to determine the electronic structure, magnetic state, and lattice stability of paramagnetic correl-
ated materials at finite temperatures, e.g., near the Mott IMT \cite{17, 19, 23, 28}.

In this paper, we study the pressure-induced evolution of electronic and magnetic properties of the late transition metal monoxides, from MnO to NiO using a state-of-
the-art self-consistent over charge density DFT+DMFT method \cite{30} implemented with plane-wave pseudopo-
tentials \cite{31}. We explore the evolution of their electronic structure and magnetic states near the pressure-
induced Mott IMT, which was shown to be accompa-
nied by a magnetic collapse – a transformation from the high-spin to low-spin state (HS-LS), all in the B1 crystal structure \cite{4, 25}. Here, we focus on their high-
temperature properties in the paramagnetic state well above the Néel temperature to exclude the complications associate with a structural phase transformation, e.g., in a low-temperature distorted rhombohedral phase. We obtain that under pressure MnO-NiO exhibit a Mott IMT which is accompanied by a simultaneous collapse of lo-
cal magnetic moments and lattice volume, with a transition pressure $p_c$ varying from $\sim$145 to 40 GPa, upon moving from MnO to CoO, and $p_c \approx$ 429 GPa for NiO. We show that in MnO, FeO, and CoO the Mott IMT and the concomitant collapse of the local moments is accompanied by a sharp crossover of the valence state, implying the importance of the valence fluctuations for understanding their electronic states in the vicinity of the pressure-driven IMT. We give a novel microscopic explana-
tion of the magnetic collapse of these compounds, re-
vealing a remarkable quantum superposition of the high-, intermediate-, and low-spin states near the Mott transi-
tion, i.e., a HS-LS and IS frustration. Our results pro-
vide a novel microscopic explanation of the magnetic col-
apse of all these compounds. In fact, in MnO the mag-
netic collapse is found to be driven by the appearance of the intermediate-spin state (IS), strongly competing with the LS state; in FeO we observe a conventional HS-
LS crossover. Most interestingly, in CoO we obtain a remarkable coexistence (frustration) of the HS and LS states, up to high compression. Overall, our results qual-
itatively improve understanding of the pressure-induced evolution of the electronic and magnetic structure in corre-
lated insulators, which may have important implica-
tions for the theoretical picture of quantum criticality of the Mott transitions \cite{8}.

II. METHOD

We employ the DFT+DMFT approach \cite{19, 25, 30} to calculate the pressure-induced evolution of the effective electronic structure of paramagnetic MnO, FeO, CoO, and NiO oxides. It starts with construction of the effective low-energy (Kohn-Sham) Hamiltonian $[\hat{H}^{KS}_{\sigma,\alpha}(\mathbf{k})]$ using the projection onto Wannier functions in order to obtain the $p$-$d$ Hubbard Hamiltonian (in the density-density approxima-
tion) \cite{32, 33}

$$\hat{H} = \sum_{\mathbf{k},\sigma} \hat{H}^{KS}_{\sigma,\alpha}(\mathbf{k}) + \frac{1}{2} \sum_{\sigma\sigma',\alpha\beta} U^{\sigma\sigma'}_{\alpha\beta} \hat{n}_{\alpha\sigma} \hat{n}_{\beta\sigma'} - \hat{V}_{DC}, \quad (1)$$

where $\hat{n}_{\alpha\sigma}$ is the occupation number operator with spin $\sigma$ and (diagonal) orbital indices $\alpha$. $U^{\sigma\sigma'}_{\alpha\beta}$ denotes the reduced density-density form of the four-index Coulomb interaction matrix: $U^{\sigma\sigma'}_{\alpha\beta} = U_{\alpha\beta\sigma\sigma'}$ and $U^{\sigma\sigma'}_{\alpha\beta} = U_{\alpha\sigma\beta\sigma'} - U_{\alpha\beta\sigma\sigma'}$. The latter is expressed in terms of the Slater integrals $F^0, F^2$, and $F^4$. For the $d$ electrons these parameters are related to the Coulomb and Hund’s coupling as $U = F^0$, $J = (F^2 + F^4)/14$, and $F^2/F^4 = 0.625$. $\hat{V}_{DC}$ is the double-counting correction to account for the electronic interactions described by DFT (see below).

We use a fully self-consistent in charge density imple-
mentation of the DFT+DMFT method in order to take into account the effect of charge redistribution caused by electronic correlations and electron-lattice coupling \cite{30}. To take into account self-consistency over charge density we evaluate charge density $\rho(\mathbf{r})$ as

$$\rho(\mathbf{r}) = k_B T \sum_{\mathbf{k},\omega_n,ij} \rho_{\mathbf{k},ij} G_{\mathbf{k},ij}(i\omega_n)e^{i\omega_n \mathbf{r},0^+}, \quad (2)$$

where summation over the Matsubara frequencies is per-
fomed taking into account an analytically evaluated asymptotic correction. In the plane-wave pseudopotential approach \cite{31} matrix elements of the charge density operator $\rho_{\mathbf{k},ij}$ in the basis of the Kohn-Sham (KS) wave functions $\psi_{\mathbf{k}}$ are defined as

$$\rho_{\mathbf{k},ij}(\mathbf{r}) = \langle \psi_{\mathbf{k}} | \mathbf{F} | \psi_{\mathbf{k}} \rangle \langle \psi_{\mathbf{k}} | \beta_j^\dagger \rangle \langle \beta_i^\dagger | \psi_{\mathbf{k}} \rangle + \sum_{lm} Q_{lm}^I(\mathbf{r} - \mathbf{R}_I) \langle \beta_j^\dagger | \psi_{\mathbf{k}} \rangle \langle \beta_l^\dagger | \psi_{\mathbf{k}} \rangle,$$  

where $I$ is an atom index, $\beta_i^\dagger(\mathbf{r})$ is the augmentation basis function, $Q_{lm}^I(\mathbf{r})$ is the augmentation function for
localized double-counting correction, evaluated from the
exclude the double-counting. Here, we use the fully lo-
interactions already described by DFT we need to in-
DFT+DMFT. Therefore, to account for the electronic
interaction contributions would be counted twice within
Sham energies from DFT already include interaction ef-
tests through the Hartree and exchange-correlation terms
Sham energies. Full charge self-
tion from DFT and the charge-density correction due
average of the KS low-energy Wannier Hamiltonian
+ \Delta \rho(r), i.e., to split the contribu-
tions, as well as the corresponding change in the atomic
coordinates and of the unit-cell shape.

III. COMPUTATIONAL DETAILS

We employ the DFT+DMFT approach as discussed above to explore the electronic structure and magnetic properties of MnO, FeO, CoO, and NiO under pressure. For the partially filled Mn, Fe, Co, and Ni 3d and O 2p orbitals we construct a basis set of atomic-centered symmetry-constrained Wannier functions, defined over the energy range window spanned by the p-d band complex. We employ the continuous-time hybridization-expansion quantum Monte-Carlo algorithm in order to solve the realistic many-body problem. The calculations are performed in the paramagnetic state at an electronic temperature \( T = 1160 \) K, i.e., well above the Néel temperature, ranging from \( T_N \approx 116 \) K to 523 K for MnO to NiO. At such a temperature MnO-NiO oxides adopt a cubic B1 crystal structure up to high pressures. We take the following values of the average Hubbard \( U \) and Hund’s exchange \( J \) as estimated previously: \( U = 8.0 \) eV and \( J = 0.86 \) eV for the Mn 3d orbitals, 7.0 and 0.89 eV for Fe, 8.0 and 0.9 eV for Co, and 10.0 and 1.0 eV for Ni, respectively. The Coulomb interaction \( U \) and Hund’s \( J \) are considered to be pressure-independent and have been treated in the density-density approximation. The spin-orbit coupling was neglected in these calculations. In our DFT+DMFT calculation we neglect by the effect of lattice and local magnetic moments entropy on the equation of states of MnO-NiO which seems to become prominent at very high temperatures \( T \gg 1160 \) K. The spectral functions
were computed using the maximum entropy method and the Padé analytical continuation procedure.

**IV. RESULTS AND DISCUSSION**

As a starting point, we calculate the total energy and fluctuating (instantaneous) local magnetic moments \( \sqrt{\langle m_z^2 \rangle} \) of the paramagnetic B1-structured MnO, FeO, CoO, and NiO as a function of the unit-cell volume using the DFT+DMFT method (see Figure 1) [25]. Overall, the calculated electronic, magnetic, and lattice properties of MnO-NiO agree well with those published previously [24][26]. We obtain \( V \approx 158.9, 144.1, 137, \) and 128 a.u.\(^3\) for the equilibrium lattice volume of MnO, FeO, CoO, and NiO, respectively. The ambient-pressure local magnetic moments of \( \sim 1.8 \mu_B \) to \( 4.8 \mu_B \) in NiO-MnO match the high-spin magnetic state of their transition metal ions. The local moments are seen to retain the HS state upon compression down to about 0.6-0.7 \( V/V_0 \). Upon further compression, all these compounds exhibit magnetic collapse -- a remarkable reduction of the local magnetic moments which results in a Mott insulator-to-metal phase transition (IMT) [25]. The resulting low-spin local moments are about 1.6\( \mu_B \), 1.1\( \mu_B \), 1.26\( \mu_B \), and 1.28\( \mu_B \) for MnO, FeO, CoO, and NiO, respectively. By fitting the DFT+DMFT total-energy results to the third-order Birch-Murnaghan equation of states (separately for the low- and high-volume regions) we obtain that magnetic collapse is accompanied by a sudden change of the lattice volume. That is, the phase transition is of first order with a significant fractional volume \( \Delta V/V \) collapse of 13.6\%, 9\%, and 11.2\% for MnO-CoO, except for NiO, where a resulting change of the lattice volume is only about 1.4\%.

Our result for the transition pressure \( p_c \) evaluated from the equation of states shows a monotonic decrease from 145 GPa, 73 GPa, to 40 GPa for MnO, FeO and CoO, respectively, while NiO has a high transition pressure \( \sim 429 \) GPa. We note that this anomalous behavior of \( p_c \) can be understood as a continuous decrease of the strength of electronic correlations and, hence, the tendency towards localization of the 3d electrons upon changing of the electron conﬁguration from 3d\(^8\) Mn\(^{2+}\) ions to 3d\(^7\) in Co\(^{2+}\) [24]. In fact, the effective interaction strength changes from \( U + 4J \) for MnO to \( U - 3J \) for CoO, while in NiO it sharply increases due to a crossover in the effective degeneracy of low-energy excitations from five-orbital (as in MnO, FeO, and CoO) to two-orbital behavior (as in NiO). It is interesting to note that the calculated transition pressure \( p_c \) (as well as the energy gap values) is very sensitive to the choice of the interaction parameters Hubbard \( U \) and Hund’s exchange \( J \). To help check this result, we perform the DFT+DMFT calculations of MnO-NiO with various sets of the Hubbard \( U \) and Hund’s \( J \) values, varying them by about 10\%. In particular, for MnO, we obtain a transition pressure \( p_c \sim 145 \) GPa, 133 GPa, and 109 GPa for the \( U/J \): 8/0.86 eV, 7/0.86 eV, and 8/0.75 eV, respectively. For FeO, it is \( p_c \sim 55 \) GPa, 73 GPa, and 80 GPa for the \( U/J \): 5/0.89 eV, 7/0.89 eV, and 8/0.89 eV, respectively. For NiO our results are \( \sim 248 \) GPa and 429 GPa respectively for the \( U/J \): 8/1 eV and 10/1 eV. In fact, our results are consistent with the behavior the effective interaction strength that changes from \( U + 4J \) for MnO to \( U - 3J \) for CoO, revealing a strong sensitivity (in terms of a percentage change) to \( J \) rather than to \( U \).

Overall, our results suggest a complex interplay between chemical bonding and electronic correlations in MnO-NiO near the Mott transition. The Mott insulator-to-metal phase transition is accompanied by a remarkable increase of the bulk modulus, varying from 137 to 263 GPa in MnO, 142/210 GPa in FeO, 184/246 GPa in CoO, and 187/188 GPa in NiO. The latter implies an anomaly in the compressibility at the phase transition point. Moreover, we obtain a substantial redistribution of electrons between the \( t_{2g} \) and \( e_g \) orbitals in the 3d shell of the spin-state active MnO, FeO, and CoO. This implies a significant change in chemical bonding of the 3d electrons. Thus, the \( t_{2g} \) orbital occupations are found to gradually increase with pressure, whereas the \( e_g \) orbitals are strongly depopulated (below 0.27 for MnO and FeO, and 0.44 for CoO). The 3d total occupancy weakly changes with pressure. Upon pressurizing to \( \sim 150 \) GPa it increases by 0.4-0.5 electrons in MnO, FeO, and CoO. It is important to note that magnetic collapse is also seen to occur in NiO, which in fact, has a 3d\(^8\) electronic con-
MnO to NiO) are Mott insulators with a large d-d energy gap of ~2–3.5 eV, which emphasizes the crucial importance of strong correlations to determine the electronic and magnetic properties of transition metal oxides. The top of the valence band is predominantly formed by transition metal 3d states, with a large contribution from the O 2p states. In Figures 1 and 5 we display our results for the k-resolved spectral functions of paramagnetic MnO-NiO obtained by DFT+DMFT for the ambient pressure Mott insulating phase and those for pressure p > p_c in a metallic state. It is important to note the contribution of the empty transition metal 4s states at the Brillouin zone Γ-point seen as a broad parabolic-like band above the Fermi energy (see Figure 4). This is in agreement with photoemission and optical experiments which e.g. for FeO report a weak absorption between 0.5 and 2.0 eV, assigned to the mixed Fe 3d-O 2p to Fe 4s transitions, while the strong absorption edge associated with the d-d transitions is found to appear in optical spectroscopy at about 2.4 eV [37].

Under pressure the energy gap in MnO-NiO gradually decreases resulting in a Mott insulator-to-metal phase transition. Upon the Mott transition, all these materials exhibit a strongly correlated metallic behavior. It is characterized by the lower- and upper-Hubbard bands to appear in their spectral function, and the quasiparticle peak at the Fermi level, associated with a substantial renormalization of the electron mass (see Figure 2). We find that the electronic effective mass evaluated by using a polynomial fit of the imaginary part of the self-energy \( \Sigma(\omega_n) \) at the lowest Matsubara frequencies \( \omega_n \) diverges at the Mott transition (upon decompression starting from the metallic phase), in accordance with a Brinkman-Rice picture of the Mott IMT [38]. We note that this divergence concurs with a drop of the spectral weight of the \( t_{2g} \) and \( e_g \) orbitals at the Fermi level (with an opening
of a Mott energy gap) and a sudden increase of the local magnetic moments in MnO-NiO. Our analysis of the spectral weight at the Fermi level and the quasiparticle weight of electronic correlations of localized 3d electrons to explain the electronic structure and lattice properties of correlated transition metal oxides. Indeed, at ambient pressure, the 3d electrons are strongly localized, as it is seen from our result for the local spin susceptibility $\chi(\tau) = \langle \hat{m}_z(\tau)\hat{m}_z(0) \rangle$, where $\tau$ is the imaginary time (see Figure 6). Indeed, $\chi(\tau)$ is seen to be nearly constant, independent on $\tau$. Upon further compression, the 3d electrons exhibit a crossover from localized to itinerant moment behavior which is associated with a Mott transition, as it is clearly seen in paramagnetic FeO, CoO, and NiO. In particular, $\chi(\tau)$ is seen to decay fast nearly to zero with the imaginary time $\tau$, which is typical for itinerant magnets.

In Figures 7 and 8 we display our results for the $t_{2g}$-$e_g$ crystal field energy splitting and the $p$-$d$ hopping matrix elements of MnO-NiO as a function of volume. The crystal field splittings are obtained from the first moments of the interacting lattice Green’s function for the 3d states as $\Delta_{t_{2g},e_g} = \text{diag} \left[ \sum_k H^{KS}(k) + \text{Re} \Sigma(\omega_n \rightarrow \infty) \right]$, where $H^{KS}(k)$ is the effective low-energy $p$-$d$ (Kohn-Sham) Hamiltonian in the Wannier basis set. Re$\Sigma(\omega_n \rightarrow \infty)$ is a static Hartree contribution from self-energy $\Sigma(\omega_n)$. We also compare our results for $\Delta_{t_{2g},e_g}$ with those obtained in the non-interacting case, with $\Sigma(\omega_n) = 0$. We observe that upon compression both the non-interacting $t_{2g}$-$e_g$ crystal field energy splittings and the $p$-$d$ $(p_z$-$d_{3z^2-r^2}$ and $p_z$-$d_{xz}/p_y$-$d_{yz}$) hopping matrix elements monotonously increase (by modulus) (i.e., as expected the transition-metal 3d bandwidth and $t_{2g}$-$e_g$ splitting monotonously increase under pressure). We note that neither $\Delta_{t_{2g},e_g}$ for $\Sigma(\omega_n) \equiv 0$ nor $p$-$d$ hopping parameters exhibit anomaly (are changing continuously) near the Mott transition. In contrast to that the Mott IMT accompanied by the HS-LS transition clearly correlates with a remarkable enhancement of the crystal-field splitting, caused by correlation effects. This change of $\Delta_{t_{2g},e_g}$ is large, about 1.5-3.2 eV for MnO-CoO, whereas for NiO it is seen as a weak anomaly at the transition point. This result implies the crucial importance of electronic correlation effects, determined by the self-energy contribution $\Sigma(\omega_n)$, which plays a significant role at the Mott IMT. Our results are consistent with a transition from localized to itinerant moment behavior of the 3d electrons at the Mott transition, in which the Mott IMT concurs with a collapse of magnetism. Indeed, under pressure, the overlap of the transition metal 3d and ligand 2p orbitals increases and hence the $p$-$d$ hybridization (and 3d bandwidth) increases, resulting in a reduction of correlation effects and metallization for $p > p_c$. This behavior concurs with an increase of crystal field splitting between the $t_{2g}$ and $e_g$ orbitals which favors the lower spin state.

Next, we analyze the pressure-evolution of the electronic structure of MnO-NiO in the vicinity of the Mott IMT. At this point, we determine a reduced density matrix of the 3d electrons as a function of lattice volume: $\rho_{\alpha\beta} = \langle \phi^N_{\alpha S_\alpha} \phi^N_{\beta S_\beta} \rangle w_{N,S_\alpha} \phi^N_{\alpha S_\alpha} | \phi^N_{\beta S_\beta} \rangle$, where $\phi^N_{\alpha S_\alpha}$ is a 3d atomic state with the occupation $N$ and spin $S_\alpha$. Its eigenvalues $w_{N,S_\alpha}$ give a probability of observing different 3d-electron atomic configurations for a given unit-cell volume. That is, the 3d electrons are seen being fluctuating between various atomic configurations with a given prob-
ability, exchanging with the surrounding medium, that gives alternative information about the nominal valence \((\text{Tr}\{S_z\}w_{N,S_z})\) and spin-state \((\text{Tr}\{N\}w_{N,S_z})\).

Our results for the pressure-evolution of the calculated valence state and spin-state configurations weights of MnO-NiO are summarized in Figures 9 and 10. Our DFT+DMFT calculations reveal that upon moderate compression (in the Mott insulating regime) all four compounds adopt a \(2^+\) oxidation state of their transition-metal ions with a nominal \(3d^N\) configuration with \(N\) varying from 5 to 8 for MnO-to-NiO, respectively. In fact, at ambient pressure, the nominal \(2^+\) oxidation state has the largest weight of above 70-80%. It reduces to about \(\leq 60\%\) upon compression to \(0.6-0.7 V/V_0\), all in the Mott insulating regime. Interestingly, at ambient pressure the weight of the first excited state corresponding to the \(3d^{N+1}\) configuration is below 20-30\%. However, it tends to increase upon compression, resulting in a remarkable crossover of the valence state of MnO-CoO. In fact, as shown in Figure 9 the Mott IMT (and the concomitant magnetic collapse transition) is found to be accompanied by a sudden change of the electronic state of Mn, Fe, and Co from a \(3d^N\) to \(3d^{N+1}\) configuration (\(3d^{N+1}\) state turns to become favorable for Mn to Co), suggesting a crossover of the nominal oxidation state from \(2^+\) to a nearly \(1^+\) state (i.e, the valence of oxygen shifts near to 1-). Below the phase transition, in a correlated metal regime, the electronic state in MnO-CoO can be characterized as a mixed-valent state with a major contribution due to the \(3d^{N+1}\) state (about 50\%), which has a substantial admixture of the \(3d^N\) and excited \(3d^{N+2}\) states.

Our results therefore suggest a possible change of the oxygen valence state under high pressure which is not \(2^-\) as at low pressure but rather varies near to \(1^-\) due to oxygen-oxygen interactions. We note that similar behavior has been proposed to occur in iron oxide FeO \(_2\), where an altered valence state of oxygen around to \(1^-\) instead of \(2^-\) value was found \[39\]. This suggests that oxygen may also have multiple valence states in oxide minerals under deep Earth conditions.

Interestingly our results for NiO also reveal a sudden change of the \(3d^8\) atomic configuration weight at the Mott transition. However, in contrast to MnO-CoO, in a correlated metal phase the \(3d^8\) (i.e., \(\text{Ni}^{2+}\)) states remain to be predominant, with a weight of above 55\% and a large \(\sim 40\%\) admixture of the \(3d^9\) excited state (below \(\sim 0.47V_0\), corresponding to \(\sim 700 \text{ GPa}\)), implying a crossover from localized to itinerant moment behavior.
under pressure. Our results therefore suggest the absence of the valence crossover in NiO. Moreover, this behavior seems to be consistent with a very slight change of the total Wannier 3d charge in NiO under pressure. It increases by $\sim 0.1$ electrons upon compression to $\sim 400$ GPa (the oxygen 2p charge respectively decreases). On the other hand, the change of the Wannier 3d charge in MnO, FeO, and CoO is more significant (up to 0.4-0.5 electrons) upon pressurizing to $\sim 150$ GPa that seems to be a consequence of emptying of the antibonding $e_g^t$ states under pressure. The latter leads to a different strength of covalent $p-d$ bonding above and below the magnetic collapse transition.

We also compute the pressure-induced evolution of the local magnetic state of paramagnetic MnO-NiO. In Figure 10 we display our results for the corresponding probabilities of the spin-states of the 3d electrons (e.g., in MnO, these are the HS: $|d^6_{S_z=5/2}| + |d^6_{S_z=3/2}|$, IS: $|d^7_{S_z=3/2}|$ + $|d^7_{S_z=1/2}|$, and LS: $|d^8_{S_z=1/2}|$ + $|d^8_{S_z=0}|$ + $|d^8_{S_z=1/2}|$ for MnO), are shown.

FIG. 10: Our DFT+DMFT results for the spin-state configurations weights of MnO, FeO, CoO and NiO as a function of relative volume $V/V_0$. Different spin-state contributions, e.g., the HS: $|d^6_{S_z=5/2}| + |d^6_{S_z=3/2}|$, IS: $|d^7_{S_z=3/2}|$ + $|d^7_{S_z=1/2}|$, and LS: $|d^8_{S_z=1/2}|$ + $|d^8_{S_z=0}|$ + $|d^8_{S_z=1/2}|$ for MnO, are shown.

In conclusion, we determine the electronic structure, magnetic state, and structural properties of correlated transition metal monoxides MnO, FeO, CoO, and NiO in the rocksalt B1 crystal structure at high pressure and temperature using the DFT+DMFT method. We obtain that under pressure MnO-NiO exhibit a Mott IMT which is accompanied by a simultaneous collapse of local magnetic moments and lattice volume, implying a complex interplay between chemical bonding and electronic correlations. We explain a monotonous decrease of the Mott IMT transition pressure $p_c$ which varies from $\sim 145$...
to 40 GPa, upon moving from MnO to CoO, and then suddenly increases to \(~429\) GPa. We provide a unified picture of such a behavior and suggest that it is primarily a localized to itinerant moment behavior transition at the Mott IMT that gives rise to magnetic collapse in transition metal oxides.

We have shown that the interplay between electronic correlations, spin state, and the lattice in the vicinity of the Mott IMT results in the formation of a complex electronic and magnetic states of MnO, FeO, CoO, and NiO under pressure. In particular, the Mott IMT and collapse of the local moments in MnO, FeO, and CoO under pressure are found to be accompanied by a sharp crossover of the valence state, implying a complex interplay between the charge, spin, and lattice degrees of freedom. This suggests a remarkable importance of the valence fluctuations for understanding the electronic state of correlated systems near the Mott transition. In fact, this is in connection to quantum critical phenomena, i.e., the quantum critical nature of the Mott transition and (possible) quantum valence criticality near the Mott transitions. Most importantly, we provide a novel microscopic explanation of the magnetic collapse of all these compounds. On the basis of our DFT+DMFT calculations we observe three distinct scenarios: a) magnetic collapse caused by the appearance of the IS state, strongly competing with the LS state in MnO; b) a conventional HS-LS crossover in FeO, and c) a remarkable coexistence of the HS and LS states (HS-LS frustration) in CoO. We propose that quantum fluctuations of the valence and spin states emerging near the Mott transition may have important implications for the understanding of quantum criticality of the Mott transitions. Finally, we point out the importance of further theoretical and experimental investigations of the above discussed correlated compounds using, e.g., x-ray absorption spectroscopy and electron energy-loss spectroscopy, which are powerful probes of a valence state.

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