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Bulk electronic structure of non-centrosymmetric EuTGe3 (T = Co, Ni, Rh, Ir) studied by hard x-ray photoelectron spectroscopy

Abstract
Non-centrosymmetric EuTGe3 (T = Co, Ni, Rh, and Ir) possesses magnetic Eu2+ ions, and antiferromagnetic ordering appears at low temperatures. Transition-metal substitution leads to changes in the unit-cell volume and in the magnetic ordering. However, the magnetic ordering temperature does not scale with the volume change, and the Eu valence is expected to remain divalent. Here we study the bulk electronic structure of non-centrosymmetric EuTGe3 (T = Co, Ni, Rh, and Ir) by hard x-ray photoelectron spectroscopy. The Eu 3d core-level spectrum confirms the robust Eu2+ valence state against the transition-metal substitution with a small contribution from Eu3+. The estimated Eu mean valence is around 2.1 in these compounds, as confirmed by multiplet calculations. In contrast, the Ge 2p spectrum shifts to higher binding energy upon changing the transition metal from 3d to 4d to 5d elements, hinting at a change in the Ge-T bonding strength. The valence bands of the different compounds are found to be well reproduced by ab initio band structure calculations.

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Bulk electronic structure of non-centrosymmetric EuTGe$_3$ ($T = \text{Co, Ni, Rh, Ir}$) studied by hard x-ray photoelectron spectroscopy

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Non-centrosymmetric EuTGe$_3$ ($T = \text{Co, Ni, Rh, and Ir}$) possesses magnetic Eu$^{2+}$ ions, and antiferromagnetic ordering appears at low temperatures. Transition-metal substitution leads to changes in the unit-cell volume and in the magnetic ordering. However, the magnetic ordering temperature does not scale with the volume change, and the Eu valence is expected to remain divalent. Here we study the bulk electronic structure of non-centrosymmetric EuTGe$_3$ ($T = \text{Co, Ni, Rh, and Ir}$) by hard x-ray photoelectron spectroscopy. The Eu 3d core-level spectrum confirms the robust Eu$^{2+}$ valence state against the transition-metal substitution with a small contribution from Eu$^{3+}$. The estimated Eu mean valence is around 2.1 in these compounds, as confirmed by multiplet calculations. In contrast, the Ge 2p spectrum shifts to higher binding energy upon changing the transition metal from 3d to 4d to 5d elements, hinting at a change in the Ge-T bonding strength. The valence bands of the different compounds are found to be well reproduced by ab initio band structure calculations.

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I. INTRODUCTION

Strongly correlated 4$f$-electron systems have been a platform for studying various anomalous phenomena, such as valence fluctuations, unconventional superconductivity, heavy-fermion behavior, and spin/charge ordering [1,2]. The ground-state properties of these compounds are characterized by competing Kondo effects or Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. Both interactions originate from the interplay of localized $f$ electrons and itinerant conduction electrons, although the former quenches the magnetic moments, while the latter leads to magnetic ordering in the ground state. The competition between the Kondo effect and RKKY interactions in Ce and Yb compounds is often discussed within the Doniach phase diagram [3]. In the vicinity of the quantum critical point (QCP), where the nonthermal parameter controlled phase transition happens at absolute-zero temperature, particularly, quantum fluctuations accommodate exotic phenomena [4].

Eu compounds exhibit very different phase diagrams from Ce and Yb compounds and the absence of a QCP. Most of the reported Eu compounds favor a Eu$^{2+}$ (4$f^7$, $J = 7/2$) valence state with an antiferromagnetic ground state. However, the energy difference between Eu$^{2+}$ and the nonmagnetic Eu$^{3+}$ (4$f^6$, $J = 0$) valence state is not very large [5] and is reachable by applying external pressure or chemical substitution. Indeed, among the most extensively studied Eu compound series with the ThCr$_2$Si$_2$-type crystal structure, pressure- or chemical-substitution-controlled first-order valence transitions and valence fluctuations are frequently reported [6]. In the Eu(Pd$_{1-x}$Au$_x$)$_2$Si$_2$ system, EuAu$_2$Si$_2$ possesses a Eu$^{3+}$ valence state and exhibits antiferromagnetic ordering below a Néel temperature $T_N$ of $\sim$ 15.5 K [7]. Substitution of smaller Pd ions decreases the lattice parameter and, by contrast, increases $T_N$. Above $x \sim 0.25$, the magnetic transition is suddenly taken over by a first-order valence transition to Eu$^{3+}$ [8]. The Eu valence deviates from integer values to so-called intermediate valence states and is $\sim$ 2.8 in EuPd$_2$Si$_2$ below 150 K [9]. A similar tendency is also reported for Eu(Pt$_{1-x}$Ni$_x$)$_2$Si$_2$ [10] and EuNi$_2$Si$_2$ [11] systems in such a way that the substitution by elements with small ionic radii works in the same way as pressure and leads to a nonmagnetic ground state. Application of external pressure shows a consistent behavior compared with chemical substitutions [12]. Due to the different ionic size between Eu$^{2+}$ and Eu$^{3+}$, the change in the Eu valence state is often assigned to Kondo volume collapse effects [13,14]. In contrast, changes in the Eu valence-state and ground-state properties are found to be independent of the volume effect in the EuRh$_2$Si$_2$ system. The conversion from divalent EuRh$_2$Si$_2$ to valence-fluctuating Eu$_2$Si$_2$ involves only an $\sim$ 1.5% volume change, indicating its origins in electronic structure changes [15]. Very recently, exotic behavior has been discovered in EuRhSi$_3$ and Eu$_2$Ni$_3$Ge$_5$ [16–18] that cannot be explained by the conventional phase diagram of

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Eu compounds. Both EuRhSi$_3$ and Eu$_2$Ni$_3$Ge$_3$ have magnetic Eu$^{2+}$ ions and exhibit antiferromagnetism below $T_N = 49$ and 19 K, respectively, at ambient pressure. Electrical resistivity measurements under pressure have reported the suppression of a magnetic ordering temperature and a successive phase transition to a nonmagnetic heavy-fermion state without a hint of a valence transition [17,18]. These behaviors are similar to those of Ce and Yb compounds and indicate the possible existence of a QCP. These new aspects of Eu compounds urge a systematic study of the electronic structure and its relation to physical properties.

Eu-based ternary germanides Eu$^+T$Ge$_3$ ($T =$ Co, Ni, Rh, Ir) and EuRhSi$_3$ are isoostructural and possess a BaNiSn$_3$-type structure ($I4mm$) which is similar to the ThCr$_2$Si$_2$-type structure, although without centrosymmetry [19]. Magnetic susceptibility measurements [19–22] and Mössbauer spectroscopy [23,24] report the presence of magnetic Eu$^{2+}$ ions in all the compounds, and localized Eu 4$f$ moments order antiferromagnetically at similar temperatures. The magnetic moments order antiferromagnetically along the $c$ axis at $T_N =$ 15.4, 13.5, and 12.3 K for EuCoGe$_3$, EuNiGe$_3$, and EuIrGe$_3$, respectively. EuCoGe$_3$ and EuIrGe$_3$ exhibit additional magnetic transitions at 13.4 and 7.5 K, respectively, due to a change in the antiferromagnetic structure [19,22]. Recently, three antiferromagnetic phases have been discovered in EuIrGe$_3$, and a helical magnetic structure based on the Dzyaloshinskii-Moriya interaction was proposed [25]. Conversely, in EuRhGe$_3$, the magnetic moments order perpendicular to the $c$ axis at $\sim 12$ K [19,22]. For each compound, the effective magnetic moments are close to the Eu$^{2+}$ ionic value of $7.90\mu_B$ [19]. All the transition metals are nonmagnetic in Eu$^+T$Ge$_3$. Despite the variation of transition-metal substitution and the change in unit-cell volume, the Eu ions seem to have a robust Eu$^{2+}$ valence state, with $T_N$ being barely affected. In the EuNi(Si$_{1-x}$,Ge$_x$)$_3$ system, transport measurements reported a monotonous decrease of $T_N$ with an increase in Ge substitution, indicating its strong connection to the volume change [26]. However, the change in $T_N$ in Eu$^+T$Ge$_3$ by transition-metal substitution does not show a proportional change with the unit-cell volume. This implies that variation of the physical properties of Eu$^+T$Ge$_3$ by transition-metal substitution is rather dominated by the change in electronic structure rather than the unit-cell volume effect. In order to study the transition-metal substitution effect on the electronic structure of Eu$^+T$Ge$_3$, we performed hard x-ray photoelectron spectroscopy (HAXPES). By using the bulk-sensitive HAXPES method, we can unambiguously determine the Eu valence from Eu 3$d$ core-level spectra and suppress the surface contribution. The Eu 3$d$ core-level spectra confirmed that the Eu$^{2+}$ valence state is robust against transition-metal substitution. The estimated Eu valence is close to 2.1. In contrast, the Ge 2$p$ core-level spectrum shifts to high binding energy by changing transition metal from 3$d$ to 4$d$ to 5$d$ elements. A similar trend was observed in the Eu 4$f$ spectrum in the valence band. We compare the measured valence-band electronic structure with ab initio band structure calculations.

II. EXPERIMENT

HAXPES measurements were performed at the GALAXIES beamline [27,28] of the SOLEIL synchrotron. The incident energy was selected by using the third order of the Si(111) monochromator ($h\nu =$ 6.9 keV), yielding a photon bandwidth of $\sim 200$ meV. The photon beam was linearly polarized with the electrical field vector in the plane of the storage ring. Photoelectrons were collected by using a hemispherical analyzer EW4000 (VG Scienta). The binding energy of the spectra was calibrated by measuring the Fermi edge of a Au film. The overall energy resolution was estimated to be $\sim 250$ meV from Au Fermi edge fitting. Eu$^+T$Ge$_3$ ($T =$ Co, Ni, Rh and Ir) single crystals were grown by the metal-flux method [19]. The grown crystals were characterized by x-ray diffraction, magnetic susceptibility, and electrical resistivity measurements. The clean surfaces of the samples were obtained by fracturing in situ under vacuum (better than $5 \times 10^{-8}$ mbar) and were immediately transferred to the analysis chamber with a base pressure of $5 \times 10^{-9}$ mbar. The samples were aligned in a

![Diagram](Image)

FIG. 1. Eu 3d core-level spectra of Eu$^+T$Ge$_3$ ($T =$ Co, Ni, Rh, and Ir). The experimental data are displayed using solid circles. The solid black lines represent the simulated spectra from atomic multiplet calculations with a $4f^7$ configuration including plasmon satellites and an integral background [29]. The arrows indicate the position of Eu$^{2+}$ components. The simulated Eu$^{2+}$ spectrum (dark blue line) and its plasmon satellites (light blue line) for EuCoGe$_3$ are shown at the bottom as an example. The difference (purple line) spectrum obtained by subtracting the simulated spectrum from the experimental one reveals the Eu$^{2+}$ components (purple shaded area).
grazing-incidence (normal-emission) geometry. In order to avoid irradiation damage, all the measurements were performed at the lowest reachable temperature of 30 K. The EuCoGe$_3$ spectra were collected within 6 h (multibunch operation mode: 450 mA while using the attenuator to reduce the beam intensity down to 15%), and those for EuNiGe$_3$, EuRhGe$_3$, and EuIrGe$_3$ (single-bunch operation mode: 16 mA) were collected within 12 h after cleaving under a pressure of 5 × 10$^{-9}$ mbar. In order to check for oxidation or contamination, we have observed wide-range and Eu 3d spectra for each compound just after the cleaving and at the end of measurement, which showed no remarkable changes. Furthermore, the accumulation of Eu 3d and valence-band spectra was divided into several sets, and reproducibility of the spectra was checked.

III. RESULTS AND DISCUSSION

Figure 1 shows the Eu 3d core-level spectra of EuTGe$_3$ (T = Co, Ni, Rh and Ir) measured at 30 K. The Eu 3d spectra are split into 3d$_{5/2}$ (1120–1145 eV) and 3d$_{3/2}$ (1150–1175 eV) components due to spin-orbit interaction. Each spin-orbit partner further splits into a Eu$^{2+}$ component at lower binding energy and a Eu$^{3+}$ component at higher binding energy representing the Eu 4$f^7\rightarrow 4f^7 + e$ and Eu 4$f^6\rightarrow 4f^6 + e$ transitions, respectively. Here $\zeta$ denotes a 3d core hole, and $e$ denotes the outgoing photoelectron. Broad structures around 1140 and 1170 eV are attributed to plasmon satellites related to the Eu$^{2+}$ 3d photoemission process. Compared to the Eu 3d spectrum of other divalent Eu compounds, such as EuRh$_2$Si$_2$ (mean Eu valence $\nu \sim 2.1$ at 300–20 K) [30] and EuNi$_2$(Si$_{0.5}$Ge$_{0.5}$)$_2$ ( $\nu \sim 2.2$ at 300 K) [31], the relative intensity of Eu$^{3+}$ components compared to those of Eu$^{2+}$ is small and buried in the tail of the Eu$^{2+}$ components and its satellite structures. As expected from magnetic susceptibility and Mössbauer measurements, the Eu valence states in the EuTGe$_3$ series are very close to Eu$^{2+}$. In order to elucidate Eu$^{3+}$ contributions, a simulation analysis was performed by carrying out atomic multiplet calculations and accounting for the line shape of the Eu 3d core-level spectra. The Eu 3d spectra were simulated by using the XTLS (version 9.01) code [32] with a 4$f^7$ (Eu$^{2+}$) ground-state configuration. The electrostatic and exchange parameters were obtained using Cowan’s atomic Hartree-Fock program with relativistic corrections [33]. The exchange parameters were scaled down to 86% of their Hartree-Fock values. The calculated spectra are convoluted with a Lorentzian function for lifetime broadening and a Gaussian to account for the experimental resolution. The broadening parameters as well as the values used for the Coulomb and exchange multiplet interactions are listed in Ref. [34]. An example of the simulation for EuCoGe$_3$ is shown in the bottom of Fig. 1. The plasmon satellites (light blue line) are reproduced by broadening the simulated Eu$^{2+}$ atomic multiplet spectrum and shifting in order to be in agreement with the experimental spectrum. Their relative intensity and the energy position of the Eu$^{2+}$ 3d components were calibrated using the Ge 2$p$ peak and its plasmon position [see inset of Fig. 2(b)]. The solid black lines in Fig. 1 represent the simulated spectra, including the atomic multiplet spectrum, plasmon satellites, and integral background [29]. The experimental spectra are fitted by adjusting the intensity of the calculated spectra such that the difference between the experimental and calculated spectra is minimized. As seen in Fig. 1, the simulations can well reproduce the multiplet structures of the experimental spectra. Since the simulations take into account only the Eu$^{2+}$ contribution, the deviations from the simulated spectrum at $\sim 1135$ and 1165 eV are assigned to the Eu$^{3+}$ contributions. We extracted the Eu$^{3+}$ component by subtracting the calculated spectrum from that of the experiment. A contribution from the Eu$^{3+}$ plasmon satellites to the Eu 3d spectrum is negligibly small and therefore not considered in this analysis. Some residual wiggling feature in the difference spectrum (purple line) originates mostly from tiny deviations in the peak positions and peak widths of the multiplet structures. The Eu valence was estimated by using the formula $\nu = 2 + I_{2z}/(I_{2z} + I_{3z})$. Here $I_{2z}$ and $I_{3z}$ denote integrated spectral intensities of the simulated Eu$^{2+}$ spectrum (dark blue line) and the extracted

![Figure 2](image-url) (a) Ge 2$p_{3/2}$ core-level spectra measured at 30 K. The inset shows the complete Ge 2$p$ spectra. (b) Binding energy of the Ge 2$p_{3/2}$ peaks of EuTGe$_3$ as a function of T (T = Co, Ni, Rh, and Ir). The inset shows an example of the fit. The dashed line represents the integral background (BG) [29].
Eu$^{3+}$ component (purple shaded area in Fig. 1), respectively. The obtained Eu valences are $v = 2.11$, 2.09, 2.08, and 2.09 ($\pm 0.01$) for EuCoGe$_3$, EuNiGe$_3$, EuRhGe$_3$, and EuIrGe$_3$, respectively. We should note that the estimated inelastic mean free path is $\sim 73$ Å for 5.7 keV photoelectrons [35]; therefore, the Eu$^{3+}$ signal is not likely to be coming from the surface states.

Figure 2(a) shows spectra with the Ge $2p_{3/2}$ component for all the compounds. The inset shows the Ge $2p$ complete spectra. The Ge $2p$ spectra tend to shift towards higher binding energy upon going from 3$d$ to 4$d$ to 5$d$ elements. In order to precisely obtain this energy shift, a fitting analysis was performed on the spectra by using Gaussian and Lorentzian functions [36]. In addition, a Mahan function [37] with $\alpha = 0.16$ is used to account for the asymmetry of the line shapes. The result of the fitting analysis is plotted in Fig. 2(b) with an example of such a fit in the inset. A large energy shift of $\sim 250$ meV is observed between EuCoGe$_3$ and EuNiGe$_3$. The energy shifts of the Ge $2p$ binding energy among EuCoGe$_3$, EuRhGe$_3$, and EuIrGe$_3$ indicate the change in bonding by transition-metal substitution.

In order to study the atomic orbital character of the valence-band electronic structure, we performed band structure calculations using the full-potential nonorthogonal local-orbital code (FPLO) [40,41]. The local-density approximation (LDA) with the Perdew and Wang flavor [42] of the exchange and correlation potential was chosen. Additionally, the strong Coulomb repulsion between the Eu 4$f$ electrons was included in a mean-field way by applying the LDA+$U$ method. The calculations were performed for the experimentally obtained lattice parameters reported in Ref. [19] with $J_H = 0.7$ eV and incident photon energy. The energy shift between EuCoGe$_3$ and EuNiGe$_3$ can be understood as a result of the energy shift of $E_F$ towards higher energy in the conduction bands with increasing 3$d$ occupation.
varying $U$ from 5 to 7 eV. It should be noted that varying $U$ changes only the energy separation between the filled and unfilled Eu 4$f$ states and does not change the results qualitatively. The calculated total and partial densities of states are presented in Fig. 3. The europium ions in the unit cell are configured such that they have a ferromagnetic arrangement in the $ab$ plane and are antiferromagnetically aligned along the $c$ axis. Therefore, the densities of states (DOSs) are symmetric for both the spin channels except for Eu 4$f$. The DOSs in the minority-spin channel are inverted and added together with the majority-spin DOSs for comparison to experiments. The majority-spin states of Eu 4$f$ (solid red line) are fully occupied and appear as a localized sharp peak around 1 eV, while the Eu 4$f$ minority-spin states (dashed red line) remain unoccupied. These results reflect the magnetic Eu 4$f$ state in all compounds. The Co and Ni 3$d$ partial DOSs (PDOSs) appear centered at $-1.5$ and $-2$ eV, respectively. An increase in the 3$d$ electron number in EuNiGe$_3$ shifts the center of the 3$d$ PDOS away from $E_F$, which decreases the hybridization to Eu 4$f$. The Rh 4$d$ and Ir 5$d$ PDOSs show a more extended nature than the 3$d$ PDOS, appearing from $E_F$ to $-6$ eV and then below $-7$ eV. The occupied Ge 4$p$ PDOS are mainly distributed from $E_F$ to $-6$ eV, hybridizing with transition metal $d$ and Eu 4$f$ PDOSs. The Ge 4$s$ PDOS appears at $-7$ to $-10$ eV. Commonly, in all four compounds, a quasi-gap-like low-DOS region appears $\sim 1$ eV above $E_F$.

The experimentally measured valence-band spectra after integral background correction [29] are displayed in Fig. 4. The HAXPES valence-band spectra cannot be directly compared to the theoretical DOSs since the photoionization cross section of Eu 4$f$ states is not the only one contributing to the spectrum. Therefore, the PDOSs are weighted with the corresponding photoionization cross sections extracted or interpolated from Refs. [43–45]. Then, the simulated theoretical spectra were convoluted with a Gaussian function (FWHM: 0.3 eV) and a Fermi-Dirac function of 30 K. We consider the Eu 4$f$, $T$ $d$, and Ge 4$sp$ states as mainly contributing to the valence band. The simulated spectra show good agreement with experimental spectra. Note that we used the DOS with the reported transport measurements [47]. The decrease in the DOS at $E_F$ from EuCoGe$_3$ to EuNiGe$_3$ can also be understood as a rigid-band shift due to an increase in 3$d$ orbital occupation by substitution of Co by Ni, which shifts the 3$d$ states to higher binding energy.

![Fig. 4. Valence-band spectra (solid circles) of Eu$T$Ge$_3$ ($T$ = Co, Ni, Rh, and Ir) after integral background correction [29] and simulated spectra (lines). The majority- and minority-spin DOSs are added together to compare with experimental spectra. Each PDOS is multiplied by the corresponding photoionization cross section and convoluted by a Gaussian (0.3 eV: FWHM) and Fermi-Dirac functions at 30 K. The dashed lines denote the sum of the displayed PDOSs. Note that the intensities of simulated EuNiGe$_3$ spectra are reduced to 50% relative to those of other compounds.](image-url)
against pressure. The dominant part of the Eu 4f DOS of EuTGe₃ is localized at ~1 eV below $E_F$, which is deeper than other Eu compounds possessing an intermediate Eu valence state or valence transition [30,48]. It hinders a charge transfer from Eu 4f to the conduction band that makes up the valence fluctuation or nonmagnetic Eu²⁺ states. Moreover, the calculated DOS of EuTGe₃ (see Fig. 3) has a quasi-gap-like region just above $E_F$ that can also prevent charge transfer. In divalent antiferromagnetic Eu₂GeAs₂, the Eu²⁻/⁴⁺ states are localized at 1–2 eV below $E_F$ [49]. X-ray absorption spectroscopy under pressure reported a change of antiferromagnetic to ferromagnetic ordering above 8 GPa. Although the Eu valence gradually increases, the Eu²⁺ magnetic moments remain up to 20 GPa [50].

Notwithstanding the small energy difference between Eu²⁺ and Eu³⁺ valence states, not all Eu-containing compounds readily manifest valence transitions/ fluctuations upon chemical substitution, pressure, magnetic field, etc. For Eu compounds containing nonmagnetic transition-metal ions, the main fingerprint to look for is the position of the Eu 4f valence band. When the occupied 4f states are pinned to $E_F$, they are more susceptible to possessing a nonintegral number of 4f electrons, and therefore, a valence transition upon chemical substitution/pressure is highly probable. For example, the calculated and measured valence-band structure of valence-fluctuating EuNi₂(P₁₋ₓGeₓ)₂ and EuNi₂(S₁₋ₓGeₓ)₂ respectively corroborate this scenario [51,52]. In this case, a strong coupling of the magnetic ordering temperatures of the Eu moments to $E_F$, i.e., the Fermi level is pinned by the 4f states of the transition-metal ions or the p states of the ligands. The integral filling combined with the energy position enhances the localized character of the Eu 4f electrons and thereby the RKKY exchange and weakens the valence fluctuations. The EuTGe₃ systems presented here belong to this latter category and naturally explain the insensitivity of $T_N$ to the different chemical substitutions.

IV. CONCLUSIONS

We have performed bulk-sensitive HAXPES and successfully revealed the electronic structure of EuTGe₃ ($T$ = Co, Ni, Rh, and Ir). The Eu 3d core-level spectrum revealed that the Eu valence states of all the compounds are almost Eu³⁺ with a negligible contribution from Eu²⁺. The estimated Eu valence is close to 2.1. The Ge 2p core-level spectrum shows the chemical shift to higher binding energy by changing transition metal from 3d to 4d and to 5d elements, indicating the change in chemical bonding between $T$ and Ge. The valence-band electronic structure was systematically studied with the support of ab initio band structure calculations. The experimental valence-band spectra show good agreement with the theoretical simulation. The Eu²⁺/⁴⁺ states are localized at ~1 eV below $E_F$ in all compounds. All the compounds have a quasi-gap-like region just above $E_F$. This favors the robust Eu²⁺ magnetic state against transition-metal substitution and also gives an explanation of its stability against external pressure.

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