Coexistence of long range magnetic order and intervalent state of Eu in EuCu₂(SiₓGe₁₋ₓ)₂: evidence from neutron diffraction and spectroscopic studies

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Experimental results of the X-ray absorption spectroscopy, Mößbauer spectroscopy (isomer shift) and neutron diffraction are presented for the series of EuCu₂(SiₓGe₁₋ₓ)₂ polycrystalline samples ($0 < x < 0.75$). Homogeneous intermediate valence state is established for Eu-ions as well as long range magnetically ordered state at the temperatures below 10–15 K. Observation of the ordered magnetic moments at Eu site gives rise to the experimental statement for the coexistence of valence fluctuations and long range magnetic order takes place in the wide range of Ge concentrations for this substance.

1. Introduction. The EuM₂X₂ ("122") compounds demonstrate a large variety of electronic and magnetic ground states and unusual physical phenomena, which are extensively studied over the last years. For instance, the reentrance of the superconductivity developing on the background of long-range magnetic order of Eu moments under external pressure occurs in EuFe₂As₂ [1]. Moreover, the transition to the intermediate valence state of Eu ions in this compound was observed in the same pressure range [2] by X-ray absorption spectroscopy above Eu L_3-edge. Another member of the "122" family, EuNi₂P₂ has been supposed to demonstrate formation of a hybridization gap [3].

The EuCu₂(SiₓGe₁₋ₓ)₂ family has been recently shown to be of particular interest [4, 5]. The rare-earth ion configuration changes from nearly integer valence $\sim 2^+$ ($4f^7$) in EuCu₂Ge₂ (magnetically ordered below

$T_N = 14\,\mathrm{K}$, with approximately full Eu²⁺ magnetic moment determined from susceptibility measurements), to a valence fluctuating (VF) state above $x \sim 0.6$. The d-metal ions in this series of substance supposed not to carry any magnetic moment at all. A striking feature of the Ge-rich region is the possible coexistence of the magnetically ordered phase with VF, which is quite unusual among f-electron compounds except few examples such as certain thulium chalcogenides [6].

In our recent work [7] the dynamical magnetic response of Eu f-electrons have been studied for EuCu₂(SiₓGe₁₋ₓ)₂ with $x \geq 0.6$ which shows that VF may exist in the concentration range of magnetically ordered state. In the present work we focused on the precise determination of the extent of valence instability of Eu in the whole range of x along with establishing of the long range magnetically ordered state by direct neutron diffraction experiment at low temperatures for $0 \geq x \geq 0.6$.

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2. Sample preparation. Samples have been prepared from high purity materials of Eu (99.99 %) and Si, Ge, Cu (better than 99.99 %) by arc melting followed by homogenization annealing at $800\,°C$ during ~ 500 h. The quality of the samples was checked carefully using X-ray diffraction, AC susceptibility, and DC magnetization measurements. X-ray diffraction analysis revealed no impurity phases within the limits of sensitivity. All compositions crystallize in the $ThCr_2Si_2$ structure (body centered tetragonal with 2 chemical formula unit per unit cell and parametric position (along c-axis) for Si/Ge, space group $I4/mmm$). The lattice constants and magnetic susceptibilities obtained were in quite good agreement with data published in [5].

3. Experimental techniques. Eu valence has been measured by X-ray Near Edge Structure (XANES) spectroscopy above Eu L_3-edge and Mößbauer spectroscopy, which provide the "fast" and "slow" fluctuating time limits of speed of interconfigurational fluctuations. The characteristic time of the Mößbauer spectroscopy is about 10^{-8} s that is much longer than corresponding value for XANES ($\sim 10^{-15}$ s).

XANES measurements in the temperature range 10–300 K have been carried out at the line A1 of the HASYLAB, DESY in transmission geometry. The Eu valence was further accessed using ^{151}Eu Mößbauer spectroscopy, in particular using the isomer shift, which gives insight in the electronic configuration of Eu. ^{151}Eu-Mößbauer spectra were recorded on a constant-acceleration spectrometer using a 30-mCi ^{151}SmF$_3$ source. The velocity calibration was performed with α-Fe at room temperature utilizing a ^{57}Co/Rh source. All Mößbauer spectra discussed herein were obtained using powder samples at room temperature and the extracted isomer shifts are reported with reference to EuF$_3$.

Three samples $EuCu_2(Si_xGe_{1-x})_2$ with $x = 0.0$, 0.4, 0.6, which corresponds to the part of magnetic phase diagram with supposed ordered ground state, have been studied by means magnetic neutron diffraction.

Taking into account large absorption cross section ($\sigma_{abs} = 4530$ barn) of natural Eu, neutrons with relatively short wavelength of 1.121 Å (Ge (111) monochromator) have been used in diffraction experiment on the 7C2 diffractometer with hot neutron source at the "Orphee" reactor at LLB (Saclay). This provides reasonable level of the transmission for thin samples. The scattering angle range where the intensive peaks are observed was $3.3° < 2\Theta < 40°$ that correponds to the momentum transfer range of $0.3 < Q < 3.8$ Å^{-1}. In this scattering angles range the transmission of the flat samples (thickness of the order of 0.16 mm of bulk material) varied from 0.75 to 0.72.

4. Experimental results. *4.1. X-ray absorption data.* XANES data for $0 < x < 1$ in the temperature range $5 < T < 300$ K show the intermediate-valence character of the f-electron state for Eu in $EuCu_2(Si_xGe_{1-x})_2$. Selected L_3-edge absorption spectra for the sample with maximum Ge-concentration ($x = 1$) are presented in Fig. 1. One can see clear

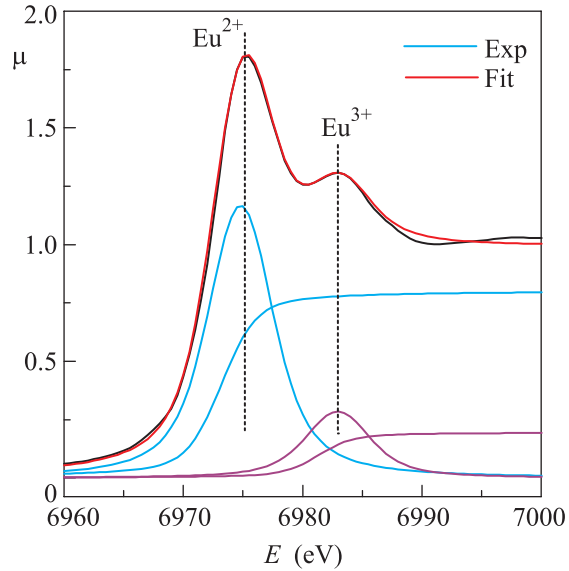Fig. 1. $EuCu_2Ge_2$ XANES spectrum at $T = 78$ K

contribution from Eu^{3+} configuration signal along with stronger one from Eu^{2+}.

Resulted Eu valence determined from the present and previous [7] XANES measurements are summarized in Table 1. These values are consistent With ones reported in earlier work by Fukuda et al. [8].

4.2. Isomer shift data. Isomer shifts have been measured for samples with $x = 0.0$, 0.4, 0.6, 0.75, 0.90 at 300 K. All Mößbauer spectra are characterized by a single spectral component. Isomer shift is in a good agreement wih literature data for $x = 0.0$ [9]. Basing on the XANES data for average valence at $x = 0.6$ and 0.9 [7] we have converted the isomer shift to the valence values for all compositions. The isomer shift data along with corresponding valence values are shown in Table 1. For concentrations $x = 0$ and 0.75 a good agreement with data obtained by Eu L_3-edge XANES.

Joint analysis of XANES and Mößbauer isomer shift spectroscopy shows that Eu valence in $EuCu_2(Si_xGe_{1-x})_2$ system is homogeneous and higher than 2+ in the whole range $0 \le x \le 0.9$.

4.3. Neutron diffraction. Neutron diffraction experiment has been carried out on the samples with $x = 0$,

Valence of Eu in EuCu₂(Si$_x$Ge$_{1-x}$)₂ determined by XANES and Mößbauer spectroscopy

Concentration x	Valence by XANES, $T = 10\,\text{K}$	Valence by XANES, $T = 300\,\text{K}$	Isomer shift, $T = 300\,\text{K}$ mm/s	Valence from scaling of isomer shift to XANES data
0	2.20(1)*⁾	2.19(1)	−9.8(1)	2.18(1)
0.4			−9.1(1)	2.24(1)
0.6	2.37(1)	2.28(1)	−8.6(1)	2.28(1)
0.75	2.68(1)	2.35(1)	−7.5(1)	2.37(1)
0.9	2.78(1)	2.52(1)	−5.6(1)	2.52(1)

*⁾Data obtained at $T = 78\,\text{K}$.

0.4, and 0.6 for a number of temperatures in the range 4–50 K. Typical time for one temperature was 6 h.

The neutron diffraction patterns for the sample with $x = 0.6$ measured at temperatures 5 and 25 K are shown in Fig. 2a.
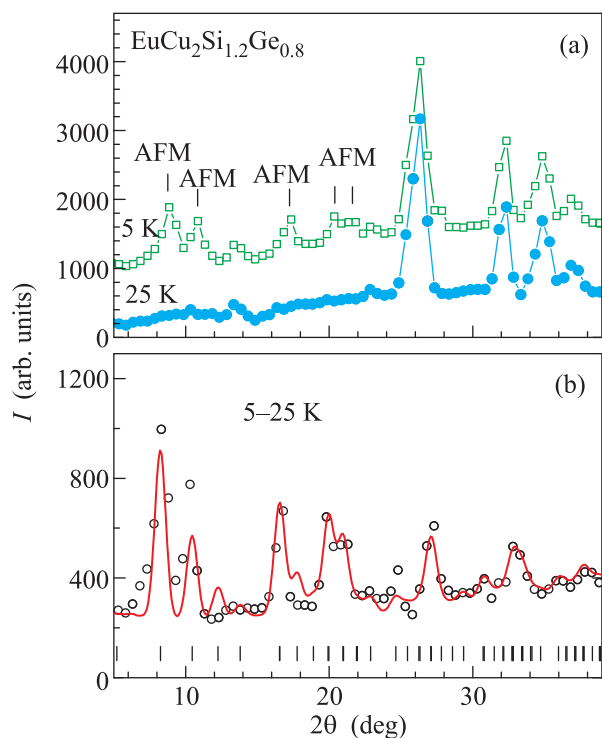

Fig. 2. (a) – Neutron diffraction patterns of EuCu₂(Si$_x$Ge$_{1-x}$)₂, $x = 0.6$, measured at $T = 5$ and 25 K. Incoming neutron wavelength $\lambda_i = 1.121\,\text{Å}$. (b) – The pure magnetic contribution at $T = 5\,\text{K}$ obtained by subtraction of the data measured at $T = 25\,\text{K}$ (circles) along with profile calculated by the Rietveld method (line). The ticks below represent calculated positions of the magnetic peaks

Appearance of additional magnetic peaks on cooling clearly demonstrates the onset of the long range an-

tiferromagnetic (AFM) order. The magnetic contribution to the diffraction patterns obtained as a difference between the patterns measured in paramagnetic (25 K) and magnetically ordered phases, is shown in Fig. 2b. For all samples, the magnetic signal looks similar. The main distinction is the variation of the relative intensity of the peaks located at $2\theta \approx 8.1°$ and $10.1°$ with the increase of the Si concentration x. This means that the symmetry of the magnetic structure is similar for all samples under study but the orientation of the magnetic moments with respect to the crystallographic axes changes with the x value.

We have performed the analysis of the magnetic contribution to the diffraction patterns by the Rietveld method. For all compositions ($x = 0, 0.4, 0.6$) we established the antiferromagnetic state with a propagation vector $\mathbf{k} = (1/3, 0, 0)$ and antiparallel orientation of Eu magnetic moments located at positions 2a – $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$ of the tetragonal crystal structure of the $I4/mmm$ symmetry.

For the EuCu₂Ge₂ and EuCu₂Si$_{0.8}$Ge$_{1.2}$ compounds it was found that the Eu magnetic moment is located in the (xy) planes. With an increase of the Si concentration to $x = 0.6$, its reorientation towards the z-axis occurs in EuCu₂Si$_{1.2}$Ge$_{0.8}$.

The obtained values of the Eu magnetic moment components are listed in Table 2 along with the corresponding values of R-factors. In the refinement procedure, we found that the calculated intensity of the magnetic peak $(1, 0, 0)$ located at $9.9°$ is somewhat lower with respect to experimental one for the EuCu₂Si$_{0.8}$Ge$_{1.2}$ sample for the best fit obtained (Table 2). As the intensity of this peak strongly depends of the orientation of the Eu magnetic moment, this may indicate a presence of microscopic regions with somewhat different orientations of the magnetic moments in EuCu₂Si$_{0.8}$Ge$_{1.2}$ sample, driven by local fluctuations of the Si concentration within the sample volume.

Eu-ion static magnetic moment obtained from the diffraction data refinement by the Rietveld method at the temperature $T = 5\,\mathrm{K}$

$X(\mathrm{EuCu_2(Si_xGe_{1-x})_2})$	M_x, μ_{B}	M_y, μ_{B}	M_z, μ_{B}	$M_{\mathrm{tot}}, \mu_{\mathrm{B}}$	R-factors
0.0: $\mathrm{EuCu_2Ge_2}$	3.1	6.0		6.7(1)	$R_p = 0.07$
					$R_{wp} = 0.09$
0.4: $\mathrm{EuGu_2Si_{0.8}Ge_{1.2}}$	3.3	4.1		5.3(1)	$R_p = 0.09$
					$R_{wp} = 0.12$
0.6: $\mathrm{EuCu_2Si_{1.2}Ge_{0.8}}$	2.6		4.6	5.3(1)	$R_p = 0.05$
					$R_{wp} = 0.07$

One can see from Table 2 that the total magnetic moment does not reach the full value of $\mathrm{Eu^{2+}}$ $(7.94\mu_{\mathrm{B}})$ even for the sample without Si $(x = 0)$.

The obtained magnetic moments in ordered state demonstrate a temperature dependence specific for order parameter. Temperature dependence of the Eu ordered magnetic moment for the $\mathrm{EuCu_2Si_{1.2}Ge_{0.8}}$, most close to the instability concentration region of the magnetic phase diagram [5], is shown in the inset to Fig. 3.
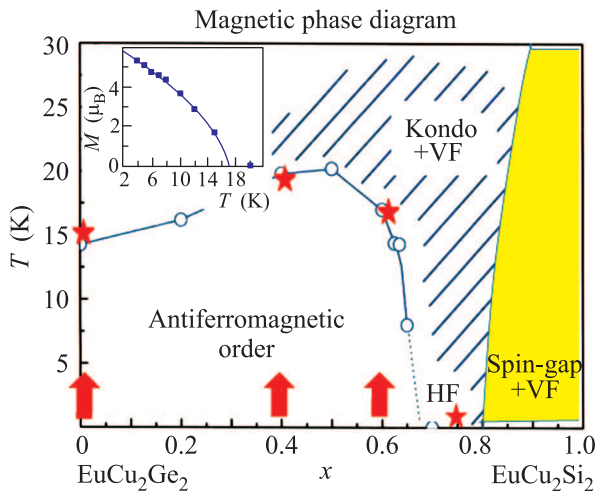

Fig. 3. Magnetic phase diagram for $\mathrm{EuCu_2(Si_xGe_{1-x})_2}$ based on the suggestion of [5]. Arrows and stars indicate compositions of our samples and corresponding T_{N} values determined in present work. Inset: temperature dependence of the Eu ordered magnetic moment for $\mathrm{EuCu_2Si_{1.2}Ge_{0.8}}$ sample and the corresponding fit by the function $M = M_0(1 - T/T_{\mathrm{N}})^a$ (see text)

It was fitted by the function $M = M_0(1 - T/T_N)^a$ with $M_0 = 6.25(5)\mu_{\mathrm{B}}$, $a = 0.60(3)$, and $T_N = 17(1)\,\mathrm{K}$.

Due to not high enough number of temperature points in magnetically ordered state for other samples only estimations of the magnetic ordering temperatures from neutron diffraction data were obtained, $T_N(x = 0) \approx 15\,\mathrm{K}$ and $T_N(x = 0.4) \approx 19\,\mathrm{K}$. Estima-

tions of the M_0 are quite speculative and does not exceed the level of $7\mu_{\mathrm{B}}$.

5. Discussion and conclusion. The results of XANES and Mößbauer isomer shift spectroscopies in $\mathrm{EuCu_2(Si_xGe_{1-x})_2}$ show that in the wide range of Ge for Si substitution the intervalent state of Eu does exist. The valence determined by both methods exceeds the 2+ by 10–20 % that is far above the estimated uncertainty of the methods used. This is in contradiction with measurements [5] of susceptibility, which provide values of the effective magnetic moment well above $7\mu_{\mathrm{B}}$. Nevertheless, measured valence is consistent with data from diffraction presented in Table 2 which show the deficit of the ordered magnetic moment of 25–30 % at 5 K. It is necessary to note that determined here valence of Eu in $\mathrm{EuCu_2Ge_2}$ is not the extreme experimental value. In the same family $\mathrm{RM_2X_2}$ the pure 2+ state defined by L_3-edge spectroscopy is realized for the Eu ion for instance in $\mathrm{Eu(FeCo)_2As_2}$ [2]. Therefore with respect to the $\mathrm{EuCu_2(Si_xGe_{1-x})_2}$ discussed here, we make conclusion that long range magnetic order exists in the material which provide clear evidence of intervalent behaviour.

Neel temperatures obtained from diffraction (denoted by stars in Fig. 3) are in exellent correspondence with the macroscopic data [5] used to draw a magnetic phase diagram of the Fig. 3. The star for $x = 0.75$ is obtained from analysis of our measurements at IN4 spectrometer [10] which have shown the absence of any evidence of long range magnetic order down to the 2.5 K contrary to the sample with $x = 0.6$ studied in the present work. The colorized area in Fig. 3 started from Si concentration above $x \sim 0.8$ corresponds to the developing of the "spin-gap" in the excitation spectra at low temperature connected to the formation of a singlet ground state for Eu-ion. This spin-gap-type of the ground state has been established in neutron spectroscopy study of the series of $\mathrm{EuCu_2(Si_xGe_{1-x})_2}$ by time-of-flight technique recently presented in [7].

The coexistence of magnetic ordering and intermediate valence state appears to be a challenging matter, as well as cases of coexistence of superconductivity with magnetic order, or coexistence of valence fluctuations and superconductivity. Nevertheless, developing of AFM long range ordering on the backgroung of valence fluctuations (characterized by quite narrow width of quasielastic signal at low temperature correspondig to ~ 0.1 THz frequency) has been fixed in 70th for binary system TmSe [11, 12] and has been treated theoretically [13] as some kind of "phase memory" for spins of a ground (degenerated) state of electronic shell.

Another approach to the problem has been presented in publication [14]. Authors suggest hypotetical phase diagram which relates the T_N with the strength of the hybridization and calculated that it can have the dependence with maximum near the instability region very similar to experimental one suggested in [5] (naturally to suppose that increase of Si-concentration results in increase of hybridization) and confirmed by present direct measurements of long range order.

Concerning the magnetic structure determined in our study it looks like not too much complicated being commensurate with atomic structure. In several available studies of magnetic structure of RM_2X_2 systems different type of commensurate and incommensurate structures for Eu moments have been published [15–18] which show not much difference from our refinement.

In summary, the main result of present work is the clear indication of the coexistence of the intermediate valent state of Eu ions in $EuCu_2(Si_xGe_{1-x})_2$ measured by X-ray absorbtion spectroscopy and Mößbauer isomer shift with long range antiferromagnetic order defined below T_N by the neutron diffraction method. Physical microscopic background for coexistence of valence fluctuations with AFM ordering could be examined by detailed spectroscopic study of the parameters of spin fluctuation state.

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