1. Introduction

The valence of Eu can be influenced by its chemical environment [1], pressure [2], temperature [3] or magnetic field [4]. Not only 4f⁶ (Eu³⁺) and 4f⁷ (Eu²⁺) configurations can be realized, but also non-integer valence states [3]. The Eu valence has dramatic consequences for the physical properties due to the different number of conduction electrons, volume, and magnetic behavior of Eu²⁺ (large, pure-spin J = 7/2 moment, ordering at low temperatures) and Eu³⁺ (J = 0 ground state with Van Vleck paramagnetism). In a first approximation, the non-integer valence can be interpreted as a fluctuating state between the two integer valence configurations that lie close in energy. Upon warming, the high-energy state, which in valence-fluctuating Eu systems is always the divalent one, becomes increasingly populated and the average valence shifts towards 2. Similarly, a magnetic field promotes the strongly magnetic divalent state, while pressure favors the non-magnetic trivalent configuration because of its much smaller volume. In Mössbauer spectroscopy, a technique that probes nuclear transitions leaving electronic states unaffected [5], an intermediate isomer shift between those of the integer Eu valence states is observed [3]. In probes such as x-ray absorption, which result in strong changes of intermediate or final
electronic states [5], one observes two lines at the positions corresponding to the integral valences [6]. At low temperatures, this simple thermal excitation picture fails, notably in EuIr2Si2 and EuNi2P2, as the valence measured in Mössbauer experiments remains non-integer down to the lowest temperatures [7, 8]. This implies the presence of a significant hybridization between 4f and conduction electrons, which results at low temperatures in a quantum mechanical mixing of the two integer valence states. This hybridization leads e.g. to a sizeable mass renormalization of the conduction electrons, as attested by the large Sommerfeld coefficient extracted from specific heat measurements [9, 10]. The optical response as a function of temperature also contradicts a simple thermal occupation scheme, and resembles remarkably that of Kondo lattice systems, where hybridization between localized and conduction electrons plays the dominant role [11]. In this work, we investigate the effect of valence fluctuations on the lattice, magnetic, and transport properties of the paradigmatic valence-fluctuating compound EuIr2Si2, by comparing with isostructural, stable-valent compounds EuCo2Si2 and EuRh2Si2, which have the same total number of electrons. We disentangle contributions from valence fluctuations at intermediate temperatures, and from an intermediate valence at low temperatures. We show that the interconfiguration fluctuation mode, which considers thermal excitation to the divalent state and the effect of hybridization on a very simple empirical level, provides only a limited description of the data.

2. Experimental details

Single crystals of Eu T2Si2 were grown by a flux method (M = Rh,Ir) [10] or by a Bridgman technique (M = Co) [12] starting from high purity elements. Temperature-dependent synchrotron powder diffraction data on crushed single crystals were collected in transmission (Debye-Scherrer) geometry at the high-resolution beamline (ID22) of the European Synchrotron Radiation Facility (particle size <32 µm, capillary of 0.3 mm diameter, λ = 0.400 737(6) Å, 3º ≤ 2θ ≤ 52º, step 2θ = 0.002º, multi-channel detector, 10 K ≤ T ≤ 293 K, liquid-helium cryostat). The Rietveld refinement was performed with the program package WinCSD [13]. The valence of Eu was investigated by means of x-ray absorption spectroscopy (XAS) performed at the former ID16 beamline of the European Synchrotron Radiation Facility (now ID20). The spectra were collected in partial fluorescence yield using an x-ray emission spectrometer equipped with a Ge (3 3 3) analyzer crystal and set to the Eu Lα1 emission line at 5.843 keV (ΔE = 0.86 eV). In this way, the intrinsic core-hole lifetime broadening of the spectra is significantly reduced which allows to detect and quantify spectral changes more easily than in conventional, total fluorescence yield XAS spectroscopy [14–16]. Magnetization data were acquired using a quantum design magnetic property measurement system. Resistivity and specific heat was measured in a quantum design physical property measurement system with a 3He option.

3. Results and discussion

3.1. Europium valence

Figure 1 shows the temperature dependence of x-ray absorption spectra at the Eu L3 edge collected in partial fluorescence yield mode. In the x-ray absorption spectra Eu2+ and Eu3+ ions give rise to two distinct resonances at about 6.973 keV and 6.981 keV, respectively. The shape of Eu L3 XAS spectra is strongly affected by shake-up effects due to the creation of the Eu 2p core-hole. This is why EuRh2Si2 shows a pronounced absorption peak at the characteristic energy of Eu3+, although it is well established that Eu is in the divalent state in this compound [12]. The relative intensities of the Eu2+ and Eu3+ absorption lines can therefore not be used directly to determine the Eu valence in the ground state, which lacks the 2p core-hole [17]. For EuCo2Si2 and EuRh2Si2 no difference is detected between spectra taken at low and high temperatures, indicating a stable Eu valence in this temperature range. For EuIr2Si2, there is a weight shift from the trivalent to the divalent Eu characteristic absorption energies upon increasing temperature. In order to quantify the corresponding valence changes with temperature we have fitted the EuIr2Si2 spectra with a linear combination of the EuRh2Si2 and EuCo2Si2 spectra using them as a reference for Eu2+ and Eu3+ absorption, respectively, thus including shake-up effects. The valence obtained in this way is shown as a function of

![Figure 1. X-ray absorption spectra for (a) EuCo2Si2 and EuRh2Si2, and (b) EuIr2Si2. Inset: Eu valence in EuIr2Si2 as a function of temperature, as determined from the XAS spectra (black triangles, see text) and Mössbauer spectroscopy [8, 18]. The gray line represents a fit to the data using (1), the resulting characteristic energies are indicated (the shading represents T_{el}).](image-url)
temperature in the inset of figure 1: it decreases from 2.83 at low temperatures to 2.36 at room temperature. These values are in good agreement with those extracted from the isomer shift in the Mössbauer spectra of polycrystalline samples [8, 18]. The non-integer valence at lowest temperatures indicates hybridization between conduction and localized 4f electrons [11].

Assuming thermal excitation from the $J = 0$ ground state of Eu$^{3+}$ to the $J = 7/2$ state of Eu$^{2+}$ at an energy $E_{\text{ex}}$, and including only the first excited $J = 1$ multiplet of Eu$^{3+}$ at $E_1$ (the next excited multiplets can be neglected because they are at much higher energies), the valence can be expressed as

$$\nu(T) = \frac{3(1 + 3e^{-E_1/kT^*}) + 2(8e^{-E_{\text{ex}}/kT^*})}{1 + 3e^{-E_1/kT^*} + 8e^{-E_{\text{ex}}/kT^*}}, \quad (1)$$

where an effective temperature $T^* = \sqrt{T^2 + T_{\text{sf}}^2}$ is introduced, that mimics the effect of hybridization by introducing a phenomenological energy width $T_{\text{sf}}$ for all configurations [19]. For a free Eu$^{3+}$ ion, $E_1 = 480$ K, while values in the range 355–505 K have been reported in Eu compounds [12, 20]. A fit of the experimentally obtained valence using (1) with $E_1 = 480$ K reproduces the experimental data quite well (see inset of figure 1(b)), yielding $E_{\text{ex}} = (390 \pm 20)$ K and $T_{\text{sf}} = (101 \pm 7)$ K. The fit procedure with $E_1$ as a free parameter failed to give physically meaningful parameter values.

3.2. Structure

All three compounds exhibit a tetragonal ThCr$_2$Si$_2$-type structure with space group $I4/mmm$ in the whole investigated temperature range. Table 1 summarizes the refined structural parameters at the lowest and the highest measured temperatures.

Table 1. Lattice parameters of Eu$_M$$_2$Si$_2$ at the highest and lowest measured temperatures. The crystal structure is of the ThCr$_2$Si$_2$-type, space group $I4/mmm$. The uncertainties resulting from the refinement are given in parentheses. The Bragg ($R_B$) and profile ($R_P$) residuals are indicated, their values are representative for those obtained at intermediate temperatures for each sample.

| Compound | Temperature | EuCo$_2$Si$_2$ | EuRh$_2$Si$_2$ | EuIr$_2$Si$_2$ |
|----------|-------------|---------------|---------------|---------------|
|          | 300 K       | 30 K          | 10 K          | 300 K         | 10 K          |
| $a$ (Å)  | 3.922 18(1) | 3.912 58(1)   | 4.09085(1)    | 4.08341(1)    | 4.08353(1)    | 4.06569(1)    |
| $c$ (Å)  | 9.835 53(1) | 9.825 45(2)   | 10.224 71(2)  | 10.192 38(4)  | 10.110 54(1)  | 10.022 33(1)  |
| $z$      | 0.3708(1)   | 0.3715(1)     | 0.3688(2)     | 0.3707(2)     | 0.3721(2)     | 0.3731(2)     |
| $V$ (Å$^3$) | 151.305(1) | 150.410(1)    | 171.111(1)    | 169.951(2)    | 168.596(1)    | 165.668(1)    |
| $R_B$    | 0.0317      | 0.0312        | 0.0347        | 0.0463        | 0.0491        | 0.0466        |
| $R_P$    | 0.0848      | 0.1124        | 0.1195        | 0.1120        | 0.0875        | 0.0941        |

Figure 2. (a) Relative expansion of the lattice parameters $a$ (full symbols) and $c$ (open symbols) with respect to the values at the lowest measured temperature for EuCo$_2$Si$_2$ (blue circles), EuRh$_2$Si$_2$ (red squares), and EuIr$_2$Si$_2$ (black triangles). The unit cell is depicted in the inset, with Eu in red, Si in blue and the transition metal in gray. (b) Parameter $z$ determining the position of Si within the unit cell for all three compounds. Previously reported values are plotted for EuCo$_2$Si$_2$ [23] (blue open circle) and for EuIr$_2$Si$_2$ [24] (black open triangle). Atomic displacement parameters $U_{11}$ (full symbols) and $U_{33}$ (open symbols) for (c) Eu, (d) transition metal and (e) Si atoms in EuIr$_2$Si$_2$ (black triangles), EuRh$_2$Si$_2$ (red squares) and EuCo$_2$Si$_2$ (blue circles). The lines are a guide to the eye.
slightly from that reported in the literature [24] and the lattice parameters show strong temperature dependence. The refined parameter $z$ for EuRh$_2$Si$_2$ is published here for the first time.

The temperature evolution of the individual structural parameters is shown in figure 2. The lattice parameters $a$ and $c$ increase monotonically upon increasing temperature for all compounds. For EuIr$_2$Si$_2$, however, the lattice expansion is substantially larger than in the stable-valent cases, in particular along the $c$ axis where it reaches almost 1% at room temperature. The $z$ parameter is weakly temperature dependent, and slightly larger for EuIr$_2$Si$_2$ than for the stable-valent cases. While thermal expansion is larger along the $c$ axis than along the $a$ axis for the divalent and valence fluctuating compounds, for the trivalent compound thermal expansion along $a$ is larger than along $c$. The latter is in line with results for RCu$_2$Si$_2$ with $R$ = trivalent La, Gd and Lu, which exhibit an expansion of about 0.3% along $a$ and 0.1% along $c$ between low and room temperatures [25]. In comparison, CaCu$_2$Si$_2$, where Ca is in a divalent configuration, shows between low and room temperatures a similar lattice expansion along $a$ but twice as large along $c$ than that of the trivalent analogues [25]. Clearly, the rare earth valence affects the bonds along the $c$ axis more strongly than along $a$, making them particularly soft in the case of fluctuating valence. Indeed, while for integer-valent rare earth compounds the bulk modulus scales linearly with $q/V$, where $q$ is the charge of the rare earth ion and $V$ the unit cell volume, analogous compounds where the rare earth valence is non-integer fall clearly below this trend [25].

Similarly, for EuIr$_2$Si$_2$, the atomic displacement parameters for Eu and $M$ atoms along $c$ ($U_{33}$) are larger and increase more rapidly upon warming than those in the basal plane ($U_{11}$), see figure 2. For EuCo$_2$Si$_2$, $U_{11}$ appears to be larger than $U_{33}$ for both Eu and Co atoms, while for EuRh$_2$Si$_2$ $U_{11}$ and $U_{33}$ are similar. Due to the smaller cross section of Si compared to that of the heavier atoms, the displacements of Si carry a much larger uncertainty so that no reliable trend can be recognized.

Figure 3(a) shows that the Si–Si distance depends strongly on the europium valence: it is largest in the divalent compound, smallest in the trivalent compound, and intermediate for the non-integer-valent case. This is in contrast to the thickness of the Si–$M$–Si trilayer (defined as the height difference between Si layers across the $M$ layer, see inset of figure 2(a)), which is dominated by the size of the transition metal ion. For both EuIr$_2$Si$_2$ and EuRh$_2$Si$_2$ the Si–$M$–Si trilayer thickness is essentially identical, in spite of the different valence state of Eu. Similarly, the Si–$M$–Si angles do not show a distinct correlation to the valence state of Eu. This suggests that the extra conduction electron contributed by Eu$^{+3}$ goes to a band dispersing along the $z$ direction, making the material more three-dimensional. This is reflected, for example, in a worse cleaving behavior of the EuIr$_2$Si$_2$ single crystals compared to EuRh$_2$Si$_2$ ones.

### 3.3. Thermodynamic and transport properties

Specific heat as a function of temperature is plotted in figure 4(a) for all three compounds. At low temperatures, the specific heat of EuIr$_2$Si$_2$ behaves as expected for a Fermi liquid, with an electronic contribution linear in temperature given by the Sommerfeld coefficient $\gamma = 33 \text{ mJ K}^{-2} \text{ mol}^{-1}$, and a phonon contribution characterized by a Debye temperature $\Theta_D = 270 \text{ K}$ [10]. This value of $\gamma$ is higher than for the stable-valent compounds (9.6 mJ K$^{-2}$ mol$^{-1}$ for EuCo$_2$Si$_2$ [12], $\sim$25 mJ K$^{-2}$ mol$^{-1}$ for EuRh$_2$Si$_2$ [10]), indicating a moderate renormalization of the effective mass in agreement with optical spectroscopy studies [11]. The Debye temperature is much smaller than for the stable-valent compounds (388 K for EuRh$_2$Si$_2$ [26], 332 K for EuCo$_2$Si$_2$ [12]). Though a smaller $\Theta_D$ is expected due to the higher mass of iridium atoms, the large thermal expansion in figure 2(a) suggests that the low value of $\Theta_D$ for EuIr$_2$Si$_2$ is related to the phonon softening induced by valence fluctuations.

EuIr$_2$Si$_2$ exhibits a clear excess specific heat with respect to the stable-valent compounds that extends over a broad temperature range, roughly 20–200 K. In an attempt to quantify this excess specific heat, we subtracted from the data for EuIr$_2$Si$_2$ an average of the specific heat of EuRh$_2$Si$_2$ and EuCo$_2$Si$_2$ weighted by the actual valence of Eu in EuIr$_2$Si$_2$. Notice that this procedure only yields an approximate estimate, since the different atomic masses of Ir, Rh and Co are not considered. The contribution of valence fluctuations to the specific heat peaks at roughly 75 K and is basically negligible below 20 K and above 200 K. This is consistent with the temperature evolution of the valence in figure 1, which shows only weak changes at the lowest and highest temperatures. Predictions for the specific heat due to valence fluctuations within a realistic model are not available, but calculations for the spinless Falicov-Kimball model suggest that for a large energy difference between the localized $f$ state and the Fermi
level, specific heat shows a Schottky-like behavior [28]. In a simple two-level Schottky model with non-degenerate ground state and an excited state at an energy $\Delta$ with a degeneracy of eight (that of a $\text{Eu}^{3+}$ configuration), a maximum at 75 K corresponds to $\Delta \sim 260$ K, a value significantly lower than that of $E_{\text{ex}}$ obtained from the thermal evolution of the valence in figure 1. The temperature dependence of the Schottky specific heat for this value of $\Delta$, plotted as a solid line in figure 4(a), roughly follows that of the excess specific heat due to valence fluctuations in EuIr$_2$Si$_2$, albeit with somewhat smaller values than the experimental data. This difference possibly reflects the lower Debye temperature of EuIr$_2$Si$_2$ with respect to the stable valent compounds, that would be consistent with the softening observed in figure 2. Accordingly, the estimated entropy associated to the valence fluctuations saturates at high temperatures at values beyond the R ln 9 expected for the Schottky model.

The peak in the specific heat contributed by valence fluctuations correlates with a peak in the magnetic susceptibility of EuIr$_2$Si$_2$, observed both for fields applied parallel and perpendicular to the tetragonal c axis, see figure 4(b). Such a broad maximum is typical of fluctuating valence compounds. At higher temperatures, the susceptibility decreases upon warming but no clear Curie–Weiss-type behavior is recovered up to room temperature. At low temperatures, the susceptibility saturates at a residual value of $0.03 - 0.04$ emu (mol Oe$^{-1}$) that is relatively high for a metal and can be at least partly ascribed to a Van Vleck contribution involving the higher $J$ multiplets of Eu$^{3+}$. A small anisotropy is observed, which decreases on increasing temperature. This anisotropy is possibly related to the crystal-field splitting of the excited multiplets of Eu$^{3+}$, and has also been reported for the trivalent Eu compound EuCo$_2$Si$_2$ [12]. The fact that the susceptibility for fields along c is smaller than for fields applied in the basal plane indicates that the $J_z = 0$ levels lie higher in energy within each $J$ multiplet [29]. Considering only the $J = 1$ excited multiplet, if the observed susceptibility at low temperatures was purely the Van Vleck contribution of Eu$^{3+}$, this would correspond to a splitting of 16 K between $J_z = 0$ and $J_z = \pm 1$ states. However, a pure Van Vleck-like contribution implies for the average residual susceptibility $\chi_0 \sim 0.036$ emu mol$^{-1}$ an energy for the first excited $J = 1$ multiplet of about $E_1 \sim 80$ K, an unrealistically low value. Since the valence of Eu at low temperatures remains far from 3, and renormalization effects are observed e.g. in the Sommerfeld coefficient, a more realistic comparison can be made with a weighted average of divalent (Curie) and trivalent (Van Vleck) contributions, in the spirit of (1), where the weight is given by the valence [19]:

$$\chi(T) = 8N\mu_B^2 \frac{2e^{-E_{\text{ex}}/kT}}{kT} + \frac{1}{E_1} + e^{-E_1/kT} \left( \frac{1}{E_1} - \frac{1}{E_1} \right)$$

and a renormalized temperature $T' = \sqrt{T^2 + T_d^2}$ is considered, as in (1). However, substituting in (2) the values for $E_1$, $E_{\text{ex}}$, and $T_d$ extracted from the fit of (1) to the valence gives a poor agreement with the experimental susceptibility data, even after addition of a constant susceptibility term $\chi_c$, see gray line in figure 4(b). A better agreement is obtained using $E_1 = 480$ K, which is represented by the black line, yielding $\chi_c = (0.0089 \pm 0.0001)$ emu (mol Oe$^{-1}$), $E_{\text{ex}} = (269 \pm 1)$ K and $T_d = (84 \pm 1)$ K. The latter parameters are quite different to those obtained from the analysis of the valence.

The dramatic effect of valence fluctuations in transport properties is shown in figure 4(c). While at lowest temperatures the resistivity of EuIr$_2$Si$_2$ and that of stable-valent EuRh$_2$Si$_2$ and EuCo$_2$Si$_2$ are of similar magnitude, the resistivity of EuIr$_2$Si$_2$ increases over two orders of magnitude upon warming in the temperature range where strong valence fluctuations are observed in the specific heat, reaching a maximum at around 160 K. Upon further warming, resistivity decreases on increasing temperature and stagnates towards room temperature. Several theoretical works [30–32] indicate the presence of a resistivity maximum as a consequence of conduction electrons scattering off valence fluctuations, although the shape of the resistivity peak depends on the particular model and parameter range. In a simple picture, the lifetime of conduction electrons decreases on increasing temperature, becoming
of the order of the characteristic valence fluctuation time and leading to a large rise in resistivity. Resistivity then saturates as the scattering becomes fully incoherent at higher temperatures. The total resistivity increase due to valence fluctuations \( \Delta \rho \) has been proposed to scale with \( \Delta \nu / T_d \), where \( \Delta \nu \) is the percent deviation from integer valence at high temperatures, with \( \Delta \rho (\Delta \nu / T_d)^{-1} \sim 750–900 \mu \Omega \text{cm} \) K for several Ce- and Yb-based valence fluctuating compounds [30].

Estimating the phonon contribution from \( \rho(T) = \rho(T_N) \) for EuRh\(_2\)Si\(_2\), yields for EuIr\(_2\)Si\(_2\) \( \Delta \rho (\Delta \nu / T_d)^{-1} \sim 1000–1250 \mu \Omega \text{cm} \) K. The origin of the large resistivity increase is evident when comparing the derivative of resistivity with respect to temperature with the specific heat contribution from valence fluctuations: both exhibit roughly the same shape, with a well-defined maximum at \( \sim 65 \) K. The correspondence of resistivity change and specific heat has been established for magnetic systems [33] and supports the observation of an excess specific heat due to valence fluctuations in EuIr\(_2\)Si\(_2\). For stable-valent compounds, resistivity shows a much slower monotonous increase on increasing temperature that can be well described by phonon scattering [12, 26].

At low temperatures, the resistivity of EuIr\(_2\)Si\(_2\) follows \( \rho = \rho_0 + AT^2 \), with \( \rho_0 = (2.67 \pm 0.03) \mu \Omega \text{cm} \) and \( A = (0.0026 \pm 0.0005) \mu \Omega \text{cm}^{-1} \) K\(^{-2}\). This dependence, as well as a specific heat varying as \( c = \gamma T \) with a moderately high \( \gamma \) value, are characteristic of a correlated metal. The ratio \( A / \gamma^2 \), known as the Kadowaki-Woods ratio [34], shows a universal value within certain groups of materials, e.g. 0.4 \( \mu \Omega \text{cm} \) mol\(^2\) K\(^2\) J\(^{-1}\) for transition metal elements [35] and 10(0.36) \( \mu \Omega \text{cm} \) mol\(^2\) K\(^2\) J\(^{-2}\) for Kondo systems with twofold (eight-fold) degeneracy [36]. In the case of EuIr\(_2\)Si\(_2\), \( A / \gamma^2 \sim 2.4 \) \( \mu \Omega \text{cm} \) mol\(^2\) K\(^2\) J\(^{-2}\), is close to the values observed for intermediate-valent EuCu\(_2\)(Si\(_0.7\)Ge\(_0.3\)) and EuNi\(_2\)P\(_2\) (2.25 and 2.7 \( \mu \Omega \text{cm} \) mol\(^2\) K\(^2\) J\(^{-2}\), respectively) [37, 38]. A further indicator of correlations is the Wilson ratio \( W = \pi^2 k_B^2 \chi_0 / (\mu_{\text{eff}}^2 \gamma) \), where \( \chi_0 \) is the Pauli susceptibility and \( \mu_{\text{eff}} \) an effective magnetic moment. In absence of correlations (as in a Fermi gas) \( W \) is 1, while for the Kondo impurity model \( W = 2 \) in the two-fold degenerate case [39]. Taking \( \mu_{\text{eff}} = 7.94 \) as for Eu\(^{2+}\), results in \( W \sim 3.9 \). This relatively large value compared to 1.15 obtained for EuCu\(_2\)(Si\(_0.7\)Ge\(_0.3\)) [37], and \( \sim 1.4 \) for EuNi\(_2\)P\(_2\), is probably related to the fact that the low-temperature valence of Eu in EuIr\(_2\)Si\(_2\) is closer to three and the system is further away from the magnetic critical point. As a consequence, the susceptibility of EuIr\(_2\)Si\(_2\) at low temperatures is dominated by the Van Vleck rather than by the Pauli contribution. This is in line with \( W = 3.1 \) for EuCo\(_2\)Si\(_2\), where Eu is trivalent and correlations are weaker (\( \gamma \sim 9.6 \) mJ K\(^{-2}\) mol\(^{-1}\)) [12].

4. Conclusions

In conclusion, two different aspects are reflected in the properties of EuIr\(_2\)Si\(_2\). On one hand, the fluctuating valence as a function of temperature manifests in a large thermal expansion, broad peaks in the excess specific heat, magnetic susceptibility and a dramatic increase in resistivity. On the other hand, the intermediate valence at low temperatures is accompanied by Fermi-liquid behavior with a moderate electron mass renormalization, as observed in specific heat, susceptibility and resistivity. The interconfiguration fluctuation model, a simple phenomenological model combining contributions from Eu\(^{2+}\) and Eu\(^{3+}\) weighted by the Bolzmann factor, and that mimics hybridization effects through a renormalized temperature, reproduces the behavior of valence and magnetic susceptibility independently, but is unable to do so with a single set of parameters, thus showing the limitations of the model for quantitative analysis of the experimental data.

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