# Temperature-dependent Eu *3d*-*4f* x-ray absorption and resonant photoemission study of the valence transition in EuNi$_2$(Si$_{0.2}$Ge$_{0.8}$)$_2$

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We study the mixed valence transition ($T_v \sim 80$ K) in EuNi$_2$(Si$_{0.2}$Ge$_{0.8}$)$_2$ using Eu 3d-4f x-ray absorption spectroscopy (XAS) and resonant photoemission spectroscopy (RESPES). The Eu$^{2+}$ and Eu$^{3+}$ main peaks show a giant resonance and the spectral features match very well with atomic multiplet calculations. The spectra show dramatic temperature (*T*) dependent changes over large energies ($\sim 10$ eV) in RESPES and XAS. The observed nonintegral mean valencies of $\sim 2.35 \pm 0.03$ ($T=120$ K) and $\sim 2.70 \pm 0.03$ ($T=40$ K) indicate homogeneous mixed valence above and below $T_v$. The redistribution between Eu$^{2+}4f^7+[spd]^0$ and Eu$^{3+}4f^6+[spd]^1$ states is attributed to a hybridization change coupled to a Kondo-like volume collapse.

An important issue of enduring interest in *f*-electron systems that exhibit mixed-valence (MV) transitions and the related Kondo effect is the role of purely ioniclike states compared to delocalized or hybridized states.[1–5] For example, in SmS, which exhibits a pressure-dependent MV transition,[6] the relevant ionic states are Sm$^{2+}4f^6$ and Sm$^{3+}4f^5$ states. It is clear that such a transition requires the role of the 5*d* electrons of Sm, or more generally the [*spd*] electrons of the conduction band.[1] The necessary condition of charge balance for SmS would indicate that the transition involves Sm$^{2+}4f^6$ and the Sm$^{3+}4f^5+[spd]^1$ electron configurations. The MV transition then occurs between two stable states, each defined by relative contributions of the $4f^n$ and $4f^{n-1}+[spd]^1$ configurations. Each state can be a homogeneous MV state having the same nonintegral valence at each site, due to a quantum-mechanical mixing of the relevant configurations.[7] In contrast, a static or inhomogeneous MV state is one in which electron configurations are different at different sites, representing one specific electron configuration at a site. While the MVs in *f*-electron systems are often homogeneous, there are exceptions.[1,8]

Many *f*-electron systems exhibit a MV transition induced by temperature (*T*), magnetic field, and/or pressure. These include the $\alpha$-$\gamma$ transition in Ce metal,[1] the pressure-induced transitions in SmS,[6] and TmTe,[9] the *T*-dependent transitions in YbInCu$_4$,[10] Tm-monochalcogenides,[11] as well as Eu-based intermetallics, EuPd$_2$Si$_2$,[12] Eu(Pd$_{1-x}$Au$_x$)$_2$Si$_2$,[13] and EuNi$_2$(Si$_{1-x}$Ge$_x$)$_2$.[14] Among *T*-induced transitions, the Eu systems exhibit the largest change in valency, $\Delta v \sim 0.3$–$0.5$.[12–14] Of these, EuNi$_2$(Si$_{1-x}$Ge$_x$)$_2$ has been extensively studied to show *T*-,[14,15] magnetic-field-,[15] and pressure-[16] induced valence transitions. By tuning composition [*x* in EuNi$_2$(Si$_{1-x}$Ge$_x$)$_2$], the transition is observed to be first-order-like for compositions close to *x* =0.8, with a hysterisis as a function of *T*, pressure, and magnetic field.[15–17] The MV transition in EuNi$_2$(Si$_{0.2}$Ge$_{0.8}$)$_2$ has thus been investigated across the critical *T* ($T_v$) of $\sim 80$ K

by magnetic susceptibility, high-energy bulk-sensitive Eu *L*-edge x-ray absorption spectroscopy (XAS), and x-ray diffraction to show that the transition is accompanied by a Kondo-like volume collapse across $T_v$.[14–17]

XAS and resonant photoemission spectroscopy (RESPES) are important techniques for studying the electronic structure (ES) of *f*-electron systems.[18–20] In XAS applied to a solid, a core electron of a particular site or element is excited to an empty state, and hence it probes site-specific angular momentum projected unoccupied states of a solid.[21] RESPES is a complementary technique that probes the resonantly enhanced partial occupied density of states (DOS) of a solid.[20] These techniques provide important insights into the physical properties of strongly correlated materials, including MV, Kondo effect, heavy fermion behavior, etc. However, recent studies using ultraviolet photoemission spectroscopy (PES) of MV systems revealed modifications of the surface ES compared to the bulk.[22–24] While signatures of *T*-dependent MV are observed, the mean valence estimated from these measurements is incompatible with bulk thermodynamic studies. Significantly, the important role of hard-x-ray (HX: $h\nu \sim 3$–$8$ keV) PES in general,[25–31] as well as soft-x-ray (SX: $h\nu \sim 1$–$1.5$ keV) PES (Ref. 22) and RESPES (Refs. 32 and 33) of *f*-electron systems, has been reiterated for studying bulk character ES.

In this work, we study the *T* dependence of the MV transition in EuNi$_2$(Si$_{0.2}$Ge$_{0.8}$)$_2$ using XAS and RESPES across the Eu 3d-4f threshold. We observe a giant resonance of Eu$^{2+}$ and Eu$^{3+}$ main peaks and dramatic *T*-dependent changes in the XAS and RESPES data. The mean valence estimated from the data is consistent with bulk-sensitive results, indicating nonintegral homogeneous mean valencies of 2.35±0.03 (above $T_v$) and 2.70±0.03 (below $T_v$). The XAS data are analyzed using atomic multiplet calculations for Eu$^{2+}$ and Eu$^{3+}$ states. The RESPES valence-band spectra as a function of energy are also consistent with atomic calculations. The *T*-dependent transition redistributes occupancies
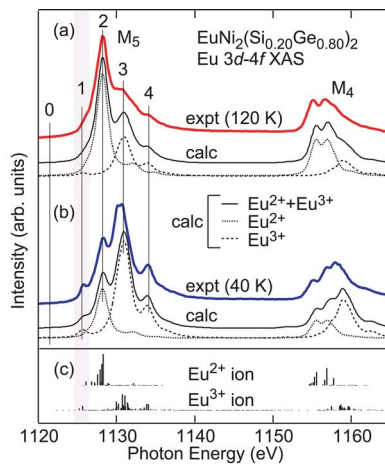
FIG. 1. (Color online) Comparison of the Eu $3d$-$4f$ XAS experimental spectra with calculated spectra at (a) $T=120$ K and (b) 40 K. The spectral intensities change strongly across $T_v \sim 80$ K, over large energy scales. The spectra are derived from intra-atomic multiplet excitations of $Eu^{2+}$ and $Eu^{3+}$ ions by broadening the discrete energy states [(c)].

of $Eu^{2+}4f^7+[spd]^0$ and $Eu^{3+}4f^6+[spd]^1$ configurations, attributed to a hybridization change coupled to a Kondo-like volume collapse.

$EuNi_2(Si_{0.2}Ge_{0.8})_2$ polycrystalline samples were prepared by melting stoichiometric amounts of constituent elements in an argon furnace.[15] $EuNi_2(Si_{0.2}Ge_{0.8})_2$ was characterized to exhibit $T_v \sim 80$ K by magnetic susceptibility. The sample was single phase with the $ThCr_2Si_2$-type structure, as confirmed by x-ray diffraction. The Eu $3d$-$4f$ XAS and RESPES experiments were performed at SX undulator beam line BL17SU of SPring-8 using a grazing incidence monochromator. The XAS measurements were carried out by recording sample drain current as a function of photon energy. The RESPES experiments used a hemispherical high energy-resolution electron analyzer, SCIENTA SES-2002. The total energy resolution at the $3d$-$4f$ threshold was about 300 meV and the vacuum was $4 \times 10^{-8}$ Pa. A clean surface was obtained by fracturing at 40 K. The measurements were performed for several fractured samples at 120 K and 40 K in a $T$ cycle to confirm reproducibility of $T$-dependent changes.

Figures 1(a) and 1(b) show the Eu $3d$-$4f$ XAS ($M_{4,5}$-edge) spectra of $EuNi_2(Si_{0.2}Ge_{0.8})_2$ obtained at a sample $T$ of 120 K (above $T_v$) and 40 K (below $T_v$), respectively. The spectra show multiple peak structures and the intensities of the peaks show large changes over a large energy range ($\sim 10$ eV in the $M_5$ region), as a function of $T$. In order to identify the character of the various features, we calculated the Eu $3d$-$4f$ XAS spectra and compared them with experimental results, as shown in Fig. 1. The calculations are atomic mutiplet calculations for the $Eu^{2+}$ and $Eu^{3+}$ free ions.[34] 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 80%.[34] The $Eu^{2+}$ and $Eu^{3+}$ discrete energy states are plotted as a bar diagram in Fig. 1(c). The discrete energy states were broadened by a Gaussian for the experimental resolution and by a Lorentzian to represent the lifetime broadening.
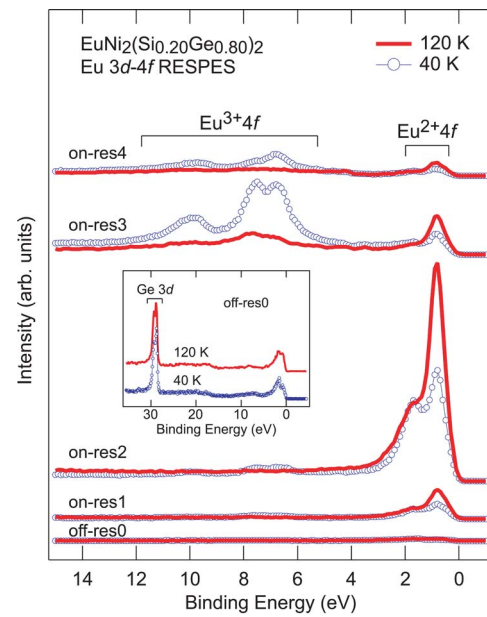


FIG. 2. (Color online) The $T$-dependent Eu $3d$-$4f$ RESPES spectra at incident photon energies marked 0–4 in Fig. 1. The inset shows the normalization procedure using off-resonance (off-res0) spectra. The resonant features originate from the partial $4f$ DOS of $Eu^{2+}$ and $Eu^{3+}$ ions. Note the absence of $T$ dependence in the $Eu^{2+}$ surface state at 1.7 eV BE (on-res2).

The calculated spectra [Figs. 1(a) and 1(b)] show a very good match with all the divalent and trivalent multiplet features, confirming that intra-atomic multiplet effects account for the observed features. The spectral intensities required to match the experiment indicate nonintegral homogeneous mean valencies of $2.35 \pm 0.03$ at 120 K, which changes to $2.70 \pm 0.03$ at 40 K. These values match with the mean valence estimated from bulk-sensitive $L$-edge XAS (Ref. 14) and HX-PES of Eu $3d$ core levels,[35] which showed a mean valence change from $\sim 2.40$ at 120 K to $\sim 2.75$ at 40 K. An important point to note is that the lowest unoccupied states with significant intensity for $Eu^{2+}$ and $Eu^{3+}$ configurations are close in energy and constitute the feature labeled 1 shaded region. This seems, at first glance, quite surprising because the $Eu^{2+}$ and $Eu^{3+}$ features are well-separated in the core levels[35] and valence band (discussed below) due to the strong on-site Coulomb correlations in the $f$ states ($U_{ff} \geqslant 5$ eV). However, in the atomic multiplet approximation for XAS, if we consider the $3d$-$4f$ excitations to be dominated by $U_{ff}$ and the core-hole attraction $U_{fc}$, the $3d$-$4f$ excitation energy difference between $Eu^{2+}$ and $Eu^{3+}$ is obtained to be $U_{ff}$-$U_{fc}$. Since $U_{ff} \sim 1.2U_{fc}$, it suggests that a lower-energy scale, such as hybridization between $f$ and conduction-band [$spd$] states, can play a major role in the MV transition.

Figure 2 shows the Eu $3d$-$4f$ valence-band RESPES obtained at $T=120$ and 40 K for energies labeled 0–4 in Fig. 1 [corresponding to incident photon energies of $h\nu$ $=1121.0$ eV (off-resonance), 1125.7 eV, 1128.2 eV, 1130.2 eV, and 1133.9 eV]. All the spectra are normalized to the Ge $3d$ shallow core levels, which do not change shape as a function of $T$ and incident photon energy, as shown in the inset for the off-resonant spectra over a larger energy scale
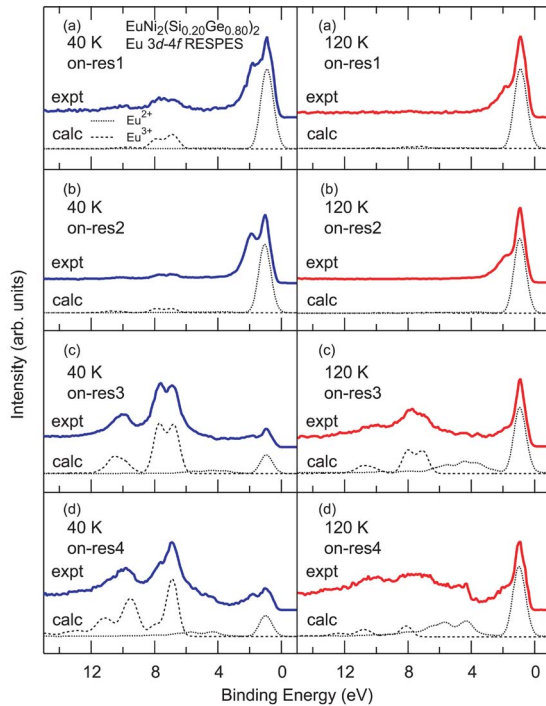
FIG. 3. (Color online) Comparison of the Eu 3$d$-4$f$ RESPES experimental spectra with atomic multiplet calculations at incident photon energies from on-res1 to on-res4, at 40 K (left panel) and 120 K (right panel).

(0–35 eV). In the off-reasonant spectra, the feature at 0.8 eV binding energy (BE) is the bulk Eu$^{2+}$ 4$f$ state, and the feature at 1.5 eV BE, composed of the Ni 3$d$ and the surface Eu$^{2+}$ 4$f$ states, has higher intensity.[24,36] This results in effectively masking the $T$-dependent changes in off-resonant spectra as the Eu$^{2+}$ 4$f$ state does not participate in the MV transition.[24,37] In contrast, the on-resonant spectra at energies on-res1-4 show dramatic changes in spectral features and intensity as a function of $T$ and incident photon energy. We discuss all the spectral features and peak assignments using atomic multiplet calculations for the RESPES data at the energies on-res1-4, shown in Fig. 3.

The spectra at the photon energy on-res1 are enhanced for the bulk Eu$^{2+}$ feature at 0.8 eV and the surface feature at 1.7 eV BE (Fig. 2). The bulk feature shows a further clear enhancement at 120 K compared to 40 K, while the surface Eu$^{2+}$ feature shows negligible change in spectral intensity with $T$. Weak features between 6 and 8 eV BE indicate $T$-dependent changes between 120 and 40 K [Fig. 3(a)], with strongly reduced intensity at 120 K. The atomic mutiplet calculations [dotted lines, Fig. 3(a)] confirm the Eu$^{2+}$ character of the feature at 0.8 eV and the Eu$^{3+}$ character between 6 and 8 eV with very weak features at higher energies.

At the energy on-res2, the Eu$^{2+}$ features are strongly enhanced, as this energy corresponds to the main peak of Eu$^{2+}$ character in XAS (Fig. 1). It is a giant resonant enhancement because the intensity increase at the bulk Eu$^{2+}$ peak is ~140 times compared to the off-resonance data at 120 K.[38] At this energy, the features between 6 and 8 eV BE, which originate in Eu$^{3+}$ states, also show a clear $T$ dependence: the spectral intensity nearly vanishes at 120 K but is observed at 40 K.

This observation confirms that the $T$ dependence is due to intrinsic mixed valency changes and not due to oxidation at high $T$, as oxidation would lead to an increase in Eu trivalency at 120 K. The calculations match the bulk Eu$^{2+}$ and Eu$^{3+}$ features.

On increasing the energy to on-res3, the Eu$^{3+}$ features are strongly enhanced with a simultaneous reduction of the Eu$^{2+}$ features. This energy being the main peak of Eu$^{3+}$-derived states in XAS, the weaker Eu$^{3+}$ multiplets are also significantly enhanced up to a BE of nearly 12 eV [Figs. 2 and 3(c)]. The Eu$^{3+}$ main peak also shows a giant resonance: ~100 times increase compared to off-resonance at 40 K. The strong $T$-dependent changes in the Eu$^{3+}$ features show that a small energy change in terms of reducing $T$ from 120 to 40 K ($\Delta T \sim 10$ meV) redistributes electronic states up to 12 eV BE in the valence band. This shows the delicate energy balance driving the MV transition. Interestingly, while the calculations match the Eu$^{2+}$- and Eu$^{3+}$-derived features as obtained at lower energies, a new feature is obtained between the main Eu$^{2+}$ and Eu$^{3+}$ features [Fig. 3(c)]. This is seen as a weak tail between 3 and 6 eV, i.e., at BEs lower than the main Eu$^{3+}$ peak. This is assigned to the intermediate spin-flip satellites, as is known from earlier work.[39] The spin-flip states (4$f^{5\uparrow,1\downarrow}$) lie between the (4$f^{6\uparrow}$) and (4$f^{5\uparrow}$) photoemission final states of Eu$^{2+}$ and Eu$^{3+}$ initial states, respectively,[39] and also exhibit $T$ dependence.[24,36] At the energy on-res4, an overall reduction of the spectral intensities of the Eu$^{2+}$ and Eu$^{3+}$ is observed, and the features are in agreement with the calculations [Fig. 3(d)]. The Eu$^{2+}$ surface state, which was nearly absent at on-res3 energy, is again recovered as a weak feature.

It has been shown that $\Delta v$, the observed change in valency with $T$, is consistent with $T$-dependent magnetic susceptibility and valency change as calculated using the interconfiguration fluctuation (ICF) model for Eu compounds,[7,13] including EuNi$_2$(Si$_{1-x}$Ge$_x$)$_2$ for $x=0.75$ and 0.8 (Refs. 14 and 15, respectively). The estimated value of energy separation between Eu$^{3+}$ and Eu$^{2+}$ for EuNi$_2$(Si$_{0.2}$Ge$_{0.8}$)$_2$ is about 770–830 K in the ICF model giving a $\Delta v \sim 0.4$ between 120 and 40 K, consistent with present experiments. A linear correlation between $T$-dependent isomer shift with composition and $T$-dependent mean valence as obtained by $L$-edge XAS (Ref. 14) is also consistent with our result. Hence, the intrinsic ES of a strongly correlated $f$-electron system undergoing a MV transition as a function of $T$ can be measured by 3$d$-4$f$ XAS and RESPES. The energy-dependent RESPES reveal the partial 4$f$ DOS in the valence band. It is surprising that the 3$d$-4$f$ XAS and RESPES data can all be explained with atomic multiplet calculations, above and below $T_v$, because it cannot explain the MV transition. Since the MV transition is coupled to a Kondo-like volume collapse in the low-$T$ phase, as is known from diffraction studies,[14,17] the volume collapse must increase hybridization between the ionic $f$ states and the conduction-band [$spd$] states. The change in occupancies is attributed to changes in hybridization above and below $T_v$.

In conclusion, the Eu 3$d$-4$f$ XAS and RESPES spectra of EuNi$_2$(Si$_{0.2}$Ge$_{0.8}$)$_2$ at 120 K and 40 K, across the MV transition at $T_v \sim 80$ K, are consistent with bulk-sensitive measure

ments. The experimental spectra correspond nicely with calculated spectra for the $Eu^{2+}$ and $Eu^{3+}$ free ion configurations in an atomic model. The mean valence was estimated to be $\sim 2.35 \pm 0.03$ at 120 K and $\sim 2.70 \pm 0.03$ at 40 K. The redistribution between $Eu^{2+}4f^7 + [spd]^0$ and $Eu^{3+}4f^6 + [spd]^1$ states is attributed to a hybridization change coupled to a Kondo-like volume collapse. Eu $3d$-$4f$ XAS is very useful for studying the bulk intrinsic ES of strongly correlated rare-earth compounds undergoing a MV transition.

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