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Brief Reports

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Covalency-driven unusual metal-insulator transition in nickelates

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Electronic structures of metallic $LaNiO_3$ and insulating $NdNiO_3$ are investigated using electron spectroscopies as well as band-structure and model-Hamiltonian calculations. It is shown that there is an increase in the transfer integral, t_{pd} in $LaNiO_3$ compared to $NdNiO_3$ though U_{dd} and Δ are very similar. A phase diagram obtained with a multiband Hubbard model explains the metal-insulator transition as well as the anomalous resistivity of $NdNiO_3$ under pressure while indicating various interesting possibilities near the metal-insulator phase line.

The electronic structure of transition-metal oxides has been of active research interest for the wide variety of physical properties these exhibit. The metal-insulator (MI) transition observed in many of these systems are yet to be understood satisfactorily. In view of the occurrence of high temperature superconductivity in the substituted cuprates,[1] similar substituted transition-metal oxide systems have been extensively studied recently using various techniques. The overall electronic structures of the undoped compounds as well as the doped ones have normally been described in terms of the well-known Zaanen-Sawatzky-Allen (ZSA) phase diagram,[2] which provides a unified basis for the metallic/insulating properties of the transition-metal compounds. The ZSA phase diagram provides a natural description for the occurrence of insulators and metals in different regimes of interaction strengths, U/t_{pd} and Δ/t_{pd}, where U, Δ, and t_{pd} are the intra-atomic Coulomb interaction strength in the Ni $3d$ manifold, the ligand to metal charge transfer energy, and the Ni $3d_{x^2-y^2}$-O $2p_x$ hopping interaction strength, respectively. The insulating compounds of the early $3d$ transition elements with $U<\Delta$ belong to the Mott-Hubbard (MH) region, while the insulating compounds of the late $3d$ transition metals belong to the charge-transfer (CT) region in terms of the ZSA classification. The gap in the charge excitation spectrum is believed to be controlled primarily by U in the MH regime and by Δ in the CT regime. It should be noted that the ZSA diagram relates directly to only such cases which do not involve any doping of charge carriers. Microscopic investigation of the electronic structure of the late transition-metal compounds belonging to the CT regime and exhibiting MI transitions in the absence of any doping, however, has not been carried out.

The recently discovered MI transitions[3-5] in the $LnNiO_3$ series (Ln is a rare earth ion) provide an interesting ground for a systematic investigation of such transitions in the charge transfer regime *without any doping of charge carriers.* Specifically, $LaNiO_3$ is a highly correlated metal, believed to be on the verge of an MI transition,[6] while $NdNiO_3$ is a *ground state* insulator.[3-5] Recently it has been reported that the resistivity of $NdNiO_3$ under pressure exhibits anomalous behavior, unexpected of a typical charge transfer insulator.[7] On the basis of extensive experimental and theoretical results, we suggest that the MI transition in this series is driven neither by a change in U nor by a change in Δ, as would be intuitively expected on the basis of the ZSA diagram for a MH and a CT insulator, respectively. Here, we provide evidence based on spectroscopic data and density of states (DOS) calculations, suggesting that the MI transition in these compounds arises from the changes in the e_g^* bandwidth. The effect of changing bandwidth arising from structural changes has indeed been suggested as a cause for the MI transition across the $LnNiO_3$ series.[5,7] We suggest that the decrease in the e_g^* bandwidth is due to an experimentally observed decrease in t_{pd} and is also possibly due to a decreasing Ni-O-Ni angle across the series. A ZSA-like phase diagram obtained from the mean-field treatment of a multiband Hubbard model provides a basis for understanding these changes and indicates interesting possibilities close to the MI phase line for the late transition-metal compounds. We show that the effect of the change in t_{pd}, normally used only as a scaling parameter, in determining the metallic or insulating property of the system depends specifically on the strength of U. Our interpretation is consistent with the anomalous pressure dependence of the MI transition in these compounds.[7]

Rhombohedral $LaNiO_3$ and $NdNiO_3$ were prepared by the standard method.[3] The He I ultraviolet photoemission (UP) spectra of these compounds, recorded at 100 K, are shown in Fig. 1(a). Figure 1(b) shows the corresponding DOS along with the Ni $3d$ and O $2p$ partial DOS, calculated using the self-consistent linear muffin-tin-orbital method within the atomic sphere approximation (LMTO ASA) with the s, p, d basis in the $R\bar{3}c$ and $Pbnm$ symmetry for $LaNiO_3$ and $NdNiO_3$, respectively.[5] The experimental spectra of $LaNiO_3$ and $NdNiO_3$ are

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remarkably similar with features appearing close to E_F (marked A and shown on an expanded scale), at about 0.9 eV (B) and 4.7 eV (D), though the features marked C and C' for $LaNiO_3$ and $NdNiO_3$ are somewhat shifted with respect to each other. The reason for this difference between C and C' is the existence of Nd $4f$ spectral intensity in $NdNiO_3$ at about 4 eV binding energy.[8] It is to be noted that we do not observe the signature of a gap at E_F in the case of insulating $NdNiO_3$. This is due to the fact that the magnitude of this gap[3] (≤ 10 meV) is much smaller than the present experimental resolution (140 meV). The considerable similarity between the experimental spectra suggests similar electronic structure in these two compounds. The valence band x-ray photoelectron (XP) spectrum of $LaNiO_3$ using Mg $K\alpha$ radiation [inset, Fig. 1(a)] indicates that the spectral intensity in the region of the features A and B increases with increasing photon energy compared to the features C and D; this suggests that the features A and B are primarily due to Ni $3d$ emission, while the features C and D have more significant O $2p$ character. Considering the electron configuration $t_{2g}^6 e_g^1$ for Ni^{3+}, it appears that the weak intensity feature A is related to the e_g^* band while the feature B is to be associated with the t_{2g}^* band.

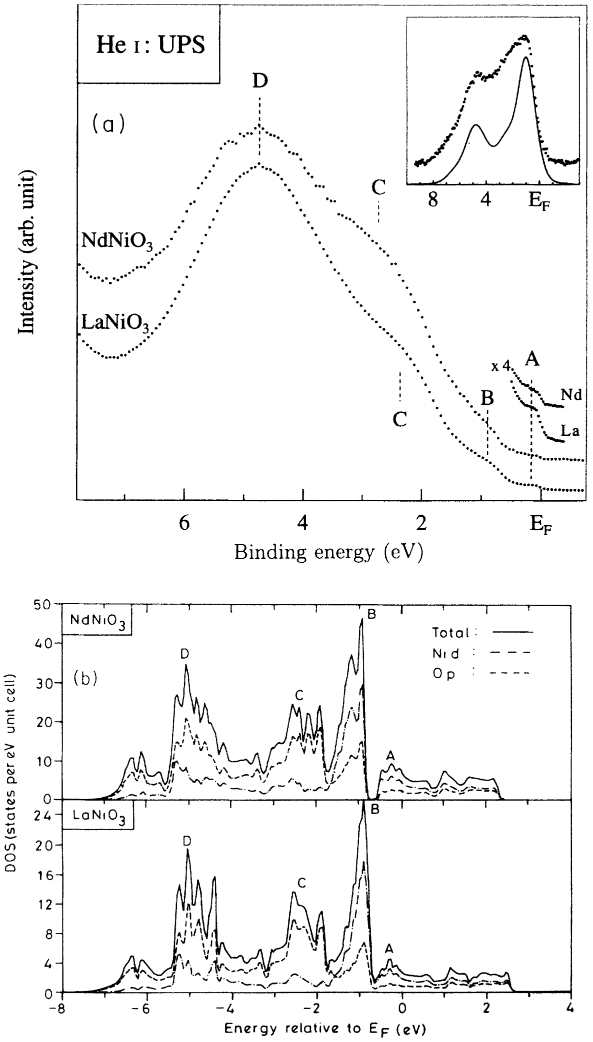

FIG. 1. (a) He I UP spectra of $LaNiO_3$ and $NdNiO_3$. The experimental (dotted line) and calculated (solid line) XP spectra of $LaNiO_3$ are shown in the inset. (b) The total DOS (solid line), Ni d (dot-dashed line), and O p (dashed line) partial DOS for $LaNiO_3$ and $NdNiO_3$ calculated within LMTO-ASA.

It is well known that a comparison of the photoemission results with the calculated DOS provides important information concerning the effects of correlation in the system. From such a comparison between Figs. 1(a) and 1(b), we can identify the parts of the DOS (marked A–D) responsible for the corresponding features in the experimental spectra. It is evident from Fig. 1 that the energy positions of the features (A–D) of the He I spectra are in good agreement with the calculated DOS. We show that the XP valence band spectrum is well described by the calculated DOS [inset, Fig. 1(a)] when we include the effects of matrix elements[9] as well as resolution and lifetime broadenings. The extra broadening in the experimental XP spectrum at about 2.5 eV binding energy [see inset, Fig. 1(a)] is attributed to correlation effects.[10] However, it appears that the effect of Coulomb correlation is not overwhelming in these cases and the electronic structure of these systems can be described within the single-particle description as a reasonable starting point. This is not to imply that the Coulomb correlation has no role to play. As we shall show later in the text, U is substantial in these compounds. Thus, we would expect to see the effects of these many-body interactions in the details of the electronic structure, as, for example, by the broadening of the spectral features in the XP spectrum compared to the calculated DOS discussed above, in close analogy to the case of uranium intermetallics.[10] One of the most obvious consequences of electron correlation in these systems is to drive $NdNiO_3$ insulating, whereas the band structure in Fig. 1(b) suggests a metallic ground state. Even in the case of metallic $LaNiO_3$, electron-electron repulsion is believed[6] to drive the system close to localization.

While it is clear that the presence of electron correlation is essential for the insulating property of $NdNiO_3$, it does not explain the differing ground state properties between $LaNiO_3$ and $NdNiO_3$, as U is expected to be similar for these two compounds. This expectation is fully justified by the Ni L_{23}-$M_{45}M_{45}$ Auger spectra of these compounds (Fig. 2). While the Auger spectrum of $LaNiO_3$ clearly exhibits the L_2- and L_3-$M_{45}M_{45}$ related

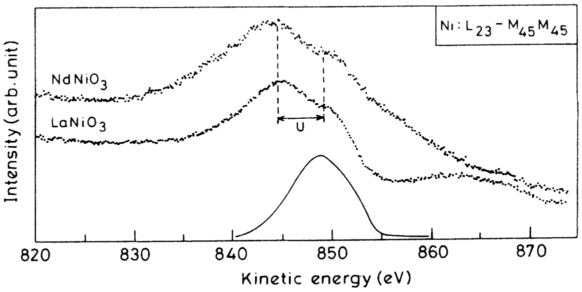

FIG. 2. The Ni L_{23}-$M_{45}M_{45}$ Auger spectra of $LaNiO_3$ and $NdNiO_3$. Comparison with the self-convoluted XP spectrum (solid line) of $LaNiO_3$ indicates U to be ~ 4.7 eV.

signals, the Auger spectrum of $NdNiO_3$ is unfortunately distorted by the presence of overlapping broad Nd M_{45}-$N_{45}V$ spectral features. Thus the L_2-$M_{45}M_{45}$ cannot be distinguished from the background, while the L_3-$M_{45}M_{45}$ spectral feature is broadened by this overlapping feature in $NdNiO_3$. However the two main features in the L_3-$M_{45}M_{45}$ spectrum can be clearly identified in the spectrum. These two spectral features appear at the same kinetic energies for $LaNiO_3$ and $NdNiO_3$ (Fig. 2). We have also shown the self-convolution[11] of the XP valence band spectrum of $LaNiO_3$ in the same figure; this comparison clearly establishes that the 849.1 eV feature is due to the presence of two uncorrelated holes, while the 844.4 eV feature is attributable to the correlated two-hole final state with no counterpart in the self-convolution of the valence band spectrum. The effective U within the Ni $3d$ manifold for both the compounds is estimated[11] to be 4.7±0.5 eV from the separation of the two spectral features (Fig. 2).

Since the late transition-metal compounds are expected to belong to the charge transfer regime, one may expect changes in the charge transfer energy (Δ) to be the driving cause for the MI transition. However, the close similarity between the He I spectra in $LaNiO_3$ and $NdNiO_3$ [Fig. 1(a)] and also the close similarity in the calculated Ni d and O p partial DOS [Fig. 1(b)] suggest very similar charge transfer energies in these compounds. It should be noted here that the weighted average separations between the Ni d and O p partial DOS in Fig. 1(b) are remarkably similar in these compounds. Thus it appears that there is no gross change in Δ between $LaNiO_3$ and $NdNiO_3$. However, a close inspection of the DOS in Fig. 1(b) shows that the e_g^* [marked A in Fig. 1(b)] related bandwidth is broader (by ~0.4 eV) in $LaNiO_3$ compared to that in $NdNiO_3$. The e_g^* bandwidth is controlled by the Ni-Ni interaction mediated via the Ni d-O p σ interaction. Thus, the Ni e_g^* bandwidth is presumably affected both by a decrease in the intracluster t_{pd} due to the longer Ni-O bond length[5] and by a decrease in Ni-O-Ni coupling due to a decrease of Ni-O-Ni angle[5] across the series.

A direct experimental evidence for the above suggestion of an increased hopping interaction strength in $LaNiO_3$ comes from an analysis of the core-level spectra. The Ni $2p$ spectral region in these two compounds are shown in Fig. 3. The standard[11,12] analysis of the core level spectrum for Ni $2p$ in $NdNiO_3$ in terms of a $(NiO_6)^{9-}$ cluster including configuration interaction, suggests t_{pd} to be 1.2±0.1 eV, with U fixed at 5.0 eV as suggested by the analysis of the Auger spectra (see Fig. 2). With increasing Δ, the satellite intensity is found to decrease monotonically. It, however, turns out that the calculated core-level spectrum does not depend sensitively on Δ and a wide range of values (Δ=1.5±2.5 eV) would be consistent with the experimental spectrum. We compare one such calculated spectrum (Δ=1.5 eV) with the experimental one in Fig. 3 to illustrate the good agreement between the two. Our analysis shows that the spectral shape as well as the satellite to main peak energy separation (ΔE_{sat}) depends mainly on t_{pd}, providing a rather reliable estimate of this interaction parameter. This is a consequence of a strongly mixed valent ground state in these compounds. The Ni $2p_{3/2}$ region in $LaNiO_3$ is extensively overlapped by the La $3d$ spectral features; however, the Ni $2p_{1/2}$ region in this compound, with peak positions corresponding to the main and satellite features at 872.2 and 881 eV, respectively, are clearly identifiable. Figure 3 clearly shows that ΔE_{sat} (9.2±0.4 eV) in $LaNiO_3$ is larger than that (7.9±0.4 eV) in $NdNiO_3$. This indicates that t_{pd} in $LaNiO_3$ is larger. Calculations based on the same configuration interaction model indicates t_{pd} to be 1.6±0.2 eV in $LaNiO_3$ to obtain the experimental ΔE_{sat}. Thus, the analysis of the core level spectra clearly indicate about a 0.4 eV increase in t_{pd} for $LaNiO_3$ compared to that in $NdNiO_3$.

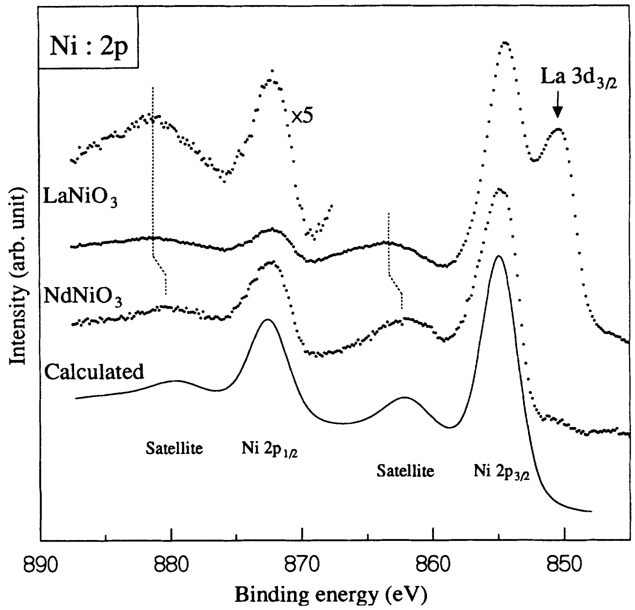

FIG. 3. The Ni $2p$ core-level spectra of $LaNiO_3$ and $NdNiO_3$. The $2p_{1/2}$ main peak and satellite region of $LaNiO_3$ is shown in an expanded scale. The calculated Ni $2p$ spectrum of $NdNiO_3$ (solid line) with Δ = 1.5 eV, U = 5 eV, and t_{pd} = 1.2 eV compares well with the experimental spectrum.

From the above evidence, it appears that the most significant change in the electronic structure between these two compounds is an increase in t_{pd}. In order to elucidate that such a change alone can drive a MI transition, as experimentally observed between $LaNiO_3$ and $NdNiO_3$, we calculate the MI phase line based on the mean-field treatment of the multiband Hubbard model that takes into account the lattice of the metal and oxygen including various transfer integrals as well as Coulomb interaction strength within the metal $3d$ manifold. The computational details are described in Ref. 13. We point out that though the model was specifically based on the structure of CuO_2 planes in La_2CuO_4, the qualitative features obtained there are also applicable to any transition-metal compound, as discussed in our earlier work.[13] According to the phase diagram in Ref. 13 and the estimated parameter strengths here, $LaNiO_3$ will be a pd (or mixed valent) metal, while $NdNiO_3$ belongs to the covalent insulator region. It has been shown earlier[13] that this in-

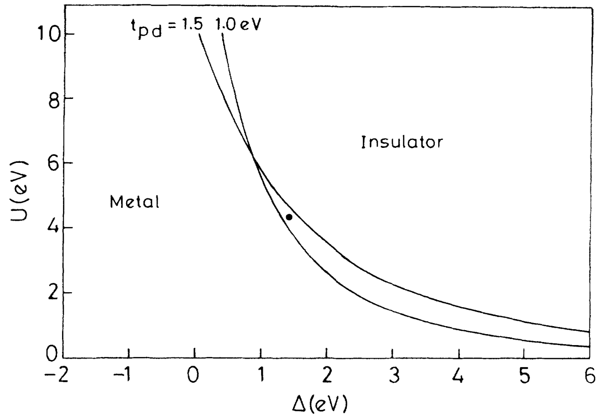

FIG. 4. The metal-insulator phase diagrams for the multiband Hubbard model using the mean-field approximation calculated for t_{pd}=1.0 and 1.5 eV. The estimated parameters for $NdNiO_3$ and $LaNiO_3$ suggest them to be in the neighborhood of the point indicated at $U \sim 4.5$ eV and $\Delta \sim 1.5$ eV.

sulating region exists only in the presence of substantial t_{pd} and thus is driven by covalency effects. In Fig. 4 we show the phase lines calculated for two different t_{pd} values, 1.0 and 1.5 eV, within this model. The two phase lines cross at about $U = U_c \simeq 6.3$ eV. If the U value is less than the critical value, there is a range of U and Δ for which the system will be metallic for larger t_{pd} (as in $LaNiO_3$), but insulating for smaller t_{pd} (as in $NdNiO_3$); we have marked one such specific U-Δ value in Fig. 4. Interestingly, if U is greater than U_c, the situation will be reversed with smaller t_{pd} value driving the system to be metallic. Moreover it is to be noticed that if t_{pd} is increased for $NdNiO_3$ with $U < U_c$, as can be done in a high pressure experiment, the system will be driven closer to the metallic state. This is indeed the observation made in the recent high pressure experiments.[7] The phase diagrams in Fig. 4 clearly show that the pressure will have an opposite effect for $U > U_c$. This resolves the conflicting claims that the pressure should drive the system more insulating for the oxides of the late transition elements[14] and the recent experimental results[7] on $NdNiO_3$.

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