

VALENCE OF CONSTITUENTS OF SELECTED RARE EARTH SILICIDES — XANES AND LAPW NUMERICAL STUDY

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The intermetallic rare earth (RE) silicides bring out a lot of attention due to their uranium based members, frustrated geometry and interesting magnetism. Although the electronic structure and magnetism are primarily determined by the rare earth and the RE-Pd/Rh hybridization it is interesting to verify a role of silicon as a “passive” spacer.

Here we report on the investigation of the chemical environment and electronic structure of Si and Pd using X-Ray Absorption Fine Structure in two different families. The XAS experiments were performed at the DAFNE-Light Laboratory of the Laboratori Nazionali di Frascati, Italy. Data were collected at room temperature, in the transmission mode.

Two families of silicides were chosen for the study. First, we elucidated similarities and differences caused by different rare earth in the same matrix for RE₂PdSi₃ series, where RE=Ce, Nd, Td, Dy, Ho, Er. The compounds crystallize in an AlB₂-type structure (space group P6/mmm). The RE ions occupy the Al-equivalent positions, while non-magnetic Pd and Si atoms should be statistically distributed on B sites. However, recent study has hinted to the existence of additional order between Pd/Si layers, which coexists with the disorder [1].

Figure 1. presents Si K edges (some are omitted for clarity) of Ce, Dy and Er based compounds as

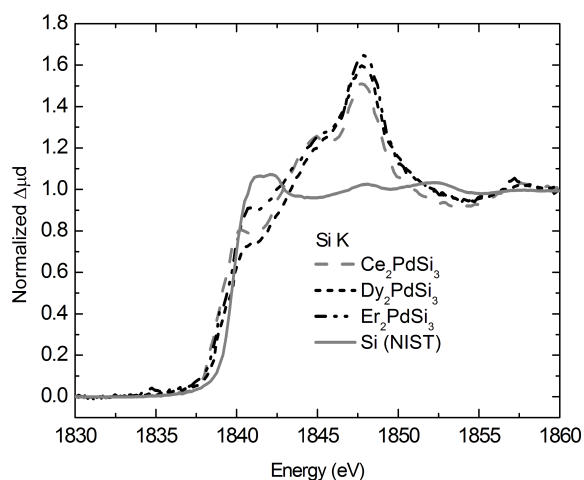


Figure 1: Si K edges of selected compounds of R₂PdSi₃ series.

well as pure silicon.

The Si K edges of the silicides are shifted to lower energies by about 0.5 eV, relative to pure Si and this shift decreases with filling of the 4*f*-shell of the RE. Such trend is consistent with the weak anionic character of Si, which is reduced by the increased screening and contraction of the radius of the lanthanide.

The Pd *L*_{III} edges were recorded with worse quality due to weak signal in the transmission mode. Figure 2. presents the edges of the respective compounds with the presented error bar estimated from the raw spectra.

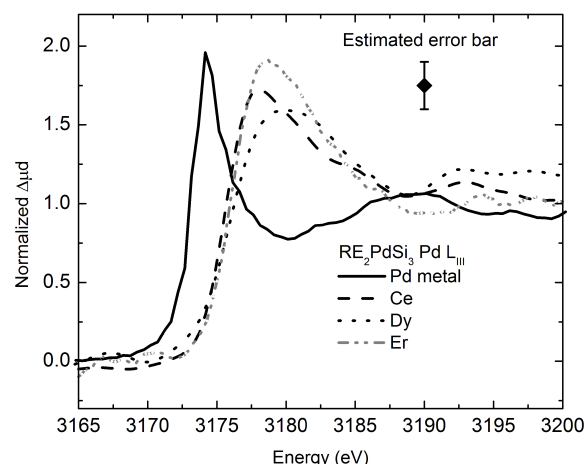


Figure 2: Smoothed Pd *L*_{III} edges of R₂PdSi₃ series.

Contrary to the Si *K*, all of the Pd *L*_{III} edges are shifted to higher energies in accordance with the cationic character of the metal. Due to significant noise, it was impossible to observe any systematic effect with the increasing atomic number of the rare earth.

The second part of the study was based on the HoRh_{*x*}Pd_{2-*x*}Si₂ series of compounds, which crystallize in the tetragonal ThCr₂Si₂-type crystal structure (space group I4/mmm). Here, the charge equilibrium of the system was imbalanced on the transition metal site by substitution of the palladium ([Kr]4*d*10) with rhodium ([Kr]4*d*85*s*1). Figure 3. presents Si *K* edges of the selected members of the family.

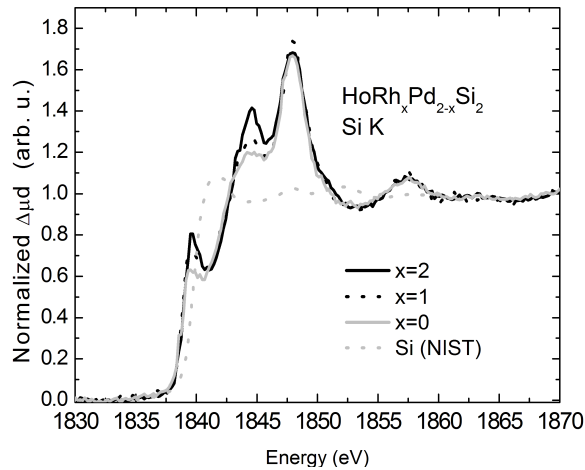


Figure 3: Si K edges of selected compounds of the $\text{HoRh}_x\text{Pd}_{2-x}\text{Si}_2$ series.

They are also shifted to lower energies in agreement with slight anionic character of the silicon. However, no change in the edge position is observed with Pd/Rh substitution. On the other hand, a clear trend can be observed in the amplitude of the edge structures situated at 1840 eV and 1845 eV, which decreases with larger Pd content. Such behaviour can be understood in term of the hybridisation between TM d and Si p states. As the TM $4d$ states are filling up and are pulled down below the Fermi's energy, they drag a part of spectral density away from the silicon $3p$ band.

In order to better comprehend the properties of both families, we concentrated on the holmium ones as the common rare earth [2, 3] and calculated theoretical densities of states using Wien2K'09 code with LDA+U formalism. Figure 4. shows that the Si K edge of HoPd_2Si_2 is well reproduced

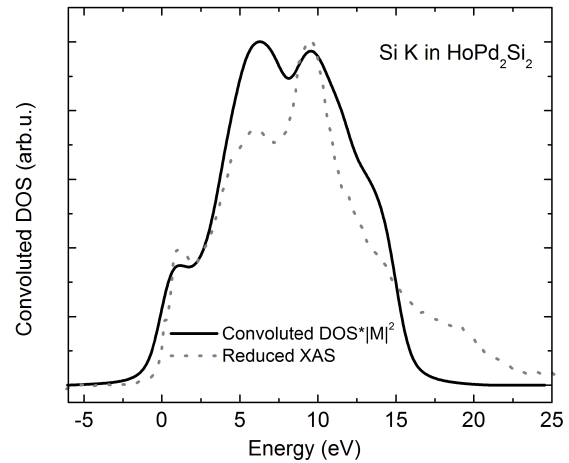


Figure 4: Comparison of calculated and experimental Si K edge in HoPd_2Si_2 .

up to 15 eV above the edge where our approximation breaks down. All features are reproduced both in the edge and its derivative.

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