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Originally published:

July 2021

Physical Review B 104(2021)4, 045119

DOI: <https://doi.org/10.1103/PhysRevB.104.045119>

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5f states in UGa₂ probed by x-ray spectroscopies

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(Received 5 January 2021; revised 23 March 2021; accepted 7 June 2021; published xxxxxxxxx)

The 5f-based ferromagnet UGa₂ with the Curie temperature $T_C = 125$ K was investigated by x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) experiments at the U- $M_{4,5}$ and Ga- K edges. The position of the U- M_4 white line, determined in the high-energy resolution fluorescence detection XAS, suggests that UGa₂ is neither a localized 5f² nor an itinerant system with 5f occupancy close to $n_{5f} = 3$. The analysis of the acquired $M_{4,5}$ XANES and XMCD spectra indicates the 5f occupancy close to 2.5 and a large orbital magnetic moment of the uranium 5f states ($3.18 \mu_B$) that is partly compensated by the antiparallel spin moment ($1.31 \mu_B$). Thus, the total 5f magnetic moment of $1.87 \mu_B$ is obtained, which is smaller than the known bulk magnetization of $3.0 \mu_B$ per formula unit, while the magnetic moments of the Ga atoms are negligible. Several methods based on density-functional theory were applied and the obtained results were compared with XAS spectral features, the Sommerfeld coefficient of the electronic specific heat, and the size of the U moments and 5f occupancies. A clear correlation is revealed between the U- M_4 white-line position of three metallic uranium compounds and the calculated uranium ionicity. It is demonstrated that only electronic structure methods taking appropriate care of orbital magnetism and related atomic multiplet effects can successfully describe all considered properties.

DOI: [10.1103/PhysRevB.00.005100](https://doi.org/10.1103/PhysRevB.00.005100)

I. INTRODUCTION

A leading theme of actinides research in solid state is the Mott transition on the 5f electronic states, taking place in pure elements between Pu and Am. Higher occupancies of the 5f states increase the total electron-electron correlation energies inside the 5f shell, and the 5f electrons eventually decrease the total energy by abandoning the formation of bonding states in favor of localized atomiclike states, which minimize the correlation energies. Enhanced actinide-actinide distances in compounds can suppress the bonding character even more, shifting the Mott transition towards less occupied 5f states. However, focusing on uranium as the most studied actinide, we see that the complete localization of the 5f states is a very rare event. Among intermetallics, there is only one binary compound, UPd₃, where the 5f localization has compelling evidence by photoelectron spectroscopy and a low density of states at the Fermi level, $g(E_F)$, to which the localized 5f states do not contribute [1,2]. One of the few binary compounds, which can be roughly classified as close to the localization regime, is UGa₂. It crystallizes in the hexagonal AlB₂-type crystal structure (space group $P6/mmm$, $a = 4.213$ Å and $c = 4.012$ Å) [3], one of the most simple binary structures, in which Ga atoms effectively separate U

atoms, increasing the shortest U-U distance to more than 4.0 Å. Such a large distance can generally explain the formation of U magnetic moments and their ferromagnetic ordering below $T_C = 125$ K [3]. The size of U moments, $\mu_U = 3.0(2) \mu_B$ determined by neutron diffraction study [4] corresponds to the low-temperature magnetization in magnetic fields along [100], which is the easy-magnetization direction. Both T_C and μ_U are higher than typical values found for other ferromagnetic uranium intermetallics, although μ_U is still lower than $3.25 \mu_B/\text{U}$ or $3.33 \mu_B/\text{U}$ expected for 5f²(U⁴⁺) or 5f³(U³⁺) configurations in the intermediate coupling scheme [5].

The electronic contribution to the specific heat with a Sommerfeld coefficient $\gamma = 11$ mJ/mol K² [6] is not much enhanced over the value 5 mJ/mol K² for the analog without 5f electrons, LaGa₂ [7], and points to the absence of large 5f contributions to the density of electronic states at the Fermi level. One reason for this could naturally be the 5f localization. Localized 5f states were suggested by earlier density-functional theory (DFT) [8] and crystal electric-field calculations [9], although there remained an uncertainty whether they are of 5f² or 5f³ type. The opposite, that is, itinerant character of the 5f states, was deduced from photoemission studies [10]. Finally, the results of magnetoresistance

and de Haas–van Alphen experiments [6] could not be convincingly explained by either the localized or itinerant model if calculating the Fermi surface in the local spin-density approximation (LSDA).

A certain indicator of localization is the observed response of magnetism to the volume compression achieved by hydrostatic pressure. For a typical band system, external pressure leads to a broadening of bands and a related reduction of the density of states at the Fermi level, leading to suppression of magnetism as the value of the Stoner product, $I \cdot g(E_F)$, where I is the Stoner parameter and $g(E_F)$ is the density of states at the Fermi level, is reduced below 1. UGa_2 behaves very differently, as the Curie temperature T_C first strongly increases (up to 154 K at $p = 14$ GPa) and then turns down [11]. Such type of behavior can be understood as insensitivity of the $5f$ moments to pressure below a certain limit. The compression initially increases the exchange coupling, probably by enhanced hybridization with non- f states. At higher pressure, roughly above 10 GPa, the moments start to be reduced, and although the coupling strength still increases, the ferromagnetism is fading in a strongly nonlinear way. Should the magnetic interactions involve fully localized states, the external pressure would have little effect on the magnetic moments and their ordering temperatures.

Determination of T_C under pressure could be performed on the basis of electrical resistivity data, which is definitely easier than determination of magnetization. To investigate the latter, the technique of x-ray magnetic circular dichroism (XMCD) can be in principle performed with a sample located in a diamond-anvil cell. The XMCD signal at the M edge of uranium can give, using the sum rules, the spin and orbital part of U magnetic moments. However, the strong absorption of several keV photons in diamond makes this experiment challenging and the XMCD experiment was so far performed and analyzed for the ambient pressure only. Here we describe results of a simpler x-ray absorption spectroscopy (XAS) experiment, accomplished as the pressure study of the $M_{4,5}$ absorption edges at room temperature and without magnetic field, reaching $p = 7.2$ GPa. Although the current instrumentation could not reach the critical pressure range, spreading above 10 GPa, the results give an interesting characterization of UGa_2 .

The position of the M absorption edge carries important information about the $5f$ occupancy, which, as we mentioned above, is one of the unresolved issues. To accurately determine the position of the edge, we performed an x-ray absorption experiment using a high-energy resolution fluorescence detection (HERFD) mode at room temperature.

II. EXPERIMENTAL DETAILS

The measurements were performed on UGa_2 single crystals grown by the Czochralski technique. A twinning with approximately 2° misalignment of the a axis between different grains was found. For spectroscopy experiments, the crystal was cut and polished to provide a flat plane perpendicular to the a axis.

The high-resolution absorption measurements were performed at room temperature at the beamline ID26 [12] of the European Synchrotron Radiation Facility (ESRF) in

Grenoble. The incident energy was selected using the $\langle 111 \rangle$ reflection from a double Si crystal monochromator. Rejection of higher harmonics was achieved by three Si mirrors at angles of 3.0, 3.5, and 4.0 mrad relative to the incident beam. X-ray absorption near-edge structure (XANES) spectra were measured in the high-energy resolution fluorescence detection mode using an x-ray emission spectrometer [13,14]. The sample, the analyzer crystal, and the photon detector (silicon drift diode) were arranged in a vertical Rowland geometry. The uranium HERFD XAS spectra at the M_4 edge were obtained by recording the maximum intensity of the $U-M_\beta$ emission line (≈ 3337 eV) as a function of the incident energy. The emission energy was selected using the $\langle 220 \rangle$ reflection of five spherically bent Si crystal analyzers (with 1 m bending radius) aligned at 75° Bragg angle. The paths of the incident and emitted x-rays through air were minimized in order to avoid losses in intensity due to absorption. The intensity was normalized to the incident flux. A combined (incident convoluted with emitted) energy resolution of 0.4 eV was obtained as determined by measuring the full width at half maximum (FWHM) of the elastic peak. The present data are not corrected for self-absorption effects. The analysis shown in this work is based on comparison of the energy position of the main transitions at the $U-M_4$ edge which is only little affected by self-absorption effects. The energy calibration was in each case related to a preceding UO_2 measurement using identical experimental conditions. Therefore, the relative accuracy between all the spectra shown can be taken as better than 0.1 eV.

The conventional XANES and XMCD spectra were measured at the beamline ID12 [15] of ESRF. The source is the first harmonic of the helical electromagnet/permanent magnet hybrid undulator, which provides high flux of circularly polarized x-ray photons and allows for reversing the helicity of the x-rays at each energy point. After monochromatization with a double-crystal Si(111) monochromator, the rate of circular polarization is reduced to about 0.35 at the M_5 edge and to 0.45 at the M_4 absorption edge. For the ambient pressure measurements performed at $T = 15$ K we used an oriented millimeter-sized single crystal of UGa_2 , where the magnetic easy axis (the [100] direction) was collinear with the k vector of the x-ray beam. The XANES spectra were recorded using the total fluorescence yield detection mode in backscattering geometry for parallel $\mu_+(E)$ and antiparallel $\mu_-(E)$ alignments of the photon helicity with respect to a 3 T external magnetic field applied along the beam direction. The XANES spectra for right and left circularly polarized x-ray beams were then corrected for self-absorption effects, which have been proven to work very well in the case of U multilayers [16], and for incomplete circular polarization rates of incident x-ray photons. The U edge-jump intensity ratio M_5/M_4 was then normalized to 3:2 according to the statistical edge-jump ratio (defined as the ratio between the occupation numbers for the two spin-orbit-split core levels $j = 3/2$ and $5/2$). This statistical U edge-jump intensity ratio M_5/M_4 is very close to the value (1.57) tabulated in the XCOM tables by Berger *et al.* [17]. A deviation of $\pm 10\%$ in the M_5/M_4 XAS edge-jump normalization (ratio of 1.5) would affect the branching ratio $B = I_{M_5}/(I_{M_5} + I_{M_4})$ by $\pm 2.5\%$ and similarly the occupation numbers of the $j = 5/2$ and $j = 7/2$

subshells $n^{5f}_{5/2}$ and $n^{5f}_{7/2}$. Further details concerning the analysis of uranium M -edges spectra in uranium magnetic compounds can be found elsewhere [18]. The XMCD spectra $\mu_+(E) - \mu_-(E)$ were obtained as the difference of the corrected XANES spectra. To make sure that the final XMCD spectra are free of any experimental artifacts, measurements were also performed for the opposite direction of the applied magnetic field.

For the high-pressure measurements performed at $T = 300$ K, a dedicated high-pressure diamond-anvil cell (DAC) with a He gas-driven membrane optimized for the tender x-ray range has been used [19]. The DAC consisted of an asymmetric diamond-anvil configuration, in which a fully perforated diamond, with a culet diameter of $600 \mu\text{m}$, and a hole diameter of $100 \mu\text{m}$ (front anvil) was complemented by a $50\text{-}\mu\text{m}$ -thick diamond disk to minimize the x-ray absorption. The back anvil was a full diamond with the same culet diameter of $600 \mu\text{m}$. The gasket was made of stainless steel. A single crystal of $80 \times 80 \times 30 \mu\text{m}^3$ was loaded inside the cell, and He gas was used as the pressure-transmitting medium. The pressure was measured *in situ* using the luminescence of a ruby chip. Using the specific DAC, we could reach a pressure up to $p = 7.2$ GPa. The XANES signal from the sample was collected in the backscattering geometry, through the thin diamond window, using a Si photodiode. As focalization system, a set of 2D parabolic Be lenses with the curvature radius of 0.2 mm together with a pair of pinholes having an aperture of 0.8 mm was used. High-order harmonics of the undulator emission were rejected using a pair of vertically focusing mirrors.

III. COMPUTATIONAL DETAILS

The electronic structure of UGa₂ was modeled by several approaches based on DFT as implemented in two different relativistic all-electron full-potential codes. This comprises the local spin-density approximation, the generalized gradient approximation (GGA), and a combination of LSDA with the Hubbard model constructed for the uranium $5f$ electrons. The Hubbard model was approximately solved using the static mean-field theory (the LSDA+ U method) and the dynamical mean-field theory (the LDA+DMFT method).

Apart from LDA+DMFT, all mentioned methods suffer from an incomplete description of orbital magnetism that stems from orbital-dependent self-interaction present in the local or semilocal approximations to DFT [20]. For this reason and in view of the importance of the orbital magnetism in uranium compounds, orbital-polarization corrected (OPC) [21,22] GGA was used to model the magnetic properties in another calculation.

It should be mentioned that the LSDA+ U method may suffer from a multitude of metastable solutions. A possible way to exhaust the solution space is occupation matrix control [23]. Here, this computationally expensive approach was not applied since, in a metal with relatively broad (> 1 eV) bands, the possibility of metastable states is largely reduced in comparison with narrow-band insulators.

A. WIEN2K

The WIEN2K code implements the linearized augmented plane-wave (LAPW) method and its extensions. The core

TABLE I. Computed equilibrium volume, lattice constants, and bulk modulus (LSDA and LSDA+ U methods) compared to the experimental data. The row labeled as LSDA* corresponds to a metastable state (a local minimum of the total energy) that is 0.37 eV/UGa₂ higher than the global minimum. All calculations are for the ferromagnetic state with moments along the [100] direction.

Method	$V_0(\text{\AA}^3)$	$a_0(\text{\AA})$	$c_0(\text{\AA})$	c_0/a_0	K (GPa)
LSDA	52.73	4.61	2.87	0.622	109
LSDA*	57.59	4.15	3.86	0.931	99
LSDA+ U (2 eV)	59.70	4.15	4.00	0.964	99
Experiment	61.79	4.21 [3]	4.02 [3]	0.954	100 ± 8 [49]

states (U up to $5d$, Ga up to $3p$) are evaluated in the muffin-tin sphere by numerically exact integration of the Kohn-Sham-Dirac equations. All higher-lying states are considered as the valence states, for which the method combines a scalar-relativistic description with spin-orbit coupling added in a second variational step. See Ref. [24] and references therein for further details. Most of the calculations were performed at the experimental lattice geometry ($a = 4.213 \text{\AA}$, $c = 4.020 \text{\AA}$) with the following parameters: the radii of the muffin-tin spheres were $R_{\text{MT}}(\text{U}) = 2.80 a_{\text{B}}$ for the uranium atoms and $R_{\text{MT}}(\text{Ga}) = 2.25 a_{\text{B}}$ for the gallium atoms, and the plane-wave cutoff K_{max} was set by $R_{\text{MT}}(\text{Ga}) \times K_{\text{max}} = 10$. The equation of state (Table I) and the properties under pressure (see Fig. 5) were obtained with smaller radii, $R_{\text{MT}}(\text{U}) = 2.45 a_{\text{B}}$ and $R_{\text{MT}}(\text{Ga}) = 2.05 a_{\text{B}}$, necessitated by the reduced interatomic distances in the compressed lattice. The default basis set containing local orbitals for semicore states (U $6s$ and $6p$, and Ga $3d$) was used in all cases. Integrals in the reciprocal space were computed with a modified tetrahedron method with Blöchl corrections using an $18 \times 18 \times 17$ sampling of the full Brillouin zone.

The LSDA calculations were performed with the Perdew-Wang (PW92) parametrization of the exchange-correlation functional [25]. The Coulomb parameter U entering the LSDA+ U functional was varied in the range 0 – 2 eV, the exchange parameter J was fixed to 0.4 eV, and the fully localized limit was taken for the double-counting correction.

The LDA+DMFT method was applied in the variant described in Ref. [26]: the *nonmagnetic* (spin-restricted) band structure calculated in the local-density approximation with the WIEN2K code was represented by a tight-binding model in the basis of the maximally localized Wannier functions (with uranium $7s$, $5f$, $6d$, and $7p$ character, and gallium $4s$ and $4p$ character) [27,28], and the DMFT self-energy for the uranium $5f$ states was computed by solving the auxiliary impurity model in a reduced Fock space using the Lanczos method. The impurity model consisted of 14 spin-orbitals for the uranium $5f$ shell and 42 spin-orbitals representing the hybridization of the $5f$ shell with its environment. The off-diagonal hybridization, induced by noncommutativity of the hexagonal symmetry at the uranium site with the spin-orbit coupling, was taken into account. The Coulomb interaction among the $5f$ electrons was considered in its full spherically symmetric form parametrized by four Slater integrals, $U = F_0 = 2.0$ eV, $F_2 = 7.09$ eV, $F_4 = 4.60$ eV, and $F_6 = 3.36$ eV. The first integral is at the upper limit of the range explored with the

299 LSDA+ U method; the other three correspond to the atomic
300 Hartree-Fock values calculated for the $U^{3+}(5f^3)$ ion and then
301 reduced to 80% to account for screening [29].

302 In our LDA+DMFT implementation, the ferromagnetic
303 solution is induced by introducing a small symmetry-breaking
304 magnetic field to the impurity model that is removed again
305 after a few iterations of the self-consistency cycle. The tight-
306 binding model stays frozen in its initial form derived from the
307 nonmagnetic LDA, and the spin (and orbital) polarization is
308 introduced only to the $5f$ states by means of the polarized
309 self-energy. Since no charge self-consistency is attempted,
310 the exchange field induced by $5f$ electrons and experienced
311 by the $6d$ electrons, and the exchange field induced by $6d$
312 electrons and experienced by $5f$ electrons, both correspond
313 to the nonmagnetic state and are thus, incorrectly, absent
314 from our description of the electronic structure. We address
315 this deficiency by introducing an empirical exchange splitting
316 Δ_{fd} to the $5f$ shell, analogously to the earlier computational
317 investigations of rare-earth systems [30,31]. The magnitude
318 of this splitting can be estimated as $\Delta_{fd} \approx I_{fd}m_d$, where m_d
319 is the magnetic moment due to $6d$ electrons and I_{fd} is the
320 intra-atomic exchange integral. The magnetic moment can
321 be approximated by its LSDA value, $m_d \approx 0.24 \mu_B$; the ex-
322 change integral can be estimated by atomic calculations, $I_{fd} \approx$
323 $0.15 \text{ eV}/\mu_B$ [32]. This yields $\Delta_{fd} \approx 35 \text{ meV}$. This small ex-
324 change splitting has a sizable effect on the magnetic moments,
325 but its influence on the spectral properties is negligible. Note
326 that the total exchange splitting in LSDA is approximately
327 1 eV, the dominant contribution being naturally the $5f$ - $5f$
328 exchange, which is incorporated in the self-energy in the
329 LDA+DMFT method. The calculations employing the esti-
330 mated exchange splitting Δ_{fd} are denoted as LDA+DMFT*.

331 The double-counting correction in the LDA+DMFT calcula-
332 tions was treated as a tunable parameter chosen to maintain
333 the $5f$ filling near the LSDA value, that is, to simulate charge
334 self-consistency. This condition implies the double-counting
335 correction $\approx 3.0 \text{ eV}$ for $U = 2.0 \text{ eV}$. We used the same
336 value in the LDA+DMFT* variant as well, since the double-
337 counting (Hartree) term should not depend on the exchange
338 splitting.

339 The Sommerfeld coefficient γ was evaluated using the
340 Fermi-liquid formula

$$\gamma = \frac{\pi^2 k_B^2}{3} \left[\frac{g_f(E_F)}{Z_f} + g_{\text{non-}f}(E_F) \right],$$

341 where $g_f(E_F)$ is the density of the uranium $5f$ states at the
342 Fermi energy E_F , $g_{\text{non-}f}(E_F)$ is the density of all other states
343 at the Fermi energy, and $Z_f < 1$ is the average quasiparticle
344 weight for the $5f$ states that is evaluated from the DMFT
345 self-energy as suggested in Ref. [33]. In static approximations,
346 such as LSDA and LSDA+ U , the quasiparticle weight equals
347 1.

348 B. FPLO

349 The full-potential local-orbital (FPLO) code [34] uses
350 a four-component (Dirac) implementation of the rela-
351 tivistic Kohn-Sham equations. The presented results were
352 obtained with fplo-18.00-52 by employing the Perdew-Burke-
353 Ernzerhof (PBE) implementation of GGA [35]. The same

354 experimental structure data as in the WIEN2K calculations
355 were used for UGa_2 . For the other two systems studied, exper-
356 imental structure data were used as well: USn_3 (space group
357 221, $a = 4.603 \text{ \AA}$) and UPd_3 (space group 194, $a = 5.769 \text{ \AA}$,
358 $c = 9.640 \text{ \AA}$). Integrations in the reciprocal space were carried
359 out with a linear tetrahedron method including Blöchl correc-
360 tions on a mesh of $24 \times 24 \times 24$ ($18 \times 18 \times 18$) intervals in
361 the full Brillouin zone for UGa_2 and USn_3 (UPd_3). Densities
362 of states (DOS) of UGa_2 were evaluated with a finer mesh
363 of $48 \times 48 \times 48$ intervals. The default FPLO valence basis set
364 was used which comprises uranium $5d$, $5f$, $6s$, $6p$, $6d$, $6f$, $7s$,
365 $7p$, $7d$, and $8s$ states as well as gallium $3s$, $3p$, $3d$, $4s$, $4p$,
366 $4d$, $5s$, and $5p$ states. All lower-lying states are treated as core
367 states.

368 The data for charge distributions (ionicities and occupation
369 numbers) and for the absolute position of the $3d_{3/2}$ level,
370 which are hardly influenced by magnetic order, were obtained
371 by nonmagnetic GGA calculations. In addition, the effect of
372 the core hole on the $3d_{3/2}$ level position was modeled on
373 a $2 \times 2 \times 2$ supercell with 24 atoms, reciprocal space mesh
374 $7 \times 7 \times 7$, and one U atom constrained to host a static $3d$ hole,
375 while the electronic structure was allowed to relax.

376 In the context of charge distribution, two comments are
377 of importance: (1) Each electronic structure method makes
378 use of an individual technique to analyze ionicities and oc-
379 cupation numbers. For example, the WIEN2K code uses a
380 separation into spheres around each nucleus and interstitial
381 volumes. The FPLO code uses a projection onto overlapping
382 local (atomiclike) orbitals, which yields comparable but not
383 equal occupation numbers as the WIEN2K code. (2) A spe-
384 cial feature of the projection onto overlapping orbitals is
385 the possibility to distinguish net and overlap contributions to
386 the occupation numbers. The net contributions relate to the
387 product of two orbitals at the same atom, while the overlap
388 contributions relate to the product of two orbitals at different
389 atoms, i.e., they can be used as a measure of hybridization
390 or delocalization. The sum of net and overlap occupations
391 are called gross occupation numbers, which in turn sum up
392 to the total electron number. The ionicity discussed below
393 is defined as the difference between the electron number of
394 the respective neutral atom and the calculated total electron
395 number of that atom.

396 Magnetic properties were evaluated by means of GGA
397 and GGA+OPC calculations. For the latter, the original OPC
398 version suggested by Eriksson *et al.* [21] was used, since it
399 should be more appropriate than later spin-dependent versions
400 for the present case of strong spin-orbit coupling.

401 IV. EXPERIMENTAL RESULTS

402 The x-ray absorption at the M edge captures the electron
403 excitations from the U $3d$ states. While M_4 corresponds to the
404 transition $3d_{3/2} \rightarrow 5f_{5/2}$, M_5 to $3d_{5/2} \rightarrow 5f_{5/2,7/2}$. The $3d_{3/2}$
405 and $3d_{5/2}$ are split by the spin-orbit coupling energy of 173 eV.
406 Hence, the M_4 edge at 3.72 keV probes the unoccupied part
407 of the $5f_{5/2}$ states, while the M_5 edge at 3.56 keV probes the
408 empty part of both the $5f_{5/2}$ and $5f_{7/2}$ states. Using circularly
409 polarized x-rays with different helicity, one can derive the
410 total orbital and spin polarization of occupied $5f$ states, that
411 is, the orbital and spin magnetic moments, expressed in terms

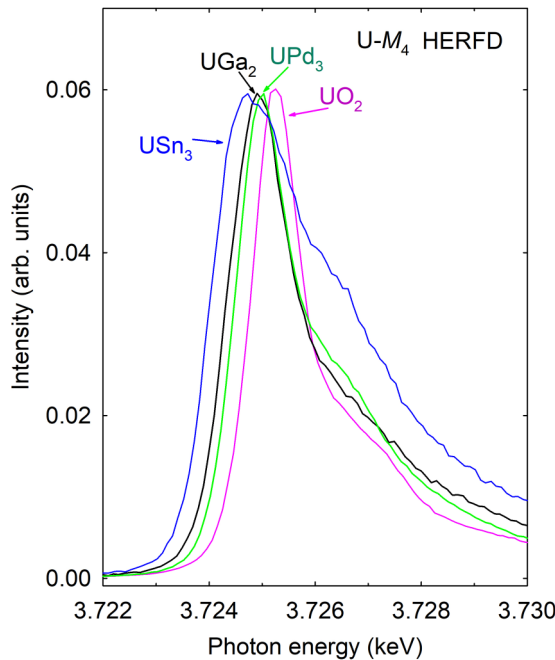


FIG. 1. U- M_4 edge of UGa₂ (black line) compared with spectra of UPd₃, UO₂, and USn₃, all from Ref. [36].

of relative dichroic signal integrated over the energy scale. The short $3d$ hole lifetime, causing the energy resolution to be principally limited to 4 eV, is not a limiting factor for the dichroic experiment, as intensities are integrated over a larger energy window. However, we can extract additional information from small energy shifts of the absorption maxima, which can reflect the bonding and/or electrostatic conditions in analogy to, e.g., energies of photoelectron spectra of core-level lines. The net shift of M edge towards lower energies with increasing $5f$ occupancy can be related to an enhanced Coulomb $3d$ - $5f$ repulsion. On the other hand, the $5f$ delocalization should have the opposite effect if the $5f$ occupancy is maintained, reflecting larger distance between the $3d$ and $5f$ orbitals. The 4-eV resolution would not allow determination of such subtle effects. For such purpose, a specific deexcitation channel can be chosen if the energy analysis of fluorescence photons is available. Choosing a “slow” deexcitation process removes the lifetime limitation. In other words, the short lifetime of the $3d$ hole is not an issue anymore if we use for example its filling via an intermediate state with a $4f$ hole. The realization of such high-energy resolution fluorescence detection spectroscopy was used in this work, using the M_β detection energy for the M_4 line yielding the combined energy resolution 0.4 eV. The present work concentrated on the M_4 line, which is narrower and small energy shifts can be easier observed than for the M_5 line.

A. M_4 -edge HERFD XAS experiment and preliminary discussion

HERFD XAS was the technique used to collect the data presented in Fig. 1, showing a detailed view of the M_4 edge. The spectrum of UGa₂ is compared with the spectra of UO₂, UPd₃, and USn₃ taken from Ref. [36], all collected using the

same experimental conditions [36] and normalized to maximum intensity. The energies of the maxima certainly depend on the energy of the initial $3d$ states (initial state effect) with respect to the Fermi level and this must be the dominant effect if the $5f$ states form a band intersected by the Fermi energy. As a final-state effect, progressing localization, similarly to the formation of a Mott gap in oxides, splits off the $5f$ spectral density from the Fermi level, and an additional energy has to be paid to reach the nearest empty $5f$ states.

Figure 1 shows that the spectrum of UGa₂ is similar to UPd₃, with localized $5f^2$ states. Not only are the maxima at very similar energies, 3724.9 and 3725.0 eV, respectively, but they are both similarly narrow. USn₃ with $5f$ band states occupied by about 2.7 electrons has the maximum at 3724.7 eV, which is not that different as the width, which is affected mainly by the extended high-energy side, indicating a much larger width of unoccupied part of the $5f_{5/2}$ band states. It has been shown previously [36] that USn₃ was partly oxidized, which explains the broadening of the U- M_4 HERFD XAS spectrum.

The shifts of the M_4 edges in metallic systems are smaller than those in uranium oxides—the latter can be clearly associated with changing the valence and $5f$ occupation from f^2 to f^0 [U(IV) to U(VI)]. The energy shift of the U- M_4 white line in the HERFD XAS mode for the U(IV) and U(VI) oxides is on the order of 2 eV, while it can vary on a smaller scale (0.2–0.4 eV) depending on details of U environment for various molecular complexes with the same U valence. In case of intermetallic systems, the energy difference between UPd₃ with presumably localized $5f^2$ state and USn₃ close to $5f^3$ is less than 1 eV. A specific feature of metallic systems is the presence of non- f conduction electrons at uranium, which can also contribute by Coulomb repulsion. In other words, changing the uranium valence in oxides changes the number of electrons transferred from uranium to ligand anions, whereas changing the $5f$ occupancy in metallic systems changes mainly the balance between the U- $5f$ states on one side and U $6d$ - $7s$ states on the other side. The $5f$ occupancy variations affect the U- $3d$ energies. The more spatially extended $6d$ or $7s$ states may affect the $3d$ energies less, but the difference is questionable. Aside from the variation of the occupancies of individual states, we can expect that the energy of the $3d$ states in the ground state can be affected by the $5f$ delocalization. Extended $5f$ states should have a lower repulsive interaction to the U- $3d$ shell than localized $5f$ states, provided equal $5f$ occupancy. In general, we cannot simply deduce the $5f$ occupancy from the M -edge energy, which, however, does not mean that inspection of the M -edge energy would be meaningless, as will be shown below.

What can be deduced from the small shift to lower energies from UPd₃ to UGa₂? Considering the effect on the $3d$ states we would have to assume a higher $5f$ occupancy. The other effect, the localization, cannot be taken responsible in UGa₂, as the $5f$ states in UPd₃ are already localized. The case of USn₃ is the other reference point, with much higher $5f$ occupancy (assumed as ≈ 2.7). There is a shift to lower energies, which is perhaps somewhat compensated by the $5f$ delocalization, yielding 3724.6 eV. The full localization of the $5f^3$ ground state would give appreciably lower energy. On the other hand, the energy shift tells us that the occupancy

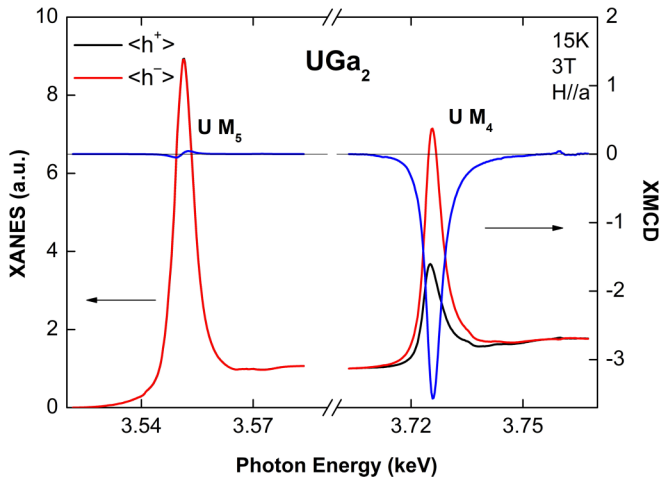


FIG. 2. X-ray absorption at the U- M_5 and M_4 edges for two different helicities (black and red) and the difference of the two helicities (blue).

is most likely higher than 2, and as the noninteger occupancy implies certain delocalization (hybridization), the occupancy cannot be different from 2 by only a small margin—because delocalization means the shift to *higher* energies. Hence we can quite reliably deduce that the HERFD XAS M_4 data indicate a certain delocalization and $5f$ occupancy higher than 2, although not reaching 3, as that would give the edge similar to USn_3 . As we will see in Sec. V, a $5f$ occupancy around 2.5 is expected for all DFT methods applied, which is not contradicting the HERFD XAS data. One has to recall at this point that the dominant bandlike character of $5f$ states is evidenced by ultraviolet photoemission spectroscopy (UPS) and $4f$ core-level x-ray photoemission spectroscopy (XPS), exhibiting the $4f$ peaks practically at the same energy as for U metal. The difference is in the existence of high-energy satellites in UGa_2 , suggesting an approach to localization [37]. Comparing XPS with HERFD XAS, one actually realizes a remarkable fact that the latter technique can detect smaller energy shifts than $4f$ core-level XPS, despite an order of magnitude higher total energies. The reason is the very sharp white line in HERFD XAS.

Besides the shifts of the M_4 white-line energy, we can try to obtain additional information from the shape of the whole spectrum, being rather diverse, as seen from Fig. 1, especially on the high-energy side. In the case of delocalized wave function of the final state, we can associate the spectrum with the unoccupied part of the appropriate density of states [38], $5f_{5/2}$ for M_4 . Its shape and width depend on differences of the $5f$ states occupation, spin-orbit, and exchange splittings as well as on the width of the $5f_{5/2}$ band, reflecting the delocalization of the $5f$ states. We can therefore compare the shape of the M_4 HERFD XAS spectrum with the $5f_{5/2}$ DOS calculated by various theoretical approaches, which can test how much the $5f$ states can be described as itinerant.

B. Uranium M -edge XMCD experiment and preliminary discussion

Figure 2 shows the XANES and XMCD spectra collected at $T = 15$ K in the magnetic field of 3 T for the M_4 and M_5

edges of uranium. The external magnetic field was applied along the a axis, i.e., the easy-magnetization direction, and its intensity is sufficient for saturation of magnetization. The spectra have the characteristics typical for magnetic uranium compounds, with the XMCD M_4 signal forming one negative peak (due to the dominance of spin-down states in unoccupied part of $5f_{5/2}$) and M_5 with both the negative and positive wiggle (as the spin-up and spin-down states largely cancel each other). Integrated intensities at each absorption edge after removal of the transitions to the continuum states give the branching ratio $B = I_{M_5}/(I_{M_5} + I_{M_4}) = 0.697 \pm 0.010$. Applying the spin-orbit sum rule [39], it is possible to determine the expectation value for the angular part of the $5f$ spin-orbit electron operator per hole $\langle w^{110} \rangle / n_h - \Delta$. Knowing n_h , which is the number of $5f$ holes, and considering a small correction term Δ due to exchange interaction with the core hole, one can further obtain the occupation numbers of the $j = 5/2$ and $j = 7/2$ subshells. From the branching ratio, $\langle w^{110} \rangle / n_h - \Delta$ is estimated to be -0.242 ± 0.01 , which can be compared to the free ion U^{4+} (-0.200) and U^{3+} (-0.308) derived from relativistic atomic Hartree-Fock calculations in intermediate coupling. This value is a bit smaller than the one reported for $UCoGe$ (-0.252) [40], for which the number of $5f$ electrons is 2.84 according to band-structure calculations [41]. Assuming a linear dependence, the $5f$ count should therefore be close to 2.5, in a good agreement with HERFD XAS measurements, which predict the value between 2 and 3 but not close to either of them. Considering $n_h = 11.5$ and using $\Delta = -0.014$, we obtain the occupation numbers of the subshells $n^{5f}_{5/2} = 2.33$ and $n^{5f}_{7/2} = 0.17$.

Using the sum rules [42,43], orbital μ_L and spin μ_S U moments can be determined, considering that the number of f holes $n_h = (14 - n_f)$ is known and taking the magnetic dipole operator $\langle T_z \rangle$ from atomic multiplets calculations [44]. We obtained $\mu_L = 3.04 \mu_B$ and $\mu_S = -1.61 \mu_B$ for $5f^3$, yielding the total moment $\mu_U = 1.43 \mu_B$. Assuming the $5f^2$ configuration increases the total moment to $\mu_U = 2.20 \mu_B$, as deduced from $\mu_L = 3.32 \mu_B$ and $\mu_S = -1.12 \mu_B$. Considering $n_h = 11.5$ and the linear scaling of $\langle T_z \rangle$ with n_h , we deduce $\mu_L = 3.18 \mu_B$ and $\mu_S = -1.31 \mu_B$. The obtained total $5f$ magnetic moment of $1.87 \mu_B$ is still substantially smaller than the known bulk magnetization of $3.0 \mu_B/U$.

It is interesting to point out that polarized neutron diffraction [45] gives moments close to $3.0 \mu_B/U$, including the suggested diffuse magnetization of $0.22 \mu_B$ parallel to the $5f$ magnetization. Considering possible errors of moments obtained from XMCD, we cannot exclude the influence of surface oxidation, which is ubiquitous to all U-based metallic systems, forming typically a 20–30-nm-thick overlayer of UO_2 upon an air exposure. While such a slab cannot be resolved in any conventional x-ray diffraction experiment, the resonant absorption conditions reduce the effective information depth to the submicrometer range. It means that the contaminated surface can represent over 10% of the probed depth, reducing the obtained moments significantly, as UO_2 being antiferromagnet provides only a very small magnetization in the field of 3 T.

Normalized XANES and XMCD spectra recorded at the K edge of Ga at $T = 15$ K and in magnetic field $\mu_0 H = 3$ T applied along the a axis are presented in Fig. 3. The XMCD

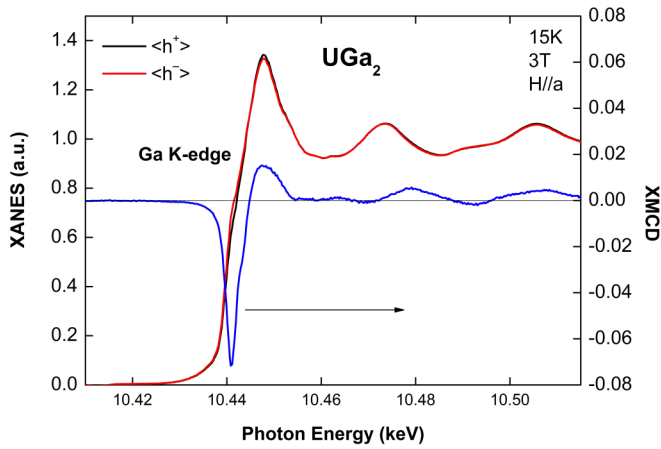


FIG. 3. X-ray absorption at the Ga-*K* edge for two different helicities (black and red) and their difference (blue).

signal at the *K* edge is weak and more intricate to interpret because it is only due to the orbital polarization of the 4*p* states. This polarization is induced both via intra-atomic spin-orbit coupling, if there is a sizable local spin moment on Ga, and via the hybridization of the 4*p* states with spin-orbit split 5*f* states of U. Positive and negative peaks show up at the XMCD Ga *K* edge accordingly [46]. The integration (up to 20 eV above the edge) of those peaks results in a negative signal, i.e., a positive orbital 4*p* moment at the Ga sites. A similar XMCD spectral shape was recorded at the Ge *K* edge in UGe₂ indicating a polarization of the Ge atoms aligned parallel to the uranium magnetic moment [47].

In addition, we performed an x-ray absorption study at high pressures (up to 7.2 GPa) at room temperature (in the total fluorescence yield mode, i.e., not HERFD). Within our experimental detection condition, the white *M*_{4,5} lines (shown in Fig. 4), each normalized to maximum intensity, are nearly the same irrespective of pressure, meaning that pressure up to 7 GPa has practically no influence on the number of 5*f* holes and on the branching ratio. This correlates with very

small changes found in LDA+*U* calculations shown below. A detailed inspection shows a very small shift of *M*₅ towards higher energies, but the shift is far below the energy resolution and has to be taken with caution.

V. COMPARISON WITH CALCULATIONS

A. Structural parameters and equation of state

The LSDA and GGA approximations to DFT are known to work well for spin magnetism and for well-screened excitations in broadband metals. Problems with the application of LSDA or GGA to narrow 5*f* bands with large orbital magnetic moments were encountered in earlier work on UGa₂. In comparison with the experimental observations, the calculated magnetic moment is too small [8], the Sommerfeld coefficient is too large [6], indicating an overestimated 5*f* density of states at the Fermi level, and the Fermi surfaces do not match the observed de Haas–van Alphen frequencies [6].

Here, the first properties to be addressed are the structure and charge distribution, which are usually both well described by local (LSDA) or semilocal (GGA) approximations. Table I summarizes the results of total energy calculations using the WIEN2K code. The *c/a* ratio of UGa₂ with space group 191 was optimized at a number of fixed volumes between 54.4 and 68 Å³ per formula unit, and the resulting energy-volume data were fitted with the Murnaghan equation of state. It turns out that the LSDA total energy at a fixed volume has two local minima as a function of *c/a*, one near *c/a* ≈ 0.65 and the other at *c/a* ≈ 0.95. The latter corresponds to the experimental observations, but for LSDA, the global minimum is found at the smaller ratio and 370 meV per formula unit below the other minimum.

Using the LSDA+*U* changes the relative balance of the two minima and the larger *c/a* ratio becomes the global minimum for *U* larger than approximately 1.5 eV. The lattice parameters obtained for *U* = 2.0 eV are in good agreement with experiment and the same holds for the bulk modulus (Table I). We should mention that also GGA+OPC yields a global minimum close to the experimental structure parameters. These

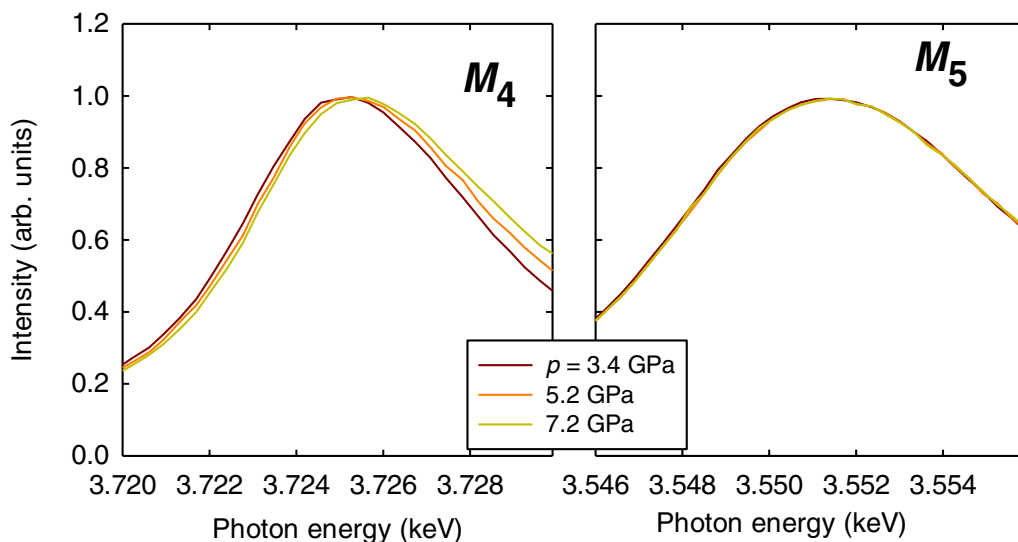


FIG. 4. U-*M*_{4,5} absorption edges of UGa₂ measured in DAC with increasing hydrostatic pressure.

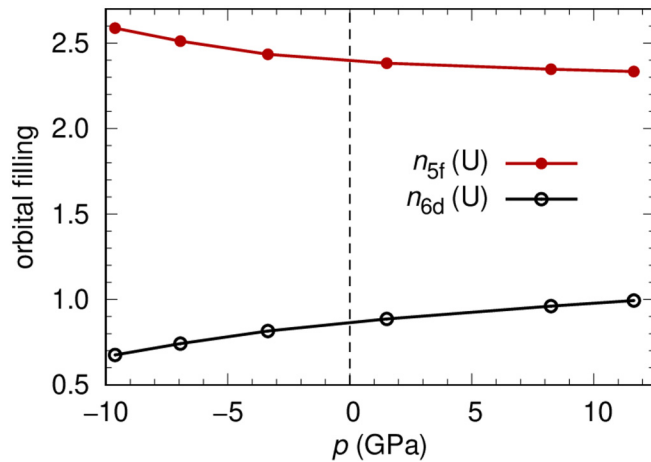


FIG. 5. Variation of the U $5f$ and $6d$ occupancy as a function of pressure (WIEN2K, LSDA+ U method with $U = 2$ eV). The absolute value of the $6d$ filling is underestimated since only the charge density inside the muffin-tin sphere ($R_{MT} = 2.65 a_B$) is counted whereas the $6d$ states are delocalized and extend to the interstitial region. In the tight-binding model used for the LDA+DMFT calculations, there are approximately 2 electrons in the uranium- $6d$ -like Wannier functions. For comparison, the related FPLO occupation numbers at zero pressure are $n_{6d} = 1.96(1.10)$ for gross (net) occupation, which can be compared with the WIEN2K values of $n_{6d} = 2.0(0.86)$ for total (muffin-tin sphere).

659 results show that LSDA fails to describe the structure of UGa_2
 660 properly and that an improved approximation is required.

661 The seemingly counterintuitive finding of two (meta)stable
 662 c/a ratios could have a rational background. Another magnetic
 663 system with a simple lattice structure, YCo_5 , is known to show
 664 an isostructural exchange-driven first-order phase transition
 665 under high pressure, which is related to a jump in the c/a
 666 ratio [48]. A possibly similar instability of UGa_2 under high
 667 hydrostatic pressure was reported in Ref. [49], where the
 668 observed transition at 16 GPa was not isostructural but to a
 669 tetragonal phase.

670 In the context of our experimental investigations of UGa_2
 671 under pressure, it is important to identify trends in the elec-
 672 tronic structure as a function of compression. In particular,
 673 we explored the stability of the $5f$ and $6d$ occupancies as a
 674 function of pressure derived from the computed equation of
 675 state (Fig. 5). We see that no dramatic changes of occupancies
 676 are envisaged. In principle, we may expect an increase of the
 677 $3d$ - $5f$ Coulomb repulsion due to volume compression, which
 678 is compensated by the reduction of the $5f$ occupancy, so the
 679 impact of pressure on the energy of initial state is expected to
 680 be small.

681 B. X-ray absorption spectra

682 Turning to the spectral properties, it is noted that DFT
 683 calculations in general can reproduce energies of core levels
 684 within a few percent. For example, using nonmagnetic GGA
 685 the FPLO method gives the $3d_{3/2}$ states at ≈ 60 eV lower
 686 binding energies (3667 eV) than the experimental energies of
 687 the white lines. As a crude approximation of the x-ray absorp-
 688 tion process, we may consider how the electronic structure is

TABLE II. Measured positions of the ascending-edge inflection points (AE) of U- M_4 edge spectra compared with FPLO occupation numbers and ionicities obtained from nonmagnetic GGA calculations. Both gross and (net) occupation numbers are given, as explained in the Section III B. UPd_3 features two different Uranium positions with accidentally the same ionicity.

Compound	AE (keV)	n_{5f}	n_{6d}	Ionicity
USn_3	3.723 86(10)	2.94 (2.60)	1.95 (1.01)	+0.63
UGa_2	3.724 24(10)	2.63 (2.40)	1.96 (1.10)	+0.90
UPd_3	3.724 43(10)	2.68 (2.39)	1.85 (0.95)	+1.01
		2.74 (2.44)	1.81 (0.94)	+1.01

689 affected by a $3d$ hole in calculations using a supercell. This
 690 static approximation of a $3d$ hole, inducing screening and
 691 repopulation of U states, is ignoring the short lifetime of the
 692 core hole. Still, such calculations can provide an interesting
 693 comparison. When considering one $3d$ hole, the binding ener-
 694 gies shift to ≈ 3787 eV, which is now 60 eV higher than the
 695 experimental white-line energies. The experimental value is
 696 interestingly just in the middle between the ground state and
 697 the state with one static $3d$ hole. Such an uncertainty of less
 698 than 2% would be very welcome in the low-energy region. It
 699 cannot compete, however, with experimental accuracy in the
 700 realm of core levels. For this reason, the following comparison
 701 between experimental and calculated spectroscopic data will
 702 be performed using relative energies or by adjusting the Fermi
 703 level.

704 Figure 1 shows U- M_4 edge spectra of different compounds
 705 where the ascending edges of the three metallic systems span
 706 a range of 0.57 eV. The question was posed, can the edge
 707 positions be used to conclude about the $5f$ occupation num-
 708 bers, $5f$ delocalization, or other quantities related to the charge
 709 distribution? To this end, nonmagnetic GGA calculations for
 710 the three metallic systems included in Fig. 1 were carried out
 711 and the occupation numbers were extracted from the FPLO
 712 population analysis; see Table II. Note that the charge distri-
 713 bution is (and was checked to be) only marginally influenced
 714 by magnetic order.

715 Inspection of Table II shows that the $5f$ occupation of USn_3
 716 is 0.2–0.3 higher than that of UGa_2 or UPd_3 , while the latter
 717 two show similar numbers. The higher $5f$ occupation of USn_3
 718 meets the expectation. On the other hand, the slightly larger
 719 n_{5f} of UPd_3 , compared with UGa_2 , would contradict the op-
 720 posite trend in the edge positions. Note that the applied GGA
 721 method largely overestimates the hybridization contribution
 722 in the case of localized states (the difference between gross
 723 and net occupation, i.e., 0.3 electrons in the case of UPd_3).
 724 However, a redistribution of the hybridization charge toward
 725 localized charge would take place inside the atom and, thus,
 726 not essentially change the ionicity. The latter determines the
 727 electrostatic potential at the atomic site, hence the position
 728 of the core level, with respect to the Fermi energy. Figure 6
 729 illustrates the described relation between ionicity and U- M_4
 730 edge position, which is almost linear for the three available
 731 data points.

732 In the following, results of several electronic structure
 733 methods will be compared with experimental results for

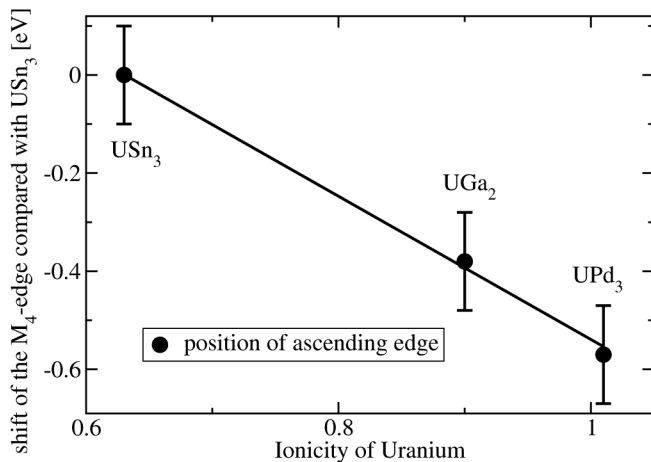


FIG. 6. Shift of the measured ascending edge inflection point vs computed ionicity of the uranium atom in three metallic compounds. The filled circles mark data points; the line is intended to guide the eye.

UGa₂ regarding the line shape of the XAS spectra. Most of these calculations will consider a ferromagnetic ground state. This is self-evident for the low-temperature data collected in the ferromagnetic state. The HERFD-XAS data were however collected at room temperature, where UGa₂ is paramagnetic. Based on the observed large paramagnetic effective moment [6,15] we can assume that the magnetic correlations at about $2 \times T_C$ exist on much longer timescale comparing to the electronic (hopping) scale. In order to model the effects of intrashell polarization in the DFT framework, it is thus appropriate to simulate the paramagnetic state with a static, ordered state. For simplicity, we have chosen a ferromagnetic state.

Figures 7 and 8 present a comparison between the HERFD XAS data and several calculated densities of U-5f_{5/2} states combined with appropriate inverse Fermi distribution ($T = 300$ K), Lorentzian broadening of 0.4 eV full width at

half maximum to simulate the finite lifetime of the core hole, and an additional Gaussian broadening of 0.8 eV FWHM. The latter value was chosen to reproduce the width of the main peak in the measured XAS for the average of the calculated spectra; see Fig. 8.

The experimental spectrum (the same data as in Fig. 1) shows a single peak with a FWHM of 1.7 eV, a shoulder at around 2 eV above the maximum, and a tail toward higher energy. The nonmagnetic GGA data have a two-peak structure before broadening (not shown) due to mixing of atomic 5f_{5/2} and 5f_{7/2} states by the ligand field, but the distance between these peaks amounts to 0.75 eV only. The resulting broadened curve (Fig. 8) has a FWHM of only 1.1 eV and lacks any visible shoulder. Additional mixing is provided by the exchange interaction in the ferromagnetic GGA calculation, yielding a very similar FWHM as the experimental main peak, but a much smaller intensity in the shoulder and tail region. If the orbital polarization is taken into account in GGA-OPC, the six m_j channels receive an additional splitting, where m_j denotes the magnetic quantum number. This results in a separation of about 1.5 eV between the two peaks. While this separation almost meets the experimental distance between the main peak and the shoulder, the intensity relations are different: the calculated shoulder is too high and the calculated tail too small.

The ferromagnetic GGA and GGA+OPC reproduce important features of the experimental spectrum, but not to a satisfactory amount. This could be related to either of the two implicit assumptions (i) a ferromagnetic state would model the situation at room temperature and (ii) a semilocal (+OPC) approximation would reasonably account for the excited-state properties.

Both assumptions can be checked by comparing the experiment with LDA+DMFT, where many-body excitations in and about the 5f shells are embedded into the DFT framework and where the paramagnetic state is accessible as well. The ferromagnetic LDA+DMFT* data are shown in the rightmost part of Fig. 7 and in Fig. 8. Both the shoulder and

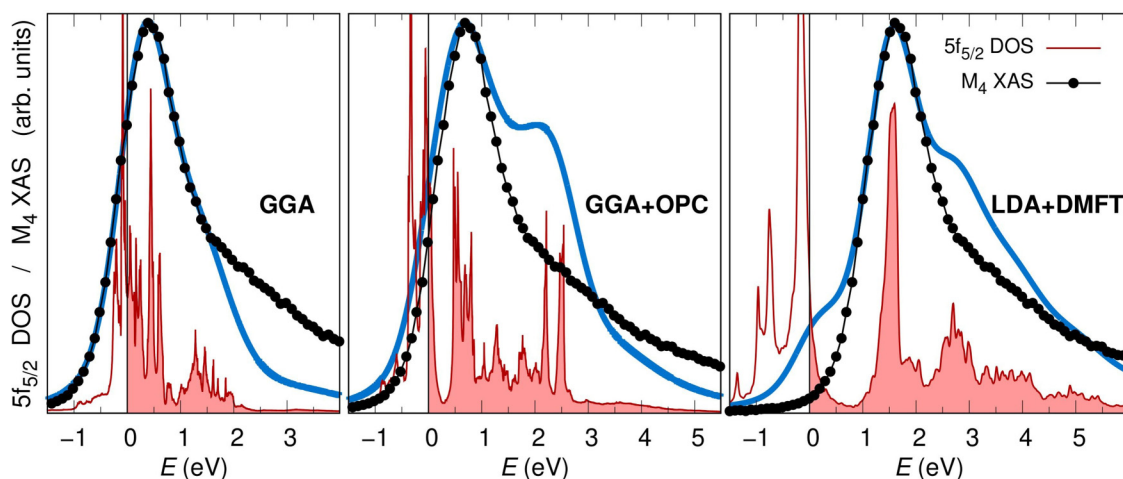


FIG. 7. Calculated M_4 spectra (thick blue lines) obtained by broadening the j -resolved densities of states ($5f_{5/2}$ -red) corresponding to ferromagnetic solutions from GGA (FPLO, left), GGA+OPC (FPLO, middle), and LDA+DMFT* (right). The black lines with dots represent the experimental data from HERFD XAS (the same as shown in Fig. 1). The experimental spectrum was aligned with the theoretical main peak.

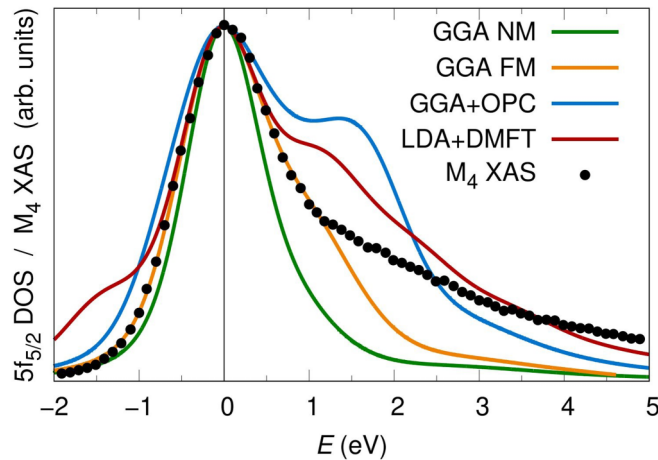


FIG. 8. Comparison of all calculated M_4 spectra (full lines) with the experimental HERFD XAS data (dots). All data are the same as in Fig. 5, but nonmagnetic GGA is added. The main peaks of all datasets are aligned.

the tail are closer in intensity to the experiment than in the GGA+OPC case. However, there is an additional shoulder at the Fermi level that is not present in the experiment or in any of the other calculations. We attribute this feature to a slight inconsistency between the $5f$ filling computed in the auxiliary impurity model and the filling evaluated from the reciprocal-space integral (the former being larger), which is due to the approximate (sparsely discretized) hybridization function. This inconsistency shifts the Fermi level down to states that should otherwise be occupied and thus invisible to XAS. To identify the individual spectral features, an analysis of the many-body eigenstates of the impurity model would be needed, which is computationally prohibitive. Nevertheless, it turns out that removing the hybridization and the crystal field from the impurity model has only a minor effect on the XAS spectrum—and the resulting *paramagnetic* atomic model is accessible to a detailed analysis. The XAS final states correspond to the $5f^4$ configurations. The main peak of the XAS spectrum is due to the $5f^4$ ground state ($J = 4$, $L \approx 6$, $S \approx 2$). The dominant contribution to the shoulder comes from two excited states that are mixtures of configurations with $S = 2$ (all four electrons aligned) and $S = 1$ (one of the electrons flipped).

To summarize the comparison of theoretical and experimental XAS line shapes, the intra-atomic magnetic correlations seem to be indispensable to explain the width of the main peak without the need of unrealistic broadening. The shoulder and the tail are probably due to the excitations to higher atomic multiplets of the $5f^4$ configuration. GGA+OPC can partly model this situation but it yields a downshift of the spectral weight from the tail region toward the shoulder. LDA+DMFT* shows a more realistic distribution of the spectral weight on the high-energy side.

C. Magnetic moments and occupation numbers

We now show and discuss the results for $5f$ occupation numbers, magnetic moments, Sommerfeld parameter, and branching ratio, listed and compared with the experimental

values in Table III. Before considering the individual quantities, we compare LSDA results obtained by the WIEN2K code with those obtained by FPLO. Within these two datasets, the occupation numbers, the uranium spin and orbital moments, and the branching ratio differ only marginally, i.e., in the last digit. This is particularly remarkable for the case of the $5f$ occupation numbers, since the projections of WIEN2K (onto real-space domains or Wannier functions) and FPLO (onto local orbitals) are different. Nonetheless, the number for muffin-tin sphere projection is almost the same as that for net projection; the same holds for Wannier vs gross projections. A significant difference is present for the unit-cell total moment, obviously due to differences in the interstitial region. A larger difference of about 20% is found for the Sommerfeld parameter, which is proportional to the DOS at the Fermi level. In a mathematical language, the DOS is a distribution and its numerical value at the Fermi level can be sensitive to small details of the band structure. Thus, it is not expected to find much better agreement among two different methods. All in all, we find a reassuringly good agreement between both codes, in accordance with previous findings regarding elastic properties [50].

All applied theoretical methods find the $5f$ occupation of 2.5–2.6 (see Table III) if muffin-tin or net occupations are evaluated, which can be considered as “localized” contributions to the $5f$ manifold. A $5f$ count of about 2.5 was indeed anticipated in the preliminary discussion of the XMCD experiment, Sec. IV B. If Wannier or gross occupations are considered, the numbers amount to 2.7–2.8, i.e., the hybridization contributions are close to 0.2 electrons for all methods. This very small sensitivity of occupation numbers with respect to the theoretical method can be understood by the dominant role of the static charge distribution among the relevant energy scales (Hartree energy).

We now turn to the spin contribution to the magnetic moment. Here and for the discussion of other data being sensitive to the magnetic state, we disregard the LDA+DMFT results, which are obtained without exchange coupling among uranium $5f$ and $6d$ states. Adding the empirically estimated exchange splitting of 35 meV to the $5f$ shell increases the moments quite substantially; see the last line of Table III. This approach, termed LDA+DMFT*, and the other theoretical methods find uranium spin moments ranging from $1.9 \mu_B$ (LSDA and LDA+DMFT*), $2.0 \mu_B$ (GGA), $2.3 \mu_B$ (GGA+OPC) to $2.4 \mu_B$ (LSDA + $U = 2$ eV). While the spread is larger than among the occupation numbers, it amounts to not much more than 10% around its barycenter.

For the discussion of the orbital magnetic moment, we disregard the data obtained by LSDA, GGA, and LSDA+ U , which are all known for deficiencies in the description of orbital magnetism, as outlined above. The two remaining methods, GGA+OPC and LDA+DMFT*, agree in the value of the uranium orbital moment, $4.6 \mu_B$.

The total unit-cell moment is almost identical to the total uranium moment, since small Ga moments and diffuse contributions compensate each other. The calculated GGA+OPC value of $2.3 \mu_B$ is 22% smaller than the experimentally determined macroscopic magnetization of $3.0 \mu_B/U$. A possible reason for this difference could be an overestimation of the spin moment in the collinear implementation of GGA+OPC

in the FPLO code. The total unit-cell moment of $2.8 \mu_B$ obtained by LDA+DMFT* is still somewhat smaller than the experimental value, but close to the experimental error bar $\pm 0.1 \mu_B$. The ratio of the orbital to spin moment, 2.0 for GGA+OPC and 2.5 for LDA+DMFT*, lies within the experimental range for both methods.

We now turn our attention to the Sommerfeld parameter γ . It is clearly overestimated in LSDA. A better description of exchange and correlation reduces its value, which is mainly due to a shift of the occupied 5f states from the Fermi level to higher binding energies. The most reliable estimates should be provided by those two methods that are not under suspicion to underestimate the orbital moment, with related distortions of the electronic DOS. The experimental value, 11 mJ/mol K², is larger than the value obtained by LDA+DMFT* and smaller than the GGA+OPC result, both deviating by about 30% from experiment. Given the discussed numerical difficulty to obtain precise values of DOS, such a difference appears to be justifiable, i.e., it is only marginally significant.

An interesting point to note is the factor of 2 difference in the Sommerfeld parameter obtained by LSDA and GGA calculations. Inspection of the DOS (not shown here) makes it clear that this is due to a slightly larger uranium spin moment in the GGA calculation (by about $0.1 \mu_B$). Such a little difference yields a larger splitting of the spin channels on the order of 0.1 eV. This way, the Fermi level becomes situated in a region of relatively low DOS in the GGA calculation while it is placed on a slope in LSDA. This example shows the strong sensitivity of low-energy properties like Sommerfeld parameter or de Haas–van Alphen data with respect to details of the DFT model used, particularly in the case of narrow-band systems and in the presence of magnetism.

Finally, we consider the branching ratio, which amounts to $B = 0.697$ according to the present experiment with an error bar of about ± 0.010 . Since the present calculations neglect core-hole effects, we use $\Delta = 0$ to evaluate the theoretical values of B . The local (LSDA) and semilocal (GGA) approx-

imations yield too-small values of $B = 0.67$, which can be understood in terms of an overestimated band dispersion. In the limit of very large dispersion, the branching ratio would tend to 0.6, while in the opposite limit of vanishing dispersion, it would tend to 1.333 for uranium. Application of LSDA+ U enhances B to 0.68, which is still somewhat smaller than its experimental value. Only the two methods that include an appropriate modeling of the orbital magnetism also provide values of the branching ratio close to the experimental range (considering the error bar): GGA+OPC with $B = 0.685$ and LDA+DMFT* with $B = 0.71$.

Summarizing the comparison of experiment with theoretical calculations, both the GGA+OPC and the LDA+DMFT* methods yield a decent, though not excellent, description of the M_4 HERFD XAS spectral shape. The results of both methods also agree, within or at least close to the error bars, with the experimental branching ratio, the Sommerfeld parameter, and the ratio between uranium orbital and spin magnetic moments. The GGA+OPC method underestimates the total magnetic moment by 22%, which is consistent with a possible overestimation of the band dispersion (bandwidth) already discussed above in the context of the GGA approximation. The total moment obtained by LDA+DMFT* is only 7% smaller than its experimental counterpart and, thus, can be considered to give a good account of the available experimental information. A reason for the remaining slight underestimation of the magnetic moments could be their sensitivity to the ligand-field splitting, which is due to the crystal electric field as well as due to hybridization. Since our discrete representation of the hybridization is a rather crude approximation in metallic systems like UGa₂, some inaccuracy of the computed crystal-field splitting has to be expected.

VI. CONCLUDING REMARKS

Our XAS spectroscopy study did not provide sufficient evidence for a clear characterization of the 5f localization/delocalization or the actual 5f occupancy. However, it can

TABLE III. Computed properties of the in-plane ferromagnetic state at the experimental lattice geometry. The magnetization was assumed along [100], the a axis, except for the LDA+DMFT calculations where it was assumed along [210], the b axis. From left to right: filling of the uranium 5f states (WIEN2K: numbers without parentheses are from the muffin-tin spheres, numbers in parentheses are from Wannier functions; FPLO: the first numbers refer to net and the second to gross occupations), uranium orbital (μ_L), spin (μ_S), and total (μ_{tot}) magnetic moments (net contributions in the case of FPLO), the total magnetic moment of the unit cell, the Sommerfeld coefficient, and the M -edge branching ratio. The difference between the uranium total moment and the unit-cell total moment comes from the spin moment residing in the interstitial region of the LAPW basis (WIEN2K, where the magnetic moment at the gallium atoms is negligible, Ga $\mu_{\text{tot}} \cong 0.01 \mu_B$), or from minor contributions at the Ga sites (FPLO).

Method	U n_{5f}	U μ_L (μ_B)	U μ_S (μ_B)	$ \text{U}\mu_L/\text{U}\mu_S $	U μ_{tot} (μ_B)	μ_{tot} (μ_B)	γ (mJ/mol K ²)	B
LSDA, WIEN2K	2.51(2.72)	2.70	-1.91	1.42	0.80	0.58	25	0.670
LSDA, FPLO	2.47(2.68)	2.70	-1.90	1.42	0.80	0.69	29	0.672
GGA, FPLO	2.47(2.68)	2.69	-2.02	1.33	0.67	0.56	15	0.670
GGA+OPC, FPLO	2.57(2.73)	4.64	-2.26	2.05	2.38	2.33	15	0.685
LSDA+ U (1 eV), WIEN2K	2.54	4.25	-2.17	1.96	2.08	1.86	10	0.682
LSDA+ U (2 eV), WIEN2K	2.58	4.70	-2.37	1.98	2.33	2.12	15	0.677
LDA+DMFT	(2.80)	(2.92)	(-1.16)	(2.52)	(1.76)	1.76	12	0.711
LDA+DMFT*	(2.76)	(4.60)	(-1.85)	(2.49)	(2.75)	2.75	8	0.709
Experiment				1.9–3.0		3.0 [5]	11 [5]	0.697

single out those situations which are entirely implausible. We can exclude the localized f^2 as well as completely localized f^3 behavior, but the HERFD XAS data do not allow for a decision between situations close to the f^2 localized state or a partly delocalized state close to f^3 , mainly due to the lack of HERFD XAS data on well-characterized U intermetallic references. Despite these limitations, a putative linear relation could be established between the U- M_4 edge positions and the calculated uranium ionicities of three intermetallic compounds.

The experimental bulk moment of $3.0 \mu_B/\text{f.u.}$ was not reproduced by XMCD (suggesting otherwise the $5f$ occupancy close to 2.5), which gives only about half of the bulk value, but we cannot exclude a certain influence of surface oxidation, or even effects of surface polishing yielding a noncollinear ferromagnetic arrangement in the topmost atomic layers. However, the $5f$ occupancy close to 2.5 suggested by the XMCD data agrees with the localized contributions to the $5f$ occupation numbers obtained in all computational approaches we applied.

The XAS spectra clearly suggest a necessity of atomic multiplets to be included in the theoretical modeling. Considering also thermodynamic data, we encounter a rather special situation: the Sommerfeld coefficient amounts to only 11 mJ/mol K^2 , suggesting a small $5f$ contribution to the electronic density of states at the Fermi level, while photoemission shows $5f$ states at or very close to E_F . This is true for historical UPS spectra on polycrystalline films [10] as well as for new high-resolution soft x-ray photoemission spectra on single crystals [37].

Other existing spectroscopy data, namely XPS, can also be tentatively linked with HERFD XAS data, as they can help to separate the effects of a deep core state from the properties of available empty electronic states. The $3d$ core-level spectra in actinides are not studied routinely, being far beyond the energy range of common XPS instrumentation. However, we can get at least a qualitative estimate from the available U- $4f$ spectra; see, e.g., Ref. [37] and references therein. The energies of the $4f_{5/2}$ and $4f_{7/2}$ lines in UGa_2 , 387.99 and 377.18 eV [10], are by $\approx 0.3 \text{ eV}$ higher than in U metal and are slightly lower than in UN, where a certain loss of the $5f$ charge can be expected due to the N bonding [51,52]. These data indicate that UGa_2 has less $5f$ electrons than U metal and they are in the same time more localized.

One should stress that in the case of U- $4f$ XPS spectroscopy, the shifts of the spectral lines in intermetallics are much smaller than in UO_2 , where the $4f$ lines shift by 3 eV towards higher energies compared with U metal [53]. This shift is much larger than in XAS, which can be related to the lack of $5f$ screening of the $4f$ hole in XPS [54]. In the charge-neutral XAS, the screening $5f$ electron is provided by the process itself and does not need to be transferred from neighbor atoms (which is not possible on the timescale of the XPS experiment).

The lack of f screening can be also taken responsible for the main XPS $4f$ lines in UPd_3 , where the $4f_{7/2}$ peak is found at 378.8 eV. However, its shoulder at 377.2 eV, which can be associated with a $5f$ -screened final state, is practically equivalent to the related main-peak energy in UGa_2 [55], only its lower intensity compared to UGa_2 indicates that the probability of $5f$ screening is much lower, due to the smaller hybridization (i.e., smaller hopping rate) in UPd_3 than in UGa_2 .

We can conclude that the spectroscopic and thermodynamic data in comparison with calculations of various kinds indicate that the $5f$ states in UGa_2 , although not fully localized, are strongly affected by atomic multiplet effects, which are not well described by LSDA or GGA. A better model was found to be GGA+OPC, where the orbital polarization of the atomic states is embedded in a Kohn-Sham scheme. Yet better, though not without room for further improvement, was the description provided by a particular LDA+DMFT implementation.

So far, the strongly correlated f systems were investigated mainly in the context of heavy fermions. UGa_2 is a strongly correlated low- γ material, though the $5f$ states are observed close to the Fermi level in photoelectron spectroscopies. The size of the magnetic moment in the ferromagnetic phase is interestingly higher than results of all computational approaches applied so far, which can signal that some part of physics is being overlooked by these theoretical methods.

It is naturally useful to seek analogies among U systems. A combination of large moments and low- γ value has been observed among metallic U systems, e.g., in UPdSn , an ordered ternary compound with crystal structure similar to that of UGa_2 , which has an antiferromagnetic ground state and $\gamma = 5 \text{ mJ/mol K}^2$ [56]. First suspected of exhibiting $5f$ localization, existing photoelectron spectroscopy data show some of the $5f$ states near E_F [57,58]. In comparison to UGa_2 , the ordered moments are lower, reaching only $\approx 2.0 \mu_B/\text{U}$.

ACKNOWLEDGMENTS

This work was supported by the **Czech Science Foundation** under Grants No. 18-02344S and No. 21-09766S. K.O.K. acknowledges support by European Research Council under Horizon 2020 Framework Programme (H2020) - **ERC** grant No. 759696. We thank Patrick Colomp of the Radioprotection services for his help at ID26 and ID12 beamlines of ESRF, Ulrike Nitzsche for maintaining the high-performance computing environment at IFW Dresden, and Shin-ichi Fujimori for fruitful discussion. During the final processing of the present paper, a separate theory article [59] has been published, which brings more details on the DFT+DMFT calculations of UGa_2 .

[1] Y. Baer, H. R. Ott, and K. Andres, *Solid State Commun.* **36**, 387 (1980).

[2] K. Andres, D. Davidov, P. Dernier, F. Hsu, W. A. Reed, and D. J. Nieuwenhuys, *Solid State Commun.* **28**, 405 (1978).

- [3] A. Andreev, V. K. Belov, A. Deriagin, V. Z. A. Kazei, R. Z. Levitin, A. Menovsky, Y. F. Popov, and V. I. Silant'ev, *Sov. Phys. JETP* **48**, 1187 (1978).
- [4] A. C. Lawson, A. Williams, J. L. Smith, P. A. Seeger, J. A. Goldstone, J. A. O'Rourke, and Z. Fisk, *J. Magn. Magn. Mater.* **50**, 83 (1985).
- [5] J.-M. Fournier and R. Troc, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman, and G. H. Lander (North-Holland, Amsterdam 1985), Vol. 2, p. 35.
- [6] T. Honma, Y. Inada, R. Settai, S. Araki, Y. Tokiwa, T. Takeuchi, H. Sugawara, H. Sato, K. Kuwahara, M. Yokoyama, H. Amitsuka, T. Sakakibara, E. Yamamoto, Y. Haga, A. Nakamura, H. Harima, H. Yamagami, and Y. Ōnuki, *J. Phys. Soc. Jpn.* **69**, 2647 (2000).
- [7] L. M. da Silva, A. O. dos Santos, A. N. Medina, A. A. Coelho, L. P. Cardoso, and F. G. Gandra, *J. Phys.: Condens. Matter* **21**, 276001 (2009).
- [8] M. Diviš, M. Richter, H. Eschrig, and L. Steinbeck, *Phys. Rev. B* **53**, 9658 (1996).
- [9] R. J. Radwanski and N. H. Kim-Ngan, *J. Magn. Magn. Mater.* **140–144**, 1373 (1995).
- [10] T. Gouder, L. Havela, M. Divis, J. Rebizant, P. M. Oppeneer, and M. Richter, *J. Alloys Compd.* **314**, 7 (2001).
- [11] A. V. Kolomiets, J.-C. Griveau, J. Prchal, A. V. Andreev, and L. Havela, *Phys. Rev. B* **91**, 064405 (2015).
- [12] C. Gauthier, V. A. Sole, R. Signorato, J. Goulon, and E. Moguiline, *J. Synchrotron Radiat.* **6**, 164 (1999).
- [13] P. Glatzel and U. Bergmann, *Coord. Chem. Rev.* **249**, 65 (2005).
- [14] K. O. Kvashnina and A. C. Scheinost, *J. Synchrotron Radiat.* **23**, 836 (2016).
- [15] A. Rogalev, J. Goulon, C. Goulon-Ginet, and C. Malgrange, *Magnetism and Synchrotron Radiation (Lecture Notes in Physics vol 565)* edited by E. Beaurepaire, F. Scheurer, G. Krill, and J. P. Kappler (Springer-Verlag, Berlin, 2001), pp. 60–86.
- [16] F. Wilhelm, N. Jaouen, A. Rogalev, W. G. Stirling, R. Springell, S. W. Zochowski, A. M. Beesley, S. D. Brown, M. F. Thomas, G. H. Lander, S. Langridge, R. C. C. Ward, and M. R. Wells, *Phys. Rev. B* **76**, 024425 (2007).
- [17] M. J. Berger, J. H. Hubbell, S. M. Seltzer, J. Chang, J. S. Coursey, R. Sukumar, D. S. Zucker, and K. Olsen (2010), <https://www.nist.gov/pml/xcom-photon-cross-sections-database>.
- [18] F. Wilhelm, J.-P. Sanchez, and A. Rogalev, *J. Phys. D: Appl. Phys.* **51**, 333001 (2018).
- [19] F. Wilhelm, G. Garbarino, J. Jacobs, H. Vitoux, R. Steinmann, F. Guillou, A. Snigirev, I. Snigireva, P. Voisin, D. Braithwaite, D. Aoki, J. P. Brison, I. Kantor, I. Lyatun, and A. Rogalev, *High Pressure Res.* **36**, 445 (2016).
- [20] F. Zhou and V. Ozoliņš, *Phys. Rev. B* **80**, 125127 (2009).
- [21] O. Eriksson, B. Johansson, and M. S. S. Brooks, *J. Phys.: Condens. Matter* **1**, 4005 (1989).
- [22] H. Eschrig, M. Sargolzaei, K. Koepernik, and M. Richter, *Europhys. Lett.* **72**, 611 (2005).
- [23] G. Jomard, B. Amadon, F. Bottin, and M. Torrent, *Phys. Rev. B* **78**, 075125 (2008).
- [24] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. H. Madsen, and L. D. Marks, *J. Chem. Phys.* **152**, 074101 (2020); D. D. Koelling, and B. N. Harmon, *J. Phys. C: Solid State Phys.* **10**, 3107 (1977).
- [25] J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- [26] J. Kolorenč, A. B. Shick, and A. I. Lichtenstein, *Phys. Rev. B* **92**, 085125 (2015).
- [27] J. Kuneš, R. Arita, P. Wissgott, A. Toschi, H. Ikeda, and K. Held, *Comput. Phys. Commun.* **181**, 1888 (2010).
- [28] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, *Comput. Phys. Commun.* **178**, 685 (2008).
- [29] H. Ogasawara, A. Kotani, and B. T. Thole, *Phys. Rev. B* **44**, 2169 (1991).
- [30] A. B. Shick and A. I. Lichtenstein, *J. Magn. Magn. Mater.* **454**, 61 (2018).
- [31] L. Peters, I. Di Marco, P. Thunström, M. I. Katsnelson, A. Kirilyuk, and O. Eriksson, *Phys. Rev. B* **89**, 205109 (2014).
- [32] M. S. S. Brooks and B. Johansson, *J. Phys. F: Met. Phys.* **13**, L197 (1983).
- [33] L. V. Pourovskii, G. Kotliar, M. I. Katsnelson, and A. I. Lichtenstein, *Phys. Rev. B* **75**, 235107 (2007).
- [34] K. Koepernik and H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999); <https://www.fplo.de/>.
- [35] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [36] K. O. Kvashnina, H. C. Walker, N. Magnani, G. H. Lander, and R. Caciuffo, *Phys. Rev. B* **95**, 245103 (2017).
- [37] S.-I. Fujimori, M. Kobata, Y. Takeda, T. Okane, Y. Saitoh, A. Fujimori, H. Yamagami, Y. Haga, E. Yamamoto, and Y. Onuki, *Phys. Rev. B* **99**, 035109 (2019).
- [38] T. K. Sham, *Phys. Rev. B* **31**, 1888 (1985).
- [39] G. van der Laan, K. T. Moore, J. G. Tobin, B. W. Chung, M. A. Wall, and A. J. Schwartz, *Phys. Rev. Lett.* **93**, 097401 (2004).
- [40] M. Taupin, J. P. Sanchez, J. P. Brison, D. Aoki, G. Lapertot, F. Wilhelm, and A. Rogalev, *Phys. Rev. B* **92**, 035124 (2015).
- [41] M. Samsel-Czekala, S. Elgazzar, P. M. Oppeneer, E. Talik, W. Walerczyk, and R. Troć, *J. Phys.: Condens. Matter* **22**, 015503 (2010).
- [42] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev. Lett.* **68**, 1943 (1992).
- [43] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, *Phys. Rev. Lett.* **70**, 694 (1993).
- [44] G. van der Laan and P. T. Thole, *Phys. Rev. B* **53**, 14458 (1996).
- [45] R. Ballou, A. V. Deriagin, F. Givord, R. Lemaire, R. Z. Levitin, and F. Tasset, *J. Phys. Colloques* **43**, C7-279 (1982).
- [46] V. N. Antonov, B. N. Harmon, and A. N. Yaresko, *J. Phys.: Condens. Matter* **19**, 186222 (2007).
- [47] Y. Inada, T. Honma, N. Kawamura, M. Suzuki, H. Miyagawa, E. Yamamoto, Y. Haga, T. Okane, S.-i. Fujimori, and Y. Ōnuki, *Physica B* **359–361**, 1054 (2005).
- [48] H. Rosner, D. Koudela, U. Schwarz, A. Handstein, M. Hanfland, I. Opahle, K. Koepernik, M. D. Kuz'min, K.-H. Müller, J. A. Mydosh, and M. Richter, *Nat. Phys.* **2**, 469 (2006).
- [49] N. R. Sanjay Kumar, N. Subramanian, N. V. Chandra Shekar, M. Sekar, and P. Ch. Sahu, *Philos. Mag. Lett.* **84**, 791 (2004).
- [50] K. Lejaeghere, G. Bihlmayer, T. Björkman, P. Blaha, S. Blügel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. Dal Corso *et al.*, *Science* **351**, aad3000 (2016).
- [51] M. S. S. Brooks, *J. Phys. F: Metal Phys.* **14**, 639 (1984).
- [52] L. Havela, F. Wastin, J. Rebizant, and T. Gouder, *Phys. Rev. B* **68**, 085101 (2003).
- [53] M. Eckle and T. Gouder, *J. Alloys Compd.* **374**, 261 (2004).
- [54] J. C. Fuggle, M. Campagna, Z. Zolnierrek, R. Lässer, and A. Platau, *Phys. Rev. Lett.* **45**, 1597 (1980).

- [55] S.-i. Fujimori, Y. Takeda, T. Okane, Y. Saitoh, A. Fujimori, H. Yamagami, Y. Haga, E. Yamamoto, and Y. Ōnuki, *J. Phys. Soc. Jpn.* **85**, 062001 (2016).
- [56] F. R. de Boer, E. Brück, H. Nakotte, A. V. Andreev, V. Sechovský, L. Havela, P. Nozar, C. J. M. Denissen, K. H. J. Buschow, B. Vaziri, P. Meissner, H. Maletta, and P. Rogl, *Physica B* **176**, 275 (1992).
- [57] L. Havela, T. Almeida, J. R. Naegele, V. Sechovský, and E. Brück, *J. Alloys Compd.* **181**, 205 (1992).
- [58] J.-S. Kang, S. C. Wi, J. H. Kim, K. A. McEwen, C. G. Olson, J. H. Shim, and B. I. Min, *J. Phys.: Condens. Matter* **16**, 3257 (2004).
- [59] B. Chatterjee and J. Koloren, *Phys. Rev. B* **103**, 205146 (2021).