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**Author:** T. Toliński, A. Kowalczyk, Grażyna Chełkowska, M. Mihalik, M. Timko

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# Valence Band and Core Levels of Ce$_5$Ni$_2$Si$_3$ Crystal Studied by X-ray Photoemission Spectroscopy

T. Toliński$^a$, A. Kowalczyk$^a$, G. Chełkowska$^b$,
M. Mihalik$^c$ and M. Timko$^c$

$^a$Institute of Molecular Physics, PAS
M. Smoluchowskiego 17, 60-179 Poznań, Poland
$^b$Institute of Physics, Silesian University
Uniwersytecka 4, 40-007 Katowice, Poland
$^c$Insitute of Experimental Physics, Slovak Academy of Sciences
Watsonova 47, 04353 Košice, Slovakia

The crystal of Ce$_5$Ni$_2$Si$_3$ was prepared by the Czochralski method. The X-ray photoemission spectroscopy was measured for the valence band and the core levels. Based on the Ce($3d$) doublet and its satellites a small value of the hybridization parameter of the $f$-states with the conduction electrons $\Delta = 4$ meV and the $f$-occupancy $n_f$ close to 1 were found. X-ray photoemission spectroscopy shows that the region between 0 and 3 eV is predominated by the Ni($3d$) and Ce($4f$) peaks. Some features of the multiplet structure of the Ce($4f$) states are also visible close to the Fermi level.

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## 1. Introduction

The Ce$_5$Ni$_2$Si$_3$ compound is a geometrically frustrated magnet with an antiferromagnetic transition at $T_N = 7.3$ K. The crystallographic structure is hexagonal of the Ce$_2$NiSi-type, space group $P6_3/m$ with the lattice constants $a = 15.9$ Å and $c = 4.3$ Å. This compound exhibits a relatively large electronic specific heat coefficient $\gamma = 263-300$ mJ K$^{-2}$mol$^{-1}$, typical of the Kondo systems [1–3]. In connection with the observations of the large effective mass and the presence of the magnetic ordering one can expect a large degree of localization of the Ce($4f$) states. To cast more light on the question of the hybridization effects and the occupancy of the $f$ states we have measured the X-ray photoemission spectra (XPS) for the core states and the valence band of the Ce$_5$Ni$_2$Si$_3$ crystal grown by the Czochralski method. The Ce($3d_{3/2,5/2}$) spin–orbit split doublet and its satellites have been analyzed based on the Gunnarsson–Schönhammer (G–S) model [4].

## 2. Results and discussion

The $Ce_5Ni_2Si_3$ crystal was grown by the Czochralski method from the melt of stoichiometric composition in Ar atmosphere. The X-ray photoemission spectra were obtained using the Al $K_\alpha$ radiation with the PHI 5700/660 Physical Electronics Spectrometer.
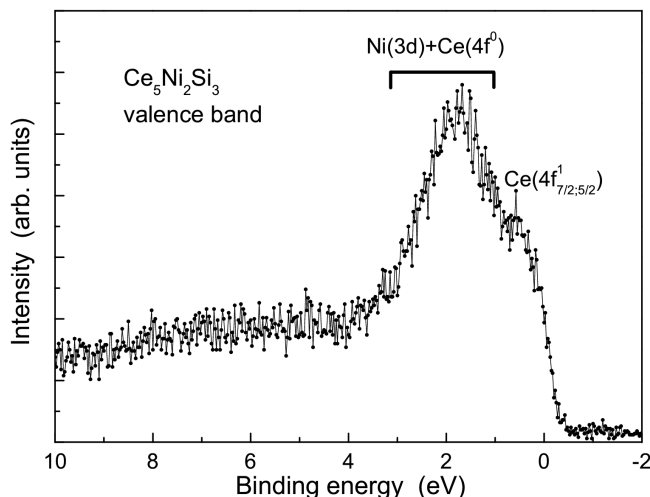


Fig. 1.   Valence band spectrum of the $Ce_5Ni_2Si_3$ crystal.

Figure 1 presents a valence band spectrum of the $Ce_5Ni_2Si_3$ crystal. As indicated in the figure in the energy range from about 0.9 eV up to 4 eV the valence band is predominated by the Ni(3d) and Ce(4f$^0$) peaks. Both contributions can be significant and as results from various studies on Ce and Ni metals and on compounds containing both the elements the contributions due to these states can be close in energy [5, 6]. The Si atoms can yield a small contribution due to $3p$ states within 1.5–4.5 eV, mixed $3s$ and $3p$ states at 7 eV and $3s$ states around 9.5 eV [7]. Close to the Fermi level some features of the multiplet structure of the Ce(4f) states can be noticed. They supposedly develop from the spin–orbit (SO) split Ce($4f_{7/2,5/2}$) final states. According to the theoretical and resonant XPS studies this SO splitting is equal to 280 meV [5, 6]. However, these subtle effects cannot be precisely identified with the standard XPS experiment and the discussed interpretation is mainly qualitative. The analysis of the valence band region suggests a localized character of the Ce(4f) states. Such an assumption is justified by the XPS measurements of the Ce(3d) core states.

Figure 2 shows the Ce(3d) doublet and satellites resulting from the modified screening of the core hole due to the various possible final states ($3d^9 4f^0$ and $3d^9 4f^2$). The G–S model shows how one can extract the values of the hybridization parameter $\Delta$ between the $f$ states and the conduction electrons, and the $f$ occu-
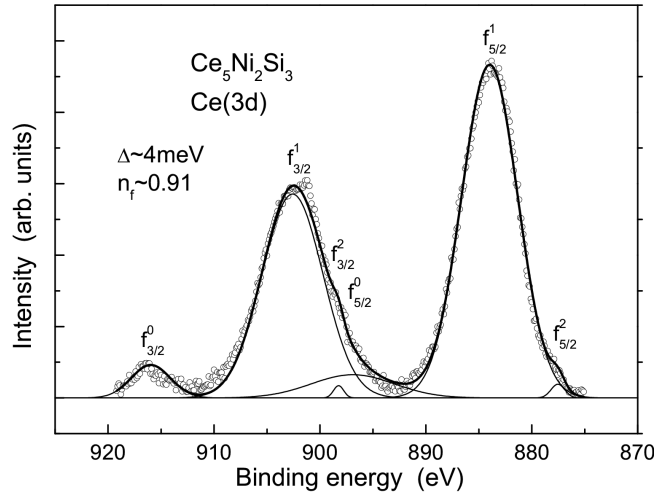
Fig. 2. Experimental (circles) Ce(3$d$) doublet and its satellites measured by XPS for the Ce$_5$Ni$_2$Si$_3$ crystal. Thick solid line presents a fit and the thin solid lines reflect the corresponding components.
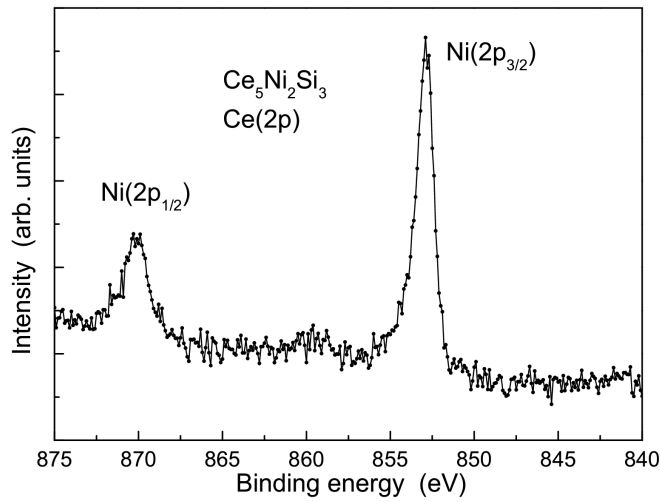


Fig. 3. XPS Ni(2$p$) doublet with a small satellite peak visible at $E_B = 860$ eV.

pancy $n_f$ based on the intensity ratios of the main peaks and the satellites. The details are provided elsewhere [4, 8]. From the analysis we have got the estimated values $\Delta = 4$ meV and $n_f = 0.91$. These values imply that the hybridization is very weak and the $f$ electrons are localized keeping mainly the Ce$^{3+}$ valence state. Further analysis of the XPS core states concerns the Ni(2$p$) doublet, which is displayed in Fig. 3. The SO split is equal to 17.25 eV. The presence of a small satellite between the main peaks usually means that the Ni contribution to the

magnetic properties of a compound is negligible by the reason of the filling of the $3d$ band.

## 3. Conclusions

The X-ray photoemission spectroscopy measurements on the $Ce_5Ni_2Si_3$ crystal revealed the predominance of the Ni($3d$) and the Ce($4f$) states at the valence band region. The position of the $f$ peaks and the analysis of the Ce($3d$) core states corroborate the localization of the $f$ electrons and the $Ce^{3+}$ valence state.

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