Mössbauer spectroscopy measurements on the 35.5 K superconductor Rb$_{1-x}$EuFe$_4$As$_4$

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The results of x-ray diffraction and $^{57}$Fe and $^{151}$Eu Mössbauer spectroscopy measurements, supplemented with $ab$ initio hyperfine-interaction parameter calculations, on the new 35.5 K superconductor Rb$_{1-x}$EuFe$_4$As$_4$ are presented. The superconductor crystallizes in the tetragonal space group $P4/mmm$ with the lattice parameters $a = 3.8849(1)$ Å and $c = 13.3370(3)$ Å. It is shown that there is no magnetic order of the Fe magnetic moments down to 2.1 K and that the ferromagnetic order is associated solely with the Eu magnetic moments. The Curie temperature $T_C = 16.54(8)$ K is determined from the temperature dependence of both the hyperfine magnetic field at $^{151}$Eu nuclei and the transferred hyperfine magnetic field at $^{57}$Fe nuclei that is induced by the ferromagnetically ordered Eu sublattice. The Eu magnetic moments are demonstrated to be perpendicular to the crystallographic c axis. The temperature dependence of the principal component of the electric field gradient tensor, at both Fe and Eu sites, is well described by a $T^{3/2}$ power-law relation. Good agreement between the calculated and measured hyperfine-interaction parameters is observed. The Debye temperature of Rb$_{1-x}$EuFe$_4$As$_4$ is found to be 391(8) K.

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I. INTRODUCTION

Discovered in 2016, AeAFE$_2$As$_4$ (Ae = Ca, Sr, Eu and $A = $ K, Rb, Cs) compounds are a new Fe-based class of superconductors with the critical temperature $T_C$ in the range 31.6–36.8 K [1–4]. Unlike in solid solutions, such as intensively studied (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ or (Sr$_{1-x}$Na$_x$)Fe$_2$As$_2$, the Ae and A atoms in AeAFE$_2$As$_4$ occupy crystallographically inequivalent positions, which changes the space group from $I4/mmm$ to $P4/mmm$. The crystal structure of these new superconductors consists of the Ae and A layers alternately stacked along the crystallographic c axis between the Fe$_2$As$_2$ slabs. Therefore, these fully ordered, stoichiometric Fe-based superconductors offer a unique opportunity to study, among other things, the relation between superconductivity and possible long-range magnetic order.

The superconductor RbEuFe$_4$As$_4$ with a critical superconducting temperature $T_C = 36.5$ K exhibits an anomaly at $\sim 15.0$ K in the magnetic-susceptibility and specific-heat data [3]. The isothermal magnetization measurements allowed the identification of this anomaly as a ferromagnetic transition [3]. The ferromagnetism in the RbEuFe$_4$As$_4$ superconductor has been suggested [3] to result from the ordering of the Eu magnetic moments. This is equivalent to assuming that the Fe atoms in RbEuFe$_4$As$_4$ carry no magnetic moment. No orientation of the magnetic moment in RbEuFe$_4$As$_4$ with respect to the crystallographic axes has been established.

The main goal of this study is to determine whether the magnetic moment in the RbEuFe$_4$As$_4$ superconductor is associated with only Eu or Fe atoms or with Eu and Fe atoms and what its orientation is relative to the crystallographic axes. To achieve this goal, $^{57}$Fe and $^{151}$Eu Mössbauer spectroscopy, supplemented by the first-principles calculations, will be utilized.

II. EXPERIMENTAL AND THEORETICAL METHODS

The Rb$_{1-x}$EuFe$_4$As$_4$ polycrystalline sample was prepared with a solid-state reaction method in an Ar atmosphere and at high temperatures, as described elsewhere [3].

An x-ray diffraction pattern was measured at 298 K in Bragg-Brentano geometry on a PANalytical X’Pert scanning diffractometer using Cu $K\alpha$ radiation in the 2θ range of 10°–120° in steps of 0.02°. The $K\beta$ line was eliminated by using a Kevex PSI2 Peltier-cooled solid-state Si detector. The chemical composition of the crystallites of the sample was determined using an energy-dispersive x-ray spectrometer (Model Octane Plus) equipped with a field-emission scanning electron microscope (Hitachi S-4800). The dc magnetization measurements were carried out using a Quantum Design magnetic property measurement system (MPMS-5).

The $^{57}$Fe and $^{151}$Eu Mössbauer measurements [5] were conducted using standard Mössbauer spectrometers operating in the sine mode, with sources $^{57}$Co(Rh) and $^{151}$Sm(SmF$_3$) at room temperature, respectively. The Mössbauer source $^{151}$Sm(SmF$_3$) is not a monochromatic source as $^{151}$Sm nuclei are located in the SmF$_3$ matrix at a sites of noncubic symmetry. By measuring the $^{151}$Eu Mössbauer spectra of a cubic EuSe compound, we determined that the electric quadrupole coupling constant [5] $eQ_zV_{zz}$ [here $e$ is the proton charge, $Q_z = 0.903$ b is the ground-state electric quadrupole moment of the $^{151}$Eu nucleus [6], and $V_{zz}$ is the principal component of the electric-field-gradient (EFG) tensor] in our source is $-3.69(13)$ mm/s, which is close to the value of $-3.6$ mm/s...
found in Ref. [7]. The precise shape of the source emission line was taken into account in the fits of the $^{151}\text{Eu}$ Mössbauer spectra.

The 14.4 and 21.5 keV γ rays were detected with a proportional counter. The spectrometers were calibrated with a 6.35-μm-thick α-Fe foil [8], and the spectra were folded. The Mössbauer absorbers consisted of a mixture of powder Rb$_{1-x}$EuFe$_4$As$_4$ and boron nitride, which was pressed into a pellet that was put into an 8-μm-thick Al disk container to ensure a uniform temperature over the whole absorber. The Mössbauer absorbers were put into a Mössbauer cryostat in which they were kept in a static exchange gas atmosphere at a pressure of $\sim 6 \times 10^{-2}$ mbar. The surface densities of the $^{57}\text{Fe}$ and $^{151}\text{Eu}$ Mössbauer absorbers were 17.23 and 29.1 mg/cm$^2$, respectively. They correspond to an effective thickness parameter $t_{\text{h}}$ [5] of 2.96 $t_{\text{h}}$ and 2.62 $t_{\text{h}}$, respectively (here $t_{\text{h}}$ is the Debye-Waller factor of the absorber). Since $t_{\text{h}} > 1$, the resonance line shape of the Mössbauer spectra was described using a transmission integral formula [9]. The Mössbauer spectra at temperatures below the magnetic transition temperature were analyzed using a least-squares fitting procedure which entailed calculations of the positions and relative intensities of the absorption lines by numerical diagonalization of the full hyperfine interaction Hamiltonian.

Ab initio magnetic moment and Mössbauer hyperfine-interaction parameter calculations were performed within the framework of density functional theory using the full-potential linearized augmented plane wave plus local orbitals method as implemented in the WIEN2K package [10,11]. The experimental lattice parameters ($a$ and $c$) and the atomic position parameters in the space group $P4/mmm$ (see below) were used in the calculations.

III. RESULTS AND DISCUSSION

A. Structural characterization

Figure 1 displays the room-temperature powder x-ray diffraction pattern of Rb$_{1-x}$EuFe$_4$As$_4$. The compound studied was shown [3] to crystallize in the tetragonal space group $P4/mmm$. A Rietveld refinement [12] of the x-ray powder diffraction data was carried out, yielding the lattice parameters $a = 3.8849(1)$ Å and $c = 13.3370(3)$ Å and the atomic positional parameters that are listed in Table I. We note (Fig. 1) that the specimen studied contains the second phases of FeAs [13] in the amount of 3.1(4) wt% and of Eu$_2$O$_3$ in the amount of 0.7(2) wt%. The values of $a$ and $c$ found here are, respectively, shorter and longer than the corresponding values in Ref. [3].

We found with energy-dispersive x-ray spectroscopy that the chemical composition of the crystallites studied was Rb$_{0.67(5)}$EuFe$_{4.17(7)}$As$_{3.83(5)}$. This indicates the existence of a significant Rb deficiency in the specimen. This deficiency induces an additional hole doping, which naturally explains the changes in the lattice parameters. The extra hole doping places the sample in an overdoped regime, which leads to a slight decrease of the superconducting transition temperature (see below).

The unit cell and the layered crystal structure of RbEuFe$_4$As$_4$ are shown in Fig. 2. The interactions between the Rb, Fe, and As atoms in the compound studied are depicted by various connecting rods. One observes that the layers of Eu atoms are completely isolated from the Fe$_4$As$_4$ blocks and that two neighboring Fe$_4$As$_4$ blocks are separated by sheets of Rb atoms along the $c$ direction.

The physical dimensions of the unit cell play an important role in some of the electronic transfer properties of the compound studied. In particular, each unit cell of RbEuFe$_4$As$_4$ is separated along the $c$ direction from its neighboring cells by two planes formed by the Eu atoms. As a direct result of the elongation of the unit cell in the $c$ direction, the RbFe$_4$As$_4$ units are practically isolated from the neighboring cells. Consequently, no direct electronic charge transfer between the neighboring RbFe$_4$As$_4$ units along the $c$ direction is expected. Hence, one can consider the Eu layers to form barriers for the conduction electrons, forbidding them from freely propagating along the $c$ direction. The absence of connecting rods in Fig. 2(b) between these layers of the Eu atoms and the RbFe$_4$As$_4$ units indicates this point. Thus, the insulating behavior of the compound studied along the $c$ axis results from strong ionic interactions between the Eu layers and the RbFe$_4$As$_4$ units, leading to the charge delocalization that exists only within the RbFe$_4$As$_4$ units. In other words, the valence electrons of the Eu atoms are completely transferred to the RbFe$_4$As$_4$ units to form the aforementioned ionic couplings.

<table>
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<th>Atom</th>
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<th>Point symmetry</th>
<th>Occupancy</th>
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<td>$\frac{1}{2}$</td>
<td>$\frac{1}{4}$</td>
</tr>
<tr>
<td>Eu</td>
<td>1$a$</td>
<td>$4/mmm$</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe</td>
<td>4$i$</td>
<td>$2mm$</td>
<td>1.0</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0.2316(2)</td>
</tr>
<tr>
<td>As1</td>
<td>2$g$</td>
<td>$4mm$</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.3362(2)</td>
</tr>
<tr>
<td>As2</td>
<td>2$h$</td>
<td>$4mm$</td>
<td>1.0</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.1273(3)</td>
</tr>
</tbody>
</table>
The tetragonal unit cell elongated along the $c$ axis rules out the possibility of any strong interaction between the Eu layers. Therefore, no magnetic coupling is expected to exist between the Eu atoms along the $c$ direction. One may thus predict that the interatomic interactions between the Eu atoms must occur in the $ab$ plane and that a two-dimensional magnetic interaction mechanism, if any, between neighboring Eu atoms in each layer should exist.

**B. Magnetic characterization**

Superconductivity and ferromagnetism of the polycrystalline sample of Rb$_{1-x}$EuFe$_4$As$_4$ were verified by magnetic measurements. As shown in Fig. 3(a), bulk superconductivity is seen from the large magnetic shielding fraction (the volume fraction exceeds 100% because of the demagnetization effect). The superconducting transition temperature $T_c$ is 35.5 K, 1 K lower than reported previously [3]. The slight decrease in $T_c$ is probably due to the existence of the Rb deficiency (see above) that induces an overdoping effect.

The field-cooled magnetic susceptibility [Fig. 3(a)] shows an upturn below 20 K and levels off at $T_c = 15.0$ K, which is defined as the Curie temperature [3]. The anomalous magnetic response reflects the Eu-spin ferromagnetism, which is manifested by the isothermal magnetization shown in Fig. 3(b). Below $T_C$, an $S$-shaped magnetic hysteresis loop, one of the hallmarks of ferromagnetism, appears. The saturation magnetization of 6.0 $\mu_B$/f.u. is close to the value of 7.0 $\mu_B$/f.u. expected for full Eu$^{2+}$-spin ferromagnetism (the deviation might be due to the existence of the FeAs and Eu$_2$O$_3$ impurities in the sample studied). In fact, the hysteresis loop at 2.0 K is superposed by superconducting signals, as seen from the bifurcation of the magnetization at high fields [Fig. 3(b)]. At 20 K, the $M(H)$ loop mainly originates from type-II superconductivity with flux pinning and Brillouin-function-type paramagnetism. No magnetic hysteresis is observed at 40 K, consistent with the loss of ferromagnetism and superconductivity at that temperature. Thus, the data presented in Fig. 3 unambiguously confirm the presence of superconductivity and ferromagnetism below their respective transition temperatures in the Rb$_{1-x}$EuFe$_4$As$_4$ specimen.

**C. Calculated magnetic moments and hyperfine interaction parameters**

The calculated magnetic moments of the Rb, Eu, Fe, As1, and As2 atoms in ferromagnetic RbEuFe$_4$As$_4$ are $-0.0038\mu_B$, 6.7095 $\mu_B$, 1.1037 $\mu_B$, $-0.0688\mu_B$, and $-0.0857\mu_B$, respectively. It is thus predicted that the magnetism of RbEuFe$_4$As$_4$
is associated predominantly with the Eu atoms and to a lesser extent with the Fe atoms. A comparison between the calculated and experimental magnetic moments carried by the Eu and Fe atoms will be made below.

$^{57}$Fe Mössbauer spectra of a nonmagnetic compound or of a magnetically ordered compound at temperatures above its ordering temperature yield two important hyperfine-interaction parameters: the quadrupole splitting (the separation between two resonance lines in an $^{57}$Fe Mössbauer quadrupole doublet) $\Delta = \frac{1}{2} e Q V_{zz} \sqrt{1 + \eta^2/3}$, where $Q$ is the electric quadrupole moment of the $^{57}$Fe nucleus (0.15 b) [14] and $\eta$ is the asymmetry parameter, and the isomer shift $\delta_0$ [5]. For a crystalline compound of known crystal structure, $V_{zz}$, $\eta$, and $\delta_0$ can also be obtained from $ab$ initio calculations [15].

The calculated values of $V_{zz}$ and $\eta$ at the 4$i$ site occupied by the Fe atoms (Table I) are $5.270 \times 10^{-20}$ V/m$^2$ and 0.8734, respectively. These values correspond to the predicted $\Delta = 0.0921$ mm/s.

The isomer shift $\delta_0 = \alpha(\rho(0) - \rho_{ref}(0))$ results from the difference in the total electron density at the Mössbauer nucleus in the compound studied, $\rho(0)$, and in the reference compound, $\rho_{ref}(0)$; $\alpha$ is a calibration constant. In calculating $\rho(0)$, relativistic spin-orbit effects were invoked to account for the possibility of the penetration of the $p_{1/2}$ electrons into the $^{57}$Fe nuclei. An $\alpha$-Fe metal (with a bcc structure and a lattice constant of 2.866 Å) was chosen as a reference compound. The calculated values of $\rho_{ref}(0)$ and $\rho(0)$ are 15309.905 and 15308.603 (a.u.)$^3$, respectively. Using the calibration constant $\alpha = -0.291$ (a.u.)$^3$ (mm/s) [16], the calculated values of $\rho(0)$ and $\rho_{ref}(0)$ lead to $\delta_0 = 0.379$ mm/s.

Finally, the calculated hyperfine magnetic field at 0 K (Fermi contact term) at $^{57}$Fe nuclei, $H_{hf}(0)$, is $-56.2$ kOe for ferromagnetic RbEuFe$_4$As$_4$. The Fermi contact term arises from a net spin-up and spin-down $s$-electron density at the nucleus as a result of spin polarization of inner filled $s$ shells by spin-polarized partially filled outer shells [5,17].

The analysis of the $^{151}$Eu Mössbauer spectra at different temperatures yields similar hyperfine-interaction parameters. The calculated values of $V_{zz}$ and $\eta$ at the $1a$ site occupied by the Eu atoms (Table I) are $-49.659 \times 10^{-20}$ V/m$^2$ and 0.0, respectively. The $\eta = 0.0$ value is expected as the point symmetry 4/mmm of the 1a sites ensures an axially symmetric EFG tensor. The calculated $H_{hf}(0)$ at $^{151}$Eu nuclei is 483 kOe for ferromagnetic RbEuFe$_4$As$_4$.

### D. $^{57}$Fe Mössbauer spectroscopy

$^{57}$Fe Mössbauer spectra of Rb$_{1-x}$EuFe$_4$As$_4$ at selected temperatures between room and liquid-helium temperatures were measured over a large velocity range (Fig. 4) in order to access the possibility of the presence of a Zeeman pattern resulting from a possible magnetic ordering of the Fe atoms in Rb$_{1-x}$EuFe$_4$As$_4$ and of a Zeeman pattern due to a magnetically ordered and Fe-containing impurity phase in the sample studied. A visual inspection of these spectra shows the absence of Zeeman patterns corresponding to the main and impurity phases with typical values of the hyperfine magnetic field $H_{hf}$. As will be shown in detail below, the large-spectral-area component of these spectra (Fig. 4) is due to Rb$_{1-x}$EuFe$_4$As$_4$ and is in the form of a quadrupole doublet with small $\Delta$ at 295.3, 191.0, and 77.9 K and a Zeeman pattern at 4.3 K.

Figure 4 shows the Mössbauer spectra of Rb$_{1-x}$EuFe$_4$As$_4$ at various temperatures down to the liquid-nitrogen temperature measured over a small velocity range. A feature on the right shoulder of the spectra indicates the presence of an impurity phase in the compound studied. Excellent fits of the spectra can be obtained with a large-spectral-area quadrupole doublet component with small $\Delta$ that originates from Rb$_{1-x}$EuFe$_4$As$_4$ and with a small-spectral-area quadrupole doublet component due to the FeAs impurity phase [18–20]. The spectral weight of the latter component, which is proportional to the product of the number of Fe atoms in the FeAs impurity and the Debye-Waller factor of the impurity, is $18(1)$% and is larger than that expected from the amount of 3.1(4) wt% of the FeAs impurity derived from the x-ray diffraction spectrum.
A feature on the right shoulder of the spectra at temperatures below the liquid-nitrogen temperature (Fig. 6) disappears because the FeAs impurity component in these Mössbauer spectra is in the form of a complex Zeeman pattern. This indicates that the magnetic ordering temperature of the impurity phase lies in the range 77.7–50.9 K (Figs. 5 and 6). This agrees with the reported Néel temperature of FeAs (77(1) K in Ref. [13] and 69.2(1) K in Ref. [20]).

The temperature dependence of $\Delta$ obtained from the fits of the spectra in Figs. 5 and 6 is shown in Fig. 7(a). A small increase in $\Delta$ with decreasing temperature is observed. Such a temperature dependence of $\Delta$ has been observed in many metallic systems. It is well described by the empirical equation

$$\Delta(T) = \Delta(0)(1 - BT^{3/2}),$$  \hspace{1cm} (1)

where $\Delta(0)$ is the value of $\Delta$ at 0 K and $B$ is a constant. The fit of the $\Delta(T)$ data [Fig. 7(a)] to Eq. (1) gives $\Delta(0) = 0.1188(2)$ mm/s and $B = 10.1(8) \times 10^{-6}$ K$^{-3/2}$. The value of $B$ is similar to that found for a wide variety of other compounds, such as the ThFeAsN superconductor [21], crystalline approximants Al$_{76}$Ni$_9$Fe$_{15}$ [22] and Al$_{13}$Fe$_4$ [23] to quasicrystals, icosahedral Al$_{60}$Cr$_{19.9}$Fe$_{0.1}$Ge$_{20}$ [24] and decagonal Al$_{70}$Co$_{15}$Ni$_{14}$Fe$_{0.1}$ [25] quasicrystals, and amorphous Zr$_{65}$Al$_{11}$Ni$_{10}$Cu$_{7}$Fe$_{0.2}$Ag$_{0.5}$ [26]. The value of $\Delta(0)$ is close to the calculated value of 0.0921 mm/s.

The Mössbauer spectra of Rb$_{1-x}$EuFe$_4$As$_4$ at 20.2 and 16.4 K are compared in Fig. 7(b). One observes that the 16.4 K spectrum is slightly, but visibly, broader than the 20.2 K spectrum. This 0.014 mm/s broadening [Fig. 7(b)] over a very narrow temperature range of 3.8 K is the consequence of the appearance at 16.4 K of a very small $H_{hf}$. We surmise that this $H_{hf}$ is transferred to the $^{57}$Fe nuclei from the ferromagnetically ordered Eu sublattice (see below). A transferred hyperfine magnetic field at a given Mössbauer nucleus results from the neighboring magnetic moments [27]. It should be stressed that this transferred hyperfine magnetic field does not result from the ordering of the Fe sublattice. Its presence constitutes direct evidence of the ordering of the Eu sublattice. Such a transferred hyperfine magnetic field at a single temperature was observed first in the EuFe$_2$(As$_{1-x}$P$_x$)$_2$ superconductors [28]. Thus, the Mössbauer spectra at 16.4 K and lower temperatures were fitted (Fig. 8) with a large-spectral-area Zeeman pattern component [the value of $\Delta$ was fixed in the fit to that obtained from the fit of the $\Delta(T)$ dependence in Fig. 7(a)] that originates from Rb$_{1-x}$EuFe$_4$As$_4$ and with a small-spectral-area Zeeman pattern component that is due to the FeAs impurity phase.

Figure 9 displays the temperature dependence of the transferred $H_{hf}$ that was derived from the fits of the spectra in Fig. 8.
As expected, $H_{hf}$ increases with decreasing temperature. The $H_{hf}(T)$ dependence was fitted using the phenomenological form [29]

$$H_{hf}(T) = H_{hf}(0) \left[ 1 - \left( \frac{T}{T_C} \right)^\alpha \right]^\beta,$$

(2)

where $H_{hf}(0)$ is the value of $H_{hf}$ at 0 K and $\alpha$ and $\beta$ are exponents describing the behavior of $H_{hf}(T)$ near 0 K and $T_C$, respectively. The fit yields $H_{hf}(0) = 6.17(2)$ kOe, $T_C = 16.63(16)$ K, $\alpha = 1.96(10)$, and $\beta = 0.21(2)$. The values of $\alpha$ and $\beta$ found here are comparable to those obtained for other compounds [30–32].

The calculations predict a nonzero, but small, value of $|H_{hf}(0)|$ at the $^{57}$Fe nuclei and of the magnetic moment carried by the Fe atoms $\mu_{Fe}$ (see above). This is at odds with the experimentally observed zero value of the intrinsic, i.e., not transferred, $H_{hf}$ down to 2.1 K and, consequently, the zero value of $\mu_{Fe}$. The failure of theory in predicting the zero values...
of $H_{hf}$ and $\mu_{Fe}$ may be related to the inherent limitations of standard density functional theory, especially as applied to the strongly correlated systems or the $d$- or $f$-electron compounds with localized electrons [33].

The temperature dependence of the center shift $\delta$ that was obtained from the fits of the spectra in Figs. 5, 6, and 8, is shown in Fig. 7(c). The center shift at temperature $T$, $\delta(T)$, consists of two terms, $\delta(T) = \delta_0 + \delta_{SOD}(T)$, where $\delta_0$ is the intrinsic, temperature-independent isomer shift and $\delta_{SOD}(T)$ is the second-order Doppler (SOD) shift. The latter is the function of the Debye temperature $\Theta_D$ [5]. The fit of the experimental data $\delta(T)$ [Fig. 7(c)] gives $\delta_0 = 0.494(2)$ mm/s and $\Theta_D = 391(8)$ K. We note that the experimental value of $\delta_0$ found here is 30% larger than the calculated $\delta_0$.

### E. $^{151}$Eu Mössbauer spectroscopy

The $^{151}$Eu Mössbauer spectra of Rb$_{1-x}$EuFe$_4$As$_4$ at temperatures between room and liquid-helium temperatures are shown in Fig. 10. The spectra in the paramagnetic temperature region (left column in Fig. 10) consist of a large-spectral-area quadrupole component in the form of an unresolved quadrupole octet [5,34] that originates from Eu$^{3+}$ ions in Rb$_{1-x}$EuFe$_4$As$_4$ and a small-spectral-area component in the form of a single line due to Eu$^{2+}$ ions in the Eu$_2$O$_3$ impurity phase. The spectral weight of the latter component is 22(1)% and is larger than that expected from the amount of 0.7(2) wt% of the Eu$_2$O$_3$ impurity derived from the Rietveld refinement of the x-ray diffraction spectrum. The Eu atoms in Rb$_{1-x}$EuFe$_4$As$_4$ are located at the 1$a$ site with the point symmetry $4/mmm$ (Table I), which ensures an axially symmetric ($\eta = 0$) EFG tensor at this site. Also, $V_{zz}$ is parallel to the $c$ axis. The temperature dependence of $V_{zz}$ derived from the fits of the spectra in the paramagnetic temperature region is shown in Fig. 11. Similar to the $(\Delta T)$ dependence in Fig. 7(a), the magnitude of $V_{zz}$ increases with decreasing temperature. The $V_{zz}(T)$ data can be fitted to the same empirical $T^{3/2}$ power-law relation [Eq. (1)] in which $(\Delta T)$ and $(\Delta 0)$ are replaced with $V_{zz}(T)$ and $V_{zz}(0)$, respectively. The fit of the $V_{zz}(T)$ data (Fig. 11) yields $V_{zz}(0) = -0.470(6) \times 10^{22}$ V/m$^2$ and $B = 2.66(42) \times 10^{-5}$ K$^{-3/2}$. The experimental value of $V_{zz}(0)$ compares very well with the calculated value of $-0.497 \times 10^{22}$ V/m$^2$.

The spectra in the magnetic temperature region (right column in Fig. 10) were fitted with a large-spectral-area Zeeman pattern component that originates from Rb$_{1-x}$EuFe$_4$As$_4$ and a small-spectral-area single-line component due to an impurity phase. The value of $V_{zz}$ was fixed in the fit to that obtained from the fit of the $V_{zz}(T)$ dependence in Fig. 10. The temperature dependence of $H_{hf}$ determined from the fits of these Mössbauer spectra is shown in Fig. 12(a). It is usually assumed that the temperature variation of $H_{hf}$ in a magnetically ordered material can be reasonably explained within the framework of the molecular field model, assuming that $H_{hf}$ is proportional to the sublattice magnetization. In terms of this model, $H_{hf}(T)$ can be expressed as

$$H_{hf}(T) = H_{hf}(0)B_J(x),$$

where $H_{hf}(0)$ is the saturation hyperfine magnetic field; $B_J(x)$ is the Brillouin function, defined as

$$B_J(x) = \frac{2J + 1}{2J} \coth \left( \frac{2J + 1}{2J} x \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right).$$
explained in the text. The solid line in (a) is the fit to Eq. (3), as determined from the fits of the spectra in Fig. 10 (right column). The previous demonstration of the Eu-spin ferromagnetism in EuFe₂As₂ systems where the Eu magnetic moments are basically along the c axis [38,39,40,41].

Indeed, the Eu-spin ferromagnetic polarization gives rise to an internal magnetic field of 4.5 kOe, which is close to the value of $H_{hf}(0)$. This phenomenon calls for a theoretical explanation.

FIG. 12. Temperature dependence of (a) the hyperfine magnetic field $H_{hf}$ and (b) the angle $\beta$ determined from the fits of the spectra in Fig. 10 (right column). The solid line in (a) is the fit to Eq. (3), as explained in the text.

The fit of the $H_{hf}(T)$ data [Fig. 12(a)] to Eq. (3) with $J = S = 7/2$ (corresponding to a free Eu$^{3+}$ ion) yields $H_{hf}(0) = 257.4(4.3)$ kOe and $T_C = 16.51(10)$ K. The $T_C$ found here is very close to the value of 16.63(16) K derived from the temperature dependence of the transferred $H_{hf}$ at $^{57}$Fe nuclei. We take a weighted average of these two $T_C$ values, 16.54(8) K, as the $T_C$ of the studied superconductor. The experimental value of $H_{hf}(0)$ is significantly smaller than the calculated Fermi contact value of 483 kOe. This discrepancy can be explained by the fact that the measured hyperfine magnetic field at the $^{151}$Eu nuclei is divided into three equally important contributions: $H_{hf} = H_c + H_{hf} + H_{op}$. Here $H_c$ is the core-polarization field (the Fermi contact term), $H_{hf}$ is due to conduction-electron polarization by the ion itself, and $H_{op}$ includes all contributions from neighboring magnetic ions [35]. Clearly, the latter two contributions when added to the Fermi contact term must account for the measured $H_{hf}(0)$. Often, the $H_{op}$ contribution has a sign opposite to that of the $H_c$ contribution [34,35].

For $^{151}$Eu Mössbauer spectroscopy [34,35], as opposed to $^{57}$Fe Mössbauer spectroscopy [36], there is no simple relation between the measured $H_{hf}(0)$ and the magnetic moment carried by Eu atoms. We note here that the calculated Eu magnetic moment of 6.7095$\mu_B$ is slightly larger than the experimental moment of 6.0$\mu_B$ at 2 K [Fig. 3(b)].

The temperature dependence of the angle $\beta$ (the angle between $V_{zz}$ and $H_{hf}$) determined from the fits of the spectra in the magnetic temperature region (right column in Fig. 10) is shown in Fig. 12(b). One observes that the $\beta$ values are close to 90°. This constitutes experimental proof that the Eu magnetic moments are perpendicular to the crystallographic c axis, that is, that they lie in the ab plane.

F. Discussion summary

A previous study concluded that RbEuFe₄As₄ bears both superconductivity and Eu-spin ferromagnetism but without any information about the Eu-spin direction [3]. Here, using the local-probe technique of Mössbauer spectroscopy, we have demonstrated that the Eu magnetic moments lie within the ab plane, akin to the case of nondoped EuFe₂As₂ in which an A-type antiferromagnetic (i.e., in-plane ferromagnetic but interplane antiferromagnetic) ordering occurs at 19 K [37–39]. Since RbEuFe₄As₄ can be viewed as a modified EuFe₂As₂ in which every other Eu layer is replaced by a Rb layer [Fig. 2(b)], one naturally expects that the Eu-layer spins in RbEuFe₄As₄ will become ferromagnetically ordered. Furthermore, the Eu spins are likely to be in the same direction as the Eu spins in EuFe₂As₂, i.e., along the crystallographic [110] direction [38,39]. We note that the Eu-spin direction in RbEuFe₄As₄ is in sharp contrast to the corresponding direction in doped EuFe₂As₂ systems where the Eu magnetic moments are basically along the c axis [28,40,41].

IV. CONCLUSIONS

We presented the results of ab initio hyperfine-interaction parameters calculations and of x-ray diffraction and $^{57}$Fe and $^{151}$Eu Mössbauer spectroscopy study of the new 35.5 K superconductor Rb₁₋₄EuFe₄As₄. We confirmed that the superconductor crystallizes in the tetragonal space group $P4/mnm$ with the lattice parameters $a = 3.8847(1)$ Å and $c = 13.3370(3)$ Å. We showed that the Fe atoms carry no magnetic moment down to 2.1 K and that the ferromagnetic order is associated with the Eu magnetic moments. The Curie temperature $T_C = 16.54(8)$ K is determined from the temperature dependence of both the hyperfine magnetic field at $^{151}$Eu nuclei and the transferred hyperfine magnetic field at $^{57}$Fe nuclei that is induced by the ferromagnetically ordered Eu sublattice. We found that the Eu magnetic moments lie in the ab plane. We observed that the temperature dependence of the principal component of the electric-field-gradient tensor is well described by a $T^{3/2}$ power-law relation at both the Fe and Eu sites. Good agreement was found between the calculated and measured hyperfine-interaction parameters. We determined that the Debye temperature of Rb₁₋₄EuFe₄As₄ is 391(8) K.
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