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Interplay between valence fluctuations and lattice instabilities across the quantum phase transition in $\mathbf{EuCu_2(Ge_{1-x}Si_x)_2}$

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Increasing Si concentrations in the $EuCu_2(Ge_{1-x}Si_x)_2$ series tunes the divalent Eu antiferromagnetic (AF) compound $EuCu_2Ge_2$ ($T_N = 14\,K$) to a nonmagnetic intermediate valence (IV) system $EuCu_2Si_2$. There is a collapse of the magnetic state and heavy quasiparticles occur at $x \sim 0.7$ corresponding to a quantum critical point (QCP). We have systematically investigated the Eu-valence and magnetic states as well as the coupling to the lattice through the QCP in $EuCu_2(Ge_{1-x}Si_x)_2$. This involved the ^{151}Eu Mössbauer effect spectroscopy and angle-resolved x-ray diffraction measurements as a function of Si concentration ($0 \leqslant x \leqslant 1$) at variable temperatures in the range 300–4.2 K. The ^{151}Eu probe indicates that the divalent Eu AF state is stable up to $x \sim 0.5$, followed by a collapse of AF ordering for $x > 0.6$, which is associated with a simultaneous sharp change of the valence state towards a nonmagnetic IV state. The crossover from the AF ordered state to the nonmagnetic IV state is found at a QCP corresponding to $x \sim 0.7$, at which the nonmagnetic IV state is inhomogeneous and exhibits an enhanced $Eu^{\nu+}$ mean valence ($\nu \sim 2.5$). We believe that the emergence of such an unusual valence state is related to the observed heavy quasiparticles at low temperatures near the QCP. Magnetic order and a nonmagnetic inhomogeneous IV state coexist in a narrow region $0.6 \leqslant x < 0.7$, which evolves to a homogeneous IV state above $x \sim 0.8$. The $ThCrSi_2$-type tetragonal structure is maintained throughout the series, although there is a precipitous increase in the c/a ratio at 10 K when the valence fluctuations become enhanced at the critical concentration $x = 0.7$. X-ray diffraction temperature scans at the critical concentration indicate conspicuous changes to steep temperature dependences of decreasing (increasing) values of a (c) lattice parameters and decreasing unit-cell volume at $T < 100\,K$, as the IV ground state become preferentially populated at low temperatures. Thus there is a clear manifestation of strong coupling between the lattice and the valence fluctuation process. A corresponding detailed phase diagram is constructed and compared with that obtained from recent external pressure studies on the system.

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I. INTRODUCTION

In recent years there has been continuous interest in investigating the ground-state properties of $4f$ intermetallic systems (mostly Ce- and Yb-based compounds) in which the spin or charge or both degrees of freedom are coupled to the lattice. Such systems possess unusual properties at low temperatures that may be tuned by an external control parameter (pressure, composition or magnetic field) in the vicinity of their magnetic quantum critical point (QCP). Some examples include cases of, heavy fermion superconductivity in $CeCu_2Si_2$ [1] and valence fluctuations at the QCP in $CeRu_{2-x}Co_xGe_2$ [2], as well as in $YbRh_2Si_2$ and $CeRh_2Si_2$ [3].

The $EuCu_2(Ge_{1-x}Si_x)_2$ series represents one of the few examples, other than that of Ce- and Yb-based rare-earth intermetallics, where such exotic electronic ground-state properties are in evidence. Si doping of the divalent Eu antiferromagnetic (AF) compound $EuCu_2Ge_2$ ($T_N = 14\,K$ [4–6]) tunes it to become a nonmagnetic intermediate valence (IV) system $EuCu_2Si_2$ [7] in the $EuCu_2(Ge_{1-x}Si_x)_2$ series. There have been extensive investigations of magnetic and transport properties of the various compositions [8–12]. Structural studies at room temperature show that the tetragonal $ThCr_2Si_2$-type lattice is maintained throughout the series [8,12]. Electrical and thermal transport indicate Kondo behavior occurs in the concentration range $0.5 \leqslant x \leqslant 0.7$. The magnetic phase diagram of $EuCu_2(Ge_{1-x}Si_x)_2$ reveals that the AF phase is stable up to $x = 0.6$ and disappears abruptly for $x > 0.65$, suggesting a magnetic QCP occurs close to $x \sim 0.65$. Near the QCP in the vicinity of $x = 0.7$, heavy quasiparticles have been found at low temperatures [8], the origin of which is not well understood. Thus, substitution of

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Ge by Si in the $EuCu_2(Ge_{1-x}Si_x)_2$ series offers the possibility of studying the crossover from the divalent AF state to a nonmagnetic IV state through a QCP and thus represents a model system for such a study in terms of the Doniach phase diagram [13].

Both earlier Eu L_{III} x-ray absorption spectroscopy (XAS) measurements of Fukuda *et al.* [9], as well as later x-ray absorption near edge spectroscopy (XANES) measurements combined with magnetic studies, on $EuCu_2(Ge_{1-x}Si_x)_2$ suggest that intermediate valence occurs throughout the series including AF $EuCu_2Ge_2$ [11,14]. The coexistence of long-range magnetic order and valence fluctuations has been also suggested to occur at Si concentrations $x \leqslant 0.65$ [11,14]. This seemingly would add to the rich physics of the phase diagram, where Kondo effect and heavy fermion behavior are also discerned. On the other hand, the most recent angle-integrated photoemission spectroscopy (AIPES) studies at 20 K of high-quality samples of $EuCu_2Ge_2$ clearly indicate that this end member is in a stable Eu^{2+} state [15]. This finding is consistent with previous reports [4–6], and with recent high pressure studies on $EuCu_2Ge_2$ [12,16].

An alternative to deploying these electron spectroscopy probes of valence ν in $EuCu_2(Ge_{1-x}Si_x)_2$ is ^{151}Eu Mössbauer effect (ME) spectroscopy. Here the hyperfine interactions between the ^{151}Eu nucleus with the surrounding electronic environment, provides pertinent information on the Eu electronic configuration and magnetic state concurrently. The hyperfine interactions result in conspicuously different signatures for divalent Eu^{2+} $(4f^7 : J = 7/2,\ L = 0)$ with a moment of 7 μ_B and nonmagnetic trivalent Eu^{3+} $(4f^6 : J = 0,\ S = L = 3)$ in a ^{151}Eu ME spectrum. This provides direct information on a microscopic level about Si-concentration induced changes of both Eu mean valence via the ^{151}Eu ME isomer shift S and the magnetic state of the Eu ions via the effective magnetic hyperfine field B_{eff} at the Eu nucleus. In particular, the isomer shift is very sensitive to the valence state of Eu. The $Eu^{3+} - 4f^6$ configuration has a higher s-electron density at the Eu nucleus than $Eu^{3+} - 4f^7$. This results in a difference of isomer shift values between Eu^{2+} (S_2) and $Eu^{3+}(S_3)$ of $\Delta S = |S_3 - S_2|$ in the range 10–13 mm/s, considerably larger than the resolution-limiting experimental resonance linewidth (~2.5 mm/s) [7]. Furthermore, the time scale of ^{151}Eu ME spectroscopy is $\sim 10^{-8}$ s, much longer than typical $\sim 10^{-13}$ s valence fluctuation times that may occur between two electronic configurations of Eu in metallic systems [17]. Thus, in such cases ^{151}Eu ME spectroscopy noticeably determines a mean valence ν of Eu with $2 < \nu < 3$, through isomer shifts that are intermediate to typical values for S_2 (−14 to −10 mm/s) and S_3 (0 to +4 mm/s). Moreover such IV cases show strongly temperature dependent S values, unlike when integral Eu^{2+} and Eu^{3+} valences are involved [5,7].

The benefits of using ^{151}Eu ME spectroscopy are thus starkly apparent, in that the Eu electronic configuration is probed via the nucleus, yielding three distinct valence signatures for the Eu^{2+}, Eu^{3+}, and IV cases. This is without having to perturb the electronic structure in the probing process as is the case with x-ray photoemission spectroscopy or AIPES, which is surface sensitive [8,15], and in XAS or XANES [9,14] where final-state effects may be a concern [18], in certain cases contributing extrinsic effects in the determination of ν. Moreover these electron spectroscopies are fast techniques with probing times of $\sim 10^{-15}$ s so that instantaneous Eu^{2+} and Eu^{3+} valences signatures are always discerned, whether for a fluctuating valence (homogeneous IV) situation $Eu^{2+} \Leftrightarrow Eu^{3+}$ or a inhomogeneous mixed-valence situation involving some static relative abundance of Eu^{2+} and Eu^{3+} sites in the sample [19]. Indeed both pressure and temperature dependent studies involving the ^{151}Eu ME probe then give a compelling indication of a stable divalent state for $EuCu_2Ge_2$ [5,16], in accord with the recent AIPES investigation of Kawasaki *et al.* [15].

In this work we present a systematic ^{151}Eu ME study of $EuCu_2(Ge_{1-x}Si_x)_2$ as a function of Si concentration $(0 \leqslant x \leqslant 1)$ over a wide temperature range (300–4.2 K). Particular experimental attention is focused in the vicinity of the QCP at $x \sim 0.7$, to concurrently monitor both valence and magnetic behavior across the magnetic quantum phase transition (QPT). Intermediate valence from charge fluctuations of the type $Eu^{2+} \Leftrightarrow Eu^{3+} + [5d, 6s]^1$ involve different Eu atomic volumes, hence such valence instabilities are expected to couple to the lattice. Therefore, we have also conducted complementary investigations involving the temperature dependence $(10\ \text{K} \leqslant T \leqslant 300\ \text{K})$ of the lattice parameters for the different Si concentrations through the QCP.

The analysis of our experimental data for the concentration dependence reveals that the collapse of AF ordering for $x > 0.6$ is associated with a simultaneous sharp increase of the Eu mean valence state towards a nonmagnetic IV state. The crossover from the magnetically ordered state to a nonmagnetic IV state is found at a QCP corresponding to a critical concentration $x_c \approx 0.7$, at which the Eu mean valence is enhanced $(\nu \sim 2.5)$. We suppose that enhanced charge fluctuations at the QCP are related to the observed heavy quasiparticles discerned near $x = 0.7$ at low temperatures [8,12]. We further find that magnetic order and nonmagnetic inhomogeneous valency coexist in a narrow region $0.6 \leqslant x < 0.7$. The temperature dependence of the isomer shift together with that of the lattice parameters reveals the nature of valence fluctuations near the QCP and what coupling there is of these to the lattice. At $x_c \approx 0.7$ two energetically close lying metastable and ground-state nonmagnetic IV configurations are discerned, whose relative abundances are driven by thermal changes of the lattice parameters a and c. We suggest a phase diagram for the effect of Si doping in $EuCu_2(Ge_{1-x}Si_x)_2$ and compare it with that constructed from our previous external pressure studies. Both cases show a first-order magnetic transition related to the QCP at $x_c \approx 0.7$ and $P_c \sim 3.6$ GPa in the Si doping and external pressure studies, respectively. This is considered indicative of the strong coupling between spin and charge degrees of freedom originating from the highly localized AF magnetically ordered Eu^{2+} configuration in $EuCu_2(Ge_{1-x}Si_x)_2$.

II. EXPERIMENTAL

Polycrystalline samples of $EuCu_2(Ge_{1-x}Si_x)_2$ for $0 \leqslant x \leqslant 1$ were from the same ingots of the samples reported in Ref. [8]. These were prepared by arc melting the constituent elements followed by annealing for one week at 800–900°C. Powder x-ray diffraction measurements confirmed single phase purity for the samples, which all crystallized in the $ThCr_2Si_2$-type structure (space group $I4/mmm$) [12]. Structural properties of the system have been determined by temperature dependent angle resolved x-ray diffraction measurements. These measurements were performed by using a Huber G670 Guinier imaging plate diffractometer (Cu–$K_{\alpha 1}$ radiation, Ge–111 monochromator, and SiO_2 as external standard), equipped with a closed-cycle He cryostat [20]. Rietveld refinements were performed with the general structure analysis system package [21,22]. Different reflection profiles from the imaging plate detector, while taking into account the Guinier diffraction geometry, were fitted using pseudo-Voigt functions with asymmetry corrections [23].

^{151}Eu ME measurements at ambient pressure in the temperature range 300–1.75 K were carried out on these samples using a 100 mCi ^{151}Sm F_3 source. Both source and absorber were kept at the same temperature in a top-loading cryostat. Mössbauer spectra were analyzed with the NORMOS software package [24], to derive pertinent hyperfine interaction parameters, isomer shift S, magnetic hyperfine field B_{eff}, and absorption areas (abundances) of spectral components. All isomer shift values are quoted relative to the SmF_3 source from here onwards.

III. RESULTS

In the following we present the results of the structural, electronic, and magnetic investigations of the $EuCu_2(Ge_{1-x}Si_x)_2$ series using x-ray diffraction (XRD) and ^{151}Eu ME probes both at variable cryogenic temperatures.

A. Concentration dependence of lattice parameters at 10 and 300 K

The lattice response to possible valence changes from the magnetic Eu^{2+} state to nonmagnetic Eu^{3+} or IV states in the $EuCu_2(Ge_{1-x}Si_x)_2$ series, is first investigated through monitoring changes of the lattice parameters a and c and unit-cell volume V as a function of Si concentration. Previous investigations have only been performed at room temperature [8,9,12], which do discern some deviations from Vegard's law at $x > 0.6$. Such a coupling of lattice and charge degrees of freedom would best show up at low temperatures [25], where a ground-state IV configuration would be preferentially populated at $x \geqslant 0.65$ suggested by the phase diagram from physical properties measurements [8,12]. The relative changes of the lattice parameters a and c of $EuCu_2(Ge_{1-x}Si_x)_2$ at 10 and 300 K as a function of the Si concentration are displayed in Fig. 1. It shows a decrease of a, c, and V with increasing x. A linear decrease of the structural parameters would be expected due to the smaller radius of Si compared with Ge. However, as is evident from Fig. 1(a), there are anomalous changes of both lattice parameters at $x \geqslant 0.6$ at both temperatures. These anomalies are more pronounced at low temperatures, particularly the abrupt decrease of a for $x > 0.6$, which gives a first indication of a valence change of Eu^{2+} towards an IV state [25].

Despite the observation of such large anomalies at $x > 0.6$, no change of the tetragonal $I4/mmm$ lattice symmetry could be detected throughout the $EuCu_2(Ge_{1-x}Si_x)_2$ series to within the experimental accuracy. The anomalies of a and c at $x \geqslant 0.6$ at low temperatures and 300 K are best seen if one plots the c/a ratio as a function of Si concentration, as shown in Fig. 2. While c/a shows a definitive increase above $x \sim 0.6$ at 300 K, it shows a more abrupt and bigger increase at low temperatures. The clear anomalous increase of c/a at low temperatures is related to the observed abrupt decrease of a above $x \sim 0.6$ [see Fig. 1(a)]. This implies a sudden decrease of the distance between the Eu–Eu atoms, which primarily determine the interatomic distances in the a direction [26], see Fig. 1(c). These observations provide compelling evidence for a change of the valence state of Eu above $x \sim 0.6$, conceivably from the stable Eu^{2+} state towards an intermediate valence state in charge fluctuation processes $Eu^{2+} \Leftrightarrow Eu^{3+} + [5d, 6s]^1$ involving different Eu atomic volumes. Si doping leads to a unit-cell volume shrinkage (similar to the effects of pressurization) where the smaller Eu^{3+} radius is energetically favored. At a critical unit-cell volume reduction $\Delta V/V_0 \sim 0.08$ the larger Eu^{2+} radius is no longer energetically favored and $Eu^{2+} \Leftrightarrow Eu^{3+}$ valence fluctuations are triggered.

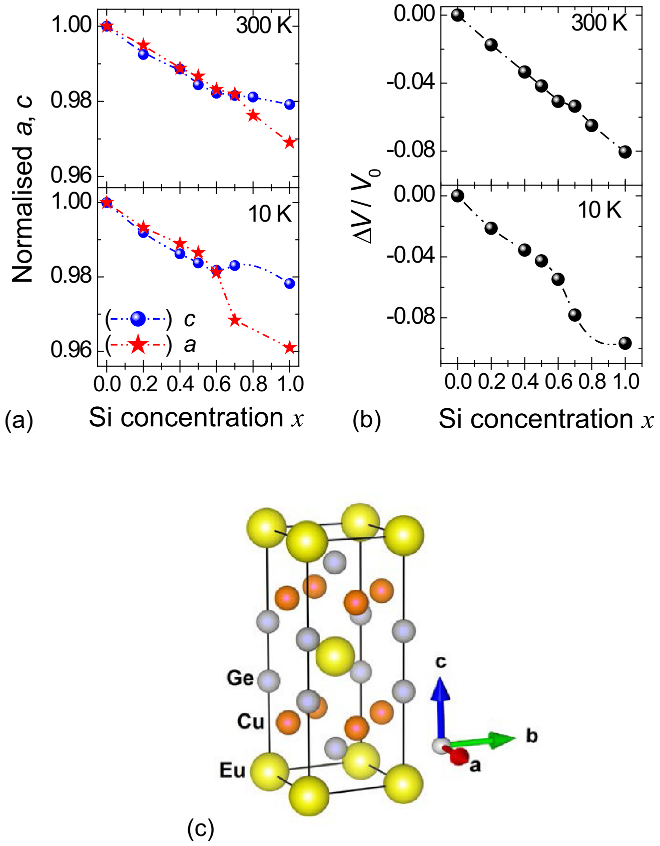

FIG. 1. Unit-cell evolution as a function of Si concentration in $EuCu_2(Ge_{1-x}Si_x)_2$ at 10 and 300 K. (a) Changes to lattice parameters a and c, normalized to the $x = 0$ case. (b) Relative change of volume $\Delta V/V_0$. Dashed lines through the data points are to guide the eye. (c) Body-centered-tetragonal unit-cell of $EuCu_2Ge_2$, $ThCr_2Si_2$-structure (SG: $I4/mmm$) [12].

B. ^{151}Eu Mössbauer effect measurements

1. Concentration dependence of the isomer shift S at 300 K

As indicated in the introduction, ^{151}Eu ME spectroscopy is an ideal tool to determine the valence state of the Eu ion in a

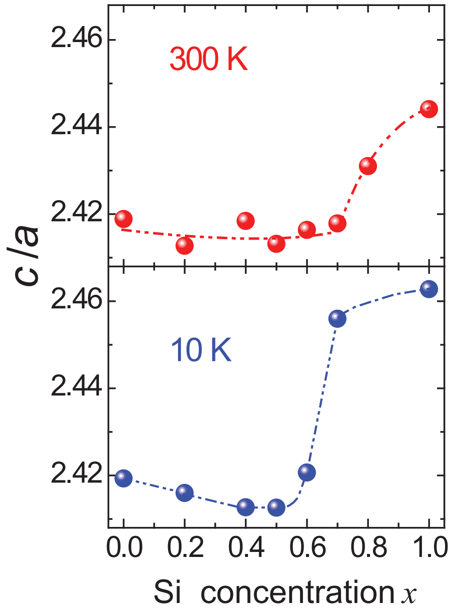

FIG. 2. The c/a ratio as a function of Si concentration at 10 and 300 K. Dashed lines through the data points are to guide the eye.

compound via the isomer shift, as there are signature values for divalent, trivalent and IV Eu states [7,27].

As shown in Fig. 3, each spectrum measured at 300 K shows a single absorption line whose S value shifts monotonically to less negative values with increasing Si concentration. For $0 \leqslant x \leqslant 0.5$, the S data shows a weak linear change. Considering the observed volume decrease between $0 \leqslant x \leqslant 0.5$ [see Fig. 1(b)], we obtain a value of $\partial S/\partial(\ln V) \sim -27$ mm/s. This value is similar to that obtained for stable divalent Eu(Pd$_{1-x}$Au$_x$)Si$_2$ for $x > 0.4$, where $\partial S/\partial(\ln V) \sim -30$ mm/s [25]. With further increasing $x \geqslant 0.6$, there is a strong nonlinear change of S tending towards the value of the intermediate valence state of EuCu$_2$Si$_2$ [7]. In fact, a linear change of S would be expected as the volume of the unit cell decreases due to Si substitution (Vegard's law). Thus, the anomalous change of S above $x = 0.5$ can be linked to the onset of a valence instability and transition to an intermediate valence state at higher Si concentrations [8]. This will be clarified when presenting the change of the isomer shift at 4.2 K as a function of Si concentration, in the discussion Sec. IV B.

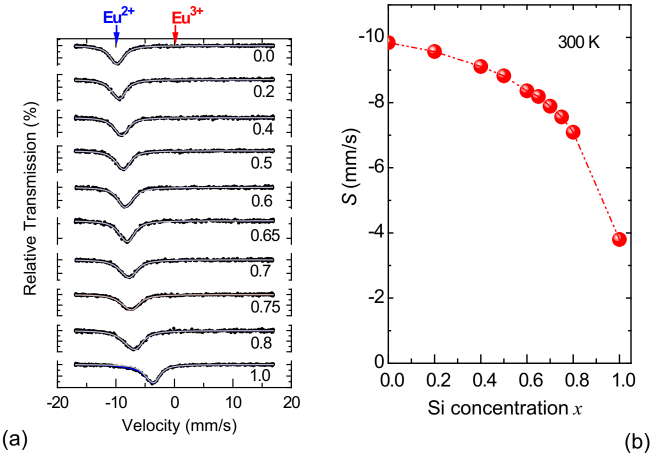

FIG. 3. (a) ^{151}Eu Mössbauer spectra at 300 K for the different Si concentrations x in the series EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$. (b) Isomer shift (S) as a function of Si concentration at 300 K. Dashed line through the data points are to guide the eye.

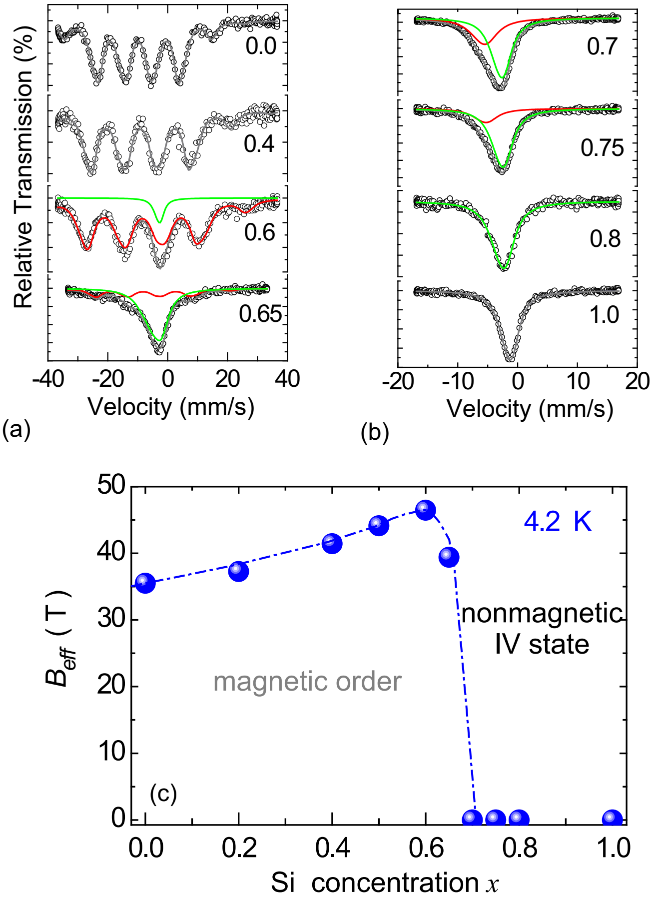

FIG. 4. (a) and (b) ^{151}Eu Mössbauer spectra of the different EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ concentrations at 4.2 K (c) Effective magnetic hyperfine field (B_{eff}) derived from the magnetically split components in (a). Dashed line through the data points are to guide the eye.

2. *Concentration dependence of the effective magnetic hyperfine field B_{eff} at 4.2 K*

A magnetic hyperfine field B_{eff} at the ^{151}Eu site in Eu compounds is only expected for Eu^{2+} ($4f^7$, $^8S_{7/2}$) in the magnetically ordered state, whereas no magnetic hyperfine field will be detected for nonmagnetic Eu^{3+} ($4f^6$, $^7F_0$).

The Mössbauer spectra at 4.2 K of EuCu$_2$(Ge$_{1-x}$Si$_x$) for all Si concentrations and the resulting change of B_{eff} with x are shown in Fig. 4. Up to $x = 0.5$ the spectra display a pure magnetic hyperfine splitting due to the magnetic ordering of the Eu^{2+} ions at low temperatures below T_N. The values of B_{eff} are typical for stable divalent Eu compounds that order magnetically [28,29]. Figure 4(c) indicates that B_{eff} at 4.2 K increases approximately linearly up to $x = 0.6$ and $\partial|B_{\mathrm{eff}}|/\partial(\ln V) \sim 229$ T. It then decreases abruptly for $x = 0.65$ and vanishes at $x = 0.7$. This indicates a magnetic quantum phase transition occurs near a critical concentration $x_c = 0.7$.

However, for $x = 0.6$ and 0.65 in Fig. 4(a), there is coexistence of a magnetically split component and an additional nonmagnetic component whose S value corresponds to an IV state ($S = -4.09 \pm 0.06\,\text{mm/sec}$ for $x = 0.6$ and $S = -2.86 \pm 0.12\,\text{mm/sec}$ for $x = 0.65$). As is shown in Fig. 13, of the Appendix, the intensity (area) of this nonmagnetic component increases appreciably from $x = 0.6$ to $x = 0.65$, while that of the magnetically split component decreases.

In the concentration range $0.7 \leqslant x \leqslant 0.75$ the system becomes completely nonmagnetic and the spectra can be fitted assuming two single lines with different values of the isomer shift and intensities. At 4.2 K the two components exhibit values of $S_I = -5.61 \pm 0.12\,\text{mm/sec}$ and $S_{II} = -2.78 \pm 0.03\,\text{mm/sec}$ for $x = 0.7$, which correspond to metastable and ground-state IV configurations of Eu, respectively. For $x = 0.75$, $S_I = -5.40 \pm 0.03\,\text{mm/sec}$ and $S_{II} = -2.60 \pm 0.02\,\text{mm/sec}$. At $x = 0.8$ and $x = 1$ only a single narrow line occurs at S_{II} values, corresponding to a homogenous IV ground-state.

Therefore the evolution of magnetic and nonmagnetic spectral components in the concentration range $x = 0.6$ to 0.8, Figs. 4(a) and 4(b), indicate a first-order magnetic to nonmagnetic transition occurs at a critical concentration $x_c \sim 0.7$. The transition from the inhomogeneous to homogeneous IV state with increasing Si concentration is best seen in Fig. 13 of the Appendix, where the change of the relative areas at 4.2 K of the different components have been plotted as a function of Si concentration. This figure demonstrates the existence of an inhomogeneous IV state for $0.6 \leqslant x \leqslant 0.75$, encompassing the critical concentration $x_c \sim 0.7$. The temperature dependence of the nonmagnetic IV states at $x_c = 0.7$ in the range $1.75\ \text{K} \leqslant T \leqslant 300\ \text{K}$ will be discussed in Sec. IV B. The inhomogeneous IV state evolves to a homogeneous IV state at $x = 0.8$ with an S value similar to that in the IV state of $EuCu_2Si_2$ [7].

IV. DISCUSSION

A. Eu mean valence in $EuCu_2(Ge_{1-x}Si_x)_2$

We analyze the Eu mean valence in the framework of the interconfigurational fluctuation model [30,31], to gain deeper insight into the change of valence of Eu in $EuCu_2(Ge_{1-x}Si_x)_2$ across the QPT at $x_c \sim 0.7$. The Eu mean valence can be determined from measured values of the isomer shift according to [7,32]:

$$S(T, V) = S_2(T, V) + (S_3 - S_2)\Delta\nu(T, V), \qquad (1)$$

where S_2 and S_3 are isomer shifts assigned to integral valences Eu^{2+} and Eu^{3+}, respectively. The quantity $\Delta\nu(T, V)$ is the occupation probability of the Eu^{3+} state. A mean valence $\nu = 2 + \Delta\nu(T, V)$ is associated with the measured values of $S(T,V)$ at different Si concentrations (volumes) and temperatures with a suitable choice of values for S_2 and S_3. We have chosen $S_2 = -9.82\,\text{mm/s}$, the isomer shift of the stable Eu^{2+} in $EuCu_2Ge_2$ ($x = 0$) and $S_3 = +0.44\,\text{mm/s}$ is the value of the stable Eu^{3+} state of $EuFe_2Si_2$ which also has the tetragonal $ThCr_2Si_2$-type structure [17]. For the integral valences this leads to a difference $S_3 - S_2 = 10.26\,\text{mm/s}$. These S_2 and S_3 values are very similar to that used in the other ^{51}Eu ME study at room temperature of the $x = 0$, 0.4, 0.6, 0.75, and 0.9 compositions of the $EuCu_2(Ge_{1-x}Si_x)_2$ series [14], except there the valences ν were normalized to that obtained from the XANES experiments for $x = 0.6$ and 0.9 at room temperature.

To obtain the actual Eu valence change as a function of Si concentration, it is first necessary to establish the change of $S_2(T, V)$ caused by the change of lattice volume due to the substitution of smaller Si atoms for Ge. This is obtained from the measured value of $\partial(S_2)/\partial(\ln V) \sim -27\,\text{mm/s}$ from the slope in Fig. 5(a) up to $x = 0.5$, which gives a change of $\Delta S_2 = -1.13\,\text{mm/s}$ for $|\Delta V/V| = 0.042$ using the volume changes in Fig. 1(b). For the Mössbauer spectra at 4.2 K for $0.6 \leqslant x \leqslant 0.75$, the S value is calculated from the weighted average values of the two spectral components [see Figs. 4(a) and 4(b)]. Our intention in taking the weighted average S value is to emphasize the evolution from a temperature independent isomer shift at $x \leqslant 0.5$ to a temperature dependent situation at $x > 0.5$.

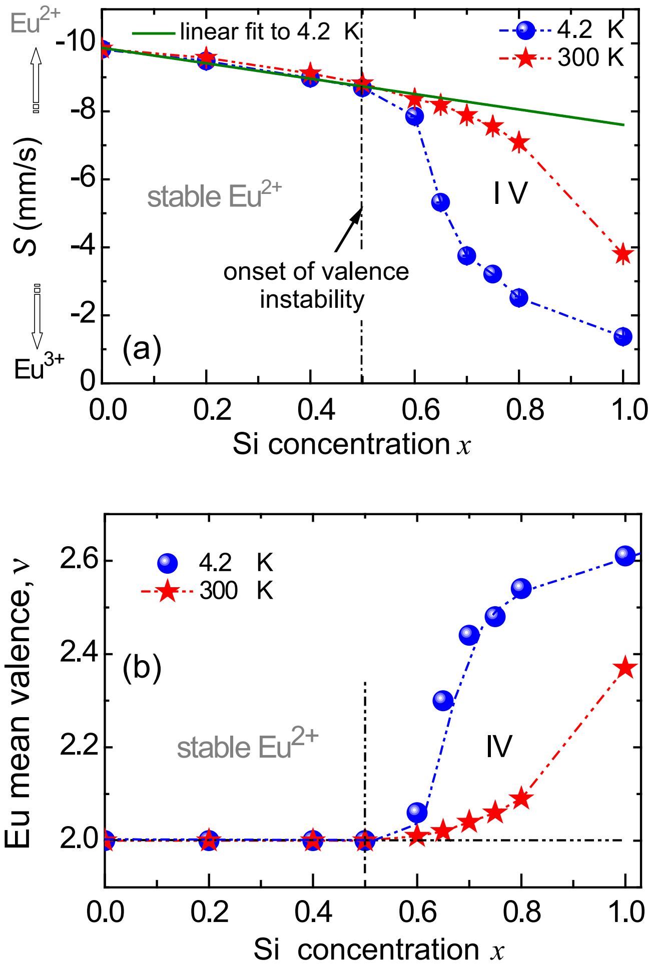

FIG. 5. (a) Depiction of the observed large temperature dependence of the isomer shift S of Eu between 300 and 4.2 K for $x > 0.5$. This confirms the onset of an intermediate valence (IV) state of Eu above $x = 0.5$. (b) Eu mean valence as a function of Si concentration in $EuCu_2(Ge_{1-x}Si_x)_2$ at 4.2 and 300 K, obtained from the measured isomer shift in (a) and Eq. (1). Dashed lines through the data points are to guide the eye.

As is evident from Fig. 5(a), S shows a linear shift to less negative values up to $x \sim 0.5$ at both 4.2 and 300 K. This is attributed to an increase of the s-electron density at the Eu nucleus with increasing x. Increasing Si substitution x leads to a decrease of the unit-cell volume, which may be considered as chemical pressure. Thus the volume-induced change of S in the concentration range $0 \leqslant x \leqslant 0.5$ amounts to $\partial S_2/\partial(\ln V) \sim -27\,\text{mm/s}$, which is relatively small and very close to that for stable divalent $\text{Eu}(\text{Pd}_{1-x}\text{Au}_x)\text{Si}_2$ compositions where $\partial(S_2)/\partial \ln V \sim -30\,\text{mm/s}$ [25,32]. This finding together with the absence of a temperature dependent isomer shift indicates that the Eu^{2+} state in $\text{EuCu}_2(\text{Ge}_{1-x}\text{Si}_x)_2$ remains stable up to $x = 0.5$.

Quite different behavior is observed for $x > 0.5$ in Fig. 5(a). There is a strong nonlinear change of S with increasing $x > 0.5$ and S exhibits an appreciable temperature dependence, which is a tell-tale signature of a valence change of the Eu^{2+} state towards intermediate valency [7].

In fact the volume-induced change of the isomer shift in Eu^{2+} metallic systems, also seen in Fig. 5(a), mainly originates from the following mechanisms [33]: (i) an increase in density of s-like conduction electrons ($6s$), (ii) an increase of the intra-atomic and interatomic $4f$ ($5d$, $6s$) exchange interactions, and (iii) promotion of a $4f$ electron into the conduction band, i.e., $4f^7 \Leftrightarrow 4f^6 + e^-$ and associated $\text{Eu}^{2+} \Leftrightarrow \text{Eu}^{3+}$ valence fluctuations. The latter mechanism, involving shielding effects of the $4f$ electrons [25], results in a major increase of the s-electron density at the Eu nucleus (i.e., dramatic change of S relative to S_2 for divalent Eu).

The concentration dependence of the Eu mean valence in $\text{EuCu}_2(\text{Ge}_{1-x}\text{Si}_x)_2$ is plotted in Fig. 5(b), as calculated from Eq. (1) and the values of the corresponding concentration dependence of S in Fig. 5(a). Figure 5(b) shows a crossover from the stable Eu^{2+} state to the IV state at $x \sim 0.5$. It further reveals a strong temperature dependence of the valence state in the IV region. Most interesting is the observation of an enhanced IV state ($\nu \sim 2.45$) across the QPT, encompassing the critical concentration $x_c \sim 0.7$ where the magnetic hyperfine field has collapsed to zero, see Fig. 4(c). Further slight increases in the valence occur for $x > 0.7$. This enhanced IV state at $x_c \sim 0.7$ is further discussed in subsections B and C.

B. Temperature dependence of the IV state across the quantum phase transition

To better understand the nature of valence fluctuations across the QPT at $x_c \sim 0.7$ in $\text{EuCu}_2(\text{Ge}_{1-x}\text{Si}_x)_2$, we have performed systematic temperature dependent ^{151}Eu Mössbauer measurements between 300 and 1.75 K in the valence instability region, i.e., for $x \geqslant 0.6$. Some temperature dependent Mössbauer spectra for such selected concentrations ($x = 0.65$, 0.7, 0.75, and 0.8) are shown in Fig. 6.

The spectra were analyzed assuming either one or two subspectra with the linewidth, isomer shift, quadrupole splitting, and spectral area as fitting parameters. The concentrations $x = 0.65$, 0.7, and 0.75 in Fig. 6 reveal basically the same features upon decreasing temperature well below 300 K. For each of these Si concentrations there are two absorption lines with different values of the isomer shift S_I and S_{II}. The isomer shifts and intensity ratios are clearly temperature dependent.

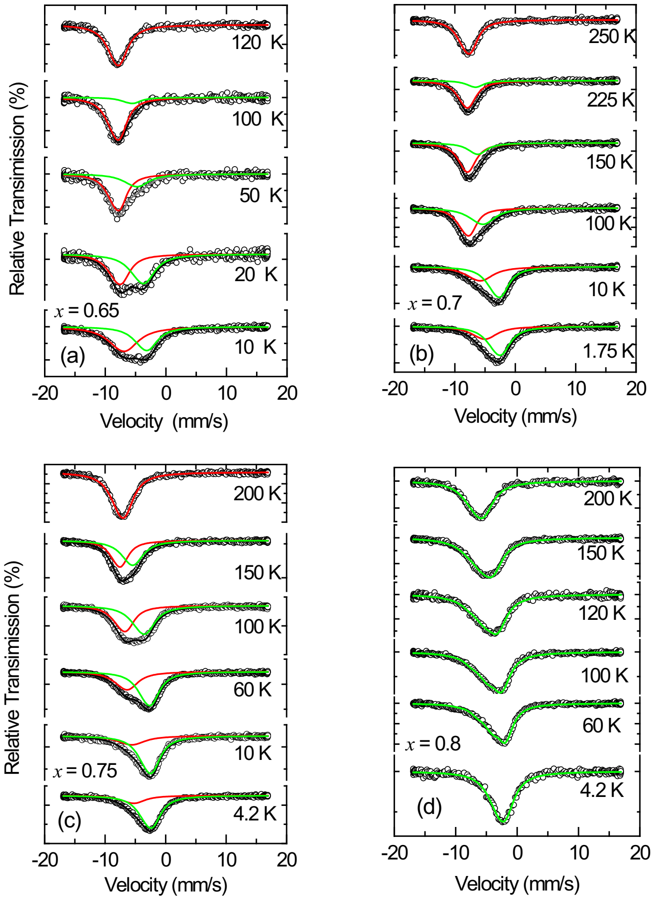

FIG. 6. ^{151}Eu Mössbauer spectra of $\text{EuCu}_2(\text{Ge}_{1-x}\text{Si}_x)_2$ at various temperatures for the IV states of $x = 0.65$ in (a), $x = 0.7$ in (b), $x = 0.75$ in (c), and $x = 0.8$ in (d). Note that for $x = 0.65$ the spectrum at 4.2 K showing coexisting magnetic and nonmagnetic IV components is in Fig. 4(a).

First consider the ME spectra for these concentrations at the lowest temperatures 10 K to 1.75 K in Fig. 6. With increasing x at these base temperatures there is definite evolution of a second IV component with S_{II} in the range -3 to -5 mm/s and a simultaneous decrease of the other IV component with more negative isomer shift values S_I in the range -7 to -8 mm/s suggestive of a metastable IV state. Figure 6 thus clearly indicates existence of an inhomogeneous IV state for $0.65 \leqslant x \leqslant 0.75$. However, at higher concentrations for $x = 0.8$, the component with the more negative value of the isomer shift (metastable IV state) disappears. Only the single line component with $S_{II} \sim -2\,\text{mm/s}$ prevails, close to that observed for the homogeneous IV compound EuCu_2Si_2 [7].

The temperature dependence of the isomer shift (4.2 K $\leqslant T \leqslant$ 300 K) in the concentration range $0.6 \leqslant x \leqslant 1$ is shown in Fig. 7(a). The S values for concentrations $0.6 \leqslant x \leqslant 0.75$ are calculated from the weighted average values of the two components in the spectra. From the calculated values of the average isomer shift we then obtain the average Eu valence $\nu(x)$ for each concentration at different temperatures using Eq. (1), as plotted in Fig. 7(b). Figure 7(b) indicates that the change of Eu mean valence with temperature in

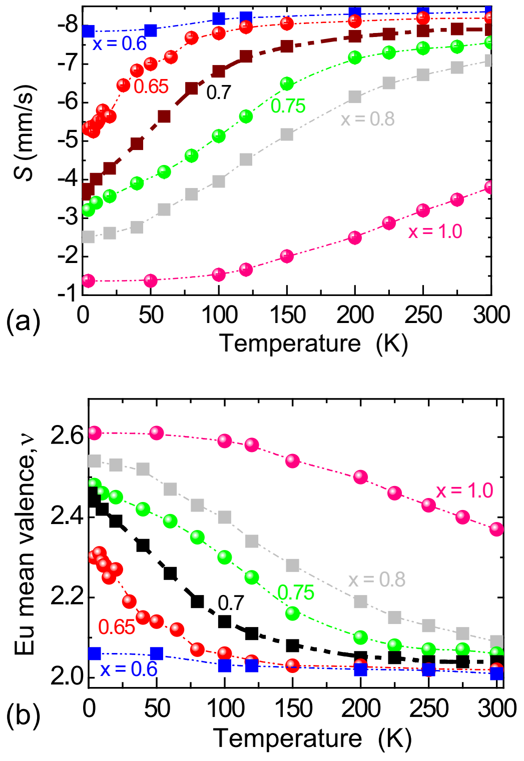

FIG. 7. (a) Temperature dependence of the average isomer shift for different $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ concentrations as deduced from the analysis of the ME spectra. (b) Corresponding Eu mean valence obtained using Eq. (1). Dashed lines through the data points are to guide the eye.

all doped samples in the region between $0.65 \leqslant x \leqslant 0.8$, is more pronounced and sharper than that observed in the homogeneous IV compound $\mathrm{EuCu_2Si_2}$ ($x = 1$). This is because higher lying (metastable) IV configurations represented by S_I are thermally accessible relative to the ground-state IV represented by S_{II}. At higher x and smaller unit-cell volumes the higher valency ground-state S_{II} becomes increasingly energetically favored. The ground-state IV configuration is also preferentially populated at low temperatures due to thermal contraction of the lattice. Moreover note that temperature dependence of $\nu(x)$ is most pronounced for the sample with the critical concentration $x_c = 0.7$ where there is a crossover to the nonmagnetic IV state, i.e., magnetic QCP in Fig. 4(c).

In addition, the onset of the S_{II} IV state for $x_c = 0.7$ is at ~225 K in Fig. 6(b), which is higher than its onset temperatures of ~100 and ~150 K for $x = 0.65$ and $x = 0.75$ just below and above x_c, respectively. This finding reveals that such charge fluctuations exist up to higher temperatures at the QCP. We believe that the existence of enhanced charge fluctuations at $x \sim 0.7$ may be responsible for the observation of heavy quasiparticles at low temperatures $0.65 \leqslant x \leqslant 0.75$ [8,12]. Information about the driving mechanism of the unusual inhomogeneous IV state across the QPT requires an investigation of the temperature dependence of the lattice parameters, as discussed in the following subsection C.

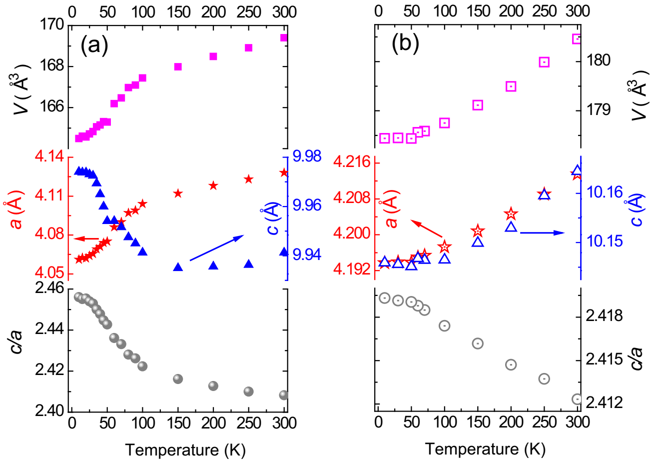

FIG. 8. Temperature dependences of: unit-cell volume and lattice parameters for (a) $x = 0.7$ of $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ in comparison with (b) the end-member $\mathrm{EuCu_2Ge_2}$.

C. Coupling of valence fluctuations to the lattice at the quantum critical point ($x_c = 0.7$)

We have shown in Sec. III A that the change of Eu valence in the $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ series is closely connected with a corresponding change of lattice parameters. As the valence state in the IV regime ($x \geqslant 0.6$) is found to be strongly temperature dependent [see Fig. 7(b)], one would expect this to manifest in the temperature dependence of the lattice parameters. In particular, the lattice parameter a in Fig. 1(c), which is very sensitive to the valence state of Eu should decrease as the valence state of Eu is shifted towards $\mathrm{Eu^{3+}}$ with decreasing temperature [25,26].

Figure 8(a) suggests such a strong coupling between valence fluctuations and lattice parameters in the IV sample at the critical concentration $x_c = 0.7$ as the temperature changes between 300 and 4.2 K. The contrasting situation where this is not the case for stable $\mathrm{Eu^{2+}}$ in $\mathrm{EuCu_2Ge_2}$ is in Fig. 8(b). The temperature-induced changes of the lattice parameters between 300 and 4.2 K of the two compositions are quite different. The stable divalent $\mathrm{EuCu_2Ge_2}$ shows a smooth evolution and small changes of a, c, and V in Fig. 8(b). Whereas in Fig. 8(a) the $x = 0.7$ IV sample reveals much larger and anomalous changes of a, c, and V, especially below ~100 K. Over the full temperature range these amount to relative changes of $\Delta a/a \sim 0.5\%$, $\Delta c/c \sim 0.2\%$ and $|\Delta V/V| \sim 1\%$ for $\mathrm{EuCu_2Ge_2}$, and ~1.7%, 0.3% and ~3%, respectively, for the $x = 0.7$ IV sample. In the IV sample the anomalous decrease in volume below ~100 K originates from the sudden decrease of a and increase of c shown in Fig. 8(a). This $x = 0.7$ sample thus experiences additional lattice pressure when decreasing the temperature below 100 K. This is expected to translate to a strongly temperature dependent shift of the Eu IV state towards the $\mathrm{Eu^{3+}}$ regime that involves a smaller atomic volume. This is revealed in Fig. 9, which shows the correlation between Eu mean valence $\nu(T)$ calculated at different temperatures 300–4.2 K and the corresponding change of unit-cell volume $V(T)$. There is a linear correlation between $\nu(T)$ and $V(T)$ below ~150 K, where $\nu(T)$ shows a steeper trajectory on route towards the $\mathrm{Eu^{3+}}$ state. Possible correlations

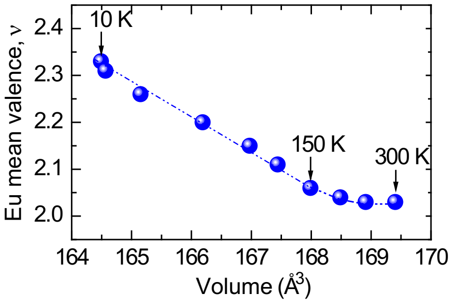

FIG. 9. Eu mean valence versus unit-cell volume of EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ for $x = 0.7$. Dashed line through the data points are to guide the eye.

between $\nu(T)$ with the lattice parameter $a(T)$ and $c(T)$ as well as the ratio $c/a(T)$ for $x = 0.7$ are plotted and discussed in Sec. 2 of the Appendix (see Fig. 14).

The consequence of such a strong temperature dependence of volume below 150 K and the evolution of the IV state is manifest in the ME spectra of the $x = 0.7$ sample above and below 100 K (see Fig. 10). Upon lowering the temperature, the ME spectra show a gradual change of population of the two IV states, S_I and S_{II}, with a simultaneous more positive shift of both IV states towards the Eu^{3+} regime. In Fig. 10(b) the isomer shifts of the two IV states (S_I and S_{II}) change rapidly below ~100 K. The simultaneous change of the respective populations can be clearly seen in Fig. 15 in the Appendix. This finding suggests the existence of two energetically closely lying IV states, whose relative abundances are driven by thermal variation of the structural parameters. Thus the change of valence with temperature tracks that of the lattice parameters and unit-cell volume in Fig. 8. The above-mentioned findings are a compelling indication that formation of such an unusual inhomogeneous IV state is intimately connected with anomalous temperature dependences of the structural parameters.

D. Magnetic phase diagram of EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$

In the following, we discuss the interplay between the antiferromagnetic order and intermediate valence in EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ across the magnetic to nonmagnetic QPT at $x_c = 0.7$. In Fig. 11, we plot the concentration dependence of the magnetic hyperfine field B_{eff} and the Eu mean valence as deduced from our ^{151}Eu Mössbauer measurements. The concentration dependence of the Néel temperature (T_N) is also presented [8]. Starting from the magnetic side of the phase diagram, B_{eff} increases with increasing Si concentration, reaches a maximum at $x \sim 0.6$ and then collapses to zero at a critical concentration $x_c \sim 0.7$ indicative of a magnetic QCP. The increase of B_{eff} with increasing x basically follows that of T_N up to $x = 0.5$. In the same concentration range the Eu mean valence is volume independent due to divalent Eu^{2+}, see Fig. 5(b). Thus the Eu^{2+}($4f^7$) magnetic ground state remains stable up to $x = 0.5$.

The enhancement of B_{eff} and T_N for $0 \leqslant x \leqslant 0.5$ ($\partial|B_{\text{eff}}|/\partial(\ln V) \sim 229\,\text{T}$) is due to both the lattice volume decrease and change of the electronic spin density in the vicinity of the Eu ions caused by the Si doping. The magnetic hyperfine field of $4f^7$ ($^8S_{7/2}$) Eu^{2+} ions in metallic systems is usually attributed to three contributions $B_{\text{eff}} = B_c + B_{ce} + B_{thf}$ [28,34]. Here $B_c = -34\,\text{T}$ is from polarization of core s electrons by the $4f$ moment, B_{ce} arises from the conduction electron polarization by the Eu ion itself, and B_{thf} includes all transferred contributions from $4f$ magnetic moments of neighboring sites.

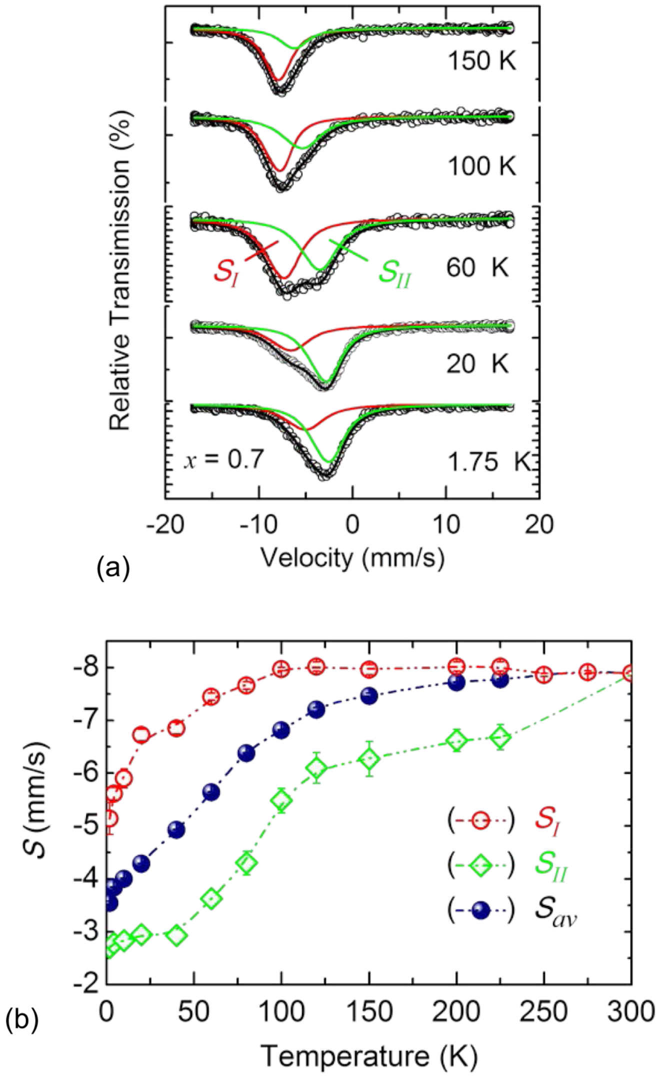

FIG. 10. (a) Eu Mössbauer spectra of EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ for $x =$ 0.7 at various temperatures. A metastable IV component (S_I) and IV ground-state (S_{II}) component is discerned at all temperatures with different relative abundances. Overall fit is the solid line through the data points. (b) Temperature dependence of the isomer shifts of the spectral subcomponents, S_I and S_{II}, for the two IV states and the weighted average value S_{av}. Dashed lines through the data points are to guide the eye.

The increase of B_{eff} with lattice or chemical pressure (i.e., increasing Si concentrations) is similar to that observed in stable divalent Eu compounds [29,34,35]. Those investigations have shown that the increase of B_{eff} with external pressure is mainly due to the increase of B_{thf}, which is caused by

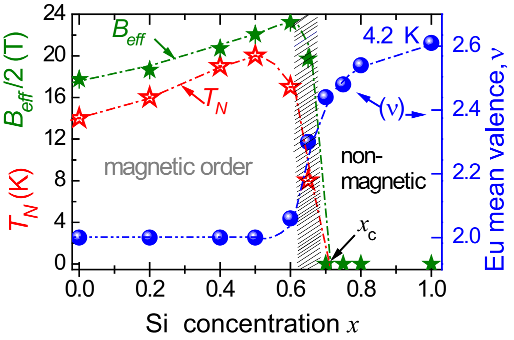

FIG. 11. Phase diagram of $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ involving both B_{eff} and Eu mean valence at 4.2 K, as a function of Si concentration. The values of T_N are taken from Ref. [8]. Hatched area marks the concentration region where there is coexistence of both antiferromagnetically ordered and intermediate valence states. Dashed lines through the data points are to guide the eye.

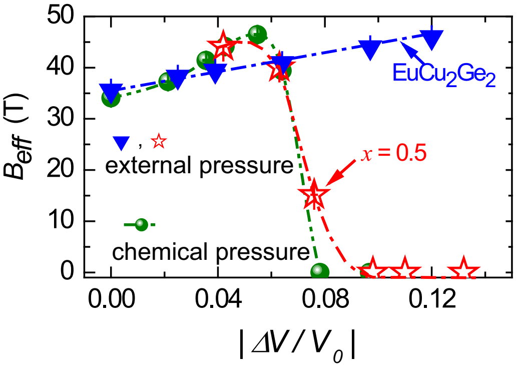

FIG. 12. Effective magnetic hyperfine field B_{eff} at 4.2 K as a function of relative change of volume due to Si chemical substitution in $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ and due to external pressure for $x = 0$ and $x = 0.5$ as reproduced from Ref. [16]. Dashed lines through the data points are to guide the eye.

the enhancement of both intra-atomic and interatomic $4f$ ($5d$, $6s$) exchange interactions. Since the strength of those interactions also determine the value of T_N, B_{eff}, and T_N react similarly to chemical pressure (see Fig. 11). This situation changes for $x > 0.5$ where B_{eff} further enhances before collapsing only when $x > 0.65$, whereas T_N is already reduced for $x = 0.6$ and completely suppressed above $x > 0.65$. The system undergoes a QPT to a nonmagnetic state at the critical concentration $x_c \sim 0.7$. The collapse of B_{eff} reflects a breakdown of magnetic order due to suppression of the $4f$ local magnetic moment with increasing Si concentration for $x > 0.65$.

By comparison the valence of $\mathrm{Eu^{2+}}$, which becomes unstable for $x > 0.5$ [see Fig. 5(b)], undergoes a precipitous increase beyond $x \sim 0.6$ and reaches $\nu \sim 2.45$ at $x_c \sim 0.7$. This indicates enhanced charge fluctuations at the magnetic QCP. Furthermore, below x_c in the regime $0.6 < x < 0.7$, there is a coexistence of magnetic ordering and inhomogeneous IV, shown in Fig. 11 as a hatched region [see also Fig. 4(a)]. This implies that collapse of the magnetic state to a nonmagnetic IV state at $x_c \sim 0.7$ is a first-order phase transition associated with simultaneous destabilization of the $\mathrm{Eu^{2+}}$ ($J = 7/2$) valence. This points to the unique feature of this system, in that tuning the highly localized AF $\mathrm{Eu^{2+}}$ state towards the nonmagnetic $\mathrm{Eu^{3+}}$ state involves simultaneously acting on both spin and charge. Thus corresponding changes to both magnetic and valence properties are to be expected in the $x_c \sim 0.7$ crossover regime. Hence in Ref. [9] (Fig. 14 of Fukuda *et al.*) and Ref. [12] (Fig. 1 of Iha *et al.*) there is reference to a steep phase boundary or line of first-order valence transitions, T_V versus x for $0.9 \geqslant x \geqslant 0.7$, which would meet the AF phase boundary at or near the magnetic QCP.

E. Comparison of substitution-induced and pressure-induced QPTs in $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$

Finally, we compare the QPT induced by chemical substitution in $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ with that induced by external pressure [16]. External pressure results in a pure volume decrease. Whereas substitution of Ge by Si not only causes a decrease of the unit-cell volume (chemical or lattice pressure), but also significantly changes the electronic structure and introduces chemical disorder. These additional effects potentially have a large impact on the magnetic and electronic properties of the system. In Fig. 12, we plot the volume dependence of B_{eff} at 4.2 K as a function of the relative change of unit-cell volume in the $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ series due to chemical substitution as well as due to external pressure on $x = 0$ and 0.5 compostions [16].

For chemical substitution, we have used the values of $\Delta V/V_0$ as obtained from our low temperature x-ray diffraction measurements, whereas those due to external pressure are taken from our compressibility measurements on the investigated samples at 300 K [16]. As shown in Fig. 12, $\mathrm{EuCu_2Ge_2}$ under external pressure of 7 GPa, corresponding to a volume reduction of $|\Delta V/V_0| \sim 12\%$, does not undergo a QPT; whereas Si substitution induces an abrupt magnetic QPT at $x_c \sim 0.7$ corresponding to $|\Delta V/V_0| \sim 8\%$. Evidently then this comparison suggests that the QPT due to chemical substitution is predominantly caused by a rather severe modification of the electronic structure. This results in a breakdown of the $\mathrm{Eu^{2+}}$ ($4f^7$) magnetic moment at a critical concentration of $x_c = 0.7$. This conclusion is strongly supported by our high pressure results on the $x = 0.5$ composition, $\mathrm{EuCu_2GeSi}$ [16]. In this case, the system could be destabilized already by applying 1.3 GPa and the pressure-induced QPT is found to occur at a critical volume reduction of $|\Delta V/V_0| \sim 10\%$ ($P_c \sim 3.6$ GPa), near to the $|\Delta V/V_0| \sim 8\%$ value induced by chemical pressure at $x_c = 0.7$. The $|\Delta V/V_0| \sim 10\%$ value associated with P_c is an upper limit, as it is based on the compressibility derived from measurements at 300 K [16]. Relative volume changes are expected to be smaller at low temperatures and will lead to a critical value smaller than that determined at 300 K.

Thus, in addition to the unit-cell shrinkage that occurs with Si doping, there will also be the development of some atomic (chemical) disorder with attendent changes to the band structure at the Fermi level. This seems to play a key role in driving the system across the QPT involving AF to nonmagnetic IV states, rather than pressure effects alone and subsequent reductions in lattice volumes.

V. SUMMARY

This work deals with a detailed study of charge fluctuations across a QPT in the ternary Eu-based intermetallic isostructural series $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$, which crystallizes in the $\mathrm{ThCr_2Si_2}$-type structure. Previous macroscopic measurements (electrical and thermal transport, and calorimetry) indicate that the initial AF state of $\mathrm{EuCu_2Ge_2}$ ($T_N = 14\,\mathrm{K}$) is stable for $0 \leqslant x \leqslant 0.6$ in the $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ series, but for $x > 0.65$ has collapsed to a nonmagnetic state where IV behavior has been identified. Consequently a QPT occurs near $x \sim 0.7$ driven by increasing Si substitution. Here we use temperature dependent ^{151}Eu Mössbauer spectroscopy (300–4.2 K) as a direct probe of the Eu electronic configuration (via the isomer shift S) and concurrently of the magnetic state (via the effective magnetic hyperfine field B_{eff}), across the identified QPT. Complementary temperature dependent XRD structural measurements (300–10 K) have also been conducted to consider the lattice response as a function of Si concentration x, especially in the vicinity of the QPT.

The analysis of the ^{151}Eu ME data indicates that the divalent Eu AF state is stable up to $x \sim 0.5$, followed by a collapse of AF ordering for $x > 0.6$, which is associated with a simultaneous sharp change of the valence state towards a nonmagnetic IV state. The crossover from the AF ordered state to the nonmagnetic IV state is found at a QCP corresponding to $x_{\mathrm{c}} \sim 0.7$, at which the nonmagnetic IV state is inhomogeneous and exhibits an enhanced Eu mean valence of $\nu \sim 2.5$. We believe that such enhanced charge fluctuations are related to the observed heavy quasiparticles at low temperatures near the QCP. The ME data further indicates that magnetic order and a nonmagnetic inhomogeneous IV coexist in a narrow region $0.6 \leqslant x < 0.7$. Temperature dependent scans at $x_c = 0.7$ reveal an inhomogeneous nonmagnetic IV state, where metastable IV and ground-state IV components coexist.

A unique feature of this $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ series is that in tuning the highly localized AF $\mathrm{Eu^{2+}}$ state towards the nonmagnetic $\mathrm{Eu^{3+}}$ state we simultaneously act on both spin and charge. Our ^{151}Eu Mössbauer microscopic probe evidences this strong coupling between spin and charge degrees of freedom in the vicinity of $x_{\mathrm{c}} \approx 0.7$, by discerning collapse of the magnetic hyperfine field B_{eff} (and hence T_N) and coexistence of magnetically ordered and nonmagnetic (IV) components at low temperatures, typical of a first-order phase transition (QPT).

Angle-resolved XRD structural measurements revealed that the $\mathrm{ThCrSi_2}$-type tetragonal structure is maintained throughout the series, although at 10 K there is a precipitous increase in the c/a ratio when the valence fluctuations become enhanced at $x_c = 0.7$. XRD temperature scans at the critical concentration shed a deeper insight on the formation of the inhomogeneous nonmagnetic IV state detected from the corresponding ME measurements. The XRD data indicates conspicuous changes to steep temperature dependences of decreasing (increasing) values of a (c) lattice parameters and decreasing unit-cell volume at $T < 100$ K, as the intermediate valence ground state become preferentially populated at low temperatures. This finding suggests the existence of two energetically closely lying IV states, whose relative abundances are driven by thermal variation of the structural parameters. Thus, our results are a clear demonstration that the formation of such an unusual inhomogeneous IV state near the QCP is intimately connected with anomalous temperature dependences of the structural parameters. By $x = 0.8$ and thereafter up to the $\mathrm{EuCu_2Si_2}$ only a homogeneous IV ground state is discerned.

We were able to construct a magnetic phase diagram and compared the QPT induced by chemical substitution (lattice pressure) in $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ with that induced by external pressure [16]. This suggested a key role of Si doping perturbations to the electronic structure likely through the effects of chemical disorder, along with the effects of chemical pressure, in driving the quantum phase transition in this series.

APPENDIX: ADDITIONAL ^{151}Eu MÖSSBAUER AND XRD ANALYSES

1. Concentration dependence of the area ratios of spectral subcomponents in the Mössbauer spectra of $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ at 4.2 K

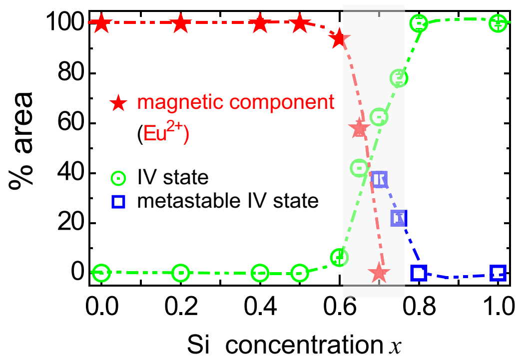

FIG. 13. Concentration dependence of the abundances (absorption area ratio) of the different components in the Mössbauer spectra in $\mathrm{EuCu_2(Ge_{1-x}Si_x)_2}$ at 4.2 K (see Fig. 4 main text). Dashed lines through the data points are to guide the eye. Shaded bar shows the Si composition range where an inhomogeneous IV state occurs.

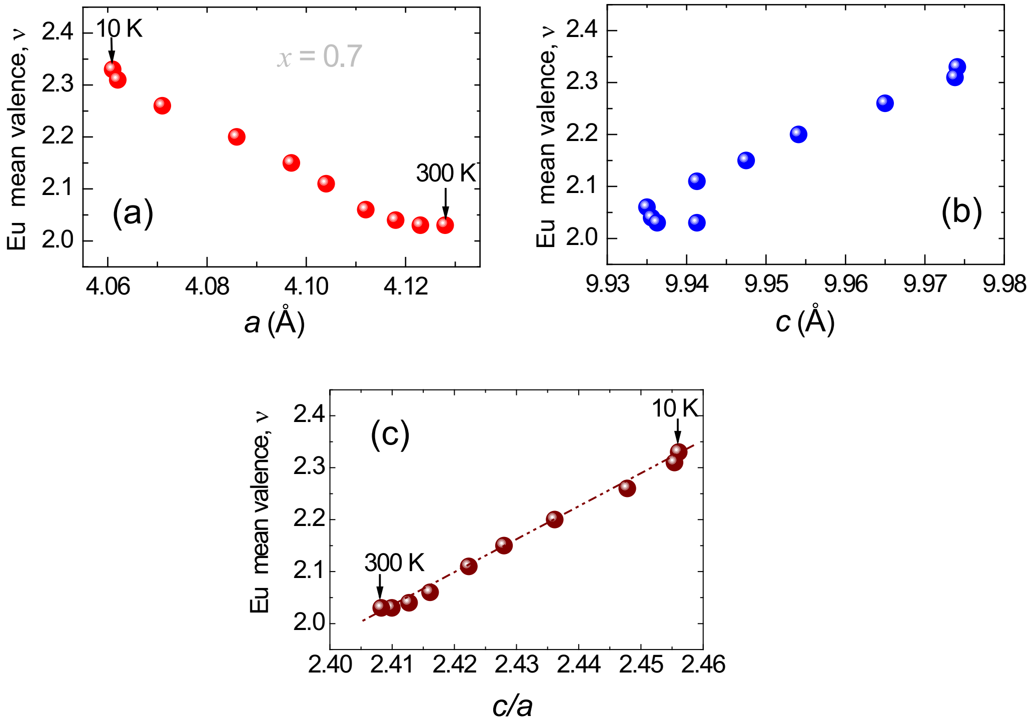

FIG. 14. Eu mean valence versus lattice parameters a, c, and the c/a ratio of $EuCu_2(Ge_{1-x}Si_x)_2$ for $x = 0.7$. Dashed line through the data points are to guide the eye.

2. Correlations between mean valence $\nu(T)$ with the lattice parameters $a(T)$ and $c(T)$ as well as the ratio $c/a(T)$ for $x = 0.7$

The lattice parameter a decreases with decreasing temperature in Fig. 8(a) of the main text. It is determined primarily by the Eu-Eu interatomic distances in the structure [see Fig. 1(c)] and therefore should be the most likely to correlate with valence changes. However, it does not show an exact linear correlation in Fig. 14(a). The behavior of c is rather complex in Fig. 8(a) of the main text, since it decreases in the range 300–150 K, then increases below 100 K and saturates below ~30 K. This results in a poor correlation with the temperature dependence of the Eu mean valence as shown in Fig. 14(b). A fairly good linear correlation is found between the change of $\nu(T)$ and c/a and with temperature, see Fig. 14(c). This indicates that the intrinsic behavior of $\nu(T)$ in $EuCu_2(Ge_{1-x}Si_x)_2$ for $x = 0.7$ is determined by the ratio of c/a as a function of temperature rather than by $a(T)$ alone.

3. Intermediate valence components at the critical concentration $x_c = 0.7$ in the $EuCu_2(Ge_{1-x}Si_x)_2$ series

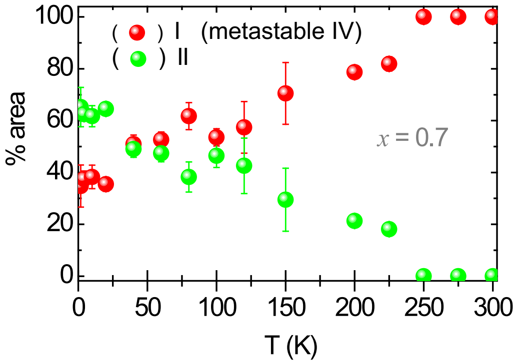

FIG. 15. Temperature dependence of the abundances (absorption area ratio) of the two IV components corresponding to isomer shifts S_I and S_{II}, respectively, in $EuCu_2(Ge_{1-x}Si_x)_2$ for $x = 0.7$ (see Fig. 10 of the main text).

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