The role of $pd$ hybridization in the metal-insulator transition in NdNiO$_3$ heterostructure

Mingjing Chen$^a$, Xingkun Ning$^a$, Guangsheng Fu$^a$, Shuang Guo$^a$, Lingyun Wang$^a$, Peng Liu$^a$, Jianglong Wang$^a$, Shufang Wang$^a$, Wei Liu$^b$, Jirong Sun$^c$, Tao Yu$^d$ and Zhidong Zhang$^b$

$^a$Hebei Key Lab of Optic-electronic Information and Materials, The College of Physics Science and Technology, Hebei University, Baoding, People’s Republic of China; $^b$Shenyang National Laboratory for Materials Science, Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS), Shenyang, People’s Republic of China; $^c$Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, People’s Republic of China; $^d$Department of Physics, South University of Science and Technology of China, Shenzhen, People’s Republic of China

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.

ARTICLE HISTORY

Received 26 April 2018

KEYWORDS

Hybridization; metal-insulator transition; XPS; XLD; EELS

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 $d^7$, $d^9\Lambda$, and $d^9\Lambda^2$ 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 bandstructure 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 $\Delta$ and their hybridization strength ($T$), which is encapsulated in the $p$-bandwidth ($W$) [18,19,11]. S. R. Barman et al.
have suggested that the MIT in this series is driven neither by a change in $U$ nor by a change in $\Delta$ 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 NdNiO$_3$/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 NdNiO$_3$ (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/cm$^2$ 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 $\times$ 10$^{-5}$ mbar ozone atmosphere. The fluxes of the effusion cells were calibrated with a quartz crystal monitor before growth. At last, an NdNiO$_3$ (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) (Thera ESCALAB 250; Al K$_\alpha$ 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 $\times$ 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 ($\rho$) 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 $\mathrm{dlog(}\rho)/\mathrm{dT}$ crosses zero is taken as $T_{MIT}$ and the change of slope in $\mathrm{dlog(}\rho)/\mathrm{dT}$ and $\mathrm{dlog(}\rho)/\mathrm{d1/T}$ is taken as $T_N$. The change of slope in $\mathrm{dlog(}\rho)/\mathrm{dT}$ 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 $\mathrm{dlog(}\rho)/\mathrm{d1/T}$ does not depend on the exact values of $T_N$. As such, the calculated values of $T_N$ used the change of slope in $\mathrm{dlog(}\rho)/\mathrm{d1/T}$ should be viewed as a rough guide and not as exact. In addition, the anomaly in $\mathrm{dlog(}\rho)/\mathrm{d1/T}$ 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) $\rho$-$T$ curves for a variety of NdNiO$_3$ 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 $T_{\text{MIT}}$ and the change of slope in $d\log(\rho)/dT$ and $d\log(\rho)/dT$ 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 3$d$ 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 change 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 Ni$^{3+}$ and Ni$^{2+}$ peaks, respectively. The presence of the areas change for the Ni$^{3+}$ and Ni$^{2+}$ ions in the interface region indicates that the charge disproportionation of the type: Ni$^{3+}$ → Ni$^{2+}$ 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 2$p$ 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 calculated 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
transfer interaction between the neighboring Ni sites is governed by the super transfer process via the O 2p state.

The core photoemission is the direct response of the \( pd \) hybridization strength \( T \) [23,24]. Figure 3(a) shows the Ni 2p spectra for all the samples. It is noted that Ni 2p 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 \( \Delta E_{\text{sat}} \) 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 2p\(_x\) 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 2p\(_{1/2}\) 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 $\Delta E_{\text{sat}}$ (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 $\Delta E_{\text{sat}}$ ($pd$ 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 ($I_\sigma$) and out-of-plane ($I_\pi$) components, is employed to elucidate Ni 3$d$ 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 $x^2-y^2$ orbital occupation then promoted the $T_{\text{MIT}}$ to higher temperatures. Figure 4(d–f) show that a $eg$ 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].
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 $d_{x^2-y^2}$ 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, Ni$^{3+}$ low-spin configuration $t_{2g}(6)e_{g}(1)$ converts to Ni$^{2+}$ low-spin configuration $t_{2g}(6)e_{g}(2)$ due to Coulomb repulsion under the $O_6$ 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 $3d^8L$ states with the Fermi energy passing through the strongly mixed Ni-O valence states (Figure 5(e) and (f)). The excitation of an oxygen 2$p$-electron into the unoccupied upper nickel 3$d$ 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 ($\Delta E_{\text{sat}}$) of the Ni 2$p$ 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 $pd$ hybridization the phase transition temperature, which might be significant for the development of multifunctional materials to the application in the microelectronic device.

Acknowledgements

The authors acknowledge the support of all the staff at beamline BL08U1A in Shanghai Synchrotron Radiation Facility (SSRF) and XMCD beamline in National Synchrotron Radiation Laboratory (NSRL).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work is supported by the National Natural Science Foundation of China [grant no. 11604073, 51372064], the Nature Science Foundation of Hebei Province [grant no. A2017201104, E2017201227], the National Science Foundation of Education Department of Hebei Province [BJ2017046], the One Province and One School fund and the Graduate Student Innovation fund Project in Hebei Province [no. CXZZBS2017023].

References

[1] Torrance JB, Lacorre P, Nazal AI, et al. Systematic study of insulator-metal transitions in perovskites RNiO3.
(R = Pr, Nd, Sm, Eu) due to closing of charge-transfer gap. Phys. Rev. B. 1992;45:8209.

[2] Torriss B, Margot J, Chaker Met al. Metal-Insulator transition of strained SmNiO₃ thin films: structural, electrical and optical properties. Sci. Rep. 2017;7:40915.

[3] Onozuka T, Chikamatsu A, Katayama T, et al. Reversible changes in resistance of perovskite nickelate NdNiO₃ thin films induced by fluorine substitution. ACS Appl. Mater. Interfaces. 2017;9:10882.

[4] Wang L, Dash S, Chang L, et al. Oxygen vacancy induced room-temperature metal-insulator transition in nickelate films and Its potential application in photovoltaics. ACS Appl. Mater. Interfaces. 2016;8:9769.

[5] Vardi N, Anouchi E, Yamin T, et al. Ramp-reversal memory and phase-boundary scarring in transition metal oxides. Adv. Mater. 2017;29:1605029.

[6] Lacorre P, Torrance JB, Pannetier J, et al. Synthesis, crystal structure, and properties of metallic PrNiO₃: comparison with metallic NdNiO3 and semiconducting SmNiO₃. J. Solid State Chem. 1991;91:225.

[7] Girardot C, Kreisel J, Pignard S, et al. Scattering investigation across the magnetic and metal-insulator transition in rare earth nickelate (R = Sm, Nd) thin films. Phys. Rev. B. 2008;78:104101.

[8] Bruno FY, Rushchanskii KZ, Valencia S, et al. Rationalizing strain engineering effects in rare-earth nickelates. Phys. Rev. B. 2013;88:195108.

[9] Kurita K, Chikamatsu A, Shigematsu K, et al. Effects of Cr substitution on the magnetic and transport properties and electronic states of epitaxial thin films. Phys. Rev. B. 2015;92:115153.

[10] Peng JJ, Song C, Wang M, et al. Manipulating the metal-to-insulator transition of NdNiO₃ films by orbital polarization. Phys. Rev. B. 2016;93:235102.

[11] Chen MJ, Ning XK, Wang ZJ, et al. Polarization and charge-transfer effect on the transport properties in two-dimensional electron gases/LaNiO₃ heterostructure. Appl. Phys. Lett. 2018;112:021601.

[12] Heo SY, Oh C, Son JW, et al. Influence of tensile-strain-induced oxygen deficiency on metal-insulator transitions in NdNiO₃₋δ epitaxial thin films. Sci. Rep. 2017;7:4681.

[13] Guo H, Li ZW, Zhao L, et al. Antiferromagnetic correlations in the metallic strongly correlated transition metal oxide LaNiO₃. Nat. Commun. 2018;9:43.

[14] Shi J, Zhou Y, Ramanathan S. Colossal resistance switching and band gap modulation in a perovskite nickelate by electron doping. Nat. Commun. 2014;5:4860.

[15] García-Muñoz JL, Amboage M, Hanfland M, et al. Pressure-induced melting of charge-order in the self-doped mott insulator YNiO₃. Phys. Rev. B. 2004;69:094106.

[16] Jaramillo R, Ha SD, Silevitch DM, et al. Origins of bad-metal conductivity and the insulator–metal transition in the rare-earth nickelates. Nat. Phys. 2014;10:304.

[17] Mazin II, Khomskii DI, Lengsdorf R, et al. Charge ordering as alternative to Jahn-teller distortion. Phys. Rev. Lett. 2007;98:176406.

[18] Imada M, Fujimori A, Tokura Y. Metal-insulator transitions. Rev Mod Phys. 1998;70:1039.

[19] Liu J, Kargarian M, Kareev M, et al. Heterointerface engineered electronic and magnetic phases of NdNiO₃ thin films. Nat. Commun. 2013;4:2714.

[20] Barman SR, Chainani A, Sarma DD. Covalency-driven unusual metal-insulator transition in nickelates. Phys. Rev. B. 1994;49:8475.

[21] Gauquelin N, Benckiser E, Kinyanjui MK, et al. Atomically resolved EELS mapping of the interfacial structure of epitaxially strained LaNiO₃/LaAlO₃ superlattices. Phys. Rev. B. 2014;90:195140.

[22] Abbate M, Zampieri G, Prado F, et al. Electronic structure and metal-insulator transition in LaNiO₃₋δ. Phys. Rev. B. 2002;65:155101.

[23] Zaanen J, Westra C, Sawatzky GA. Determination of the electronic structure of transition-metal compounds: 2p x-ray photoemission spectroscopy of the nickel dihalides. Phys. Rev. B. 1986;33:8060.

[24] Groot F de, Kotani A. Core level spectroscopy of solids. Boca Raton (FL): CRC Press Taylor & Francis Group; 2008.