Local Correlations, Non-Local Screening, Multiplet Effects and Band Formation in NiO

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NiO is a benchmark system in solid state physics. It crystallizes in the NaCl structure, has a partially filled 3d shell (Ni^{2+} $3d^8$), and is an antiferromagnetic insulator with a Néel temperature of 523 K [1]. It was pointed out early by *de Boer* and *Verwey* [2] that many of the properties of the 3d transition metal compounds do not agree with the predictions of band theory, e.g., standard band theory predicts NiO to be metallic. A qualitative explanation was proposed in terms of the *Mott-Hubbard* model [3,4] in which the on-site Ni 3d-3d Coulomb interaction plays a decisive role.

An early *ab initio* attempt to fix the shortcoming of band theory was to treat NiO as a *Slater* insulator in which the doubling of the unit cell allows for the existence of a gap [5–7]. However, the calculated gap of about 0.2 eV [5] turned out to be much too small: a combined photoemission (PES) and bremsstrahlung-isochromat (BIS) spectroscopy study showed that the band gap is 4.3 eV [8] and established thereby the correlated nature of NiO. The inclusion of a self-interaction-correction (SIC) or *Hubbard U* term to the density-functional formalism may provide a justification for the magnitude of the experimental band gap [9,10].

Yet, one of the most direct methods to critically test the accuracy of the different approaches, is to determine the excitation spectrum associated with the introduction of an extra particle into the system [13]. Curve (a) in Figure 1 displays the valence band X-ray photoemission spectrum (XPS, $hv = $ 1486.6 eV) of an *in situ* cleaved NiO single crystal. This spectrum represents essentially the Ni 3d spectral weight since the photoionization cross section of the O 2p is relatively small [14]. One can clearly observe from curve (e) in Figure 1 that the Ni 3d density of states calculated by band theory (in the local density approximation, LDA) does not match at all: it has a *Fermi* cut-off and the line shape is completely different. The inclusion of the *Hubbard U* in the calculations (LDA+U) does not solve the line shape problem, see curve (d). All this
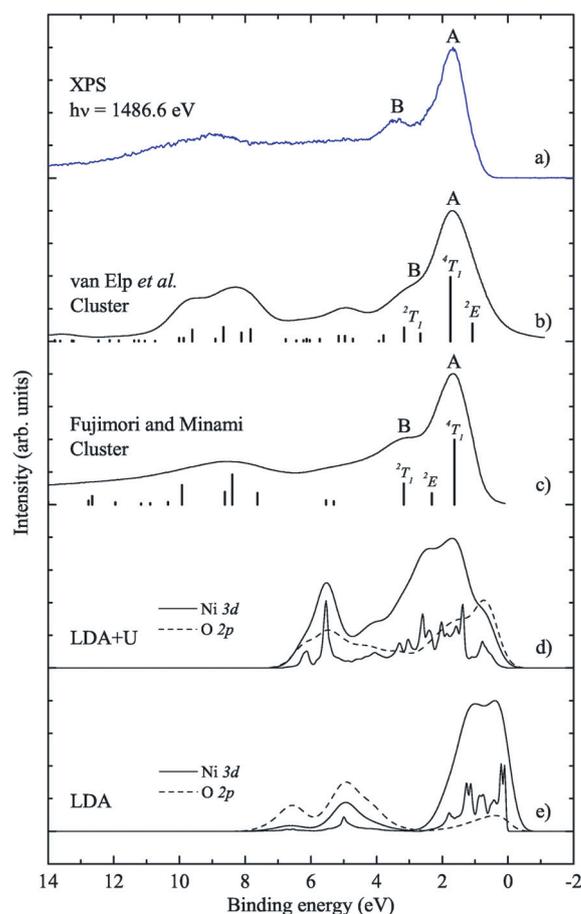
Fig. 1: Valence band XPS (1486.6 eV) spectrum of an *in situ* cleaved NiO crystal. The results of two single-site cluster calculations (reproduced from Refs. [11] and [12]), and LDA and LDA+U calculations are also included for comparison.

demonstrates the shortcomings of mean field theories to describe spectra associated with the fundamental one-particle *Green's* function of the system [10,15].

A completely different approach is to give up the translational symmetry of the system in order to focus on the local correlations and, especially, the dynamics of the propagation of the injected particle.

Curve (c) of Figure 1 shows the Ni 3*d* spectral weight from an early cluster configuration-interaction calculation by *Fujimori* and *Minami* [12], which also includes the full atomic multiplet theory. The agreement with the experimental spectrum is extremely good. Nevertheless, a later cluster calculation by *van Elp et al.* [11] arrived at a less satisfactory result: peak B has almost disappeared in the calculation, see curve (b). The prime motivation to use a different set of model parameters in [11] is to infer that the first ionization state is low spin (^2E) [16] rather than the *Hund's* rule high spin (^4T), analogous to the case of *Zhang-Rice* singlets in the cuprates [17,18]. Recent developments combining LDA with dynamical mean field [19–22] or GW approaches [23] yield Ni 3*d* spectral weights which deviate in important details from the experimental spectrum. These discrepancies between the experiment and the later theoretical simulations [11,19–22] do not provide confidence that one has made progress in understanding the nature of the first ionization state.

The issues that we address in this work are threefold. First of all we have to establish whether the XPS valence band spectrum in Figure 1 is truly representative for bulk NiO. There are reports in the literature claiming that certain satellite peaks in the Ni 2*p* spectrum are due to surface effects [24–26]. Second, we have to determine to what extent a single-site many body approach can be utilized to describe the electronic structure of NiO for which band formation is also essential. Third, we need to identify the nature of the first ionization state in the framework of a local *ansatz*. To this end we measured the valence band of NiO utilizing the more bulk-sensitive hard X-ray photoelectron spectroscopy (HAXPES) and we investigated experimentally the electronic structure of NiO impurities in MgO.

The XPS data (*hv* = 1486.6 eV) on *in situ* cleaved NiO single crystals were recorded using a *Vacuum Generators* twin crystal monochromator Al-K_α source and a *Scienta* SES-100 analyzer, with an overall energy resolution set to 0.35 eV. The HAXPES data (*hv* = 6500 eV) were taken at the Taiwan beamline BL12XU of SPring-8 in Hyogo, Japan using an *MB Scientific* A-1HE analyzer. The overall energy resolution was set to 0.35 eV. The NiO impurity in MgO system was prepared *in situ* as 10 nm − 20 nm thin films on polycrystalline Ag by means of molecular beam epitaxy. The meas-
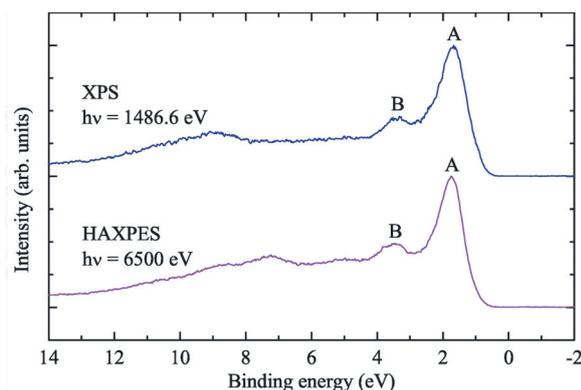
Fig. 2: Valence band photoemission spectra of an *in situ* cleaved NiO single crystal recorded using 1486.6 eV (XPS) and 6500 eV (HAXPES) photons.

urements were performed at the 11A1 Dragon beamline of the NSRRC in Hsinchu, Taiwan. The photoemission spectra were recorded at the *Cooper* minimum of Ag 4*d* (*hv* = 140 eV) [14,27] using a *Scienta* SES-100 analyzer with an overall energy resolution set at about 0.15 eV.

In Figure 2 we show the valence band photoemission spectra of a freshly cleaved NiO bulk crystal, taken with a photon energy of 1486.6 eV (XPS) and 6500 eV (HAXPES). By increasing the photon energy we increase also the kinetic energy of the outgoing photoelectron and, thus, also the inelastic mean free path. One can estimate that the probing depth is then enhanced from about 15 Å to roughly 80 Å [28]. We observe that the spectra are very similar. We, thus, conclude that the XPS data as displayed in Figures 1 and 2 is representative for the NiO bulk material and that the contribution of surface effects [24–26] can be safely neglected. To be specific: peak B is intrinsic for bulk NiO. We would like to note that increasing the photon energy from 1486.6 eV to 6500 eV does not alter much the Ni 3*d* character of the spectrum. The O 2*p* photoionization cross section relative to that of the Ni 3*d* remains very small, it changes from 1/13 to only 1/10 [29], meaning that peak B truly belongs to the Ni 3*d* spectral weight and not to the O 2*p* [21].

The valence band spectrum of the $Ni_{0.05}Mg_{0.95}O$ impurity system is shown in Figure 3 together with the spectrum of an MgO reference thin film grown simultaneously under identical oxygen and substrate conditions. The spectra are normalized to their O 2*s* core level intensities (not shown here). Both are dominated by the O 2*p* valence band, yet,

there are clear differences between them due to the presence or absence of the 5% NiO impurity. The difference spectrum multiplied by a factor of 6 is given by the red curve in Figure 3. This curve represents the Ni $3d$ spectral weight of the NiO impurity. Remarkable is that it is different from the spectrum of bulk NiO as shown in Figures 1 and 2. The impurity spectrum lacks specifically peak B which is prominently present in the bulk spectrum.

To interpret and understand the impurity spectrum, we have performed simulations using the well-proven configuration-interaction cluster model [30–32]. Within this method we have treated the Ni impurity within a NiO_6 cluster which includes the full atomic multiplet theory and the local effects of the solid. It accounts for the intra-atomic $3d$–$3d$ Coulomb and exchange interactions, the atomic $3d$ spin–orbit coupling, the local crystal field, and the O $2p$–Ni $3d$ hybridization. This hybridization is taken into account by adding the $3d^9\underline{L}$ and $3d^{10}\underline{L}^2$ states to the starting $3d^8$ configuration, where $\underline{L}$ denotes a hole in the O$2p$ ligands. The simulations have been carried out using the program XTLS 8.3 [30].

The bottom curve in Figure 3 shows the Ni $3d$ one-electron removal spectrum from the cluster calculation. The agreement with the experiment is very satisfactory. In order to achieve this, we have started the calculations by using parameter values which were suggested from earlier studies on NiO [11,30,33,34]. We then fine-tune the parameters describing the octahedral crystal and ligand fields,
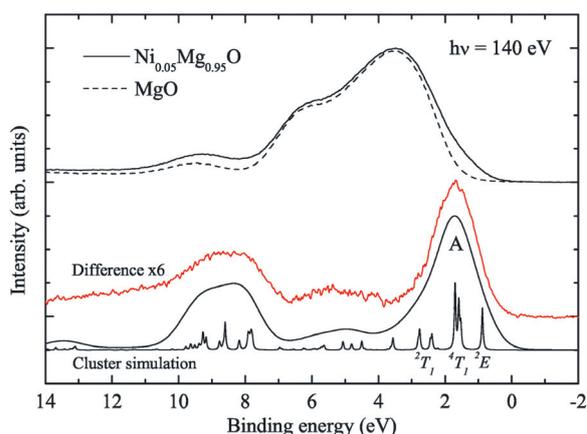
and also the difference between the *Hubbard U* and the O $2p$–Ni $3d$ charge transfer energy [35]. The crucial issue here is to obtain a main line (peak A) without having another feature appearing at about 2 eV higher energies (peak B) as was the case in the simulations by *Fujimori* and *Minami* [12] and by *van Elp et al.* [11]. This has implications for the energetics of the states making up the valence band as we explain in the following.

A detailed look at the cluster calculations displayed in Figure 1 shows that peak A is given by the $^4T_1$ final state of the Ni $3d^7$ multiplet structure while peak B is due to the $^2T_1$. Avoiding the appearance of peak B means that the energy splitting between these two states must be made smaller, e.g., 1 eV or less. This is what we have done in our simulation in Figure 3, using different but equally reasonable parameter values [35]. The consequences for the physics are, yet, quite far reaching. Given the fact that various X-ray absorption studies find an effective octahedral crystal and ligand field splitting of about 1.65 eV [33,34], i.e., the splitting between the isospin $^2T_1$ and ^2E states, we arrive at the conclusion that the ^2E must be lower in energy than the $^4T_1$ by 0.65 eV or more. This is what we read from our results in Figure 3. In other words, our impurity study provides the spectroscopic evidence that the first ionization state has a compensated-spin character rather than the *Hund's* rule high-spin. This in turn justifies that the ground state of a hole doped NiO system may indeed be low-spin in nature [16].

Fig. 3: Extraction of the NiO impurity valence band photoemission spectrum: Valence band spectra of $Ni_{0.05}Mg_{0.95}O$ and an MgO reference, together with the resulting difference spectrum. Also included is the result of a single-site configuration-interaction cluster calculation.
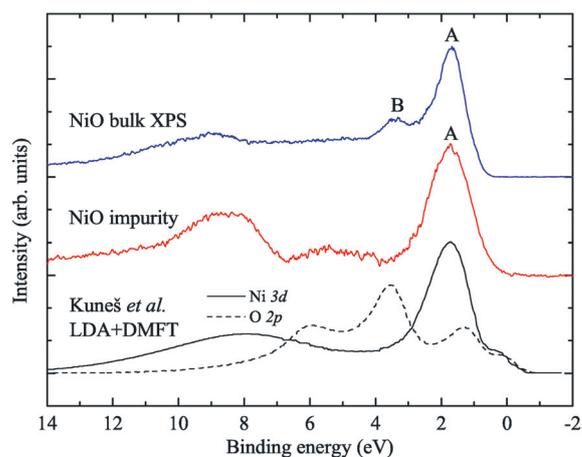
Fig. 4: Comparison of the valence band photoemission spectra of bulk NiO and NiO impurity in MgO. Also included are the simulated Ni $3d$ and O $2p$ spectral weights of the NiO valence band from a LDA+DMFT calculation (reproduced from Ref. [21]).

We now return to the problem of the bulk NiO valence band spectrum. Figure 4 shows the Ni $3d$ spectral weight taken with XPS and compares it with the spectra of the NiO impurity and of the single-site LDA+DMFT calculation [21]. One can clearly observe that peak B is absent in the impurity as well as in the Ni $3d$ spectral weight of the single-site calculation (the photoionization cross section of O $2p$ is much lower, it does not contribute significantly to the spectrum). In fact, one could infer that the calculation reproduces quite well the impurity spectrum, with perhaps some discrepancies due to the incomplete implementation of the multiplet structure of the on-site Coulomb interactions. Yet, the discrepancy with the bulk spectrum strongly suggests that the origin of peak B must be sought in non-local correlations, i.e., effects which cannot be included in a single-site approach.

Our suggestion is that peak B is due to non-local screening processes involving the formation of low-energetic coherent many body states on neighboring NiO clusters, which are of the ^2E type as we have shown above. The mechanism is similar as proposed earlier for the Ni $2p$ core level spectrum of bulk NiO [36], but the application of it for the valence band requires a careful analysis. If one starts to interpret the valence band of bulk NiO from a local or impurity *ansatz*, then one has to make an estimate about how well each of these states will retain their local character upon band formation. This is in particular difficult to calculate for the ^2E state, which is a state in which a hole is injected in an e_g orbital starting from the $3d^8$ $^3A_2$ ground state [34]. This hole can be expected to readily propagate in the lattice since the hopping between the Ni $3d(e_g)$ and O $2p(\sigma)$ orbitals are rather large [11,36], yet, it may leave behind an energetically costly wake of wrong spins in the antiferromagnetic lattice. In any case, it would not be meaningful to describe its band formation as a low-energy screening process involving neighboring ^2E states [37].

However, for the main peak of the bulk NiO spectrum, i.e., the $^4T_1$ state, we infer that we can make a meaningful approximation by using the coherent ^2E screening model. The $^4T_1$ consists of a hole injected into the t_{2g} orbital, and its ability to move is rather limited since the overlap between the Ni $3d(t_{2g})$ and O $2p(\pi)$ is small. One could con-
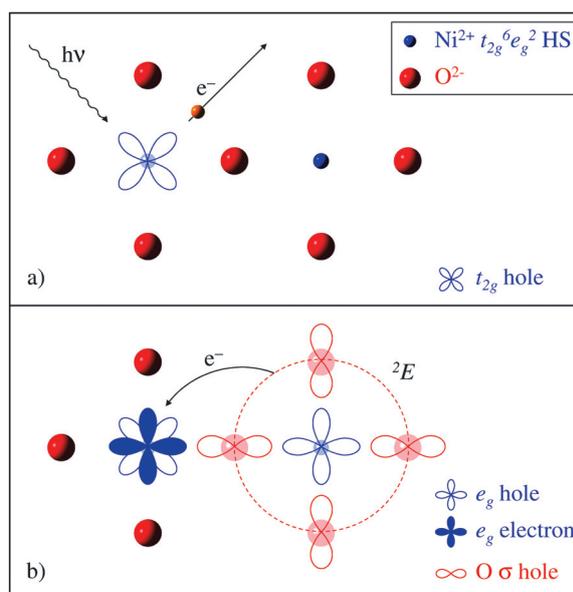
Fig. 5: Non-local screening in valence band photoemission on NiO: (a) Creation of the atomic-like (quasi-core) $4T_1$ hole state by the photoemission process. (b) Screening by a next neighbor NiO_6 cluster producing a coherent low-energetic ^2E hole state there.

sider the $^4T_1$ as a localized quasi-core state. We then can invoke the non-local screening process as follows: after the creation of the $^4T_1$ state, an e_g electron from a neighboring NiO cluster hops onto the Ni site, leaving behind a coherent ^2E hole state on that neighbor. A sketch for this process is given in Figure 5. These two states are energetically almost degenerate [36], and the Ni $3d(e_g)$ and O $2p(\sigma)$ hybridization between them is then strong enough to produce two peaks: not only the main peak A but also the satellite peak B. A multi-site cluster calculation has been carried out to describe this process quantitatively in the cuprates [38].

We have succeeded to determine reliably the Ni $3d$ valence band spectra representative for bulk NiO as well as for NiO as an impurity system. From the impurity data we are able to extract the local electronic structure and the correlations herein, thereby establishing firmly the compensated-spin character of the first ionization state. By comparing the bulk with the impurity system, we were able to identify features in the bulk NiO spectrum which are caused by screening processes involving local quasi-core valence band states and non-local low-energetic many body states.

References

[1] *W. L. Roth*, Phys. Rev. **110** (1958) 1333.

[2] *J. H. de Boer and E. J. W. Verwey*, Proc. Phys.Soc. London **49** (1937) 59.

[3] *N. F. Mott*, Proc. Phys. Soc. London, Sect. A **62** (1949) 416.

[4] *J. Hubbard*, Proc. R. Soc. London, Ser. A **276** (1963) 238.

[5] *T. Oguchi et al.*, Phys. Rev. B **28** (1983) 6443.

[6] *K. Terakura et al.*, Phys. Rev. Lett. **52** (1984) 1830.

[7] *K. Terakura et al.*, Phys. Rev. B **30** (1984) 4734.

[8] *G. A. Sawatzky and J. W. Allen*, Phys. Rev. Lett. **53** (1984) 2339.

[9] *A. Svane and O. Gunnarsson*, Phys. Rev. Lett. **65** (1990) 1148.

[10] *V. I. Anisimov et al.*, Phys. Rev. B **44** (1991) 943.

[11] *J. van Elp et al.*, Phys. Rev. B **45** (1992) 1612.

[12] *A. Fujimori and F. Minami*, Phys Rev B **30** (1984) 957.

[13] *C.-O. Almbaldh and L. Hedin*, "Handbook on Synchrotron Radiation" edited by *E. E. Koch*, Vol. **1b**, North-Holland, Amsterdam (1983) 607.

[14] *J. J. Yeh and I. Lindau*, At. Data Nucl.Data Tables **32** (1985) 1.

[15] *V. I. Anisimov et al.*, Phys. Rev. B **48** (1993) 16929.

[16] *P. Kuiper et al.*, Phys Rev. Lett. **62** (1989) 221.

[17] *F. C. Zhang and T. M. Rice*, Phys. Rev. B. **37** (1988) 3759.

[18] *H. Eskes and G. A. Sawatzky*, Phys. Rev. Lett. **61** (1988) 1415

[19] *X. Ren et al.*, Phys. Rev. B **74** (2006) 195114.

[20] *J. Kuneš et al.*, Phys. Rev. Lett. **99** (2007) 156404.

[21] *J. Kuneš et al.*, Phys. Rev. B **75** (2007) 165115.

[22] *Q. Yin et al.*, Phys. Rev. Lett. **100** (2008) 066406.

[23] *H. Jiang et al.*, Phys Rev. B **82** (2010) 045108.

[24] *L. Sangaletti et al.*, Solid State Commun. **103** (1997) 421.

[25] *L. Soriano et al.*, Phys. Rev. B **75** (2007) 233417.

[26] *I. Preda et al.*, Phys. Rev. B **77** (2008) 075411.

[27] *S. L. Molodtsov et al.*, Phys. Rev. Lett. **85** (2000) 4184.

[28] *C. J. Powell and A. Jablonski*, Surf. Interface Anal. **29** (2000) 108.

[29] *M. B. Trzhaskovskaya et al.*, At. Data Nucl. Data Tables **77** (2001) 97.

[30] *A. Tanaka and T. Jo*, J. Phys. Soc. Jpn. **63** (1994) 2788.

[31] *F. M. F. de Groot*, J. Electron. Spectrosc. Relat. Phenom. **67** (1994) 529.

[32] See the "Theo Thole Memorial Issue", J. Electron. Spectrosc. Relat. Phenom. **86** (1997) 1.

[33] *D. Alders et al.*, Phys. Rev. B **57** (1998) 11623.

[34] *M. W. Haverkort et al.*, Phys. Rev. B **69** (2004) 020408.

[35] Parameters used for the calculation of the NiO_6 cluster (in eV): $\Delta = 5.0$, $U_{dd} = 6.5$, $10Dq = 0.5$, $T_{pp} = 0.8$, $V(e_g) = 2.2$, $V(t_{2g}) = V(e_g)/1.5$, ζ see Ref. [30], *Slater* integrals 70% of *Hartree-Fock* values of the free Ni^{2+} ion.

[36] *M. A. van Veenendaal and G. A. Sawatzky*, Phys. Rev. Lett. **70** (1993) 2459.

[37] *M. Taguchi et al.*, Phys. Rev. Lett. **100** (2008) 206401.

[38] *A. Tanaka*, J. Phys. Soc. Jpn. **68** (1999) 3493.

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