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High-kinetic-energy photoemission spectroscopy of Ni at 1*s*: 6-eV satellite at 4 eV

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Electron correlations are responsible for many profound phenomena in solid-state physics. A classical example is the 6-eV satellite in the photoelectron spectrum of Ni. Until now the satellite structure has only been investigated at the *L* shell and more shallow levels. Here we report a high-kinetic-energy photoemission spectroscopy (HIKE) investigation of Ni metal. We present 1*s* and 2*p* photoelectron spectra, obtained using excitation energies up to 12.6 keV. Our investigation demonstrates that the energy position of the satellite relative to the main line is different for the 1*s* and the 2*p* levels. In combination with electronic structure calculations, we show that this energy shift is attributed to unique differences in the core-valence coupling for the *K* and $L_{2,3}$ shells in 3*d* transition metals, resulting in different screening of the core holes.

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Core and valence level photoelectron spectra provide direct and important information on correlation effects in matter. Particularly, photoelectron spectroscopy provides insight of how the dual atomic particlelike character and itinerant wavelike character of the electron manifest themselves in the physical properties of a material. This dual character is expressed through the appearance of a complicated satellite structure. The spectral shapes for these systems can still not be fully calculated by *ab initio* methods despite extensive efforts.[1–3] This makes the detailed interpretation of these spectra particularly important. Much attention has been paid to the so-called 6-eV satellite seen in the Ni $2p_{3/2}$ core-level spectrum as well as in the valence electron spectrum for Ni metal. The satellites have been interpreted as shake-up features connected to the narrow-band character of the Ni 3*d* band. A common interpretation for the core-level satellite is that it is dominated by a screened $2p^5 3d^9$ final-state configuration while the main line corresponds to a $2p^5 3d^{10}$ state.

The Ni 2*p* photoelectron spectrum from Ni metal was first studied in Ref. 4. A strong satellite associated to the Ni $2p_{3/2}$ line was found at 6-eV higher binding energy relative to the main line. The structure was attributed to a "surface plasmon" and this started the long controversy on the "Ni 6-eV satellite." A similar structure had already been observed in the valence bands of Ni. In 1975 Hüfner and Wertheim[5] proposed a phenomenological model including correlation effects for the core-level satellite. This has since then become a classical problem in core photoemission of metals, and one can find surveys in, e.g., Hüfners monography.[6] In 1980 Mårtensson and Johansson[7] applied a Born Haber cycle approach in combination with fully screened and localized excitonic states and got a remarkably good theoretical description of the Ni core-level satellites. More recent attempts to obtain a fully satisfactory description of the correlation effects in Ni from first principles have followed (see, e.g., Refs. 8–13). Very recently, a study was made where the satellite is again attributed to a surface plasmon,[14] as was the original idea from Ref. 4.

We have added independent experimental information on this fundamental problem by recording the satellite spectra for the deep Ni 1*s* core level. The reason has been lack of a suitable excitation source to reach this deep core level. The Ni 1*s* core electron has a binding energy of 8.33 keV and can therefore not be reached by using, e.g., a Cu $K\alpha$ excitation source (photon energy 8047 eV) for x-ray photoelectron spectroscopy. A study of the satellite structure for the Ni 1*s* core photoelectron line has therefore been missing up to now. In the last years the third generation synchrotron facilities have made possible a new technique, high-kinetic-energy photoemission (HIKE). [Also referred to as hard x-ray photoelectron spectroscopy (HAXPES)]. Using crystal monochromators in very highly resolving mode ($E/\Delta E \approx 100\,000$) and using a new generation of ultra-high-resolution electron spectrometers ($E/\Delta E \approx 100\,000$), it is possible to obtain very high-resolution photoelectron spectra in the range 2–12 keV excitation energy.

The measurements we present here were performed at the KMC-1 beamline at BESSY using the HIKE experimental station.[15] The analysis system of the HIKE station consists of the R4000 electron analyzer provided by VG Scienta, which is optimized for high kinetic energies up to 10 keV. The energy resolution of the analyzer was set to 0.25 eV. The KMC-1 beamline is equipped with three sets of double crystal monochromators, Si(111), Si(422), and InSb(111), which provides an excitation energy range varying from 1.7 to 12.0 keV. The present investigation employed excitation energies in the range of 8.7–12 keV. In this case, the total experimental resolution is given by the Si(422) double crystal monochromator which varies from 0.7 eV to approximately 1.2 eV. The Ni samples were prepared by sputtering of pure Ni onto a Si(111) substrate. The base pressure in the sputtering

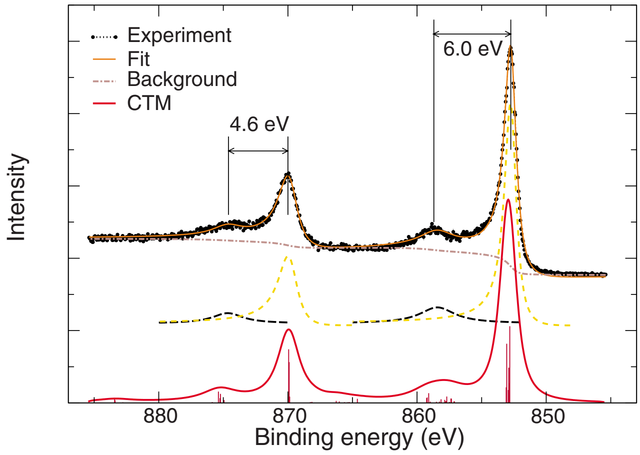

FIG. 1. (Color online) Ni $2p$ photoelectron spectrum recorded at 6.03 keV photon energy is shown together with a curve fit of the experimental spectrum (including the fitted Shirley background) and CTM calculations (see text). We find the satellite to be positioned at 6 eV relative to the $2p_{3/2}$ line, while it is positioned at 4.6 eV relative to the $2p_{1/2}$ line.

system was better than 1×10^{-8} mbar. The film thickness was about 50 nm.

In Fig. 1 we present the Ni $2p$ core photoelectron spectrum obtained at 6.03 keV excitation energy. This corresponds to a kinetic energy of the electrons of about 5.2 keV. The electron inelastic mean-free path is thus approaching 10 nm for this high kinetic energy, and the surface contribution is consequently almost negligible.[16] The spectrum has been fitted using Doniach-Sunjic line profiles[17] for each peak (satellites and main lines) and Shirley backgrounds[18] for each spin-orbit component. The satellite structure associated with the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ core photoelectron lines are found at 6.0 ± 0.2 and 4.6 ± 0.2 eV lower kinetic energies with respect to the main lines. The uncertainties are mainly due to the difficulties to determine the background contribution to the spectral density. Note that measurements so far have been made with excitation energies which are expected to result in substantial surface contributions to the spectra. The lifetime width of the Ni $2p$ core levels compared to the surface core-level shift is too large to permit a surface component to be measured directly. However, in Ref. 19 the surface and bulk spectra could be separated based on the fact that they have different angular variations due to photoelectron diffraction effects. The surface core-level shift was measured to be -0.31 eV for the main Ni $2p_{3/2}$ peak and -0.7 eV for the corresponding satellite.

In Fig. 2, we show the Ni $1s$ photoelectron spectrum recorded at 12.6 keV excitation energy, resulting in a kinetic energy of the emitted photoelectron in excess of 4 keV. This means that the electron mean-free path is similar to that for the $2p$ spectrum above. The experimental results are shown together with the corresponding theoretical calculations for the same core level. The fits were obtained in the same way as described for the $2p$ levels above (see Fig. 1). Also the $1s$ spectrum shows a strong satellite although in this case the satellite energy is found to be only 4.0 ± 0.3 eV. Again we find that the uncertainty is mainly attributed to difficulties in the background determination.

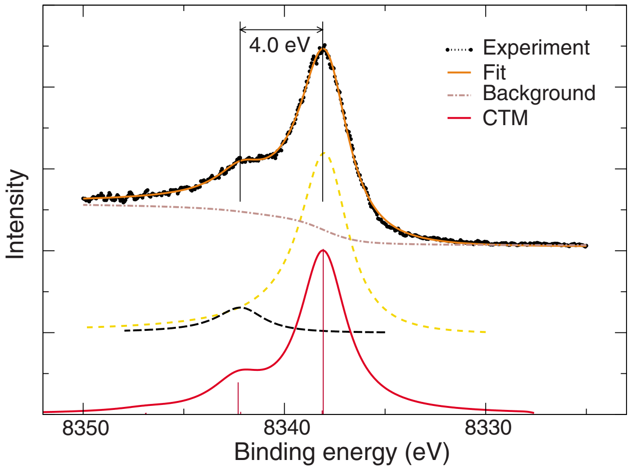

FIG. 2. (Color online) The Ni $1s$ photoelectron spectrum recorded using 12.6 keV excitation energy is shown together with the fitted results and multiplet calculations. The satellite is found at 4.0 eV relative to the main line.

Hence, we find very different satellite energies for the different core levels. The satellite positions are 4.0, 4.6, and 6.0 eV for the $1s$, $2p_{1/2}$, and $2p_{3/2}$ core levels, respectively.

The pronounced shell dependence gives strong evidence against the interpretation that the satellites are due to plasmon losses, and these results thus clearly show that the recent reinterpretation in Ref. 14 is not tenable. Instead, the difference in satellite energy can be described within the $3d$ shake-up model. In Ref. 7 the energy of the $3d$ shake-up was calculated within a complete screening model. The energy of both the $2p_{1/2}$ and $2p_{3/2}$ satellites was calculated to be 4.6 eV. In Ref. 20 the consequences of the $2p^5 3d^9$ multiplet effects were further analyzed. The $2p_{1/2}$ satellite has a relatively narrow multiplet pattern, and hence the observed satellite energy corresponds closely to the calculated energy for the configuration average. For the $2p_{3/2}$ satellite the multiplet pattern extends over several eV. For the low-energy multiplets the effective core hole $3d$ Coulomb interaction is too small for the satellite states to appear as split-off discrete states. The observed satellite is instead due to the high-energy multiplets. These are calculated to be more intense and they form a distinct structure at 6 eV, consistent with the calculated position of the configuration average.

An important difference between a $1s$ and $2p$ core hole is their degree of localization as well as screening, which influences the $3d$ valence states. To obtain insight into the different screening processes at the $1s$ and $2p$ edges, we have performed density-functional theory (DFT) supercell calculations including a Ni $1s$ or a $2p$ core hole. The calculations were performed within the local-density approximation.[21] We used the full potential linearized augmented plane-wave (FPLAPW) band-structure method as implemented in the WIEN2K package.[22] These calculations include self-consistent screening processes of all electrons in the supercell of 32 atoms. The results (not shown) demonstrate that the presence of a $1s$ core hole has a weaker influence on the $3d$ states as compared to a $2p$ core hole. In particular, for a $2p$ core hole, the center of gravity of the $3d$ DOS is pulled down deeper below the Fermi energy.

To calculate the spectra we have used a configuration interaction model for the initial and final states,[23] which derives from Cowan's code.[24] We modeled both initial and final states as a mixture of $3d^8$, $3d^9$, and $3d^{10}$ configurations. The initial state of $16\% d^8 + 47\% d^9 + 37\% d^{10}$ is the commonly accepted representation of the metallic nickel ground state.[12,13] As our DFT calculations have shown, one should expect that the $1s$ core hole state will be described by a configuration closer to the initial state than the $2p$ core hole state. The transfer of valence states toward lower energies in the presence of a $2p$ core hole implies a stronger localization tendency of the $3d$ states leading to a stronger onsite Coulomb repulsion U_{2p}. Furthermore, the core hole potential Q_{1s} is lower than Q_{2p} because of the smaller spatial extent of $1s$ states and, consequently, smaller overlap with valence $3d$ band states. Taking these facts together, we estimate the following set of parameters for the excited atom: $Q_{1s} - \Delta_{1s} = 3$ eV, $U_{1s} = 3$ eV, $Q_{2p} - \Delta_{2p} = 3.85$ eV, $U_{2p} = 5.15$ eV, and $T_{1s,2p} = 1.4$ eV, where $\Delta_{1s,2p}$ and $T_{1s,2p}$ are charge-transfer energies and mixing integrals for systems with a $1s$ or $2p$ core hole, respectively.[13] With these parameters we computed the $1s$ and $2p$ photoemission spectra using the charge-transfer multiplet (CTM) theory.[23,24] They are shown in Figs. 1 and 2, together with experimental data and fits, which clearly reveal the main lines (dashed yellow curves) and satellites (dashed black curves). The measured and computed photoelectron spectra compare very well. At the $2p_{3/2}$ and $2p_{1/2}$ edges the computed satellite appears at 6.0 and 4.6 eV, respectively, while at the $1s$ edge it appears at 4.0 eV. These satellite positions coincide with the experimental ones.

In summary, we have used high kinetic photoelectron spectroscopy to investigate the bulk electronic structure of Ni metal at the $1s$ and $2p$ regions, and we are able to use the data for the $1s$ level to complete the picture. Unexpectedly, we find that the correlation satellites are located at different energies relative to the main photoelectron line for different levels. Both the $1s$ and $2p$ photoemission spectra of bulk metallic Ni can be consistently explained by the same theoretical approach. We have identified the physical mechanism leading to the shift of the $1s$ satellite to be due to the difference in $1s$ core hole screening and localization.

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