ESR investigation of the spin dynamics in 
$(\text{Gd}_{1-x}\text{Y}_x)\text{PdSi}_3$

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**Abstract**

We report electron-spin resonance measurements in polycrystalline samples of $(\text{Gd}_{1-x}\text{Y}_x)\text{PdSi}_3$. We observe the onset of a broadening of the linewidth and of a decrease of the resonance field at approximately twice the Néel temperature in the paramagnetic state, this characteristic temperature coincides with the electrical resistivity minimum. The high-temperature behaviour of the linewidth is governed by a strong bottleneck effect.

**Key words:** Electron Spin Resonance, Gd alloys, magnetoresistance

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**1 Introduction**

It is of general believe that due to the close $f$-shell Gd ions do not show exotic magnetic behaviour in solid-state environment. However, recently it has been reported that some Gd alloys exhibit interesting phenomena including large magnetoresistance effects [1,2,3,4]. A metal-to-insulator-like transition has been reported for Gd$_5$Ge$_4$ [5]. In addition, a large number of the Gd-based intermetallics reveal large negative magnetoresistance (MR) effects arising from peculiar magnetic precursor effects [6]. Recently, the Gd transition-metal silicides and germanides with 2:1:3 stoichiometry ($\text{AlB}_2$-type hexagonal structure [7]) came into focus, as some of these compounds even show a Kondo-like minimum in the temperature dependence of the resistivity well above the magnetic ordering temperatures [4,8,9]. In polycrystalline Gd$_2$PdSi$_3$ ($T_N = 21$ K), the compound of interest in this article, a pronounced minimum occurs

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at about 45 K, which has been confirmed in single crystalline Gd$_2$PdSi$_3$ Saha et al. [10]. The minimum persists even when diluting the Gd sublattice by Y in (Gd$_{1-x}$Y$_x$)$_2$PdSi$_3$ [4]. Chaika et al. investigated the electronic structure for $R_2$PdSi$_3$ with $R=$La, Ce, Gd and Tb by photoemission and band-structure calculations [11] and found that in Gd$_2$PdSi$_3$ the Gd 4$f$ level is far below the Fermi level and hence should not significantly hybridize with the band states. In order to shed some light on the unusual magnetic and electronic properties of this compound we systematically investigated the spin dynamics of (Gd$_{1-x}$Y$_x$)$_2$PdSi$_3$ by electron-spin resonance (ESR).

2 Experimental details and results

The samples were prepared by arc melting and are taken from the same batch as those used in previous investigations by Mallik et al. [4]. ESR measurements were performed in a Bruker ELEXSYS E500 CW-spectrometer at X-band frequencies ($\nu \approx 9.47$ GHz) equipped with a continuous He-gas-flow cryostat in the temperature region $4.2 < T < 300$ K. The polycrystalline samples were powdered, placed into quartz tubes and fixed with paraffin. ESR detects the power $P$ absorbed by the sample from the transverse magnetic microwave field as a function of the static magnetic field $H$. The signal-to-noise ratio of the spectra is improved by recording the derivative $dP/dH$ with lock-in technique.

2.1 ESR spectra and intensity

Typical ESR spectra are presented in Fig. 1 and illustrate the evolution of the Gd resonance with Y concentration $x$ (left column) and temperature $T$ (right column). As expected, no ESR signal could be observed for $x = 1$. For $x < 1$, within the whole paramagnetic regime the spectrum consists of a broad, exchange narrowed resonance line, which is well fitted by a Dysonian line shape [12]. As in the present compounds the linewidth $\Delta H$ is of the same order of magnitude as the resonance field $H_{\text{res}}$, both circular components of the exciting linearly polarized microwave field have to be taken into account. Therefore the resonance at the reversed magnetic field $-H_{\text{res}}$ has to be included into the fit formula for the ESR signal, given by

$$\frac{dP}{dH} \propto \frac{d}{dH} \left\{ \frac{\Delta H + \alpha(H - H_{\text{res}})}{(H - H_{\text{res}})^2 + \Delta H^2} + \frac{\Delta H + \alpha(H + H_{\text{res}})}{(H + H_{\text{res}})^2 + \Delta H^2} \right\}$$

(1)

This is an asymmetric Lorentzian line, which includes both absorption and dispersion, where $\alpha$ denotes the dispersion-to-absorption ratio. Such asymmetric line shapes are usually observed in metals, where the skin effect drives electric
Fig. 1. ESR spectra of \((\text{Gd}_{1-x}\text{Y}_x)_{2}\text{PdSi}_3\). Left column: various Y concentrations \(x\) at \(T = 100\) K. Right column: temperature evolution of the ESR spectrum for \(x = 0\). Solid lines represent the fits using the Dysonian line shape, Eq. (1).

and magnetic microwave components out of phase in the sample and therefore leads to an admixture of dispersion into the absorption spectra. For samples small compared to the skin depth one expects a symmetric absorption spectrum \((\alpha = 0)\), whereas for samples large compared to the skin depth absorption and dispersion are of equal strength yielding an asymmetric resonance line \((\alpha = 1)\). At high Y concentrations the spectra are nearly symmetric with respect to the resonance field in accordance with the pure absorption spectra for \(\alpha = 0\). With decreasing \(x\) they become more and more asymmetric corresponding to an increasing parameter \(\alpha\). To check, whether the skin effect is the reason for the asymmetric line shape, we have to estimate the skin depth \(\delta = (\rho/\mu_0\omega)^{0.5}\) from the electric resistance \(\rho\) and the microwave frequency \(\omega = 2\pi \times 9\) GHz \((\mu_0 = 4\pi \times 10^{-7}\) Vs/Am). Using the resistivity values determined by Mallik et al. [4] - for example at 60 K for \(x = 0\), \(\rho = 0.25\) m\(\Omega\)cm - we find a skin depth \(\delta = 5.7\) \(\mu\)m. Therefore the skin depth is comparable to or even smaller than the grain size \((\approx 40\mu m)\) in accordance with the asymmetry of the ESR spectra. The large increase of the linewidth on decreasing temperatures (see Fig. 1, right column) results in an increasing uncertainty in determining both, resonance field \(H_{\text{res}}\) and dispersion-to-absorption ratio \(\alpha\) accurately, because both quantities are correlated, while the linewidth remains relatively unaffected. As the resistivity of the present compounds \(T \leq 150\) K changes by only 20\% [4], it is reasonable to fix the parameter \(\alpha\) for \(T < 50\) K at a value determined for \(T > 50\) K, where \(\alpha\) is found to be nearly temperature independent (e.g. \(\alpha = 0.7\) for \(x = 0.2\)). The integrated intensity \(I_{\text{ESR}}\) of the resonance line measures the spin susceptibility \(\chi_S\) of the ESR probe, \(I_{\text{ESR}} \sim \chi_S\). In the case of nonzero dispersion the intensity is determined by \(I_{\text{ESR}} = A \cdot \Delta H^2(1 + \alpha^2)^{0.5}\), where \(A\)
Fig. 2. Temperature dependence of the ESR intensity $I_{\text{ESR}}$ and the magnetic susceptibility $\chi$ (taken from Ref. 5) and the corresponding reciprocal values (inset) in $(\text{Gd}_{1-x}\text{Y}_x)\text{PdSi}_3$. The solid lines in the inset represent fits using a CW behavior. $T_N = 15$ K denotes the amplitude of $dP/dH$ and $(1+\alpha^2)^{0.5}$ takes changes of the dispersion into account. However, one has to be careful with this formula on approaching $\alpha = 1$. If the skin depth is small compared to the grain size, the microwave probes only a small fraction of the sample and changes of the resistivity with temperature also change this fraction. Then the ESR intensity is not a sensible measure of the spin susceptibility anymore. Fortunately, the relative changes of the resistivity are small in the temperature regime of interest, and hence the ESR intensity is even useful, when $\alpha$ approaches unity. Figure 2 shows both $I_{\text{ESR}}$ and the susceptibility data from Mallik et al. [4] for $x = 0.2$. Good agreement between the two sets of data can be observed throughout the whole concentration range in the paramagnetic regime. The peaks in the intensity appear at $T = 20, 15$ and 8 K for $x = 0, 0.2$ and 0.5 respectively. Below the Néel-Temperature $T_N$ we still observe a distorted resonance signal for $x \leq 0.5$ as shown in Fig. 3 for $x = 0.2$, but due to the reasons mentioned above deviations between ESR intensity and the magnetic susceptibility appear. The inverse quantities $1/I_{\text{ESR}}$ and $1/\chi$, which are sketched for $x = 0.2$ in the inset of Fig. 2, exhibit a linear temperature dependence in the paramagnetic regime ($T > T_N$). The samples with $x = 0, 0.2$ and 0.5 follow a $(T - \Theta_{\text{CW}})^{-1}$ Curie-Weiss (CW) law, with positive Curie-Weiss temperatures $\Theta_{\text{CW}}$ of 25, 17 and 6 K, respectively. For $x > 0.5$ the reciprocal ESR intensities $1/I_{\text{ESR}}$ show no deviations from a Curie law ($\Theta_{\text{CW}} = 0$). The resonance lines below $T_N$ (Fig. 3) exhibit a splitting into a broad absorption band with decreasing temperature, which can be interpreted in terms of antiferromagnetic powder spectra with a small antiferromagnetic gap [13]. However, the observation of resonance lines below $T_N$ is a rather unusual feature of intermetallics [21].
Fig. 3. ESR spectra of $(\text{Gd}_{0.8}\text{Y}_{0.2})_2\text{PdSi}_3$ for $T \leq T_N$ (4-15 K), which have to be multiplied by the given amplification factors in order to get the original amplitude.

2.2 Temperature dependence of the ESR linewidth and the resonance field

Generally, the ESR linewidth $\Delta H$ measures the spin-spin relaxation rate $1/T_2$ of the Gd-spins, whereas the resonance field $H_{\text{res}}$ or effective $g$-value ($\bar{\omega}_L = g\mu_B H_{\text{res}}$) gives information about the local static magnetic field at the Gd site. The linewidth is plotted versus temperature for all investigated samples in Fig. 4. As the temperature is lowered, the linewidth shows a monotonous behaviour that can be fitted very well with a linear function $\Delta H = c \cdot T$. Then the linewidth passes a minimum at $T_{\text{min}} \approx 2T_N$ and increases drastically while approaching the transition temperature to the magnetically ordered state. This feature is clearly seen for $x \leq 0.5$, whereas for higher Y concentrations we can only detect the onset of a line broadening in the temperature range investigated.

In Fig. 5 we show the temperature dependence of the resonance field $H_{\text{res}}$ for all samples under investigation. Again, we have to distinguish between the Gd-rich concentration range $x \leq 0.5$ and the samples with $x \geq 0.8$: At high temperatures $H_{\text{res}}$ is nearly constant for all concentrations and yields a $g$-value $g \approx 1.99$ slightly below the free-electron value. For $T < 100$ K and $x \leq$
Fig. 4. Temperature dependence of the ESR linewidth $\Delta H$ in $(\text{Gd}_{1-x}\text{Y}_x)_2\text{PdSi}_3$. The solid lines represent a linear fit for $T > T_{\text{min}}$, yielding a concentration dependence (inset) of the slope according to eq. (2).

0.5 we observe a dramatic shift of the resonance to lower fields, which coincides with the onset of the line broadening mentioned above. Finally, a distinct kink and an upturn to higher fields follows. The peak-like minima for $x = 0, 0.2, 0.5$ are found at 20, 15 and 6 K respectively. These temperatures are consistent with the ESR intensity and the magnetic-ordering temperatures obtained from measurements of the heat capacity and the magnetic susceptibility [4].

Fig. 5. Temperature dependence of the ESR resonance field $H_{\text{res}}$ in $(\text{Gd}_{1-x}\text{Y}_x)_2\text{PdSi}_3$. 
3 Discussion

The temperature dependencies of the $g$-value and the Gd-ESR linewidth bear important information on the interaction between the localized Gd-4f spins and the conduction electrons (for a review on the theory of ESR in metals, see e.g. Barnes [14], for experimental reviews see Taylor [15] and Elschner and Loidl [16]). Due to its half-filled 4f shell ($4f^7$, spin $J = S = 7/2$) the orbital momentum of Gd$^{3+}$ vanishes ($L = 0$), and therefore the Gd spin does not relax directly to the lattice. But the energy is transferred via the exchange interaction to the conduction electrons, which themselves couple to the phonons of the lattice. This process is usually known as Korringa relaxation and yields a linear increase of the resonance linewidth $\Delta H_K \propto bT$ with increasing temperature $T$, where the slope $b$ is proportional to the squared electronic density of states $N^2(E_F)$ at the Fermi energy.

This holds as long as the back-scattering rate $\delta_{ei}$ of the conduction electrons to the Gd ions is small compared to the scattering rate $\delta_{el}$ of the conduction electrons to the lattice. If however the former becomes comparable or even larger than the latter, the so called bottleneck effect occurs and the Korringa law is modified by the ratio $B = \delta_{el}/\delta_{ei}$ of both rates. This results in a reduced linear increase following [14]:

$$\Delta H(T) = \Delta H_K(T) \frac{B}{1 + B}$$

(2)

As the back-scattering rate $\delta_{ei}$ is proportional to the concentration of the localized spins (here $\delta_{ei} \sim \text{Gd concentration (1-x)}$), it is possible to prove the influence of the bottleneck effect in a given compound by the dependence of the linewidth on the concentration of magnetic ions.

The inset of Fig. 4 shows the slope $c$ of the linear high-temperature increase of the linewidth $\Delta H(T) = c \cdot T$ in $(\text{Gd}_{1-x}Y_x)_2\text{PdSi}_3$ as a function of the Gd-concentration $(1-x)$. It is well fitted by eq. (2), assuming a constant electron-lattice relaxation rate $\delta_{el}$, where $B$ can be expressed as $B = A/(1 - x)$ with a constant parameter $A$. The resulting Korringa rate $b = 10 \text{ Oe/K}$ is typical for usual metals and related intermetallic compounds (e.g. LaCu$_2$Si$_2$ [20]). Hence, at high temperatures the system behaves like a regular metal under the strong influence of the bottleneck effect for all Gd concentrations. Usually in unbottlenecked metallic hosts the $g$-value of Gd differs from the value in non-metallic hosts by $\Delta g = N(E_F)J_{ie}(0)$ with the coupling constant $J_{ie}$ between the Gd-spins and the band states [14]. The fact that at high temperatures the $g$ value is not strongly shifted from $g = 1.997$, which is usually observed for Gd$^{3+}$ in insulators [16], is in accordance with the strong bottleneck. The 122-type compounds have been intensively investigated by ESR by
Kaczmarska and coworkers during the last 15 years [19]. They found that the
ESR behaviour of dense Gd systems depends on the transition metal with
the thermal broadening parameter $c$ decreasing with increasing number of $d$
electrons from Co to Cu. For GdPd$_2$Ge$_2$ a value of 2.0 Oe/K was found,[18]
which is enhanced in comparison to 1.2 Oe/K for Gd$_2$PdSi$_3$ (see Fig. 3). This
result is in agreement with regard to the relative Gd concentration, which is
higher in the latter compound.

The increase of the resonance linewidth and the shift of the resonance field
towards lower temperatures on approaching magnetic order is a common fea-
ture of intermetallic compounds containing rare-earth ions like Gd as reported
in the experimental review by Taylor and Coles [21]. Generally, for antiferro-
magnetic compounds they find no ESR signal below $T_N$, but a broadening of
the line at about $1.5T_N < T < 10T_N$. Some systems like Pd$_3$Gd and EuAl$_4$,
however, show an ESR signal also below $T_N$, which has been attributed this
as common to materials which undergo metamagnetic transitions in magnetic
fields comparable to the resonance field [21]. Exactly such a behaviour has
been reported for Gd$_2$PdSi$_3$. At 2 K Saha et al. observed two metamagnetic
transitions in fields of 3 and 9 kOe [10]. On approaching $T_N$ from below both
transitions coincide at about 3 kOe, the value of the resonance field. Together
with the spectra we observed below $T_N$ (see Fig. 3) for $x \leq 0.5$, we conclude
that our system belongs to the same peculiar class of intermetallics as Pd$_3$Gd
and EuAl$_4$.

Apart from the existence of these signals and the suggested connection to
metamagnetism, we found another very interesting feature:
To analyze the linewidth in $(\text{Gd}_{1-x}\text{Y}_x)\_2\text{PdSi}_3$ at low temperatures in more
detail, we remind the magneto-resistance effects, which indicate the impor-
tance of the scattering of the conduction electrons on the localized Gd spins.
Indeed, the comparison of the resistivity data reported by Mallik et al. [4]
with the EPR linewidth shows that the onset of the line broadening and the
resonance shift (Fig. 5) coincides with the increase of resistivity for $x \leq 0.5$.
In Fig. 6 we show the ESR linewidth and resistivity for the pure compound
using a scaling that reveals the similarity of the increase in resistivity and
linewidth. Unfortunately, only limited resistivity data has been reported for
EuAl$_4$ [21] and Pd$_3$Gd making it difficult to judge unambiguously, whether a
correlation between linewidth and resistivity could be another common prop-
erty of those materials. To date, the origin of such a behaviour cannot easily
be explained, but due to the fact that the Gd 4f level in Gd$_2$PdSi$_3$ is about
2 eV below the Fermi level the Kondo effect cannot be responsible for the
observed minima [11], which is in agreement with the fact that the Korringa
rate and therefore the density of states at the Fermi level is independent on $x$.
A comparison with other metallic systems reveals that also in many ordered
and disordered magnetic compounds a minimum of the ESR linewidth can
be found at twice the critical temperature [16]. The increase of the linewidth
is attributed to spin fluctuations, which could also give rise to the resistivity
behaviour. Another system where a correlation between ESR linewidth and resistivity has been observed is Fe doped La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ [22], where localization effects were considered to explain that feature. Indeed, a localization scenario has also been proposed by Mallik et al. in order to explain the resistivity minimum in (Gd$_{1-x}$Y$_x$)$_2$PdSi$_3$ [4]. Very recently, Eremin et al. [1] gave an explanation for the magneto-resistance effects of another Gd alloy, namely GdI$_2$, which orders ferromagnetically close to room temperature [3,2]. The concomitant anomalous peak in the resistivity has been attributed to scattering of the 5$d$ conduction electrons by localized 4$f^7$ electrons as a result of the specific topology of the Fermi surface. A similar mechanism could also account for the correlation in resistivity and linewidth in (Gd$_{1-x}$Y$_x$)$_2$PdSi$_3$.

4 Conclusion

In conclusion we performed electron-spin resonance measurements in (Gd$_{1-x}$Y$_x$)$_2$PdSi$_3$. On approaching magnetic order, both the ESR linewidth and the resonance field are correlated with the resistivity minimum for $x \leq 0.5$. The high-temperature behaviour of the linewidth can be well described by a strong bottleneck effect, yielding a constant density of states at the Fermi level. The observation of antiferromagnetic-resonance-like absorption lines below the Néel temperature can be attributed to a metamagnetic transition in a magnetic field comparable to the resonance field. High-Field ESR measurements in single crystals should be performed in order to investigate the frequency and field dependence of the resonance lines. Thus, it should be possible to separate the influences of metamagnetic transitions, spin fluctuations and localization.
scenarios. Hopefully, such investigations will also trigger theoretical studies on localization effects in compounds with stable localized moments, which do not show a Kondo effect.

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