

Hard X-ray Photoemission Spectroscopy of Temperature-Induced Valence Transition in $\text{EuNi}_2(\text{Si}_{0.20}\text{Ge}_{0.80})_2$

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We investigate the temperature-induced mixed valence transition in $\text{EuNi}_2(\text{Si}_{0.20}\text{Ge}_{0.80})_2$ using Hard X-ray (5940 eV) photoemission spectroscopy (HX-PES), with a probing depth larger than 5 nm. The Eu 3*d*, Ni 2*p* and Ge 2*p* core-level states are studied below and above the critical valence transition temperature, $T_v = 80$ K. HX-PES spectra at 40 K and 120 K show the mixed valence transition, with clear changes in the divalent and trivalent Eu 3*d* chemically shifted features, and negligible changes in the Ni 2*p* and Ge 2*p* states. The Eu 3*d* spectral shapes match very well with the results of the atomic calculations of the Eu^{2+} and Eu^{3+} configurations, confirming intra-atomic multiplet features. The Eu 3*d* HX-PES spectra indicate a mean valence of 2.70 ± 0.03 at 40 K which changes to 2.40 ± 0.03 at 120 K, in good accord with the results of bulk Eu L-edge X-ray absorption spectroscopy measurements.

KEYWORDS: $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$, Hard X-ray photoemission, temperature-induced valence transition, rare-earth compounds

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Many rare-earth compounds^{1–5)} exhibit a valence transition induced by temperature, magnetic field and/or pressure. These include SmS ,⁶⁾ YbInCu_4 ,^{7–9)} TmTe ¹⁰⁾ as well as the Eu-based intermetallics, such as EuPd_2Si_2 ,^{11,12)} $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ ^{13–17)} and $\text{Eu}(\text{Pd}_{1-x}\text{Au}_x)_2\text{Si}_2$.¹⁸⁾ Among these systems, the Eu-based systems are unique in terms of the rather large change in valency between the Eu^{2+} ($4f^7$) and Eu^{3+} ($4f^6$) configurations that they exhibit as a function of temperature.^{4,5,11–18)} For example, the mean valence of the Eu ion in $\text{EuNi}_2(\text{Si}_{0.2}\text{Ge}_{0.8})_2$ changes from nearly trivalent (~ 2.75) in the low temperature phase to nearly divalent (~ 2.35) in the high temperature phase, across the critical temperature (T_v) of ~ 80 K.^{13–17)} This is a larger change as a function of temperature than, for instance, that of YbInCu_4 , which shows a change of mean valence from ~ 2.95 to ~ 2.85 across a sharp valence transition at ~ 42 K,⁷⁾ although larger changes as a function of pressure have been known, e.g., as in YbAl_2 .¹⁹⁾ The temperature dependent transition in YbInCu_4 has been recently measured by high resolution X-ray absorption and resonant inelastic X-ray scattering (RIXS) experiments at the L-edge (~ 8.95 keV), establishing RIXS as a quantitative probe of the Yb 4*f* electron occupation number.⁷⁾ In contrast, Soft X-ray (SX) photoemission experiments on YbInCu_4 showed a gradual change preceding the transition and a mean valence different from the RIXS measurements, which was attributed to surface effects.⁸⁾

Many Eu compounds crystallizing in the ThCr_2Si_2 tetragonal structure are known to exhibit the mixed valence transition. $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ exhibits a temperature-,^{13–16)} magnetic field-¹⁴⁾ and/or pressure-¹⁷⁾ induced valence

transition. The temperature dependent mixed valence transition of Eu ions in $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ was investigated across the critical temperature (T_v) of ~ 87 K by magnetic susceptibility,¹⁴⁾ Eu L-edge X-ray absorption spectroscopy (XAS),¹⁴⁾ and X-ray diffraction¹⁵⁾ studies. The Eu L-edge X-ray absorption experiment of $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ indicated a mean valence at 40 K of about 2.75 which changes at 120 K to ~ 2.35 . While the Eu 3*d* core-level X-ray photoemission spectroscopy (XPS)¹⁶⁾ of $\text{EuNi}_2(\text{Si}_{0.25}\text{Ge}_{0.75})_2$ ($T_v \sim 115$ K) using a SX Al $K\alpha$ source ($h\nu = 1486.6$ eV) was expected to yield a similar valence change as for the $x = 0.79$ composition, the spectra showed a much larger Eu^{2+} component than expected and the mean valence was estimated to be 2.17 at 33 K and 2.08 at 300 K. This result being different from that of the Eu L-edge XAS, it was attributed to the fact that, with the kinetic energy of Eu 3*d* photoelectrons being around 330 eV, the spectra obtained from the XPS reflect the surface electronic structure.¹⁶⁾

The surface versus bulk electronic structure of correlated *d* and *f* electron systems has been a controversial issue for many years e.g. valency changes^{8,16)} and the Kondo effect⁷⁾ on the surface can be different compared with that in the bulk; another issue is in the context of a surface related enhancement of correlation effects.^{19–22)} A recent advance in Hard X-ray photoemission spectroscopy (HX-PES) using a fixed photon energy of nearly 6 keV is very important for the investigation of surface versus bulk electronic structure of solids.^{23,24)} This is based on the increased probing depth by increasing the photon energy for excitation, so that the inelastic mean free path becomes much longer (>5 nm), which facilitates a genuine bulk electronic structure measurement. HX-PES has been applied to studies on a high dielectric constant HfO_2 thin film grown on Si for metal–

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oxide–semiconductor (MOS) applications²³⁾ as well as for the intrinsic electronic structure of molecular beam epitaxy grown thin films of Ga:Mn:N, a diluted magnetic semiconductor.²⁴⁾ At a photon energy of nearly 6 keV, the kinetic energy of the emitted photoelectrons, for example, from Eu 3*d* core states is about 4800 eV, so that the estimated inelastic mean free path becomes longer than 5 nanometers.²⁵⁾ For a kinetic energy of around 330 eV, as used in a previous XPS study,¹⁶⁾ the mean free path is ~ 0.8 nm,²⁵⁾ which is clearly surface sensitive. Hence, it is very important to study the temperature dependent valence transition in $\text{EuNi}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ with HX-PES.

The present study provides the first core-level photoemission measurements which show the large change in mixed valency as a function of temperature across T_v . The result confirms that HX-PES probes the intrinsic electronic structure of a rare-earth system consistent with bulk Eu L-edge XAS measurements, and which is otherwise very difficult using SX core-level PES.

We used polycrystalline samples which were prepared by melting stoichiometric amounts of constituent elements in an argon furnace. $\text{EuNi}_2(\text{Si}_{0.2}\text{Ge}_{0.8})_2$ was characterized to exhibit $T_v = 80$ K by magnetic susceptibility. The sample was single phase with the ThCr_2Si_2 -type structure, as was confirmed by X-ray diffraction,¹⁵⁾ although small inhomogeneities in composition cannot be ruled out. The sharp change in the lattice parameters¹⁵⁾ and magnetic susceptibility¹⁴⁾ data suggest negligible role of inhomogeneities or mixed phase in the sample. The Eu 3*d* HX-PES experiment was performed at an undulator beam line BL47XU of SPring-8, using a hemispherical high energy-resolution electron analyzer, SCIENTA SES-2002. The X-ray energy was chosen to be 5940 eV and the details of the experimental setup are described elsewhere.²⁴⁾ The total energy resolution was about 400 meV. The vacuum of the analyzer chamber was around 2×10^{-7} Pa. The sample temperature was controlled within an accuracy of ± 2 K. A clean surface was obtained by fracturing at 40 K and a temperature cycle (40–120–40 K) was used to confirm the results of the temperature dependent measurements.

Figure 1 shows the Eu 3*d* HX-PES spectra of $\text{EuNi}_2(\text{Si}_{0.2}\text{Ge}_{0.8})_2$ obtained with 5940 eV photons at sample temperatures of 40 K and 120 K. An integral background has been subtracted from the raw data. The spectra show multiple peak structures at both temperatures, but the intensities of the peaks show drastic changes as a function of temperature. The Eu 3*d*_{5/2} and 3*d*_{3/2} components correspond to the splitting due to spin–orbit interaction, and each component consists of the low binding energy divalent and the high binding energy trivalent components separated by the chemical shift, as labeled in the spectra. As is clearly seen in the spectra, the intensity ratio of the divalent component to the trivalent component depends on temperature: the trivalent components exhibit higher intensity at 40 K as compared to the divalent components. In contrast, the divalent components show higher intensity at 120 K, as compared to the trivalent components. In order to confirm the divalent and trivalent character of the various features, we have calculated the Eu 3*d* divalent and trivalent spectra and compare them with the experimental Eu 3*d* HX-PES spectra, as shown in Fig. 2. The calculation of Eu 3*d* spectra

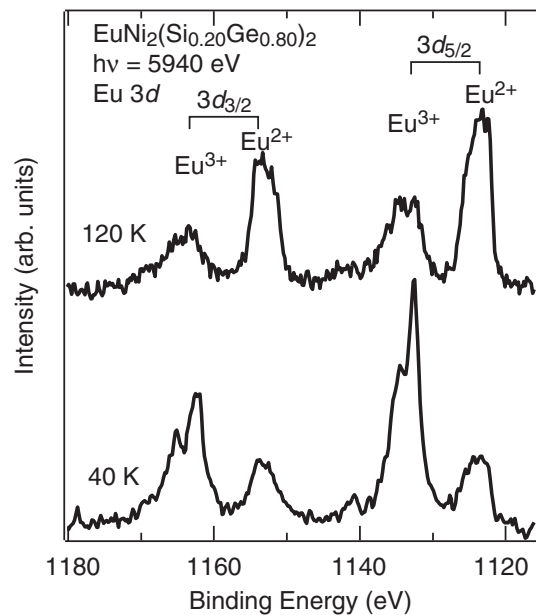


Fig. 1. Hard X-ray Photoemission spectra of the Eu 3*d* core-levels measured using $h\nu = 5940$ eV at 40 K and 120 K.

has been performed for the free Eu^{2+} and Eu^{3+} ions. The Slater integrals and spin–orbit coupling constants are calculated by the Hartree–Fock method with relativistic corrections. As usual, the Slater integrals are reduced to 90% and the details of the calculations are well-known.²⁶⁾ The Eu^{2+} and Eu^{3+} discrete energy states are plotted as a bar diagram in Fig. 2 (lower panels). The discrete energy states were broadened with a Gaussian caused by the experimental resolution and with a Lorentzian to represent the lifetime broadening. The calculated spectra show a very good match with all the divalent and trivalent multiplet features, confirming that intra-atomic multiplet effects account for the observed features. A recent study on a heavy fermion system, $\text{PrFe}_4\text{P}_{12}$, also showed that the valence band *f* character states show a good match with the results of atomic multiplet calculations.^{27,28)} The present study, as well as the study on $\text{PrFe}_4\text{P}_{12}$ indicate that while the core level and valence band spectra for mixed valent or heavy fermion systems can be reproduced using an atomic model, it is clear that the atomic model cannot explain the mixed valence transition or heavy fermion behavior. In order to estimate the mean valence at 40 K and 120 K, the calculated spectra for the divalent and trivalent Eu ions were summed up, maintaining the ratio between intensities of well-separated features as obtained by experiment. This was necessitated by the fact that the divalent character states are mixed with the trivalent states, as is understood from the discrete energy level bar diagrams shown in Fig. 2. The mean valence estimated from such an analysis indicates a value of 2.70 ± 0.03 at 40 K, which changes to 2.40 ± 0.03 at 120 K. These values match very well with the mean valence estimated from Eu L-edge XAS results¹⁴⁾ which showed a mean valence change from ~ 2.75 to ~ 2.35 .

In order to check whether the mixed valence transition in $\text{EuNi}_2(\text{Si}_{0.2}\text{Ge}_{0.8})_2$ is directly reflected in the Ni and Ge states, we have also measured the Ni 2*p*_{3/2} and 2*p*_{1/2} as well as the Ge 2*p*_{3/2} HX-PES spectra as a function of temper-

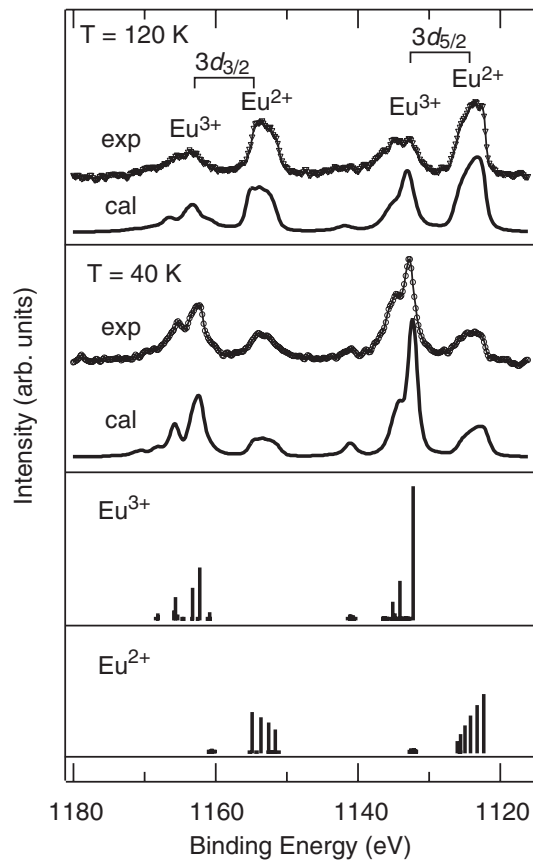


Fig. 2. Comparison of the HX-PES experimental spectra with calculated spectra. The bar diagram represent the Eu^{2+} and Eu^{3+} discrete energy states. The spectral features are consistent with intra-atomic multiplets of the Eu^{2+} and Eu^{3+} ions, as seen in the calculated spectra obtained by broadening the discrete energy states.

ature, as shown in Figs. 3(a) and 3(b), respectively. The Ni $2p$ and Ge $2p$ spectra are similar to elemental Ni and Ge spectra. Further, both the spectra show negligible changes between 40 K and 120 K. The data thus clearly show that the Ni and Ge $2p$ states do not exhibit any chemically shifted features as seen in the Eu $3d$ core-levels and also do not change across the mixed valence transition. The results thus indicate that the Ge and Ni states scarcely participate in the mixed valence transition and the transition is driven by valency changes occurring only in the Eu derived electronic states. First principles calculations have indeed shown that the mixed valence transition is a transition between two states, but both with non-integral mean valency of the rare-earth derived states as observed in the present study.^{29–31)}

The success of the present HX-PES results in revealing the mixed valence transition consistent with bulk measurements, as compared to the SX-PES results¹⁶⁾ is attributed mainly to the larger probing depths of the present technique. It is also noted that the present studies adopted fracturing the sample surface in ultra-high vacuum as compared to the scraping method used for surface preparation in the earlier study. Most importantly, HX-PES is shown to reliably probe the intrinsic electronic structure of a strongly correlated f electron system undergoing a mixed valence transition as a function of temperature.

We measured the Eu $3d$ HX-PES spectra of $\text{EuNi}_2(\text{Si}_{0.2}\text{Ge}_{0.8})_2$ at 40 K and 120 K, across the mixed valence

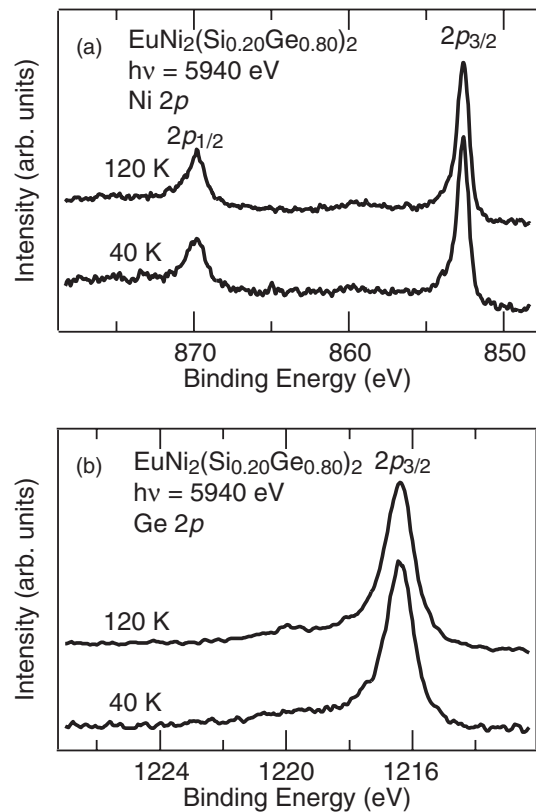


Fig. 3. (a) Hard X-ray photoemission spectra of Ni $2p$ core-levels measured using $h\nu = 5940$ eV at 40 K and 120 K showing negligible change across the mixed valence transition at $T_v = 80$ K. (b) Hard X-ray photoemission spectra of Ge $2p_{3/2}$ core-level measured using $h\nu = 5940$ eV at 40 K and 120 K also do not show changes across $T_v = 80$ K.

transition at $T_v = 80$ K. The intensities of the chemically shifted divalent and trivalent components reflect the bulk values of mean valence above and below the critical temperature. The experimental spectra correspond well to the calculated spectra for the free Eu^{2+} and Eu^{3+} ion configurations in an atomic model, and confirm that the fine structure in the experimental spectra are intra-atomic multiplet effects, although an atomic model cannot explain the mixed valence transition. Using the calculations for the Eu^{2+} and Eu^{3+} configurations, the mean valence was estimated to be 2.70 ± 0.03 at 40 K and 2.40 ± 0.03 at 120 K, consistent with bulk measurements of Eu L-edge XAS. Core-level PES using HX is shown to be very important for studying the bulk intrinsic electronic structure of strongly correlated rare earth compounds which are known to exhibit strong surface effects.

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