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bandstructure results

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Electronic structure and the metal–insulator transition in LnNiO_3 ($\text{Ln} = \text{La, Pr, Nd, Sm}$ and Ho): band structure results

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Abstract. We report detailed band structure results on the series LnNiO_3 with $\text{Ln} = \text{La, Pr, Nd, Sm}$ and Ho . LaNiO_3 is shown to be a pd metal, expected to be close to localization due to correlation effects; the other four compounds are suggested to be covalent insulators. There is a systematic reduction in the bandwidths with increasing atomic number of the rare-earth ion. Using a tight-binding analysis of the *ab initio* results, the reduction in the bandwidth is related to the changes in the intercluster hopping interaction strengths arising from the structural changes driven by the lanthanide contraction across the series.

In the series LnNiO_3 ($\text{Ln} = \text{rare earth}$), the first member LaNiO_3 is a strongly correlated metallic oxide [1], while other members with $\text{Ln} \neq \text{La}$ are insulators at $T = 0 \text{ K}$ [2–5]. However, these compounds exhibit an insulator–metal (MI) transition at finite temperatures, the transition temperature (about 130 K, 200 K and 400 K for $\text{Ln} = \text{Pr, Nd}$ and Sm , respectively) increasing systematically with the atomic number of the rare-earth ion. Thus it appears that the compounds become increasingly more insulating with heavier rare earths and hence require higher transition temperatures to drive them into a metallic state. While it is clear that the intra-atomic Coulomb interaction U_{dd} is crucial in driving the systems insulating, it is also to be noted that this intra-atomic quantity is not expected to change significantly from one nickelate to the other. The possibility that the MI transitions have a magnetic origin can also be eliminated, since in several systems in this series the magnetic transition occurs at a considerably lower temperature than the MI transition temperature [3, 4]. Recently, we have experimentally established [6] that there is a change in the effective Ni 3d–O 2p hopping interaction strength between LaNiO_3 and NdNiO_3 which appears to be primarily responsible for their differing ground state properties. On the basis of structural data, it has been suggested [4] that the e_g^* bandwidth would decrease across the series because of a decrease in the effective coupling between the neighbouring Ni sites. It is known [4] that there is a systematic increase of Ni–O distance and a decrease of Ni–O–Ni angle across the series. Both of these effects can contribute to reducing the e_g^* bandwidth. Here we theoretically investigate whether there is indeed a systematic change in the electronic structure in general, and in the e_g^* bandwidth in particular, in this series of compounds responsible for the transformation into an increasingly insulating state. Thus, we have carried out detailed scalar-relativistic self-consistent band structure calculations for these compounds with $\text{Ln} = \text{La, Pr, Nd, Sm}$ and Ho within the linearized muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA). Band structures of these compounds can be compared meaningfully, as all the compounds form in closely

related distorted perovskite structures. The present results clearly show that there is a systematic decrease in the bandwidths across the series arising from these structural changes. Furthermore, we analyse the band structure results in terms of a tight-binding model in order to extract various hopping interaction strengths. This analysis suggests that the reduction in the e_g^* bandwidth is primarily driven by changes in the intercluster hopping due to the distortion of the Ni–O–Ni angle rather than by changes in the intracluster hopping due to changes in Ni–O distances.

We perform LMTO–ASA calculations for the real crystal structure of LaNiO_3 with two formula units per unit cell in the $R\bar{3}c$ symmetry with a rhombohedral distortion of the perovskite structure, and for the other LnNiO_3 compounds with four formula units in the $Pbnm$ space group with orthorhombic distortion [3–5]. In this method [7], spheres are inscribed around each atom whose radii are so chosen that the sum of volumes of the spheres equals the volume of the unit cell. This space-filling criterion has been satisfied with reasonable overlap of atomic spheres in all of these cases without any empty spheres. Self-consistency was achieved with 68 and 64 irreducible k points in the Brillouin zone for $R\bar{3}c$ and $Pbnm$ systems, respectively, and the density of states calculated with 125 and 150 irreducible k points of the Brillouin zone.

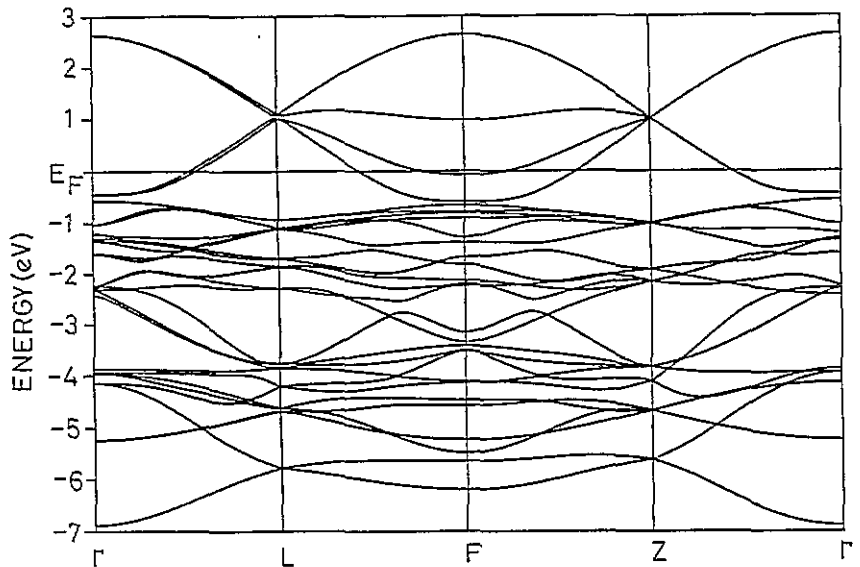


Figure 1. Band dispersions in LaNiO_3 along four symmetry directions.

We show the band dispersions between -7 eV and $+3$ eV of E_F along four symmetry directions for LaNiO_3 (figure 1) and the corresponding total density of states (DOS) and the Ni d and O p partial DOS (figure 2) calculated with the s, p, d and f basis in each atomic sphere. figure 2 clearly shows that there are four groups of identifiable DOS features, marked in the figure. Four bands spread approximately between -0.5 eV and $+2.5$ eV are found to cross the Fermi level; these bands centred around 1 eV above E_F are formed essentially by covalent mixing of Ni d and O p states. Approximately one fourth of these bands are occupied. There is a set of six bands with small dispersion appearing between -0.5 eV and -1.5 eV (figure 1); these bands give rise to a peaked DOS at about -0.9 eV with majority Ni d character and are fully occupied. Noting the electron configuration of $t_{2g}^6 e_g^1$

for Ni^{3+} , the group of four bands centred around +1.0 eV arising from two Ni atoms per unit cell is attributed essentially to Ni d (e_g)-O p_σ σ -interaction forming the antibonding e_g^* band, while the set of six relatively flat bands around -0.9 eV is due to Ni d (t_{2g})-O p_π π -interaction forming the antibonding t_{2g}^* band. We point out that the calculated bandwidths are in agreement with high-energy spectroscopic results [6]. The corresponding bonding e_g and t_{2g} bands can also be identified from figs.1 and 2. Thus, the four strongly dispersing bands approximately between -4 eV and -7 eV are associated with the bonding e_g band, while the relatively flat bands approximately between -3.8 eV and -4.8 eV are attributed to the bonding t_{2g} band. These two groups together give rise to overlapping DOS features between -6.5 and -3.5 eV (figure 2). The remaining eight bands appearing between -1.5 eV and -3.5 eV, and exhibiting considerable dispersion, have essentially O p character with only small covalent admixture of Ni d. Thus, these are essentially the non-bonding O p bands, arising primarily from O-O interactions giving rise to prominent DOS features between -2 and -3 eV (figure 2). The above assignments are approximate to the extent that the distortion of the lattice in LaNiO_3 from the ideal cubic perovskite structure leads to a mixing of various symmetries.

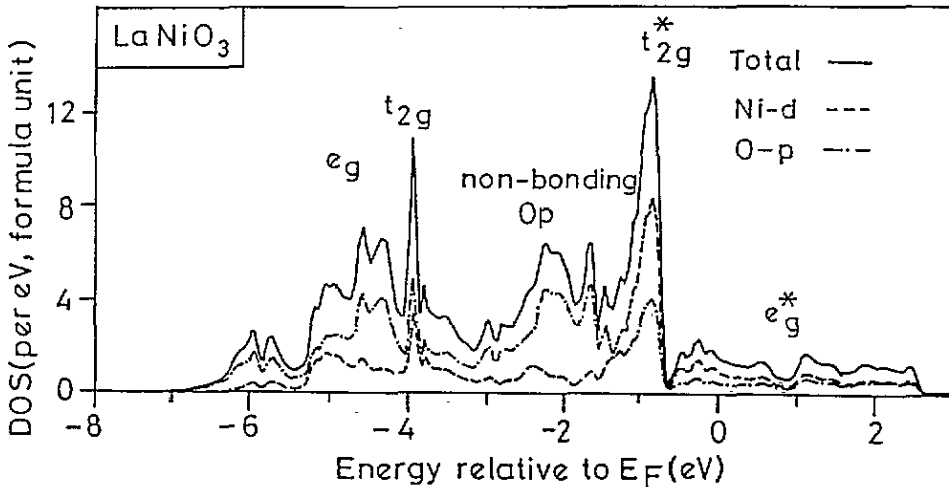


Figure 2. Total, Ni d and O p partial densities of states for LaNiO_3 .

The average energy separation between t_{2g} and t_{2g}^* bands is approximately 3.5 eV, while that between the e_g and e_g^* bands is approximately 6.0 eV. The mean energies of the various bands, and thus the mean energy differences as well, are controlled by various intracuster energetics of the NiO_6 octahedra. Thus, it is possible to model this in terms of the linear combination of atomic orbitals (LCAO) approach. We denote the effective charge transfer energy with respect to the centroid of the oxygen p band as Δ ($= \epsilon_d - \epsilon_p$). The p_σ and p_π levels split by $+\delta$ and $-\delta$ from the oxygen p-band centroid due to oxygen-oxygen interaction with $\delta = (pp\sigma) - (pp\pi)$. We denote the Ni d (e_g) transfer integral with the symmetry-adapted oxygen p_σ orbitals as $t_\sigma = \sqrt{3}(pd\sigma)$ and the corresponding transfer integral for the π -interaction as $t_\pi = 2(pd\pi)$. Here the parameters $pp\sigma$, $pp\pi$, $pd\sigma$ and $pd\pi$ are the usual Slater-Koster parameters [8]. LCAO analysis for this model shows that $\Delta = 0.5 \pm 0.4$ eV, $\delta = 0.5 \pm 0.4$ eV, $t_\sigma = 2.9 \pm 0.3$ eV and $t_\pi = 1.6 \pm 0.2$ eV would yield mean energies of the e_g , t_{2g} , t_{2g}^* and e_g^* bands at about -4.9 eV, -4.2 eV, -0.8 eV and 0.9

eV, assuming the non-bonding p-band centroid at -2.5 eV. From the figure, we find that the mean energies and energy differences are in very good agreement with the band structure calculations. While such an analysis suffers from oversimplification, we believe that it does provide an approximate idea about the various electronic interaction strengths. It should also be noticed that while the present LCAO approach completely ignores the important effects due to Coulomb interactions, the band structure calculation is also performed within an effective independent particle approximation where Coulomb interactions are averaged over the occupied orbitals. It is interesting to note that the estimate of t_{σ} here is in good agreement with the estimate (3.2 ± 0.4 eV) of the same quantity from an analysis of the Ni 2p core-level photoemission spectrum from LaNiO_3 [6].

We have verified that the effect of discarding the f states from the basis on the electronic structure of LaNiO_3 is negligible, as the results are very similar over the entire range to those in figure 2 calculated including the f states in the basis. In particular, the DOS and partial DOS corresponding to the t_{2g}^* and the e_g^* bands are nearly identical in the two sets of calculations. Since the electronic structure is expected to be dominated by Ni 3d–O 2p interactions, this is not a surprising result. Moreover, the main discussions in the present work are related to the systematic changes in the t_{2g}^* and e_g^* bands; thus, it appears that the neglect of f states from the basis does not vitiate the conclusions to any significant extent. Moreover, the effect of the f states in the electronic structure of LnNiO_3 is expected to be largest for LaNiO_3 and to decrease with increasing atomic weight of the rare earth (Ln) due to 4f contraction. Thus, we have treated the 4f level of the rare-earth ions in the following as a core level, while including only the s, p and d basis for the band structure calculations of LnNiO_3 compounds with $\text{Ln} \neq \text{La}$. Figure 3 shows the total and partial Ni d and O p DOS for PrNiO_3 , NdNiO_3 , SmNiO_3 and HoNiO_3 . The overall features in these figures are very similar to one another and also to those for LaNiO_3 (figure 2). Thus we find four distinct groups in the DOS in each case and the origin of these features is the same as that in LaNiO_3 . Moreover the mean energies of these four groups of DOS features are also very similar. This indicates that an LCAO analysis considering only the intra- NiO_6 cluster interactions will yield results very similar to those obtained for LaNiO_3 . Besides these remarkable similarities in the overall descriptions, there are some specific and important differences in the details of the electronic structures of the various compounds. The most important distinction is observable in terms of the bandwidth of the e_g^* bands which we show on an expanded scale for all the five compounds in the inset of figure 3. It is obvious from the figure that there is a systematic decrease in e_g^* bandwidth with increasing atomic number of lanthanide in LnNiO_3 . This decreasing bandwidth across the series is also observable in terms of an increasing energy gap between the t_{2g}^* and e_g^* bands in these compounds at about -0.7 eV below E_F .

It is to be noted here that the e_g^* and t_{2g}^* bandwidths depend almost entirely on the Ni–O–Ni hopping interactions, controlled by the Ni–O distance and Ni–O–Ni angle in these compounds. The average Ni–O distance and Ni–O–Ni angle show small but systematic changes across the series. Thus, the Ni–O distances are 1.933, 1.944, 1.946, 1.955 and 1.938 Å and Ni–O–Ni angles are 164.8° , 157.6° , 156.0° , 151.8° and 151.5° for La, Pr, Nd, Sm and Ho compounds respectively. These structural changes are related to the changing size of the Ln^{3+} ion due to the well known lanthanide contraction across the rare-earth series [4]. An increase of the Ni–O distance as well as a decrease of the Ni–O–Ni angle from the ideal value of 180° in the cubic perovskite would tend to decrease the width of the e_g^* band. However, the Ni–O distance affects the bandwidth by changing the *intracluster* Ni 3d–O 2p hopping interaction strength, while the Ni–O–Ni angle determines the Ni 3d–O 2p–Ni 3d *intercluster* hopping. In order to understand the intercluster behaviour, it is

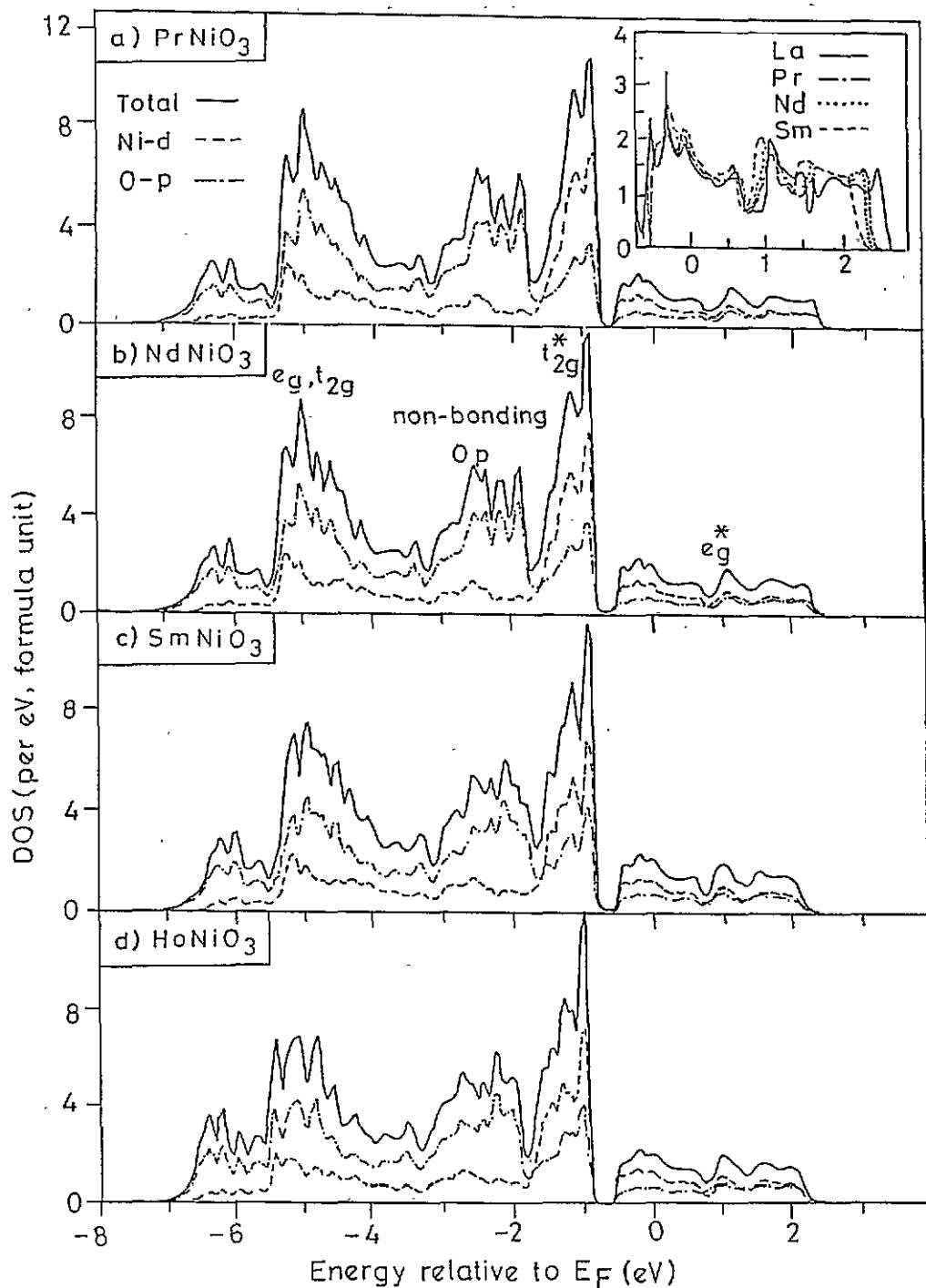


Figure 3. As in figure 2 but for (a) PrNiO_3 , (b) NdNiO_3 , (c) SmNiO_3 and (d) HoNiO_3 . The inset shows the comparison of bandwidths for the e_g^* bands of LnNiO_3 with $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$ and Sm .

essential to go beyond the simple LCAO analysis presented earlier involving only a single NiO_6 octahedron. Thus, we have analysed the LMTO results of figures 2 and 3 in terms of a parametrized tight-binding model to obtain estimates of various interaction parameters.

The tight-binding Hamiltonian was set up with nearest-neighbour interaction, considering only M 3d and O 2p orbitals as the relevant ones. We have estimated the various parameter strengths by fitting the band dispersion or DOS obtained within this model to the corresponding quantity calculated by the LMTO method. Results obtained from such a least-square-error fitting are given in table 1. From this table we find that for LaNiO_3 the estimates are similar to those obtained on the basis of an isolated NiO_6 cluster alone. For example, the value of t_σ ($=\sqrt{3}(\text{pd}\sigma)$) obtained from tight-binding analysis is the same as that from LCAO analysis and the values of Δ are also very similar. Here we point out that these estimates are also consistent with those obtained from an analysis of experimental spectroscopic results [6]. It is to be noted that all the interaction parameters for the other LnNiO_3 compounds with $\text{Ln} \neq \text{La}$ are very similar to those for LaNiO_3 . In particular, the values of $\text{pd}\sigma$ are quite comparable. This indicates that the intracluster interactions are relatively unchanged among the various nickelates. Thus the systematic change in the e_g^* bandwidth across the series must arise from the monotonic decrease of Ni–O–Ni angle affecting the intercluster hopping.

Table 1. Estimates of tight-binding parameters obtained by least-squared-error fitting of LMTO results.

Compound	$\text{pd}\sigma$ (eV)	$\text{pd}\pi$ (eV)	$\text{pp}\sigma$ (eV)	$\text{pp}\pi$ (eV)	Δ (eV)
LaNiO_3	-1.66	0.85	0.91	-0.37	0.67
PrNiO_3	-1.51	0.77	0.76	-0.31	0.74
NdNiO_3	-1.58	0.79	0.80	-0.37	0.89
SmNiO_3	-1.68	0.75	0.89	-0.36	0.65
HoNiO_3	-1.80	0.72	0.91	-0.37	0.65

The band structure calculations presented here show LaNiO_3 to be a metal in agreement with the observed resistivity behaviour. However, it is to be noticed that the bandwidth of the relevant e_g^* band in LaNiO_3 is 3.5 eV, a value that is close to the intra-atomic Coulomb interaction strength, U_{dd} ($\sim 4.7 \pm 0.5$ eV), in this compound estimated from Auger spectroscopic results [6]. Thus, $U \geq W$ suggests that the system is close to Mott localization and the expected ground state behaviour is that of a strongly correlated almost localized metal, in agreement with the suggestions based on transport experiments [1]. However, the present results suggest that even LnNiO_3 with $\text{Ln} \neq \text{La}$ would be metallic with a finite density of states at E_F . This is a well known difficulty [9] of local density approximation methods in describing insulating states in the presence of Coulomb interactions. Several new methods have been suggested in the recent times to overcome this drawback [10] and it would be interesting to see if these improved methods would yield the ground state of the insulating compounds correctly. On the other hand, in the limit of $U \geq W$, it may be expected that even a small decrease of the bandwidth may drive the system to an insulating ground state. Since the intra-atomic Coulomb strength, U_{dd} , is experimentally known [6] to be very similar for LaNiO_3 and NdNiO_3 , and is not expected to be very different for PrNiO_3 , SmNiO_3 and HoNiO_3 , it is reasonable to expect that the observed decreasing bandwidth across the series (inset in figure 3) and therefore an increasing U_{dd}/W , is, at least partly, responsible for the observed increasingly insulating behaviour of LnNiO_3 . Thus, these four compounds appear to be just localized insulators appearing close to the metal-insulator

phase line in terms of ZSA [11] or the modified [12] phase diagrams. In this context, it should be recalled that the recent calculation [12] of the ZSA-like phase diagrams based on a multiband Hubbard model indicated the presence of a new phase, termed the covalent insulator, in between the charge-transfer (CT) insulator and the p-d metal regions. It was suggested that the compounds of late transition metal oxides with $U > \Delta$ must belong to this phase, if they exhibit an insulator–metal transition in the absence of carrier doping. The ground state wave function corresponding to the covalent insulator region is characterized by a strongly mixed valence state. The present calculations show that there is strong mixing between the Ni d and O p states over the entire energy range and, in particular, for the e_g^* band. Moreover, it has been shown [12] that the insulating/metallic property in the vicinity of this region in the presence of a large U and small Δ is sensitively dependent on the effective transfer integral. The band structure results presented here, with evidence for a small effective Δ (≈ 0.7 eV) and changing bandwidths of the e_g^* band, clearly suggests that the compounds with $\text{Ln} \neq \text{La}$ indeed belong to the covalent insulator region of the modified phase diagram [12].

In conclusion, we have presented detailed band structure results for LaNiO_3 , PrNiO_3 , NdNiO_3 , SmNiO_3 and HoNiO_3 . The analysis shows LaNiO_3 to be a pd metal close to being localized due to electron correlation effects. A systematic narrowing of the bandwidths is observed for increasing atomic number of the rare-earth ion. By analysing LMTO results in terms of a parametrized tight-binding model, this effect has been related to the changes in the structural aspects of the compounds induced by the lanthanide contraction across the series affecting primarily the effective intercluster transfer integrals. On the basis of the strengths of various interaction parameters, it is suggested that the insulating compounds, PrNiO_3 , NdNiO_3 , SmNiO_3 and HoNiO_3 , derive their ground state insulating property from the simultaneous presence of electron correlation and strong covalency effects, and that these compounds belong to the covalent insulator regime of the modified ZSA diagram.

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References

- [1] Sreedhar K, Honig J M, Darwin M, McElfresh M, Shand P M, Xu J, Crooker B C and Spalek J 1992 *Phys. Rev. B* **46** 6382
Rajeev K P, Shivashankar G V and Raychaudhuri A K 1991 *Solid State Commun.* **79** 591
- [2] Vassiliou J K, Hornbostel M, Ziebarth R and Disalvo F J 1989 *J. Solid State Chem.* **81** 208
- [3] Lacorre P, Torrance J B, Pannetier J, Nazzal A I, Wang P W and Huang T C 1991 *J. Solid State Chem.* **91** 225
- [4] Torrance J B, Lacorre P, Nazzal A I, Ansaldo E J, and Niedermayer Ch 1992 *Phys. Rev. B* **45** 8209
Garcia-Munoz J L, Rodríguez-Carvajal J, Lacorre P and Torrance J B 1992 *Phys. Rev. B* **46** 4414
- [5] Demazeau G, Marbeuf A, Pouchard M and Hagenmuller P 1971 *J. Solid State Chem.* **3** 582
- [6] Barman S R, Chainani A and Sarma D D 1994 *Phys. Rev. B* **49** 8475
- [7] Anderson O K 1975 *Phys. Rev. B* **12** 3060
Skriver H L 1984 *The LMTO Method* (Berlin: Springer)

- [8] Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
- [9] Pickett W K 1989 *Rev. Mod. Phys.* **61** 433
- [10] Svane A and Gunnarsson O 1993 *Phys. Rev. Lett.* **65** 1148
Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev. B* **44** 943
MacKrodt W C, Harrison N M, Saunders V R, Allan N L, Towler M D, Apra E and Dovesi R 1993 *Phil. Mag.* **68** 653
Massida S, Posternak M and Baldereschi A 1992 *Phys. Rev. B* **46** 11 705
- [11] Zaanen J, Sawatzky G A and Allen J W 1985 *Phys. Rev. Lett.* **55** 418
- [12] Sarma D D, Krishnamurthy H R, Seva Nimkar, Mitra P P, Ramasesha S and Ramakrishnan T V 1992 *Pramana—J. Phys.* **38** L 531
Seva Nimkar, Sarma D D, Krishnamurthy H R and Ramasesha S 1993 *Phys. Rev. B* **48** 7355