Strong coupling between Eu\(^{2+}\) spins and Fe\(_2\)As\(_2\) layers in EuFe\(_{1.9}\)Co\(_{0.1}\)As\(_2\) observed with NMR

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A combination of x-ray diffraction, magnetization, and \(^{75}\)As nuclear magnetic resonance (NMR) experiments were performed on single-crystal EuFe\(_{1.9}\)Co\(_{0.1}\)As\(_2\). The strength of the hyperfine interaction between the \(^{75}\)As nuclei and the Eu\(^{2+}\) \(4f\) states suggests a strong coupling between the Eu\(^{2+}\) moments and the Fe\(_1\)Co\(_{0.1}\)As\(_2\) layers. Such a strong interlayer coupling may be due to an indirect exchange interaction between the localized Eu\(^{2+}\) \(4f\) moments, mediated by the Fe \(3d\) conduction electrons. Magnetic susceptibility as well as \(^{75}\)As-NMR measurements reveal a decrease of the SDW transition temperature to \(T_{\text{SDW}} = 120\,\text{K}\) as a result of Co doping. A change of the slope in the temperature dependence of the NMR frequency of the \(^{75}\)As lower-satellite line was observed at 225 K. At the same temperature also a change of the satellite line shape was found. These changes of the NMR spectra may be caused by the formation of a nematic phase below 225 K in EuFe\(_{1.9}\)Co\(_{0.1}\)As\(_2\).

I. INTRODUCTION

The discovery of superconductivity in iron-based arsenides at temperatures up to 56 K\(^1\)\(^7\) has triggered extensive interest in their physical properties and the underlying mechanism of high-temperature superconductivity. The undoped parent compounds adopt a tetragonal structural state at room temperature, which consists of [Fe\(_2\)As\(_2\)]\(^2+\) layers separated by \([Ln_2O_2]\)\(^2+\) \((Ln = \text{lanthanoid})\) layers\(^8,9\) or \(A^2+\) \((A = \text{Ca, Sr, Ba, Eu})\) layers.\(^10,13\) At low temperatures, the parent compounds undergo a structural phase transition from a tetragonal to an orthorhombic phase, accompanied\(^14\) or followed\(^13\) by a spin density wave (SDW) transition of the itinerant Fe moments. The superconducting (SC) state can be achieved either by electron or by hole doping of the parent compounds, leading to a suppression of the SDW formation.\(^6,16–18\) The suppression of the magnetic transition in connection with the simultaneous formation of a SC state is reminiscent of cuprates and heavy fermion systems, therefore suggesting that the SC state in these systems is unconventional as well.

EuFe\(_2\)As\(_2\) is a particularly interesting member of the iron arsenide AFe\(_2\)As\(_2\) (‘122’) family, since the A site is occupied by a Eu\(^{2+}\) \(S\)-state (orbital moment \(L = 0\)) rare-earth ion with a \(4f^7\) electronic configuration with a total electron spin \(S = 7/2\), corresponding to a theoretical effective magnetic moment of 7.94 \(\mu_B\). Figure 1 shows the crystal structure of EuFe\(_2\)As\(_2\). This compound is built up by [FeAs\(_2\)]\(^−\) layers, separated by layers of magnetic Eu\(^{2+}\) ions. EuFe\(_2\)As\(_2\) exhibits both a SDW ordering of the Fe moments and an antiferromagnetic ordering of the localized Eu\(^{2+}\) moments below 190 K and 19 K, respectively. The presence of magnetic phase transitions at 19 K and 190 K in EuFe\(_2\)As\(_2\) was seen by Mössbauer spectroscopy\(^19\) and is confirmed by neutron diffraction.\(^20\) In contrast to the other ‘122’ systems, where the substitution of Fe by Co leads to superconductivity,\(^21,22\) the compounds containing Eu\(^{2+}\) exhibit the onset of a superconducting transition but seem to be hindered to reach zero resistivity at ambient pressure.\(^23\) Reentrant superconducting behavior was also observed in a EuFe\(_2\)As\(_2\) crystal under applied pressure up to 2.5 GPa.\(^24,25\) Only above 2.8 GPa a sharp resistive transition to a zero-resistivity state is achieved.\(^25\)

Bulk superconductivity is also observed in EuFe\(_{2-x}\)Ni\(_x\)As\(_2\). No superconductivity was detected in EuFe\(_{2-x}\)Ni\(_x\)As\(_2\) where isovalent P substitution of the As site acts as chemical pressure on EuFe\(_2\)As\(_2\). Only above 2.8 GPa a sharp resistive transition to a zero-resistivity state is achieved.\(^25\)

In order to investigate the coupling between the Eu and Fe\(_1\)Co\(_{0.1}\)As\(_2\) layers as well as to study the magnetic transitions in EuFe\(_{1.9}\)Co\(_{0.1}\)As\(_2\), a combination of x-ray diffraction, magnetization, and \(^{75}\)As nuclear magnetic resonance (NMR) experiments were performed on single crystals. Magnetic susceptibility as well as \(^{75}\)As-NMR measurements reveal a decrease of the SDW transition temperature to \(T_{\text{SDW}} = 120\,\text{K}\) for EuFe\(_{1.9}\)Co\(_{0.1}\)As\(_2\). It was found that the \(^{75}\)As NMR spectra are characterized by a negative frequency shift with respect to the \(^{75}\)As-NMR Larmor frequency. This shift is significantly larger than the one observed in BaFe\(_{2-x}\)Ni\(_x\)As\(_2\). \(^{30–32}\) The temperature dependence of the shift follows a Curie-Weiss type behavior with a Curie-Weiss temperature close to the one determined from the magnetization data. The estimate of the hyperfine coupling constant between the Eu\(^{2+}\) nuclei and the Eu \(4f\) states suggests a strong coupling between the Eu\(^{2+}\) magnetic moments and the Fe\(_1\)Co\(_{0.1}\)As\(_2\) layers.

II. EXPERIMENTAL DETAILS

Single crystals of EuFe\(_{1.9}\)Co\(_{0.1}\)As\(_2\) were grown out of Sn flux. The chemical composition of the single crystals was determined on freshly cleaved samples using...
TABLE I. Crystallographic and structure refinement parameters of the single crystal EuFe$_{1.9}$Co$_{0.1}$As$_2$. The diffraction study was performed at 295(2) K using MoK$_\alpha$ radiation with $\lambda = 0.71073$ Å. The lattice is tetragonal, $I4/mmm$ space group with $Z = 2$, atomic coordinates: Eu on 2a (0, 0, 0), Fe/Co on 4d (0, 1/2, 1/4), As on 4e (0, 0, $z_{\text{As}}$). A full-matrix least-squares method was employed to optimize $F^2$.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Empirical formula</td>
<td>EuFe$<em>{1.9}$Co$</em>{0.1}$As$_2$</td>
</tr>
<tr>
<td>Unit cell dimensions (Å)</td>
<td>$a = 3.9104(1)$</td>
</tr>
<tr>
<td></td>
<td>$c = 11.9434(3)$</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>182.629(8)</td>
</tr>
<tr>
<td>$z_{\text{As}}$ (atomic coordinate)</td>
<td>0.6388(1)</td>
</tr>
<tr>
<td>$R_{\text{int}}$ (Å)</td>
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</tr>
<tr>
<td>Calculated density (g/cm$^3$)</td>
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<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
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<td>Absorption correction type</td>
<td>Numerical</td>
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<tr>
<td>$F(000)$</td>
<td>362</td>
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<tr>
<td>Crystal size (µm$^3$)</td>
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</tr>
<tr>
<td>Theta range for data collection (deg)</td>
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</tr>
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<td></td>
<td>$-5 \leq k \leq 7$</td>
</tr>
<tr>
<td></td>
<td>$-22 \leq l \leq 17$</td>
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<tr>
<td>Reflections collected/unique</td>
<td>884/243 $R_{\text{int}} = 0.0463$</td>
</tr>
<tr>
<td>Completeness to 2θ</td>
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<tr>
<td>Data/restraints/parameters</td>
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<td>Goodness-of-fit on $F^2$</td>
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<tr>
<td>Final R indices [$I &gt; 2\sigma(I)$]</td>
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<td></td>
<td>$wR_2 = 0.1020$</td>
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<tr>
<td>R indices (all data)</td>
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<td></td>
<td>$wR_2 = 0.1039$</td>
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<tr>
<td>$\Delta\rho_{\text{max}}$ (e/Å$^3$)</td>
<td>4.538 and $-3.776$</td>
</tr>
</tbody>
</table>

$F_0^2$ with eight variables converged at $R_1 = 2.70\%$. Further details of the structure refinement are shown in Table I. No additional phases (impurities, twins, or intergrowing crystals) were detected by examination of the reconstructed reciprocal space sections measured at room temperature (Fig. 2). In the Co-substituted crystal the room-temperature lattice parameter $c$ is reduced and the lattice parameter $a$ is increased relative to the Eu$_{1.9}$Co$_{0.1}$As$_2$.

III. RESULTS AND DISCUSSION

A. Single crystal x-ray diffraction

X-ray diffraction experiments at room temperature revealed a good quality of the EuFe$_{1.9}$Co$_{0.1}$As$_2$ crystal. The average mosaic spread was estimated to be $\simeq 0.9^\circ$. The lattice constants for the tetragonal unit cell based upon the refinement of 689 reflections are $a = b = 3.9104(1)$ Å, $c = 11.9434(3)$ Å, $V = 182.629(8)$ Å$^3$. The average residual for symmetry equivalent reflections is $R_{\text{int}} = 4.63\%$ and $R_e = 4.01\%$. The structure was solved with XS$^{39}$ and subsequent structure refinements were performed with XL.$^{40}$ Because of the almost equal number of electrons, Co and Fe atoms were considered as one atom. The final anisotropic full-matrix least-squares refinement on $F_0^2$ with eight variables converged at $R_1 = 2.70\%$. Further details of the structure refinement are shown in Table I. No additional phases (impurities, twins, or intergrowing crystals) were detected by examination of the reconstructed reciprocal space sections measured at room temperature (Fig. 2). In the Co-substituted crystal the room-temperature lattice parameter $c$ is reduced and the lattice parameter $a$ is increased relative to the Eu$_{1.9}$Co$_{0.1}$As$_2$.

FIG. 2. The reconstructed $hk0$ reciprocal space section of the single crystal EuFe$_{1.9}$Co$_{0.1}$As$_2$. 

FIG. 1. (Color online) Tetragonal crystal structure of EuFe$_2$As$_2$ at room temperature, consisting of [Fe$_2$As$_2$]$^{2-}$ layers separated by Eu$^{2+}$ layers.
Here $C$ denotes the Curie-Weiss constant, and $\Theta$ the Weiss temperature. Analyzing the data with Eq. (1) in the temperature range from 30 K to 120 K yields $C = 2.43(5) \times 10^{-4}$ m$^3$ K/mol and $\Theta = -21.34(7)$ K. The Curie-Weiss $C$ constant corresponds to an effective magnetic moment of $\mu_{\text{eff}} = 8.7 \mu_B$, which is slightly larger than the theoretical value of the magnetic moment of a free Eu$^{2+}$ ion ($\mu_{\text{free}} = 7.94 \mu_B$). The negative value of $\Theta$ infers that the interaction between the Eu$^{2+}$ moments is ferromagnetic. Therefore, one can expect that the intralayer arrangement of the Eu$^{2+}$ spins is ferromagnetic as in the parent compound EuFe$_2$As$_2$. A clear drop in the susceptibility at the SDW transition temperature was observed in BaFe$_2$As$_2$. In the case of EuFe$_2$As$_2$ the large signal from the Eu$^{2+}$ spins makes it impossible to directly observe the SDW anomaly. However, after subtracting the Curie-Weiss contribution $\chi_{\perp \text{CW}}(T)$ from $\chi_{\perp}(T)$, a small anomaly in $\chi_{\perp \text{res}}(T) = \chi_{\perp}(T) - \chi_{\perp \text{CW}}(T)$ is visible at around 120 K (Fig. 3(b)). This behavior resembles that observed in EuFe$_2$As$_2$ and BaFe$_2$As$_2$ which was ascribed to the SDW transition of the Fe moments.

C. Nuclear magnetic resonance

In this section we present $^{75}$As nuclear magnetic resonance (NMR) studies in single crystal EuFe$_{1.0}$Co$_{0.1}$As$_2$. NMR is a powerful and extremely sensitive microscopic tool to probe both, magnetism and the local structure in a solid. $^{75}$As has a large quadrupolar moment ($Q = 0.3$ b) that interacts with the local electric field gradient (EFG) in the crystal. The nuclear spin Hamiltonian describing the interactions of the investigated nucleus with the external magnetic field and the crystal electric field gradient at the nuclear site is given by the expression

$$H = \gamma h (1 + K_\alpha) I_\alpha H_0 + \frac{h v_Q}{2(2I_z^2 - 1) + \eta(I_z^2 - I_x^2)} [I_x^2 - I_y^2]$$

(2)

Here $K_\alpha$ ($\alpha = x, y, z$) is the relative magnetic shift in the $\alpha$ direction, $I_\alpha$ are the nuclear spin components, $H_0$ is the external magnetic field, $\gamma$ is the gyromagnetic ratio, and $v_Q$ is defined as

$$v_Q = \frac{3 e Q V_{zz}}{2(2I_z^2 - 1)}$$

(3)

where $V_{zz}$ denotes the major principal axis of the EFG tensor, and $\eta$ the EFG asymmetry parameter defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$ ($0 < \eta < 1$). We use the standard convention $V_{xx} < V_{yy} < V_{zz}$ since the principal axis of the EFG tensor as well as the magnetic shift tensor are defined by the symmetry of the nuclear site, the resonance frequency of a particular nuclear transition depends on the field direction relative to the crystalline axes.

In the absence of a static magnetic field, the remaining term gives rise to double degenerate energy levels, between which nuclear quadrupole resonance (NQR) transitions can be induced. $^{75}$As has a nuclear spin $I = \frac{5}{2}$ and thus two double degenerate $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$ energy levels. In the presence of a large external magnetic field $H_0$ a splitting of the $^{75}$As spectrum into a central line, arising from the central transition $(\frac{3}{2}, -\frac{1}{2})$ and two satellite lines due to the $(\pm \frac{3}{2}, \pm \frac{3}{2})$ transitions occurs. A representative $^{75}$As NMR spectrum of the central transition at 295 K is shown in the inset of Fig. 4. In the paramagnetic state...
the diagonalization of the Hamiltonian \[\text{Eq. (2)}\] yields angular dependence of the frequency of the central line. Using the inset illustrates the $^{75}$As NMR central line shape at 295 K. The squares represent the calculated frequencies as described in the text. The solid line represents a Gaussian fit.

The $^{75}$As nuclei interact with the localized Eu-4$f$ moments. A similar behavior across the SDW transition was also reported for spin-lattice relaxation measurements in AFes$_2$As$_2$ (A = Ba, Ca, Sr). However, in contrast to these findings, in our case $1/T_2$ increases again upon further cooling. This increase reflects the dominant Eu$^{2+}$ contribution in the spin-spin relaxation process. The SDW transition below 120 K is also reflected in the temperature dependence of the central line intensity with decreasing the temperature across the SDW transition. The temperature dependence of the wipeout fraction, defined as $F = [A_1(295 \text{ K}) - A_1(T)]/A_1(295 \text{ K})$ is displayed in the inset of Fig. 5(b). The wipeout fraction is a measure for an unobserved signal intensity, and the dashed line is to guide to the eye. (b) Temperature dependence of the central line frequency is fully determined by the temperature behavior of $K$. In Fig. 6(a)
we present the temperature dependence of the shift \( K \) in the temperature range from 100 and 300 K for \( H \parallel c \) and \( H \perp c \). Compared to the magnetic shift data for AFe\(_2\)As\(_2\) (A = Ba, Ca, Sr),\(^{33–36}\) our observed shifts are significantly larger, negative, and show a completely different temperature dependence. The temperature dependence of the relative magnetic shift \( K \) above 117 K is well described by a Curie-Weiss behavior:

\[
K(T) = K_0 + \frac{C_K}{T + \Theta}.
\]

The inset of Fig. 6(a) presents the inverse of the temperature dependent part of the shift for \( H \perp c \) as a function of temperature. Below the SDW transition \( T_{\text{SDW}} = 120 \) K the data deviates from the Curie-Weiss behavior. This deviation can be understood when considering that above \( T_{\text{SDW}} \) both the Eu and Fe sublattices are in the paramagnetic state, and both contribute to the shift, while below \( T_{\text{SDW}} \) only the Eu\(^{2+}\) moments contribute. An analysis of the data for \( H \perp c \) using Eq. (4) yields \( \Theta = -18.9(9) \) K, \( K_0 = 0.17(25)\%. \) The value of \( \Theta \) is in fair agreement with the value \( \Theta = -21.34(7) \) K determined from the magnetic susceptibility measurements.

This suggests that the Curie-Weiss part of the shift arises from the hyperfine coupling between the \( ^{75}\)As nuclei and the Eu\(^{2+}\) moments. The remaining constant part of the shift \( K_0 \) could be related to the coupling of \( ^{75}\)As with the itinerant 3d electrons in the Fe\(_2\)As\(_2\) layer, including an orbital shift. However, the value of \( K_0 \) is a factor two smaller than the total \( ^{75}\)As magnetic shift reported for BaFe\(_{1.8}\)Co\(_{0.2}\)As\(_2\).\(^{36}\) The contribution of Eu to the magnetic shift \( K_{\text{Eu}} \) can be related to the susceptibility \( \chi_{\text{Eu}} \) of the localized Eu 4f moments as follows:

\[
K_{\text{Eu}} = \frac{A_{\text{Eu}}}{g N_A \mu_B} \chi_{\text{Eu}},
\]

where \( A_{\text{Eu}} \) is the \( ^{75}\)As hyperfine coupling constant with the 4f moments, \( N_A \) and \( \mu_B \) are the Avogadro number and Bohr magneton, respectively. Figure 6(b) shows \( K_{\perp} \) vs. \( \chi_{\perp} \) as obtained from the susceptibility measurements. The solid line is a linear fit.
the temperature dependence of the satellite line frequency can be seen at 225 K as shown in Fig. 7(a). The inset of Fig. 7(a) illustrates a typical $^{75}$As-NMR spectrum of the low-frequency satellite at 263 K. The spectra exhibit an asymmetric lineshape in the investigated temperature range. We analyzed the asymmetry of the satellite line shape at different temperatures by calculating its skewness (see Fig. 7(b)), defined as the asymmetry of the satellite line shape at different temperatures. We analyzed the skewness at 263 K. The spectra exhibit an asymmetric lineshape.

In order to get more quantitative NMR results for a possible nematic phase, the angular dependence of the full $^{75}$As NMR spectrum (central line and both satellite lines) was measured at 181 K. The dominant contribution to the magnetic shift stems from the Eu$^{2+}$ 4$f$ moments (see above), and it is acceptable to assume that this contribution does not have a strong $ab$ anisotropy. Therefore, we reduced the parameter set to $K_{z} = K_{y} = K_{ab}$, $K_{c}$, $\nu_{Q}$, and $\eta$. Analysis of the angular dependence of the full spectrum using the diagonalization of the Hamiltonian [Eq. (2)] yields $K_{ab} = -0.059(1)$, $K_{c} = 0.069(2)$, $\nu_{Q} = 7.51(17)$ MHz, and $\eta = 0.044(3)$. The change in $\nu_{Q}$ compared to the value $\nu_{Q} = 7.39(24)$ MHz obtained at 261 K in the tetragonal phase is small. The slight increase of $\eta$ may reflect the lower symmetry of the As site in a possible nematic phase. However, further experiments are needed to clarify the presence of a nematic phase in EuFe$_{1.9}$Co$_{0.1}$As$_{2}$. Resistivity measurements on detwinned$^{39}$ single crystals could provide more information by probing the in-plane electronic anisotropy.

**IV. SUMMARY AND CONCLUSIONS**

In summary, the magnetic properties of a EuFe$_{1.9}$Co$_{0.1}$As$_{2}$ single crystal were investigated by x-ray diffraction, magnetization, and $^{75}$As NMR experiments. It was found that the temperature dependence of the $^{75}$As magnetic shift as well as the spin-spin relaxation rate follow a Curie-Weiss type behavior, implying that the $^{75}$As nuclei interact with the localized Eu 4$f$ moments in the Eu layer. A large value of the hyperfine coupling constant between the $^{75}$As nuclei and the Eu 4$f$ moments suggests a strong coupling between the Eu and Fe$_{1.9}$Co$_{0.1}$As$_{2}$ layers. Due to such a strong interlayer coupling the antiferromagnetic interaction between the localized Eu$^{2+}$ 4$f$ moments is probably mediated by a Ruderman-Kittel-Kasuya-Yosida (RKKY) type interaction. Evidence for a SDW transition at 120 K was obtained from magnetic susceptibility as well as from $^{75}$As-NMR measurements. A change of the slope in the temperature dependence of the frequency of the $^{75}$As lower-satellite line is observed at 225 K. In addition, at the same temperature also a maximum in the temperature behavior of the skewness is detected. These findings may indicate a phase transition to an electron nematic state below 225 K.

**ACKNOWLEDGMENTS**

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37. APEX2 version 2009.9 (Bruker AXS Inc., 2009).

38. SAINT version 7.68A (Bruker AXS Inc., 2009).


