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Electronic States of UNi₂ from Photoemission Spectroscopy

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We measured the angle-resolved ultraviolet and X-ray photoemission spectra of UNi₂ single crystal. The valence band angle-resolved ultraviolet photoemission spectra were compared to the accessible band structure calculations. For UNi₂ the lowest binding energy strong emission at about -0.1 eV comes from U 5*f* states and overlaps with the Fermi edge. A small feature at -0.6 eV was ascribed also to U 5*f* electrons with more localised character. The higher-energy two-peak structure at about -1.2 eV and -2.1 eV comes from Ni 3*d* states. X-ray photoemission spectroscopy shows the standard two-line spin-orbit splitting of the Ni 2*p* states and of the U 4*f* states. Some hybridisation of the Ni 3*d* and U 5*f* state was observed in the spectra. The pronounced satellites to the Ni 2*p* and 3*p* states, associated with the on-site Coulomb repulsion and other electron correlation energies, were observed.

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1. Introduction

The uranium may have localised as well as delocalised 5*f* electrons in intermetallic compounds. The hybridisation of the 5*f* electron states either with the conduction band or with the ligand valence states gives rise to the itinerant or localised behaviour. The theory of so-called dualism of the U 5*f* electrons in intermetallic uranium compounds was developed [1].

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The Laves phase UNi₂ orders ferromagnetically below $T_C = 24$ K [2–6], with spontaneous magnetic moment of $\mu_s = 0.081 \mu_B/\text{f.u.}$ at 4.2 K oriented along the b -axis. Susceptibility measurements in the paramagnetic region and pressure experiments are consistent with the description of UNi₂ as a weak itinerant ferromagnet due to $5f$ electrons [3, 6]. From the polarised neutron scattering measurements [6] the total magnetic moment is $\mu = 0.066 \mu_B$ ($\mu_U = 0.082 \mu_B$ and $\mu_{Ni} = 0.015 \mu_B$; assuming U³⁺) or $\mu = 0.076 \mu_B$ ($\mu_U = 0.094 \mu_B$ and $\mu_{Ni} = -0.013 \mu_B$; with U⁴⁺) and is comparable with the bulk magnetisation data [2, 3].

2. Experiments

UNi₂ single crystal was grown by the Czochralski method in a tri-arc furnace [3]. UNi₂ crystallises in the hexagonal MgZn₂ structure. Laue patterns and neutron diffraction showed that the investigated single crystals were of very good quality.

The room temperature valence band (VB) spectra were detected with the angle-resolved ultraviolet photoemission spectrometer (ARUPS) equipped with the high-energy resolution analyser and LEED/AES spectrometers from Omicron. The spectra were recorded as a function of the incident angles θ of ultraviolet radiation and the angle Φ of outgoing electrons with respect to the surface normal. The energy resolution of the spectrometer was about 40 meV. The high intensity ultraviolet helium source from Focus with energy 21.2 eV was used. Surfaces were cleaned by heating up to 500–700°C and annealed them *in situ* in UHV down to the lowest pressure 10^{-11} mbar as well as by argon sputtering. The surface cleanness and the influence of annealing and argon sputtering were checked by the Auger electron spectra (AES) of oxygen and of carbon as well as of all constituent elements. The standard procedure was used to subtract the background from secondary electrons.

The core-level and valence band X-ray photoemission (XP) spectra were measured with monochromatised Al K_α radiation (1486.6 eV) at room temperature, using a PHI 5700/660 spectrometer with a hemispherical mirror analyser and with an energy resolution of about 0.3 eV, under a vacuum of about 10^{-10} Torr. The Fermi level ($E_F = 0$) was referred to the gold $4f$ -levels binding energy at 84.0 eV. The samples were cleaved in the UHV chamber.

3. Results and their analysis

Figure 1 show the ARUPS spectra of UNi₂. A peak at about -0.1 eV very close to the Fermi energy at $E_F = 0$ eV was observed which was enhanced in the He(II) spectrum (not shown because they are the same as published in [7]). It suggests that the feature has a dominant U $5f$ character in a good agreement to that reported earlier [7–10]. At lower binding energy the spectra are dominated by a broad emission from -0.5 to -3.0 eV, which is due to the Ni $3d$ states as proved by the experimental [7–9] and theoretical papers [8, 10–12]. A qualitative

comparison of the theoretically calculated density of states (DOS) [8] with an ARUPS spectrum for $\theta = 40^\circ$ and $\Phi = 0^\circ$, Fig. 2, shows very good agreement as far as the binding energies of all features (cf. the arrows in Figs. 1 and 2) and their relative intensities are considered. The small feature at about -0.6 eV (hardly seen, shown by arrow in Fig. 1) is ascribed to more “localised” U $5f$ states hybridised with Ni $3d$ as compared to more “itinerant” U $5f$ electrons at -0.1 eV (cf. Fig. 2 and [8–10]).

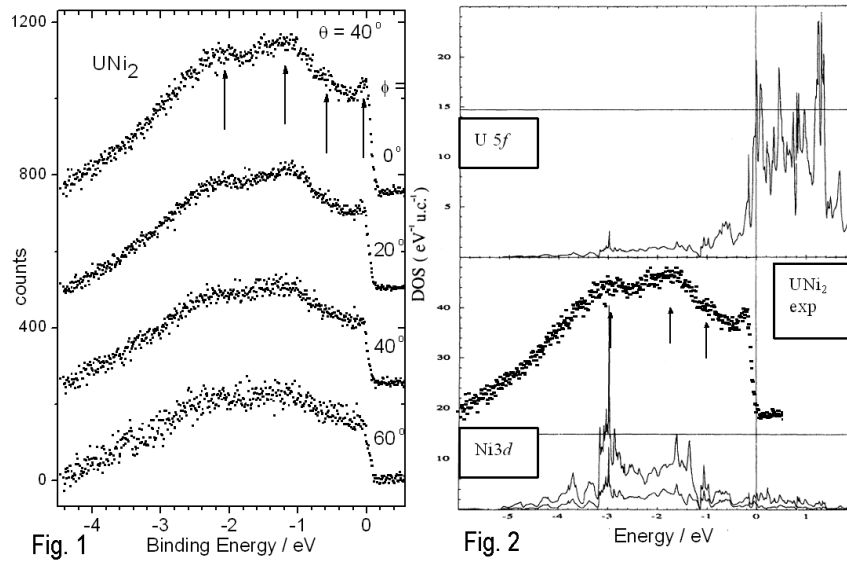


Fig. 1. The ARUPS spectra of UNi_2 . Fig. 2. The ARUPS vs. theoretical DOS [8].

The partial site-projected densities of U $5f$ and Ni $3d$ states (DOS) in Fig. 2 were calculated [8] using the linear muffin-tin orbital method (LMTO) within the atomic sphere approximation (ASA) and the spin-orbit interaction was included in a self-consistent manner. Our ARUPS spectra are in qualitative good agreement with the calculations [8] as well as with the similar calculations performed in [11, 12]. It turned out that the U $5f$ spectral DOS is dominated by the peak just below or even at E_F , which corresponds with the features spreading from -0.06 eV to -0.10 eV depending on the emission angle θ (see Fig. 1) due to some small energy dispersion. There are no published calculations of electron dispersion curve. Unpublished preliminary results [11] show rather flat subbands of $3d$ and $4f$ electrons in the valence band. All the calculations showed that there is only a very small amount of Ni $3d$ character at E_F , which originates from hybridisation with the U $5f$ states. The main Ni $3d$ -contributions to VB are concentrated to the region from -1 eV to -3 eV. That is why the two-peak structure, which is developing to one broad peak at high photon energy XP-VB spectrum at about

–1.5 eV (see Fig. 3), was ascribed totally as coming from the Ni 3*d* DOS contribution. Therefore, the experimental finding [7] that the peak at about –2.1 eV may come from localised U 5*f* states attributed to uranium oxide UO₂ is still debatable because some oxidation of the surface was observed in the Auger spectrum, in the He(II) spectrum as a small broad peak at about 22 eV of O 2*p* emission and from the lack of clear low-energy electron diffraction (LEED) reflections (not shown here).

The total X-ray photoemission spectrum of UNi₂ is presented in Fig. 3 together with the VB spectrum, Ni 2*p* spectrum, and the lower binding energy part of the spectrum in extended energy scale.

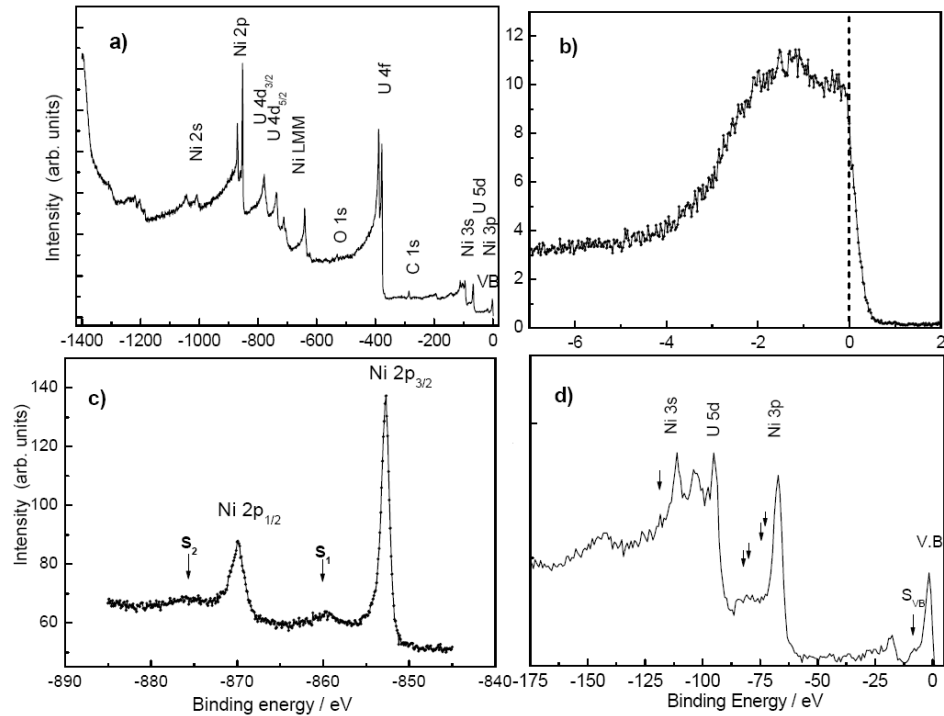


Fig. 3. (a) The total XP spectrum of UNi₂, (b) the XP valence band spectrum, (c) the XP Ni 2*p* spectrum, and (d) the lower binding energy part of the total XP spectrum with the satellites indicated by arrows.

The VB–XP spectrum is shown in Fig. 3b to be compared to the ARUPS spectra in Fig. 1. The energy width of both VB spectra are the same but the tenfold difference in energy resolution is clearly seen. The spin–orbit split spectrum of the Ni 2*p* and U 4*f* electrons is typical (see Fig. 3a). The well-known satellites to 2*p*, 3*p*, 3*s* states and also to VB for metallic Ni and its compounds (cf. e.g. [13, 14]) are indicated by arrows in Figs. 3c and d. The satellite lines which are visible at

-7.2 eV (S_1) and -5.5 eV (S_2) above the $2p_{3/2}$ and $2p_{1/2}$ peaks, respectively, are associated with not completely filled Ni 3d band and with the on- d site Coulomb repulsion correlation energy U_{dd} . Analysis of the Ni 2p core-level spectrum and of some Auger lines allows for an estimate of the correlation parameters using the scheme of configuration interactions within a cluster model [15–17]. It will be presented elsewhere.

4. Conclusions

1. The U 5f electrons in UNi₂ must be considered in a larger part as itinerant and are participating in the Fermi surface as well as shall be included in the self-consistent calculations as the other valence electrons. Presumably, some smaller part of those electrons (cf. the small feature at -0.6 eV in ARUPS spectra in Figs. 1 and 2) must be treated as more localised.

2. The hybridisation together with a large difference of electronegativity (amounting into a charge transfer from U to Ni) leads to the shift of the filled part of the Ni 3d band from E_F (cf. the emissions at -1.2 eV and -2.1 eV in the spectra in Figs. 1 and 2), so that those electrons are participating to the Fermi surface to much smaller extent than the uranium electrons.

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