ORDER, DISORDER, AND PHASE TRANSITION
IN CONDENSED SYSTEM

Gd$^{3+}$ Electron Spin Resonance Spectroscopy
on LaO$_{1-x}$F$_x$FeAs Superconductors$^1$

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Abstract—We report an electron spin resonance (ESR) spectroscopy study on polycrystalline samples of the
LaO$_{1-x}$F$_x$FeAs ($x = 0$ and 0.1) compound with small levels of Gd doping (2% and 5%). The Gd ESR signal
is found to be sensitive to the magnetic phase transition from the paramagnetic to the spin density wave
(SDW) state occurring in the parent LaO$_{1-x}$F$_x$FeAs compounds at $T_{SDW} \approx 130$ K. Interestingly, the analysis
of the low-temperature ESR spectra of the c-axis oriented Gd$_{1-x}$La$_x$OFeAs samples gives evidence for the
magnetically nonequivalent Gd sites and also for sites having a different local charge environment. The analysis
of the temperature dependence of the ESR linewidths gives evidence for a coupling of the localized 4$f$
electrons of Gd to the conduction electrons in the FeAs layers. The ESR data reveal that the fluorine substi-
tution, which provides electron doping, suppresses the SDW order and enhances the density of states in the
electronic bands stemming from the $xz$ and $yz$ orbital states of Fe to which the 4$f$ electrons are most strongly
coupled.

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1. INTRODUCTION

Superconductivity discovered in Fe pnictides [1] in
2008 has attracted a huge interest to these materials.
There are several families of Fe pnictides that all have
a common structural element: namely the FeAs layers
that are responsible for superconductivity. These layers
are sandwiched along the crystallographic $c$-axis by
single-atom layers of Ba, Eu, Ca, etc. (the 122 family,
e.g., BaFe$_2$As$_2$), layers of Li, such as in LiFeAs (the 111
family), or by double atom RO layers in ROFeAs (the
1111 family). Here, $R$ is a rare earth element. In this
paper, we focus on a representative of the 1111–type
family, LaO$_{1-x}$F$_x$FeAs. Electron doping in 1111 com-
ounds is achieved by partial substitution of fluorine
for oxygen. The parent, undoped compounds are
semimetallic and exhibit a magnetic phase transition
at a temperature $T_{SDW}$ in the range 120–140 K
depending on the $R$ element [2–7]. Mössbauer spec-
troscopy, μSR and neutron diffraction experiments
show that the ground state is an antiferromagnetic
commensurate spin density wave (SDW) with an
ordered Fe magnetic moment $\sim 0.5 \mu_B$ [3, 7–9]. The
magnetic phase transition is always preceded by a
structural transition from the tetragonal to the ortho-
rhombic phase occurring at a temperature $T_{ST}$ that is

by 10–20 K higher than $T_{SDW}$ [4–7, 10]. The fluorine
doping results in a suppression of the SDW order and
gives rise to superconductivity with a maximum $T_c$
exceeding 55 K in SmO$_{1-x}$F$_x$FeAs [2, 11].

Understanding the nontrivial nature of magnetism in
Fe pnictides, which evolves from a long-range static
to a slowly fluctuating short-range order type upon
charge carrier doping (see, e.g., [12] and the refer-
ces therein), calls for the use of local probe tech-
niques. In this paper, we explore the possibilities of
electron spin resonance (ESR) spectroscopy to gain
insights into the magnetic and electronic properties of
LaO$_{1-x}$F$_x$FeAs. No intrinsic ESR signal associated
with the resonance of the Fe moments can be observed
in this compound. This is likely because $d$ electrons
stemming from Fe are delocalized in the FeAs layers
and experience strong momentum scattering. Owing
to a substantial spin–orbit coupling, this could cause a
strong spin relaxation and, consequently, very broad
ESR linewidths. We therefore introduced a special
ESR spin probe in LaO$_{1-x}$F$_x$FeAs by doping the sam-
ple with a few percent of Gd at a nonmagnetic La site.
The Gd$^{3+}$ ion has a half-filled 4$f$ shell, which gives rise to
the maximum possible spin value $S = 7/2$, whereas
the orbital moment $L$ is completely absent. Therefore,
the well-localized magnetic moment of Gd has a pure
spin nature and is not sensitive to phonon-mediated

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La2O3, and LaF3 in a stoichiometric ratio. All materials were prepared as described in [10] using FeAs, Gd, La, Fe0.98La0.02OFeAs, and LaF3. The resulting powders were mixed and pressed into pellets in Ar atmosphere, and subsequently annealed in an evacuated quartz tube in a two-step synthesis.

Due to the complications in crystal growth, large single crystalline samples are not available. To perform ESR experiments where the magnetic field should be applied parallel to the local symmetry axis of the Gd ion (crystallographic c-axis of the compound), we effect the c-axis alignment of the Gd1−xLaxOFeAs (y = 0.02 and 0.05) samples. The sample was ground to a fine powder, then mixed with epoxy resin, and hardened while rotating in the magnetic field 1.5 T. The X-ray diffraction data of the aligned powder samples were collected at room temperature using a PANalytical X’Pert PRO system (Philips) with CuKα-radiation (Fig. 1). The presence of highly intense [001] reflections that dominate the pattern (Fig. 1, arrows) points to a sufficiently high quality of the alignment. Reflections with Miller indices different from [001] (Fig. 1, asterisks) are also visible in the background, but their intensity is strongly suppressed compared to the pure powder pattern. In the oriented powder pattern, there are additional reflections, marked with the symbol “p.” They are attributed to the sample holder (plasticine).

3. SAMPLE PREPARATION

The polycrystalline samples of Gd1−xLa0.02OFeAs (x = 0, 0.1 and y = 0.02, 0.05 nominal content) were prepared as described in [10] using FeAs, Gd, La, La2O3, and LaF3 in a stoichiometric ratio. All materials were homogenized in a mortar. The resulting powders were pressed into pellets in Ar atmosphere, and subsequently annealed in an evacuated quartz tube in a two-step synthesis.

4. SAMPLE CHARACTERIZATION

The temperature dependence of the static magnetic susceptibility χ of 2% and 5% Gd-doped LaOFeAs samples is shown in Figs. 2a, 2b with squares. It can be fitted with high accuracy using the Curie-Weiss law (solid lines). This fit enables an accurate estimate of the actual Gd content in the sample, which is shown together with the nominal content in
Table 1. Nominal and actual Gd contents as derived from the magnetization analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal y</th>
<th>Actual y</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{1-y}$Gd$_y$OFeAs</td>
<td>0.020</td>
<td>0.016</td>
</tr>
<tr>
<td>La$_{1-y}$Gd$_y$OFeAs</td>
<td>0.050</td>
<td>0.048</td>
</tr>
<tr>
<td>La$<em>{1-y}$Gd$<em>y$O$</em>{0.9}$Fe$</em>{0.1}$As</td>
<td>0.050</td>
<td>0.049</td>
</tr>
</tbody>
</table>

Table 1. As can be seen, the real content does not differ significantly from the nominal one in all cases. To label the samples in what follows, we use the nominal content values. By subtracting the Curie—Weiss fit from the measured data, we extract the susceptibility of the FeAs layers $\chi_{Fe} = \chi - \chi_{Gd}^{Gd}$ these samples. The results of the subtraction are shown with dashed lines in Figs. 2a, 2b for both 2 and 5% doped LaOFeAs samples. It can be clearly seen that at temperatures in the range 120–150 K, $\chi_{Fe}$ experiences characteristic changes: the monotonic quasilinear decrease of the susceptibility turns into a rapid downturn, after which $\chi_{Fe}$ begins to increase again. This behavior is quite similar to the known temperature dependence of $\chi$ of the parent LaOFeAs samples without Gd doping [19] and is attributed to the respective structural and magnetic phase transitions. But because the Gd magnetic susceptibility overwhelms the susceptibility of the FeAs layers in our samples, it is quite difficult to obtain accurate transition temperatures from the static magnetometry data.

Fortunately, the phase transition temperatures ($T_{ST}$, $T_{SDW}$, and $T_c$) of 2 and 5% Gd-doped LaO$_{1-x}$Fe$_x$As samples can be determined more precisely from the electrical resistivity measurements, which are not sensitive to Gd magnetism. In the case of samples without fluorine (Figs. 3a, 3b), the resistivity shows a behavior qualitatively similar to that of the LaOFeAs parent compound [7, 10]. The electrical resistivity exhibits a clear anomaly at $T_{ST} = 148$ K, which is associated with the tetragonal-to-orthorhombic structural phase transition. In addition, the resistivity derivative shows a peaklike anomaly at $T_{SDW} = 130$ K, related to the magnetic transition. The assignment of the phase transitions is described in [7, 10]. Compared to the pure LaOFeAs, our Gd-doped samples show somewhat reduced transition temperatures, possibly due to increased disorder in the system. The Gd$_{0.05}$La$_{1-x}$O$_{0.9}$Fe$_{0.1}$As sample with 10% fluorine doping does not give any evidence of the structural and the SDW transitions, but shows a transition to the superconducting state at $T_c = 25$ K (Fig. 3c), similar to what is observed in the Gd-free case [6].

5. ESR MEASUREMENTS AND DISCUSSION

ESR measurements were performed at the X-band frequency ~9.5 GHz in the temperature range 5–300 K. The typical powder ESR spectra at $T = 130$ K are shown in Fig. 4a and Fig. 4b for 2% and 5% doped samples. To fit the spectra, we used two lines of Dysonian shape, shown as dashed lines in Figs. 4a, 4b. Below, we call them the broad and narrow components. The Dysonian ESR line shape is a result of mixing of absorption and dispersion at the instant of resonance, which occurs if the microwave penetration depth is comparable to or smaller than the sample size. This is typical for the conducting systems like the present samples. The peculiar line shape and the necessity to use two lines for a fit are explained by the powder averaging of the fine structure of the Gd ESR signal. Because Gd$^{3+}$ is a spin-only ion with $S = 7/2$ and $L = 0$, the value of its isotropic $g$-factor is very close to 2.

The 8-fold degeneracy of the spin levels in the ground state is lifted by the crystal field (CF) only slightly due to the small admixture of the high-energy multiplet with $L > 0$ [20, 21]. In this case, the CF potential acts only as a small perturbation to the Zeeman energy, giving rise to a zero field splitting of the Gd energy levels in the ground-state multiplet of the order of 0.01–0.1 mK (see Fig. 5a). According to the
ESR selection rules ($\Delta S_z = \pm 1$), the ESR spectrum consists of seven absorption lines: the central transition $|+1/2\rangle \rightarrow |-1/2\rangle$ with the highest intensity and six satellites $|\pm 3/2\rangle \rightarrow |\pm 1/2\rangle$, $|\pm 5/2\rangle \rightarrow |\pm 3/2\rangle$, and $|\pm 7/2\rangle \rightarrow |\pm 5/2\rangle$. The resonance field of the main transition ($|+1/2\rangle \rightarrow |-1/2\rangle$) is almost independent of the angle between the symmetry axis $z$ and the external magnetic field due to the $g$-factor isotropy (see Fig. 5b). By contrast, the satellites change their positions under rotation of the magnetic field with respect to $z$ from $H \parallel z$ to $H \perp z$. Hence, the powder averaging of the spectra leads to its transformation to the shape shown in Figs. 4a, 4b (see also, e.g., [22]).

Information on the CF splitting and the accurate value of the magnetic field acting on the Gd ion, which actually defines the position of the central line, can be extracted from the two-component fit of the Gd ESR signal. The narrow component models the main transition. Its resonance field is determined by the local field at the Gd site. The broad component mimics the effect of the powder averaging of the satellites. Various contributions to the powder ESR linewidth can exist in metals [22]. Therefore, the width of the broad component measures the crystal field splitting, the local magnetic field, if there are magnetically nonequivalent Gd sites and the Korringa relaxation process (see below).

In Figs. 6a, 6b, the temperature dependences of the resonance field of the narrow component $H_{\text{res}}$ and of the width $\delta H$ of the broad component are shown for the 2 and 5% Gd-doped LaOFeAs samples. Component $H_{\text{res}}$ is practically constant down to the magnetic phase transition temperature $T_{\text{SDW}} = 130$ K, where it begins to shift to lower fields. The shift amounting to $\approx 7$ mT is similar for both samples. At temperatures above $T_{\text{SDW}}$ and $T_{\text{ST}}$, the width $\delta H$ of the broad and narrow components decreases linearly in $T$ as the temperature decreases (Fig. 6b). This kind of behavior occurs when localized magnetic moments in a metallic host interact with conduction electrons. This interaction causes the so-called Korringa relaxation pro-

**Fig. 4.** Experimental ESR spectra (data points) and a two–component fit of the spectra (dashed lines) of (a) La$_{0.98}$Gd$_{0.02}$OFeAs and (b) La$_{0.95}$Gd$_{0.05}$OFeAs.

**Fig. 5.** (a) Crystal field and Zeeman splitting of the energy levels of the Gd$^{3+}$ ion (top) and the corresponding ESR spectrum arising due to the ESR selection rule $\Delta S_z = \pm 1$ (bottom). (b) Dependence of the position of the fine structure components of the Gd ESR spectrum on the angle $\theta$ between the magnetic field direction and the symmetry axis $z$; $H \parallel z$ corresponds to $\theta = 0^\circ$ and $H \perp z$ corresponds to $\theta = 90^\circ$. Dashed lines in (a) and (b) are powder-averaged spectra.
cess [22, 23]. The relaxation-driven part of the linewidth is given by

$$\delta H \sim [N(\epsilon_F)J]^2 T.$$  \hspace{1cm} (1)

According to Eq. (1), the slope $\delta H/dT$ is proportional to the electronic density of states $N(\epsilon_F)$ at the Fermi energy $\epsilon_F$ and to the coupling constant $J$ between conduction and localized $4f$ electrons [22, 23]. The Korringa relaxation affects the linewidths of all lines in the fine structure [22]. In our case, in the high-temperature regime $T > T_{SDW}$, both components of the fit of the powder spectrum of the parent, i.e., F-undoped compounds exhibit narrowing, which is linear in $T$ (Fig. 6b). This suggests that the temperature-dependent part of the linewidth above the SDW transition is determined by the Korringa relaxation of Gd spins due to the interaction with conduction electrons. Here, the Korringa slope is $\delta H/dT \approx 0.045$ mT/K. Our finding corroborates the ESR results on EuFe$_2$As$_2$ single crystals [24], where the spin relaxation of Eu$^{3+}$ ions, which are isoelectronic with Gd$^{3+}$ ions, is also driven by the Korringa mechanism. Notably, the Korringa slope is much bigger in that case, $\delta H/dT \approx 0.8$ mT/K, most likely due to a smaller distance between the R layers and the FeAs layers in the 122 family compared to the interlayer distance RO–FeAs in the 1111 family.

As can be seen in Fig. 6b, as the temperature decreases below $T_{ST} = 148$ K, the linewidth of the broad component $\delta H(T)$ starts to increase and reveals a jump at $T_{SDW} = 130$ K, which is more pronounced in the case of the 5% doped sample. This anomaly, albeit much smaller in size, is also visible in the $\delta H(T)$ dependence of the narrow component. Possibly, the initial broadening in this temperature range is due to the change in the fine structure of the Gd$^{3+}$ ESR signal, which is related to the structural transition, whereas the subsequent jump at $T_{SDW}$ can be associated with the magnetic order in the FeAs layers. At even lower temperatures, the linewidths continue to narrow with almost the same $\delta H/dT$ slope as at $T > T_{SDW}$. This is different from the situation in EuFe$_2$As$_2$, where the Korringa mechanism ceases to work below $T_{SDW}$; in [24], this was ascribed to a spacial confine-

2A small anomaly at around 60 K visible in the data on the 5% Gd-doped sample seems to be a sample-specific artefact, which finds no correspondence with other physical properties of the compound.
ment of conduction electrons to FeAs layers at $T < T_{SDW}$. Our data suggests that this scenario is not applicable to the LaOFeAs compound. Already above the SDW transition, the conduction electron density at the Gd site in LaOFeAs is much smaller than that at the Eu site in EuFe$_2$As$_2$, as is evidenced by the differences in the Korringa slopes, but it seems to be unaffected by the SDW transition.

In contrast to the parent compound, the fluorine-doped sample does not reveal any anomalies until reaching the superconducting transition temperature $T_c$ (Fig. 6c). The Korringa slope $\delta H/dT$ amounts to $\sim 0.06$ mT/K in this case. This value is appreciably higher than that in the sample without fluorine. Because $\delta H/dT \propto \sqrt{N(e_f)}$ according to Eq. (1), the doping of 10% of fluorine implies an increase in the electronic density of states at the Gd site by about 16%. At this point, we recall the multiband character of the electronic states in Fe pnictides. Obviously, the localized 4$f$ electrons of Gd interact predominantly with the two “out-of-plane” bands derived from the $yz$ and $y\hat{z}$ orbital states of Fe, whereas the $xy$ “in-plane” band should be much less effective in the Korringa relaxation. The enhancement of the Korringa relaxation upon the fluorine doping suggests that the doped electrons are not confined exclusively to the FeAs planes, but indicates a 3-dimensional character of the electronic density of states.

To resolve the Gd$^{3+}$ fine structure, we have measured ESR on the $c$-axis-oriented 2 and 5% Gd-doped LaOFeAs samples. At temperatures above $T_{SDW}$ and $T_{ST}$, a single Lorentzian line \(^3\) without a fine structure is observed. The fine structure is not seen most likely because of the Korringa broadening of individual components in the high-temperature regime, and also because of the poor signal-to-noise ratio due to a small susceptibility of Gd ions at high temperatures in this strongly diluted sample. A reduction of the Korringa relaxation together with a concomitant $1/T$ increase of the Gd susceptibility upon cooling enables observation of the Gd$^{3+}$ ESR fine structure below $T \sim 80$ K (Fig. 7). As expected, the resolution of the fine structure depends on the concentration of Gd ions and on the orientation of the magnetic field with respect to the crystallographic directions.

As can be seen in Figs. 8a, 8b, the best resolution is achieved for the smallest Gd concentration of 2% and for the direction of the external field parallel to the $c$-axis of the samples. In this case, at least 12 absorption lines are visible in the spectrum. \(^4\) Remarkably, the ESR spectrum of a single Gd$^{3+}$ ion, according to its spin value $S = 7/2$, should comprise at most 7 lines. We note that no additional forbidden transitions ($\Delta S = \pm 2, \pm 3, \ldots$) are expected in this case because the external magnetic field is parallel to the symmetry axis [20, 21]. A straightforward explanation for the excess number of the ESR lines is possible assuming the presence of magnetically nonequivalent Gd sites. Indeed, they can arise due to the antiferromagnetic SDW order in the FeAs layer. According to the known alignment of Fe spins in the SDW, which is similar in the entire 1111 family of Fe-based superconductors (see, e.g., [3, 9]), there are two magnetically nonequivalent positions of the R ion, which experience a local internal field of alternating sign induced by the ordered Fe moments. The arrangement of Fe spins in the FeAs layers and of local fields at the R site are sketched in Fig. 9.

To prove this conjecture, we have performed a simulation of the low-temperature Gd$^{3+}$ ESR spectrum assuming two magnetically nonequivalent Gd sites. According to the local crystal field symmetry [25, 26], the energy levels of the Gd$^{3+}$ ion can be described using the effective spin Hamiltonian of the form [20, 21]

$$\mathcal{H}_{\text{eff}} = g \mu_B \mathbf{H} \cdot \mathbf{S} + B_2^0 \mathbf{O}_2^0 + B_4^0 \mathbf{O}_4^0 + B_6^0 \mathbf{O}_6^0.$$  \hspace{1cm} (2)

The first term in (2) accounts for the Zeeman interaction. Here, $g$ is a g-factor, $\mu_B$ is the Bohr magneton, $\mathbf{H}$ is the orientation axis of the samples (the $c$ axis).  In this case, at least 12 absorption lines are visible in the spectrum. \(^4\) On the ESR spectra measured at $T \sim 4$ K, shown in Figs. 8a, 8b, we see that in contrast to other lines, the ESR line at the field 1.5 T does not exhibit any changes upon changing the angle $\theta$ between the magnetic field and the $c$ axis of the sample. This suggests that this line is not a part of the Gd spectrum and, most probably, is an artefact signal due to a small amount of uncontrollable Fe impurity.

\(^3\) Because of the fine grinding of the powder and its dilution in the epoxy resin for the purpose of orientation in the magnetic field, the microwaves can thus fully penetrate in the interior of the oriented sample. Therefore, the ESR lineshape changes from a Dyssonian to a Lorentzian.

\(^4\) On the ESR spectra measured at $T = 4$ K, shown in Figs. 8a, 8b, we see that in contrast to other lines, the ESR line at the field 1.5 T does not exhibit any changes upon changing the angle $\theta$ between the magnetic field and the $c$ axis of the sample. This suggests that this line is not a part of the Gd spectrum and, most probably, is an artefact signal due to a small amount of uncontrollable Fe impurity.
is the sum of the applied magnetic field \( H_0 \) and the internal field \( H_{\text{int}} \), and \( S \) is the spin. In the next terms in (2), \( O_n^m \) are Stevens operators describing the symmetry of the crystal field and \( B_n^m \) are phenomenological crystal field parameters (CFP).

The best modeling of the experimental ESR spectra, taking two magnetically nonequivalent positions into account, is shown in Fig. 10a. The set of CFP used for this simulation is presented in Table 2. The \( g \)-factor obtained from the fit is equal to 1.99, which is the usual value for the Gd\(^{3+} \) ion [20–22]. The internal magnetic field obtained from this simulation is \( H_{\text{int}} \approx 7.8 \) mT. It is interesting to compare this value with the expected strength of the dipolar field \( H_d \) at the \( R \) site due to the antiferromagnetically ordered Fe moments. With the known positions of the atoms in the unit cell of LaOFeAs and the magnitude of the ordered Fe moment, it is possible to calculate \( H_d \) using the formula

\[
\mu_0 H_i = \frac{\mu_0}{4\pi} \left( \frac{3 (\mathbf{m} \cdot \mathbf{r}) I - m_i r_i}{r^5} \right), \quad i = x, y, z, \tag{3}
\]

where \( H_i (i = x, y, z) \) is the component of the magnetic field \( H_d \) created by the magnetic dipole moment in the Cartesian coordinate system, \( \mathbf{r} \) is the vector connecting the position of the dipole and the point where the magnetic field is calculated, and \( \mathbf{m} \) is the vector of the magnetic moment. Under the assumption that Fe moments are pointlike dipoles of the strength \( 0.5/\mu_\text{B} \) located just at the crystallographic position of Fe, the dipolar calculation according to Eq. (3) yields the value of the internal dipole field \( 38 \) mT. This value is much larger than that obtained from the modeling of the ESR spectrum. This is not surprising because in
the antiferromagnetically ordered FeAs layers, the spin density is largely delocalized in the form of the SDW, which reduces the dipolar field acting on the Gd ions compared to the pointlike dipole approximation. To obtain the agreement with the measured value, the substantially reduced value 0.1\(\mu_B\) of the Fe magnetic moment must be used in Eq. (3).

The model Gd ESR spectrum shown in Fig. 10a reproduces the main features of the experimental spectrum rather well. But it lacks the left and right outermost lines at 0.2 T and 0.48 T, respectively. To account for them, we have to assume the occurrence of an additional Gd site with a distinct crystal field, also subjected to an alternating internal field. This assumption allows reproducing all lines in the experimental spectrum (Fig. 10b). The best agreement is achieved with the sets of the crystal field parameters CFP1 and CFP2 listed in Table 2. The spectral weight of the additional crystallographic site with CFP2 is about 30% of the main site with CFP1. We note that the second site is characterized by a much larger uniaxial second-order and fourth-order CF parameters and, compared to the main site (Table 2). Because a unique crystallographic R site is expected in the regular structure, it is feasible that these additional sites are located at (or close to) the surface of the fine powder particles of the oriented samples. Such sites could have a substantial weight in the micron-size particles owing to the enhanced surface-to-volume ratio.

6. SUMMARY

The ESR measurements of lightly Gd-doped samples of the LaO\(_{1-x}\)F\(_x\)FeAs compound, which is a representative of the 1111 family of Fe pnictide superconductors, establish Gd\(^{3+}\) ions as a sensitive ESR probe of magnetic, structural and electronic properties of this compound. In the parent, i.e., not fluorine-doped, samples, the change of the extent of the Gd\(^{3+}\) ESR fine structure reflects the occurrence of the structural phase transition. In addition, the antiferromagnetic SDW order manifests itself in the shift and broadening of the powder spectra and in the additional splitting of the fine structure of the ESR spectrum of the c-axis-oriented sample. The analysis of these spectra yields two magnetically nonequivalent R sites at low temperatures due to the SDW order in the FeAs layer. The spin density wave creates a dipolar field alternating in space, of the order of ~7.8 mT on the Gd ions. Additional features in the spectra could be assigned to the occurrence of Gd sites with distinct crystal field parameters, which are possibly located at the surface of the fine powder particles of the oriented samples. The coupling of the localized 4\(f\) electrons of Gd to the conduction electrons is manifested by an increase in the linewidths linear in \(T\) due to the Korringa relaxation mechanism. The data give evidence that the electronic density of states at the R site in LaOFeAs is significantly reduced compared to the 122-family representative EuFe\(_2\)As\(_2\). The ESR measurements on the fluorine-doped sample reveal an enhancement of the Korringa slope of the \(\delta H(T)\) dependence, implying an increased density of electronic states at the Fermi energy with respect to the parent samples. Taking a multi-band character of the electronic structure of Fe pnictides into account, this finding implies that the electrons doped due to the F substitution contribute to the density of states of the “out-of-plane” bands stemming from the \(xz\) and \(yz\)
orbital states of Fe to which the localized 4f electrons are mostly coupled.

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