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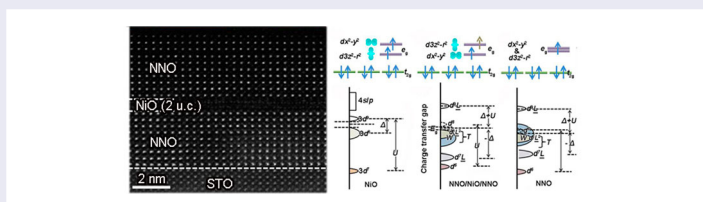
The role of pd hybridization in the metal-insulator transition in NdNiO_3 heterostructure

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ABSTRACT

Understanding and controlling phase transition in the transition-metal oxides is interesting from the fundamental physics point of view. The pd hybridization are of considerable issue to tune the phase transition temperature. Here, the transport properties of the NdNiO_3 with artificial ultra-thin NiO insert layer have been investigated. The relationship between the essential parameters of the pd hybridization (T) and the metal-insulator transition (MIT) temperature has been clearly elucidated a monotone decreasing relationship. This work realized the combination of the engineering hybridization and the phase transition temperature, which might be significant for the development of multifunctional materials in the transition-metal oxides.



IMPACT STATEMENT

The pd hybridization are of considerable issue to tune the phase transition temperature. Here, the pd hybridization have been tuned and elucidated a monotone decreasing relationship with the metal-insulator transition temperature.

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KEYWORDS

Hybridization;
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1. Introduction

Metal-insulator transitions (MIT) accompanied by huge resistivity changes are widely observed in condensed-matter systems. The interest in RNiO_3 (RNO ; R = rare earth) has recently been revived by a systematic study on MIT [1–8]. As the quantum criticality of the MIT and the associated magnetic transition has been a key issue in correlated electron systems for decades, understanding and controlling MIT in this specific family is not only interesting from the fundamental physics point of view but also provides great opportunities for future electronic devices [9–14].

The ground state in RNiO_3 can be described by a strong mixture of d^7 , $d^8\bar{L}$, and $d^9\bar{L}^2$ configurations. Until to now, there is a debate about whether nickelates are Mott-Hubbard (MH) insulator, charge-transfer (CT) insulator, negative CT insulator, Heitler-London insulator or even band insulator [1,15–18]. Early band-structure calculations and valence-band photoemission show that three essential parameters are the key issue to drive the interactions in these materials: the d - d Coulomb interactions U , the energy CT energy Δ and their hybridization strength (T), which is encapsulated in the p -bandwidth (W) [18,19,11]. S. R. Barman *et al.*

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have suggested that the MIT in this series is driven neither by a change in U nor by a change in Δ based on extensive experimental and theoretical results [20]. The spectroscopic data and density of states (DOS) calculations suggested that the MIT in these compounds arises from the changes in the e_g bandwidth. According to their Hartree–Fock band-structure calculations on the p - d model, the decrease in the e_g bandwidth is due to an experimentally observed decrease in T [18,20].

Here, we perform a detailed study on an intensively studied model system, namely, heterostructure composed of NdNiO₃/NiO (NNO) to investigate the relationship between the hybridization strength and MIT. NNO belong to a pd metal. NiO is a prototype covalent insulator. One of the probes sensitive to the high-energy scale of the problem is core photoemission which could direct response of the pd hybridization strength (T). In addition, the magnitude of the covalency W also has been investigated. The change of the essential parameters of T or W is in accordance with the induced MIT.

2. Experimental section

2.1. Sample fabrication

The NdNiO₃ (8 u.c.) was grown on STO (001) substrates by pulsed laser deposition (PLD) using a XeCl ($\lambda = 308$ nm) excimer laser. The laser flux is 1 J/cm² with a repetition rate of 2 Hz. Then the NiO films with the thickness of 1, 2 and 3 u.c. were grown by molecular beam epitaxy (MBE) at 550°C in a 2.5×10^{-5} mbar ozone atmosphere. The fluxes of the effusion cells were calibrated with a quartz crystal monitor before growth. At last, an NdNiO₃ (8 u.c.) cap layer has been deposited on the samples by PLD. All the samples have been abbreviated NNO, NNO-1, NNO-2 and NNO-3 for the NiO thickness of 0, 1, 2 and 3 u.c. The NNO and NiO pure films as reference samples were also grown on STO under the same conditions.

2.2. STEM

The scanning transmission electron microscopy (STEM) was operated at 200 kV (JEM-2400FCS, JEOL Ltd.). Electron energy loss spectroscopy (EELS) spectra were obtained using a monochromatic aberration corrected STEM, equipped with a double Wien filter monochromator and a Gatan Image Filter system (Tridiem ERS, Gatan, Inc.). The final energy resolution determined by the full-width at half-maximum of the zero-loss peak is 0.6 eV. For high loss mapping, a 8 s pixel dwell time and 0.2 eV channel dispersion were used. The background signal of all the EELS spectra was subtracted by using a classical power law fitting.

2.3. XPS and XAS

The high-energy core photoemission has been determined by X-ray photoelectron spectroscopy (XPS) (Therma ESCALAB 250; Al K α source, 1486.60 eV, Energy step: 0.1 eV) experiments. Oxygen K -edge and Ni L -edge X-ray absorption spectroscopy (XAS) are performed at beamline BL08U1A of Shanghai Synchrotron Radiation Facility (SSRF) carried out in total electron yield (TEY) mode at room temperature with an energy resolution of 0.1 eV. The background vacuum level was 8×10^{-7} Torr.

2.4. Transport properties measurement

The transport properties are measured in a Quantum Design Physical Property Measurement System (PPMS).

3. Results and discussion

High-quality NNO/NiO/NNO have been obtained with the thickness of the NiO insert layer increased from 0 to 3 u.c. Detailed structure characterizations can be found in Figure S1. Figure 1(a) shows the temperature-dependent resistivity (ρ) for the NNO films with different thicknesses of NiO insert layer. Note that the T_{MIT} and the Néel temperature (T_N) were obtained from taking the derivative of the R vs. T plots in the cooling progress, as shown in Figure 1(b–e). The temperature at which $d\log(\rho)/dT$ crosses zero is taken as T_{MIT} and the change of slope in $d\log(\rho)/dT$ and $d\log(\rho)/d1/T$ is taken as T_N . The change of slope in $d\log(\rho)/dT$ is taken as T_N due to the spin scattering. It is noted that the spin-fluctuation is weak in antiferromagnetic systems. The change of slope in $d\log(\rho)/dT$ does not depend on the exact values of T_N . As such, the calculated values of T_N used the change of slope in $d\log(\rho)/dT$ should be viewed as a rough guide and not as exact. In addition, the anomaly in $d\log(\rho)/d1/T$ can reflect the energy gap of magnetic insulators which is much more sensitive with the phase transition, gives an alternative way of determining the values of T_N . The results are shown in Figure 1(b–e) for the four films studied. For the films on the tensile STO substrate, the MIT shifts to higher temperatures with increasing the NiO thickness. Figure 1(b–e) also show that T_{MIT} increases from 63 K for the NNO(8 u.c.)/NiO(1 u.c.)/NNO(8 u.c.) to 135 K for the NNO(8 u.c.)/NiO(3 u.c.)/NNO(8 u.c.). The Néel temperature increased from 30 K to 86 K with increasing the NiO thickness.

For large U in the NNO, the presence and magnitude of a band gap is basically determined by the two important parameters in the multi-band Hubbard theory model: the ligand p -bandwidth (W) and the p - d

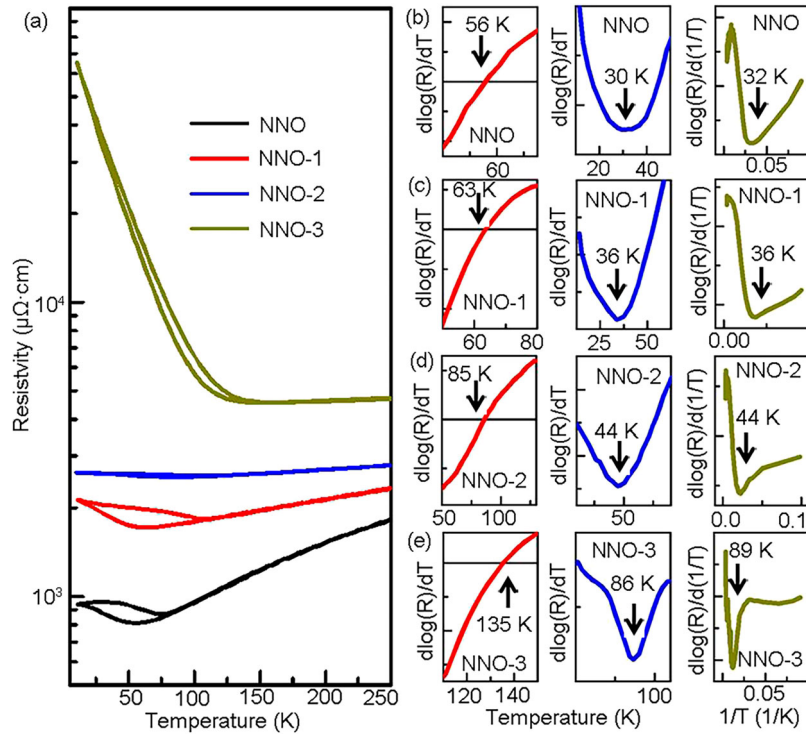


Figure 1. (a) ρ - T curves for a variety of NdNiO₃ films with different NiO insert layer thicknesses (t) grown on STO substrate. (b–e) show the metal-insulator and Néel transitions derived by $d\log(\rho)/dT$ crosses zero is taken as T_{MIT} and the change of slope in $d\log(\rho)/dT$ and $d\log(\rho)/d(1/T)$ is taken as T_N .

hybridization (T) [20,21]. Figure 2(a) shows the representative EELS spectra of the NNO-1. The fine structure of the O- K core edges was measured from pre-selected areas in Figure 2(b) (open circles). The EELS curves of NNO at the O- K core edge exhibited four well-defined peaks in Figure 2(b). The O- K edge onset around 528.5 eV (peak labeled A) corresponds to the Ni 3d band region. It is noted that this peak decreases near the interface and almost disappears in the NiO layer. EELS studies have connected the appearance of shoulder peak around 530.5 eV (peak labeled B) with such changes in this local crystal field [22]. The O K -edge EELS spectra revealed spectral weight of the pre-peak derived from Ni-O hybridized states reduced in the NNO layers. In order to see the spectra change across the interface clearly, Figure 2(c) summarizes the relative area of the pre-peaks (A) and the shoulder peaks (B), which is calculated by the integral of the area of these peaks, with the area of the bulk NNO and NiO set to 100% for the Ni³⁺ and Ni²⁺ peaks, respectively. The presence of the areas change for the Ni³⁺ and Ni²⁺ ions in the interface region indicates that the charge disproportionation of the type: Ni³⁺ $\rightarrow$ Ni²⁺ occurs occurred within about 2~3 u.c. thickness in the interface region. At the interface, a reduced pre-peak corresponds to a smaller hybridization of Ni and O compared to the NNO. A CT implies changes lies in the transfer interaction between the Ni e_g and O

2p orbitals and the MIT may be viewed as electronically driven [18].

To further elucidate the electronic structure for these heterostructures, the XAS measurements on the O K -edge have been performed. Figure 2(d) shows the XAS results obtained at the threshold energy around 528.5 eV and the values of the pre-peak width decreased with increasing the thickness of the NiO insert layer. The atomic resolved pre-peak width for the O- K edge onset around 528.5 eV (peak labeled A) in Figure 2(c) have been calculated. Interestingly, the values of the pre-peak width decreased across the NNO/NiO interface for all the samples, as shown in Figure 2(e). Aberration-corrected electron microscopy is a key tool for understanding the properties of materials as it provides a means by which the electronic and atomic structure can be investigated at sub-angstrom resolution. However, the XAS gives the results of the average values of the total heterostructures. Figure 2(f) shows that the pre-peak widths calculate from the XAS and the EELS, a measure of a degree of pd hybridization T or covalency W , scales almost mono decreased with increasing the thickness of the NiO insert layer. Microscopically, the decreasing W as a function of the NiO thickness can be attributed to longer in-plane Ni-O bonds or bond angle distortion, Whereas the bond angle distortion would decrease the one-electron bandwidth W , since the effective d electron

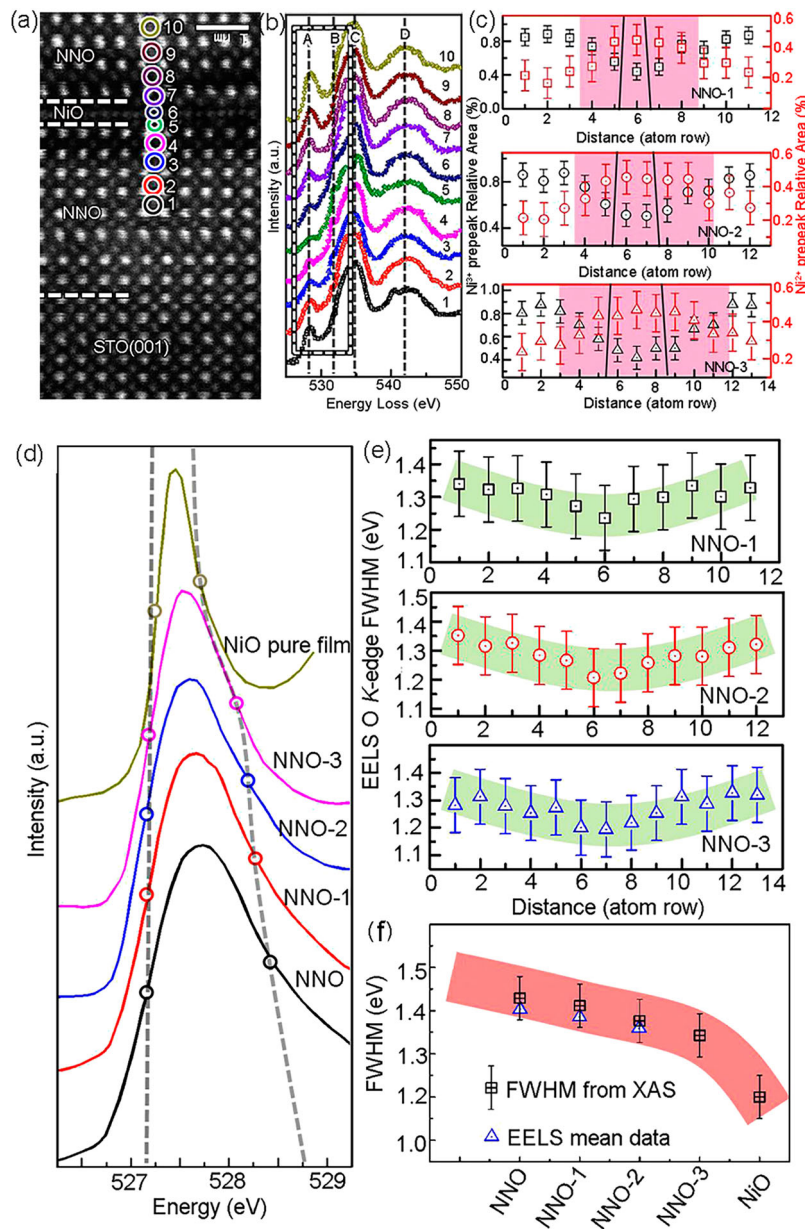


Figure 2. (a) HAADF STEM image of a typical heterostructure of NNO/NiO(1 u.c.)/NNO. (b) Recording the EELS O *K*-edges fine structures evolution across the NNO/NiO(1 u.c.)/NNO interface. (c) The relative area of the pre-peaks (A) and the shoulder peaks (B). (d) The resulting XAS obtained at the threshold energy around 528.5 eV for all the NNO/NiO/NNO heterostructures. (e) The values of the pre-peak width decreased across the NNO/NiO interface for all the samples calculate from the EELS. (f) The pre-peak widths calculated from the XAS and the EELS VS the thickness of the NiO insert layer.

transfer interaction between the neighboring Ni sites is governed by the super transfer process via the O 2*p* state.

The core photoemission is the direct response of the *pd* hybridization strength *T* [23,24]. Figure 3(a) shows the Ni 2*p* spectra for all the samples. It is noted that Ni 2*p* spectra consist of a main peak and an associate satellite peak located at about $\Delta E_{\text{sat}} = 8.2 \pm 0.1$ eV and $\Delta E_{\text{sat}} = 6.5 \pm 0.1$ eV higher binding energy than the main peak for the pure NNO and NiO films, respectively. The ΔE_{sat} decreased evidently with increasing the thickness of the NiO insert layer. The satellite to main

peak energy separation depends mainly on Ni 3*dx*²-*y*²-O 2*p*_x hopping interaction strength, *T*, providing a rather reliable estimate of this interaction parameter [23]. Figure 3(b) summarizes the relative area of the satellite intensity, which is calculated by the integral of the 2*p*_{1/2} satellite area, with the area of NiO to 100%. It is noted the satellite intensity increase monotonically with increasing the thickness of NiO insert layer. In a CT insulator, if the CT energy is small compared to *T*, the *pd* hybridization to the ground state becomes substantial [1,6,18]. Interestingly, as shown in Figure 3(b), the

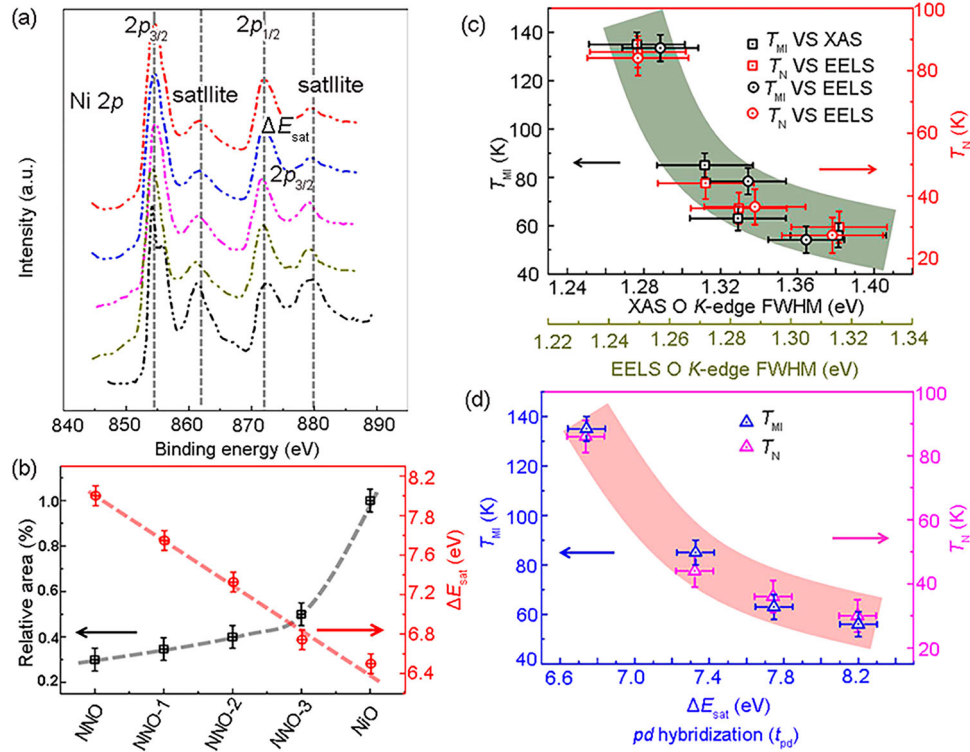


Figure 3. (a) The Ni 2p spectra for all the samples. (b) Summarizes the relative area of the satellite intensity and the satellite to main peak energy separation for all the NNO/NiO/NNO heterostructure. (c) and (d) The MIT temperature and Néel temperature shows a monotone decreasing relationship with the XAS or EELS O *K*-edge pre-peak width (a measure of a degree of covalency *W*) and the values of the ΔE_{sat} (a measure of a degree of *pd* hybridization *T*).

satellite to main peak energy separation, a measure of a degree of hybridization *T*, decreased with increasing the thickness of NiO insert layer, showing a monotone decreasing relationship. Figure 3(c) and (d) show that the MIT temperature and Néel temperature exhibit a monotone decreasing relationship with the XAS or EELS O *K*-edge pre-peak width (covalency *W*) and the values of the ΔE_{sat} (*pd* hybridization *T*). Here, we provide direct evidence based on spectroscopic data, suggesting that the MIT in these compounds arises from the changes in the bandwidth and *pd* hybridization *T*. The *pd* hybridization strength *T* are directly correlated with the phase transition temperature.

With the established strongly altered *pd* hybridization *T* or covalency *W*, we investigated the orbital properties of these engineered states on Ni sites in order to understand the change of phase transition. To this end, the orbital polarization has been measured by x-ray linear dichroism (XLD). To analyze the Ni *L*-edge XLD in a qualitative way, the difference between the XAS in-plane (I_{σ}) and out-of-plane (I_{π}) components, is employed to elucidate Ni 3d orbital occupation. In general, Ni *L*₂-edge arises largely from the unoccupied Ni dx^2-y^2 and $d3z^2-r^2$ states. Figure 4(a–c) shows that, the artificial NiO insert layer would be accompanied by a reduction of x^2-y^2

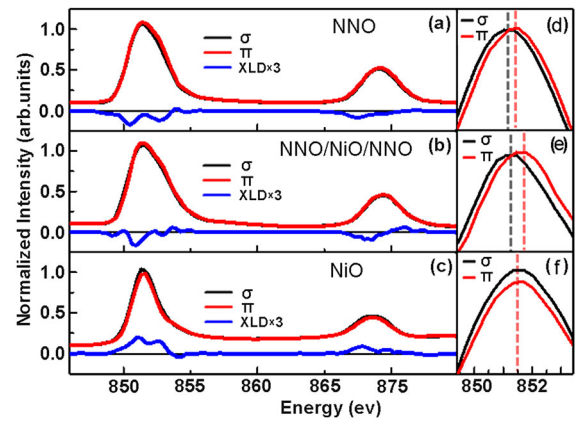


Figure 4. (a)–(c) The XAS spectra measured with linearly polarized light for NNO films, NNO/NiO/NNO heterostructures and NiO films on STO substrate. The normalized difference spectra [$I_{\sigma}-I_{\pi}$] are shown directly below the corresponding spectra. (d)–(f) The XAS of all the samples at Ni *L*₂-edge showing the Ni *e_g* band splitting of $d3z^2-r^2$ (red line) and $d x^2-y^2$ (black line) orbitals. Red and black dashed lines are guidelines for peak center positions.

orbital occupation then promoted the T_{MIT} to higher temperatures. Figure 4(d–f) show that a *e_g* band splitting have been found for the NNO with ultra-thin NiO insert layer which was not observed in tensile-strained ultra-thin NNO films on STO substrate (Figure 4(d)) [10]. It

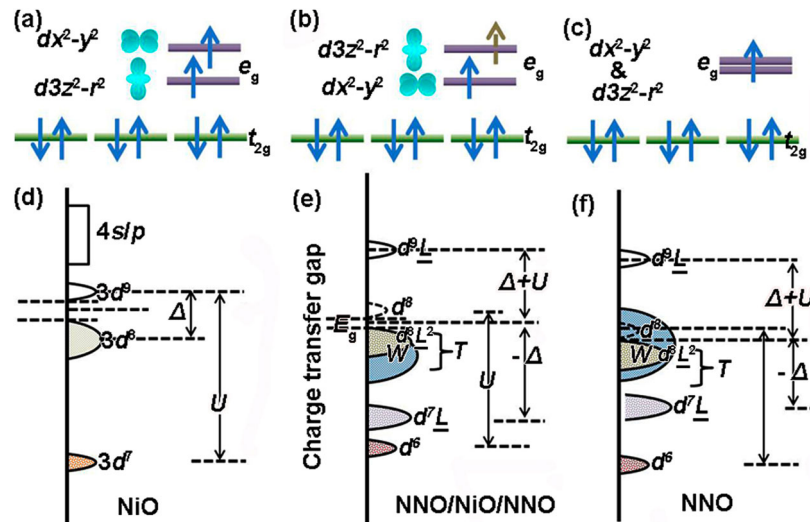


Figure 5. (a–c) Sketch of the engineered electronic, orbital and spin states for bulk NiO, bulk NNO/NiO and NNO, respectively. (d–e) Sketch of the energy bands for bulk NiO, bulk NNO/NiO and NNO, respectively. In NNO with NiO insert layer, it forms peculiar electronic configuration (Ni $3d^7$, $3d^8$ and $3d^8\bar{L}$), and e_g band splitting, forming a charge-transfer gap.

is noteworthy that the out-of-plane absorption is higher in energy than the in-plane absorption at Ni L_2 -edge for the NNO with ultra-thin NiO insert layer, while the contrary is the case for the NiO pure film (Figure 4(e–f)). The difference implies the e_g band splitting between the states with Ni dx^2-y^2 and $d_{3z^2-r^2}$ orbital character, as schematically illustrated in Figure 5(a–c). According to the experimental results, on the one hand, we herein propose an electron doping strategy by chemical route to inject an extra electron to the e_g orbital. With one more electron, Ni³⁺ low-spin configuration $t_{2g}(6)e_g(1)$ converts to Ni²⁺ low-spin configuration $t_{2g}(6)e_g(2)$ due to Coulomb repulsion under the O_h symmetry. The strong Coulomb repulsion between electrons in the single e_g orbital of $t_{2g}(6)e_g(2)$ induces a large MH splitting (as for the case of NiO in Figure 5(d)) and, consequently, helps to make the AF ground states stable. On the other hand, within the Sawatzky–Allen–Zaanen scheme, the electronic configuration of CT-metal NNO is a mixture of low-spin $3d^7$ and high-spin $3d^8\bar{L}$ states with the Fermi energy passing through the strongly mixed Ni–O valence states (Figure 5(e) and (f)). The excitation of an oxygen $2p$ -electron into the unoccupied upper nickel d band forming the charge gap, as shown in Figure 5(e). Therefore, as the ligand bandwidth W decreases or the transfer integral p – d hybridization T increases, the band gap tends to increase.

4. Conclusion

We investigated the transport properties of the NNO with different thicknesses of the ultra-thin NiO insert layer. The energy splitting (ΔE_{sat}) of the Ni $2p$ XPS spectra

(p – d hybridization T) and the O K -edge pre-peak width (covalency W) have been investigated. The relationship between the essential parameters of the bandwidth or the hybridization T and the MIT temperature has been clearly elucidated a monotone decreasing relationship. This work realized the combination of the engineering p – d hybridization the phase transition temperature, which might be significant for the development of multifunctional materials to the application in the microelectronic device.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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