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# Pressure-induced electronic phase transition in compound $\text{EuCu}_2\text{Ge}_2$

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**Abstract.** We report the high-pressure XANES study of the electronic phase transition from  $4f^7$  to  $4f^6$  configuration of europium in the rare-earth compound  $\text{EuCu}_2\text{Ge}_2$ . The hydrostatic pressure dependence of the europium valence was obtained in a wide pressure range (1-30 GPa) at room temperature. It was found that upon the pressure increase above 20 GPa the europium valence does not reach the integer value +3 but stabilizes at 2.87. The experimental results were supported by the band structure calculations in the framework of DFT, which allowed us to discuss the features of  $3d$ - $4f$  hybridization in this system. The study also compares the mechanisms of external and “chemical” pressure by the Si substitution in Ge site in series  $\text{EuCu}_2(\text{Si}_x\text{Ge}_{1-x})_2$ .

## 1. Introduction

Compounds  $\text{EuCu}_2\text{X}_2$  ( $\text{X} = \text{Si}, \text{Ge}$ ) crystallize in the  $\text{ThCr}_2\text{Si}_2$ -type structure (tetragonal space group  $I4/mmm$ ) which is famous for a variety of fascinating phenomena such as valence fluctuations, “heavy-fermion superconductivity”, non-Fermi liquid states, Kondo insulators, etc. [1-4]. These compounds are usually highly sensitive to the impacts like electron/hole doping or pressure, which lead to the modification of their electronic structure near Fermi level and eventually to various phase transitions. That is how the superconductivity was recently found in  $\text{EuFe}_2\text{As}_2$  under compression [5]. The compound  $\text{EuCu}_2\text{Ge}_2$  is antiferromagnetic ( $T_N \approx 15$  K) at ambient conditions and at the same time shows the intermediate valence state of europium with a value of 2.15 [6]. We talk about electronic phase transition in terms of transition between  $4f$  electronic configurations of rare-earth element or the valence instability. Recently it has been reported in [6] that silicon substitution in Ge site in series  $\text{EuCu}_2(\text{Si}_x\text{Ge}_{1-x})_2$  leads to a chemical compression and induces the transition from the magnetically ordered state ( $x < 0.65$ ) to a heavy-fermion state ( $0.65 < x < 0.85$ ) and then to a nonmagnetic strong valence fluctuating state which is accompanied by the Eu valence increase from 2.15 in  $\text{EuCu}_2\text{Ge}_2$  to 2.67 in  $\text{EuCu}_2\text{Si}_2$ . The suppression of the magnetic ordering may be due to the predominance of the contribution from non-magnetic  $\text{Eu}^{3+}$  ( $4f^6$ ,  $J = S = 0$ ). Thus, the europium valence might be an indicator of certain electronic and magnetic properties in this system. In this way we decided to



investigate the valence in pure parent compound  $\text{EuCu}_2\text{Ge}_2$  under the high hydrostatic pressure and to compare the results with the chemical pressure effects observed in  $\text{EuCu}_2(\text{Si}_x\text{Ge}_{1-x})_2$ .

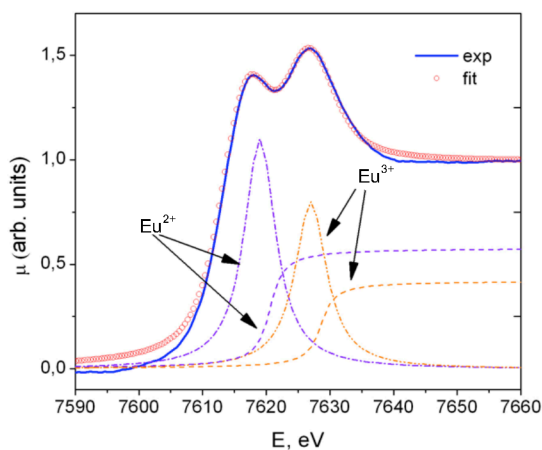
## 2. Experiment

The X-ray absorption experiment was carried out at the hard X-ray energy dispersive beamline ODE of synchrotron SOLEIL (France). The high pressure was generated by the diamond anvil cell (DAC) and controlled using the ruby luminescence. The XANES spectra were measured at  $\text{Eu-L}_2$  absorption edge in a wide pressure range 1-30 GPa.

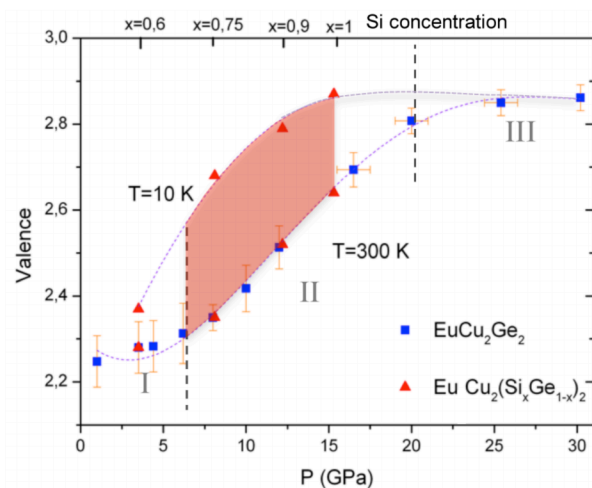
The separation of the spectral components arising from different europium valence states was done by fitting the experimental XANES, corrected for a polynomial background, with combination of Lorentzian (representing the absorption resonance) and arctangent (describing the transitions to the continuum) curves of constrained widths and energy positions (Fig. 1). In this approach the amount of Eu ions in each valence state is assumed to be proportional to the area under the corresponding Lorentzian curve or, equivalently, to its weight in the fitting formula. Europium valence state at ambient pressure in  $\text{EuCu}_2(\text{Si}_x\text{Ge}_{1-x})_2$  was explored in our earlier XANES experiment at the  $\text{Eu-L}_3$  absorption edge [7].

## 3. Results and Discussion

The resulting pressure dependence of europium valence is shown in Fig. 2. We can point out the three characteristic regions. In the first region from 1 to 6 GPa the valence changes very slightly with the pressure increase. Probably it is caused by the exchange-spin interaction in the presence of the long-range magnetic order. The transition between the first and the second regions (with the value of valence around 2.3) corresponds to the suppression of magnetic order in series  $\text{EuCu}_2(\text{Si}_x\text{Ge}_{1-x})_2$ . After this the strong magnetic interaction is replaced by the pure valence fluctuations and in the second region the europium valence begins to grow rapidly. However, the most interesting is the region above 20 GPa in which the valence begins to stabilize. The highest valence value ( $\sim 2.87$ ) obtained under the pressure of 30 GPa in compound  $\text{EuCu}_2\text{Ge}_2$  is very close to the europium valence in compound  $\text{EuCu}_2\text{Si}_2$  at low temperature (4 K) [3,6-7]. In such a way the following question arises: does the europium valence in these compounds reach the integer value +3 at all?



**Figure 1.**  $L_2$  absorption edge of Eu in  $\text{EuCu}_2\text{Ge}_2$  at room temperature and pressure 10 GPa. The fitting with  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  contributions is shown.

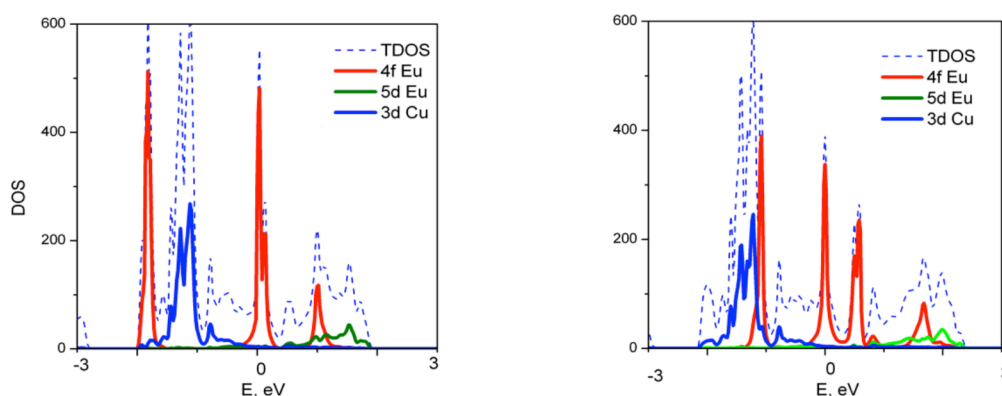


**Figure 2.** The diagram of Eu valence behaviour in the system  $\text{EuCu}_2(\text{Si}_x\text{Ge}_{1-x})_2$  vs. temperature, Si concentration and external pressure applied to the pure  $\text{EuCu}_2\text{Ge}_2$ , obtained in our X-ray absorption experiments.

Extrapolation of the saturation region shows that the valence may reach the integer value at pressure  $\sim 80$  GPa. It is also possible that above 30 GPa the  $\text{EuCu}_2\text{Ge}_2$  experiences a sharp transition to the stable phase with europium valence +3 as it was observed for cerium [8]. However, the situation when the valence transition stops at the intermediate phase is also known [9], and thus we do an attempt to propose the mechanism for the valence stabilization in  $\text{EuCu}_2\text{Ge}_2$  using the theoretical calculations of electronic structure.

### 3.1 DFT calculations

*Ab initio* electronic structure calculations were performed within the density-functional theory (DFT) using a full-potential linearized augmented plane-wave (FP-LAPW) approach using the EXCITING code [10]. The Perdew, Burke, Ernzerhof (PBE) gradient corrected local spin density approximation (LSDA-GGA) for the exchange correlation (XC) potential has been used. To account for the Coulomb correlation interaction within the Eu 4*f* shell, the PBE XC potential corrected according to GGA+U method was additionally considered. For europium the *U* and *J* parameters values of 2.7 and 1.1 eV have been taken, respectively. The pressure was modeled in the approximation of uniform compression by variation of the elementary cell volume, which was chosen because of the absence of exact information on the lattice deformation in  $\text{EuCu}_2\text{Ge}_2$  under high pressure.



**Figure 3.** Density of states for the different elementary cell volumes in  $\text{EuCu}_2\text{Ge}_2$  (from left to right: cell's scale =100%, 95 %)

Based on the results of DFT calculation we propose a qualitative model for the formation of europium intermediate valence state by the peculiar hybridization between Cu 3*d* and Eu 4*f* electronic levels. In the consequence of Coulomb interaction between localized electrons the localized 4*f* level of Eu splits into few components (Fig. 3) and one of them overlaps with Cu 3*d* subband under pressure. The saturation region with the maximum value of the europium valence at high pressure is probably due to the saturation of the 4*f*-3*d* overlap when the narrow 4*f* level reaches the middle of the wide 3*d* subband and the overlapping area becomes almost independent of levels position. According to this model, the value +3 of europium valence in compound  $\text{EuCu}_2\text{Ge}_2$  is unreachable.

### 3.2 “Chemical” vs. hydrostatic pressure

As Fig. 2 shows the “chemical” (top horizontal axis) and external (lower horizontal axis) pressures have a nonlinear relation and, consequently, a different effect on the europium valence. This fact has been also partially confirmed by the DFT calculations of  $\text{EuCu}_2\text{Ge}_2$  and  $\text{EuCu}_2\text{Si}_2$  compounds electronic structure.

At ambient pressure the Cu 3*d* DOS maximum in compound  $\text{EuCu}_2\text{Si}_2$  is situated higher in energy than in compound  $\text{EuCu}_2\text{Ge}_2$  and with increasing pressure it slightly moves down from the Fermi level. Thus  $\text{EuCu}_2\text{Ge}_2$  under pressure and  $\text{EuCu}_2\text{Si}_2$  have different energy position of Cu 3*d* levels. But in spite of that the saturation of europium valence under high pressure was obtained in compound  $\text{EuCu}_2\text{Si}_2$  as well in the previous inelastic neutron scattering experiment [11].

It was expected that the application of external pressure of the order of 2 GPa would lead to a noticeable valence change (quantitative evaluation of the relation between valence and pressure up to 5 GPa for  $\text{EuCu}_2\text{Si}_2$  was given in [1]), which is experimentally manifested in renormalization of the magnetic spectrum. However, external pressure did not produce a significant change in the structure of the magnetic response nor in its temperature dependence. This fact can be explained in the way of compensation of two main reasons for renormalization of the magnetic spectrum. On one hand, it is a high hybridization of  $f$ -electrons with the conduction band states, and on another, it is an opposite renormalization expected due to the shift of the average valence to +3. Therefore it is possible that the compound  $\text{EuCu}_2\text{Si}_2$  has only quantitative difference but similar (with  $\text{EuCu}_2\text{Ge}_2$ ) physical reasons for the stabilization of the europium valence under high pressure.

#### 4. Conclusion

The pressure dependence of europium valence in  $\text{EuCu}_2\text{Ge}_2$  has been obtained in a wide pressure range using the XANES spectroscopy. It was found that the mechanisms of the “chemical” and external pressure most likely affect the europium valence in a different way. However, the stabilization of europium valence near the similar value of 2.9 was obtained for both Si-substituted and pure compound. Based on the DFT calculations the qualitative model of hybridization between  $4f$  level and  $3d$  subband has been proposed, which explains the stabilization of valence at high pressure and predict that even at a higher compression it will stay below +3.

#### 5. Acknowledgements

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