

Exchange-induced negative- U charge order in N-doped WO_3 : A spin-Peierls-like systemMuhammad N. Huda,^{*,†} Yanfa Yan, Su-Huai Wei, and Mowafak M. Al-Jassim
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An unconventional spin-Peierls-type distortion was found in a nonmagnetic atom N doped pseudo-one-dimensional WO_3 system. The periodicity of the initial ferromagnetic WO_3 :N is doubled in one direction, and the band gap opens up due to this distortion. The magnetic moment at the N site is asymmetric in the distorted system, and the interaction between the localized spin is very weak. We show that the large exchange interaction of the nitrogen $2p$ atomic orbital and the pseudo-one-dimensional W-O-W chain in monoclinic WO_3 structure is the origin of this spin-Peierls-like transition that leads to the stabilization of an unusual negative- U charge-ordered system.

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I. INTRODUCTION

Spontaneous transition of materials from a symmetric lattice system to a distorted one due to electronic or spin interaction with phonons has generated much interest because of their potential applications in piezoelectric, magnetoelectric, and magneto-optical applications. In the conventional spin-Peierls transition,¹ the spin related lattice instability occurs in a crystal containing a soft, quasi-one-dimensional spin chain of half-integer spin with antiferromagnetic (AFM) arrangement. A finite magnetoelastic coupling between the spins in one dimension leads to a dimerization of the spins (forming a spin singlet) and doubles the periodicity of the crystal in the chain direction. The spin-Peierls transition has been observed only in AFM system containing $3d$ transition metal ions or post transition ions, such as CuGeO_3 .² This is partly because ferromagnetic (FM) coupling in strictly one dimensional chain is not possible.³ In this paper, we show that the monoclinic WO_3 , which can be considered as a quasi one dimensional system because of the weak interchain interactions, can sustain an unusual spin-Peierls transition from a ferromagnetic to a charge ordered, negative- U (Ref. 4) ground state when it is doped with sufficient concentration of N substituting on the oxygen site. The origin and nature of the magnetism and spin-Peierls transition in this system are discussed below.

WO_3 in the ground state monoclinic structure is a semiconductor with a direct band gap of 2.7 eV.⁵ It has many interesting physical properties such as electrochromical effect⁶ and superconductivity.⁷ Recently, it has also been considered for applications in photoelectrochemical water splitting.⁸ Collective magnetic moment in doped WO_3 has not been discovered yet. Achieving magnetism in such a $5d$ transition metal oxide is not straightforward, mainly due to the larger delocalized nature of W $5d$ orbital compared to transition metal $3d$ states. Recently, however, it has been shown both theoretically and experimentally that magnetism in several oxide compounds can be induced by hole doping at the oxygen site by nonmagnetic dopants such as N and C.^{9,10} This is because the oxygen atomic $2p$ orbital is much localized with large spin-exchange interaction parameters, even larger than the $3d$ transition metals. The spin-polarization in such systems can be further enhanced if the

impurities with localized $2p$ orbital defect levels are forced to be confined in lower-dimensional system¹¹ such as in WO_3 . However, the presence of the magnetic moment in a “soft” one dimensional system may induce lattice instability due to spin-phonon coupling. In this paper, we show by first-principles density functional theory (DFT) calculations that nitrogen doping in WO_3 can create collective magnetic moments. Moreover, we find that at relatively large N concentration ($\sim 4\%$), a spin and charge ordering can occur at the N_O site, results in a Peierl’s-type periodic lattice distortion. We show that the large exchange interaction in the W-O-W chain structure in monoclinic WO_3 plays an important role in stabilizing this unusual negative- U charge-ordered system.

II. METHODS

The total energy and band structure calculations are performed using the local density approximation (LDA)¹² to the DFT and the projected augmented wave (PAW) method,¹³ as implemented in the Vienna *ab initio* simulation package (VASP 4.6.21).¹⁴ The LDA calculation produces a very good agreement with the experimentally measured volume for WO_3 (see Ref. 8). The cutoff energy for the basis set is 400 eV, and the Brillouin zone (BZ) integrations were performed using the second-order Methfessel-Paxton method.¹⁵ The calculated lattice constants (and volume) of the pure WO_3 were kept fixed in the defect calculations. To check the final conclusion, we relaxed the volume of some of the relevant structures fully, and found that the final conclusion was not affected by this relaxation. However, the internal ion positions were always relaxed until the force on each of them is 0.01 eV/Å or less. For ion relaxation, a $2 \times 2 \times 2$ Monkhorst-Pack¹⁶ k -point sampling was used; however, for density-of-states (DOS) plots, a more refined $8 \times 8 \times 8$ (or $4 \times 8 \times 8$, for a supercell doubled in one direction) k -points sampling was used. It should be mentioned here, that magnetic interaction calculated with only LDA may provide erroneous conclusions, especially for $3d$ magnetism. However, in the present study, the magnetic moments are mainly originated from N $2p$ bands, and the contribution from W $5d$ bands are small, which are relatively more delocalized than $3d$ bands. So LDA is expected to provide a reasonable qualitative picture here. We have previously tested different

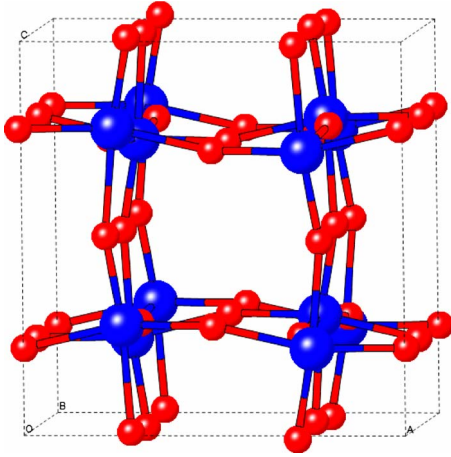


FIG. 1. (Color online) A unit cell of WO_3 . It has ABO_3 type perovskite structure with a vacant A position. Blue (larger dark gray) and red (smaller gray) are the W and O atoms, respectively.

N-doping configurations within WO_3 supercell at various concentrations.⁸ In this paper we are particularly interested in the exchange induced pseudo-one-dimensional phenomenon as described below. This mechanism may also occur in other “soft” one dimensional system where exchange interaction plays a pivotal role.

III. RESULTS AND DISCUSSIONS

The smallest monoclinic unit cell of WO_3 consists of 8 W atoms and 24 O atoms. The monoclinic WO_3 can be considered as a deformed perovskite structure, ABO_3 , where the A site ions are missing and the B site is occupied by W.¹⁷ The WO_3 structure can also be considered as consisting of W-O-W-like chains, where the chains are connected across the W atoms, as seen in Fig. 1. The interchain O-O interactions are rather weak. The valence band maximum (VBM) of WO_3 is mainly composed of O $2p$ orbital, and the conduction band minimum (CBM) has major contribution from W $5d$ orbital.⁸ When an oxygen atom is substituted by a nitrogen atom in WO_3 , a VBM derived N defect level (or defect bands at high N concentration) with N $2p$ orbital character appears above the VBM. The system could be spin polarized when the hole carrier density is sufficiently large. Figure 2 shows the total DOS and N $2p$ partial DOS (p -DOS) when 4% oxygen are replaced by N. Partially occupied N- $2p$ state is clearly seen at the Fermi level, which is responsible for the magnetic moment ($1\mu_B$ per N) found in the unit cell. The exchange splitting of the N- $2p$ band is about 0.4 eV. The corresponding nonmagnetic configuration was found to be 0.09 eV higher in total energy than the ground state ferromagnetic phase. As in all the d^0 magnetic system, the magnetic moment here is not exactly local to the N atom; rather we found that the N atom carried about 60% of the total magnetic moments. It has been known that in this type of d^0 magnetic system, the spin polarization and magnetic interaction is not a monotonic function of impurity concentration. To test this, we doubled the primitive unit cell in one direction and reduced the N atom concentration by half to about 2%. At this lower level of

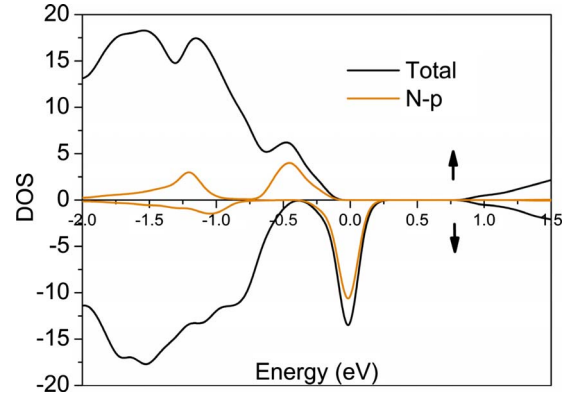


FIG. 2. (Color online) Total DOS and N p p -DOS for N substitution in WO_3 at the level of 4% doping. For clarity, the N p p -DOS is multiplied by a factor of 3. The arrows in the figure represent up spin (\uparrow) and down spin (\downarrow).

doping, we find that the system is still spin polarized with one μ_B per N atom, which results from a completely empty band above the VBM. The distance between two magnetic N atoms in this structure is more than 14 Å, so a mutual N-N interaction to sustain a FM state is unlikely. On the other hand, substituting all the O atoms in a given chain by N atoms leads to a nonmagnetic state due to the broadening of the N- p band.

Our calculations above with one N impurity in the monoclinic primitive unit cell (4% N) indicate that the system is spin polarized and can be FM. However, the high DOS at the Fermi level (Fig. 2) also give an indication that a Peierls¹⁸ or Jahn-Teller¹⁹ type distortion may occur in this system, because the density of states at the Fermi energy can be directly related to the electron-phonon coupling.²⁰ To test the possibility of such distortion, we have constructed a larger supercell. In this larger supercell the spin at N sites can have either FM or AFM configuration. We found that the FM configuration is 0.08 eV lower in energy than the AFM configuration. However, despite this high-exchange energy this FM configuration was not stable. Interestingly, a spin-charge ordering, associated with a lattice distortion in one direction has been found upon further relaxation of the bigger supercell. Figure 3 shows the structure of W-N-W chain segment before and after the lattice distortion of the FM phase. In both cases, the net magnetic moment per two N atoms in the

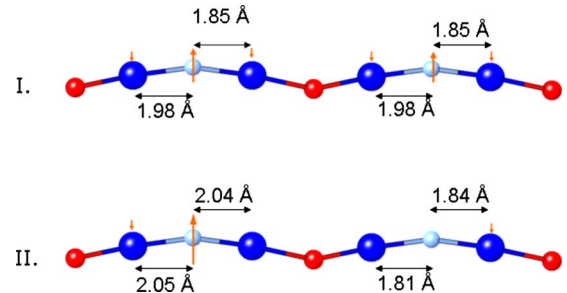


FIG. 3. (Color online) W-N-W chain segments in x direction are shown, before (Scenario-I) and after (Scenario-II) charge ordering. Light blue (small light gray), blue (large dark gray), and red (small gray) are the N, W, and O atoms, respectively.

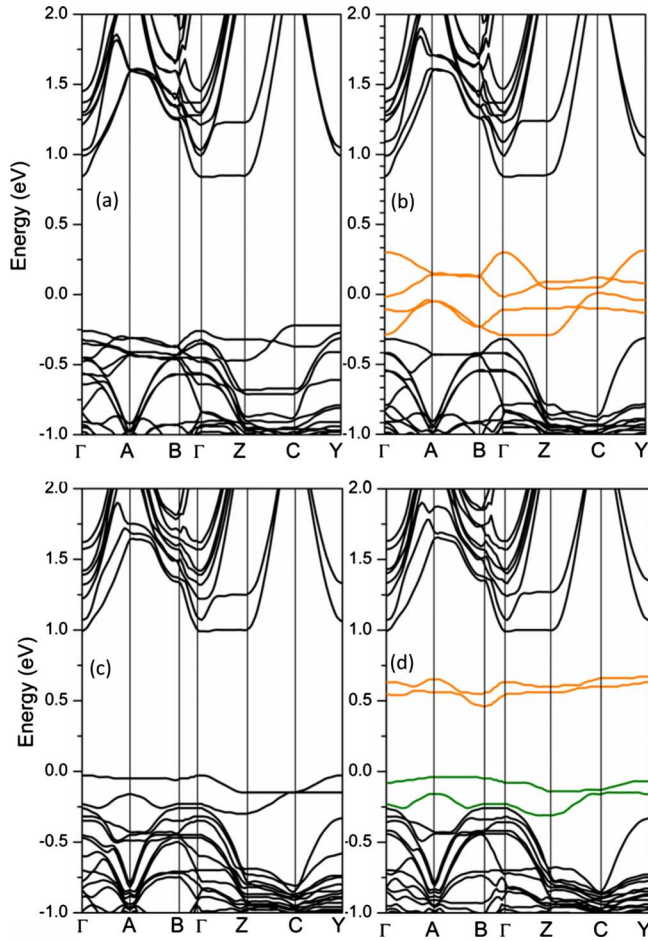


FIG. 4. (Color online) Band structure of N substituted WO_3 before [spin up (a) and spin down (b)] and after charge ordering [spin up (c) and spin down (d)]. The band gap opening is seen in the later case. The orange bands at VBM in (b) are the partially filled N p band; whereas in (d) the unoccupied and occupied N p bands after band gap opening are shown in orange (light gray) and in green [dark gray above VBM in (d)] bands, respectively.

supercell remained $2\mu_B$, but, surprisingly, the physical situations in the two cases are completely different. First of all, in the symmetric case (Scenario-I), all the substitutional N-atoms have the same magnetic moments, and all the corresponding W-N bond lengths in each primitive cell were equal. However, in the distorted case (Scenario-II), one of the N atoms, N^- , in the chain received an extra electron, and become nonspin polarized, whereas the other N-atom, N^+ , loses the electron and becomes a magnetic ion with a magnetic moment of $2\mu_B$. Here, “-” and “+” sign represents the nominal defect charge state. Consequently, the W-N distances showed significant distortions. The N^+ -W bonds ($\sim 2.04 \text{ \AA}$) is much longer than the N^- -W bonds ($\sim 1.82 \text{ \AA}$). This distortion runs periodically along the W-N chain. It leads to a band gap opening at the Fermi level and energy lowering of 0.10 eV per N atom.

Figure 4 shows the band structure for these two scenarios as described above. In Scenario-I [Fig. 4: (a) spin up (b) spin down] with a symmetric FM configuration, the system has partially filled intermediate bands in the band gap in the

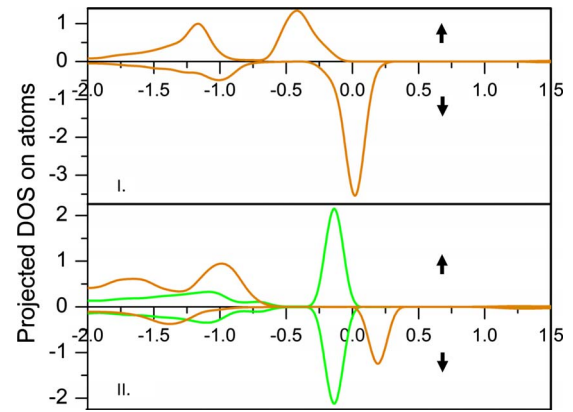


FIG. 5. (Color online) N p p -DOS for symmetric (Scenario-I) and charge ordered (Scenario-II) WO_3 :N. In (II), the two N atoms in the supercell are distinguished, the one which received electrons is in green (light gray), and the one which possesses the magnetic moment is in orange (gray). The arrows in both the scenarios represent up spin (\uparrow) and down spin (\downarrow).

spin-down channel. These bands have mainly the N- p character, as discussed above, with some W- d and O- p I contribution. However, in Scenario-II [Figs. 4(c) and 4(d)], where we have the spin and charge-ordering-induced distorted W-N chain, the band structure shows a splitting of the partially occupied band with a nonzero band gap in the spin-down channel, as expected from the Peierl’s type distortion. The splitted upper band is completely unoccupied, and the lowering of the occupied split-off bands lowers the total energy of the system. The DOS plot in Fig. 5 shows an interesting feature for Scenario-II: the upper unoccupied band mainly comes from the N atom, which has lost an electron, whereas the highest occupied band has contribution mainly from the nonmagnetic N atoms. This clearly shows the spin and charge localization in Scenario-II. To examine the spin effect in the distortion, we have performed nonspin polarized calculations on the undistorted FM system (Scenario-I), and no distortion has been found upon further relaxation. The non-spin polarized calculation also showed that the system is metallic. This clearly demonstrates that spin-exchange interaction plays an important role in the lattice distortion, cell doubling, and band-gap opening.

In earlier studies^{21,22} by model Hamiltonian approach, it has been shown that for half-filled band in one dimension without spin, no dimerization took place at lower electron-phonon coupling strength. However with spin, dimerization took place at all coupling strength. In a later study,²³ which includes quantum phonon fluctuations within the molecular crystal model, similar results were also presented. It showed that although at strong electron-phonon coupling dimerization took place in both spin-less and spin-1/2 systems, Peierl’s dimerization can be destroyed by quantum phonon fluctuations for spin-1/2 electron systems. However, these studies did not consider FM system explicitly. In addition, lattice distortions due to these interactions are also important for the discussion of superconductivity. Creation of a negative- U site has shown to play an important role in this.²⁴ However, discussion on the origin of these sites and their effect on the electronic and magnetic properties of a system

are limited in the literature, especially by first principle theories. A previous DFT study consider charge disproportionate system in BaBiO_3 ($\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$), but a “LDA- U ” (not “+”) like method was needed to achieve this.²⁵

For the present study on WO_3 , LDA was sufficient to show the negative- U effect in the pseudo-one-dimensional system. Also, as discussed above, our LDA ground state results showed no distortion for nonspin polarized case and “dimerization” took place only in spin-polarized case. The charge redistribution accompanied by lattice distortion around the N sites resulted in large energy gain in our present system. The amount of energy gain in this system may be used as an indicator of the strength of electron-phonon coupling.²⁶ It is known that the strength of the mass enhancement parameter (λ) can be related to the electron-phonon coupling strength. In the frozen-phonon approximation, this mass enhancement can be related to the distortion seen in the present case. Comparing the dispersion of the highest-occupied band in Figs. 4(b) and 4(d), one can see that the effective mass of the electrons enhanced significantly due to the distortion created by the charge ordering. Physically, this mass enhancement is a result of the localization of the extra electron at the N^- -site in Scenario-II of Fig. 3. In fact, a higher negative- U would in general enhance the effective mass of the carrier further.

Now, can the magnetization in scenario-II lead to long range ferromagnetic order? To answer this question, we have performed an even larger supercell (4 unit cell in the chain direction) calculation with full relaxation. We found that in this case the distance between the two magnetized N atoms is more than 14 Å. Consequently, the total energy difference between the AFM and FM is insignificant. So a long-range magnetic correlation may be unlikely here. It is possible that the overall state of the distorted system will be paramagnetic.

The periodic distortion observed in this system resembles the famous spin-Peierls distortion in quasi-one-dimension system.² However, it also shows its unique features. (i) The conventional spin-Peierls occurs only in AFM system, but in this case, $\text{WO}_3:\text{N}$ was ferromagnetic before the distortion, after distortion the system is paramagnetic. (ii) In conventional spin-Peierls system the magnetic moment is derived from transition or post-transition metals that has d -orbital induced multivalence character, but in $\text{WO}_3:\text{N}$, the magnetic

moment was caused by the nonmagnetic atom N substituting on O site. The negative- U ($2\text{N}^0 \rightarrow \text{N}^+ + \text{N}^-$) behavior of N in WO_3 is quite unusual as the process has to overcome the onsite Coulomb repulsion interactions. We find that this unconventional spin-Peierls distortion is stabilized by large spin-exchange interaction of the N $2p$ states and the large interatomic Coulomb interactions. Figures 4 and 5 show that, when one electron moves from one N to the other N, forming N^+ and N^- atoms, due to the strong spin-exchange interaction, the energy levels of the occupied majority spin N^- $2p$ states move down in energy significantly, therefore, lower the total energy, which is also associated with the local lattice distortion to compensate Coulomb repulsion. The resulting interatomic interaction between the charged ions also lowers the total energy, which is significant in the oxide with small bond lengths. Furthermore, the soft quasi-one-dimensional chain in monoclinic WO_3 also makes it easier to reduce the strain energy caused by the charge transfer. These combined effects lead to the unconventional ferromagnetic spin-Peierls distortion, which stabilized this negative- U , charge-ordered system with $2\mu_B$ total magnetic moment per two N atoms.

IV. CONCLUSIONS

In conclusion, the occurrence of charge ordering caused by spin related instability has been found in N doped WO_3 . The periodicity of the ferromagnetic $\text{WO}_3:\text{N}$ is doubled in one direction, and a band gap opens up due to this distortion. After the distortion the system was found to be paramagnetic. This unconventional ferromagnetic spin-Peierls transition is explained as a spin exchange driven negative- U effect. The large exchange parameter of atomic $2p$ orbitals and pseudo-one-dimensional nature of WO_3 are found to be responsible for these effects.

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