ESR investigation of the spin dynamics in (Gd1-xYx)2PdSi3

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ESR investigation of the spin dynamics in $(Gd_{1-x}Y_x)_2PdSi_3$

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1. Introduction

It is of general belief that due to the close f-shell, Gd ions do not show exotic magnetic behavior in solid-state environment. However, it has recently been reported that some Gd alloys exhibit interesting phenomena including large magnetoresistance (MR) effects [1–4]. A metal-to-insulator-like transition has been reported for Gd_5Ge_4 [5]. In addition, a large number of the Gd-based intermetallics reveal large negative MR effects arising from peculiar magnetic precursor effects [6]. Recently, the Gd transition-metal silicides and germanides with 2:1:3 stoichiometry (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_2PdSi_3 ($T_N = 21$ K), the compound of interest in this article, a pronounced minimum occurs at about 45 K, which has been confirmed in single crystalline Gd_2PdSi_3 by Saha et al. [10]. The minimum persists even when diluting the Gd sublattice by Y in $(Gd_{1-x}Y_x)_2PdSi_3$ [4]. Chaika et al. investigated the electronic structure for R_2PdSi_3 with R = La, Ce, Gd and Tb by photoemission and band-structure calculations [11] and found that in Gd_2PdSi_3, the Gd 4f 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 $(Gd_{1-x}Y_x)_2PdSi_3$ 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

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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 shown 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 ΔH is of the same order of magnitude as the resonance field H_{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 $-H_{\mathrm{res}}$ has to be included into the fit formula for the ESR signal, given by

$$\frac{\mathrm{d}P}{\mathrm{d}H} \propto \frac{\mathrm{d}}{\mathrm{d}H} \times \left\{ \frac{\Delta H + \alpha(H - H_{\mathrm{res}})}{(H - H_{\mathrm{res}})^2 + \Delta H^2} + \frac{\Delta H + \alpha(H + H_{\mathrm{res}})}{(H + H_{\mathrm{res}})^2 + \Delta H^2} \right\} \qquad (1)$$

This is an asymmetric Lorentzian line, which includes both absorption and dispersion, where α denotes the dispersion-to-absorption ratio. Such asymmetric line shapes are usually observed in metals, where the skin effect drives electric 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 α. 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 ρ and the microwave frequency $\omega = 2\pi \times 9$ GHz ($\mu_0 = 4\pi \times 10^{-7}$ V s/A m). Using the resistivity values determined by Mallik et al. [4]—for example at 60 K for $x = 0$, $\rho = 0.25$ mΩ cm—we find a skin depth $\delta = 5.7$ µm. Therefore, the skin depth is comparable to or even smaller than the grain size (≈40 µm) in accordance with the asymmetry of the ESR spectra. The large increase in the linewidth on decreasing temperatures (see Fig. 1, right column) results in an increasing uncertainty in determining both, resonance field H_{res} and dispersion-to-absorption ratio α 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 α for $T < 50$ K at a value determined for $T > 50$ K, where α is found to be nearly temperature independent (e.g. $\alpha = 0.7$ for $x = 0.2$). The integrated intensity I_{ESR} of the resonance line measures the spin susceptibility χ_{S} of the ESR probe, $I_{\mathrm{ESR}} \sim \chi_{\mathrm{S}}$. In the case of non-zero dispersion the intensity is determined by $I_{\mathrm{ESR}} = A\Delta H^2(1 + \alpha^2)^{0.5}$, where A 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 in 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 α approaches unity. Fig. 2 shows both I_{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

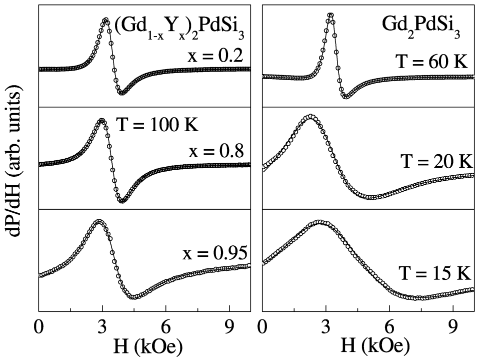

Fig. 1. ESR spectra of $(\mathrm{Gd}_{1-x}\mathrm{Y}_x)\mathrm{PdSi}_3$. Left column: various Y concentrations x at $T = 100$ K. Right column: temperature evolution of the ESR spectrum for $x = 0$. Solid lines represent the fits using the Dysonian line shape, Eq. (1).

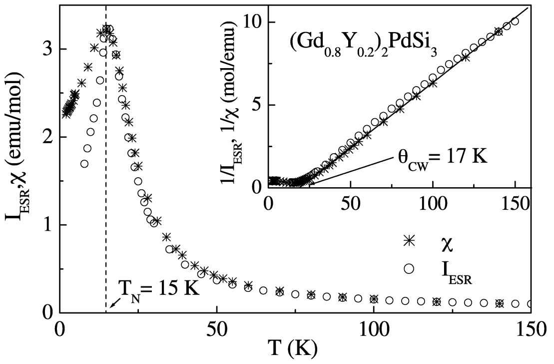

Fig. 2. Temperature dependence of the ESR intensity I_{ESR} and the magnetic susceptibility χ (taken from Ref. [4]) and the corresponding reciprocal values (inset) in $(\mathrm{Gd}_{1-x}\mathrm{Y}_x)_2\mathrm{PdSi}_3$. The solid lines in the inset represent fits using a CW behavior.

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 $1/I_{ESR}$ 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 $(T - \Theta_{CW})^{-1}$ Curie–Weiss (CW) law, with positive Curie–Weiss temperatures Θ_{CW} of 25, 17 and 6 K, respectively. For $x > 0.5$ the reciprocal ESR intensities $1/I_{ESR}$ show no deviations from a Curie law ($\Theta_{CW} = 0$). 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 [21,22].

2.2. Temperature dependence of the ESR linewidth and the resonance field

Generally, the ESR linewidth ΔH measures the spin–spin relaxation rate $1/T_2$ of the Gd-spins, whereas the resonance field H_{res} or effective g-value ($\bar{\omega}_L = g\mu_B H_{res}$) 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 behavior that can be fitted very well with a linear function $\Delta H = cT$. Then the linewidth passes a minimum at $T_{min} \approx 2T_N$ 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.

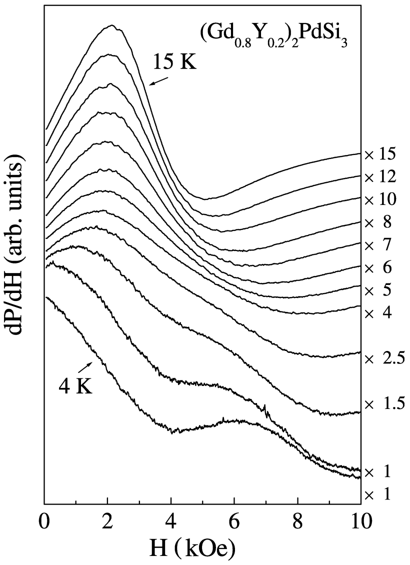

Fig. 3. ESR spectra of $(Gd_{0.8}Y_{0.2})_2PdSi_3$ for $T \leq T_N$ (4–15 K), which have to be multiplied by the given amplification factors in order to get the original amplitude.

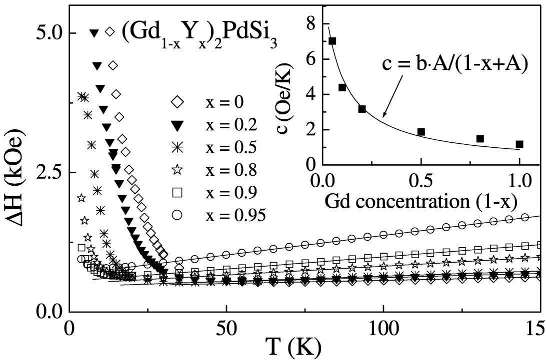

Fig. 4. Temperature dependence of the ESR linewidth ΔH in $(Gd_{1-x}Y_x)_2PdSi_3$. The solid lines represent a linear fit for $T > T_{min}$, yielding a concentration dependence (inset) of the slope according to Eq. (2).

In Fig. 5 we show the temperature dependence of the resonance field H_{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_{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 $x \leq 0.5$ 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 follow. 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].

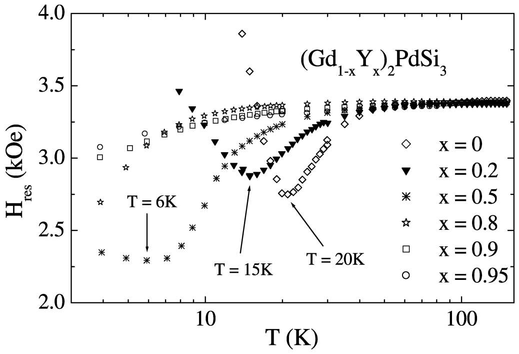

Fig. 5. Temperature dependence of the ESR resonance field H_{res} in $(Gd_{1-x}Y_x)_2PdSi_3$.

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. However, 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 δ_{ei} of the conduction electrons to the Gd ions is small compared to the scattering rate δ_{el} of the conduction electrons to the lattice. However, if 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]:

$$\Delta H(T) = \Delta H_K(T)\frac{B}{1+B} \tag{2}$$

As the back-scattering rate δ_{ei} is proportional to the concentration of the localized spins (here $\delta_{ei} \sim$ 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 $\Delta H(T) = cT$ in $(Gd_{1-x}Y_x)_2PdSi_3$ as a function of the Gd-concentration $(1-x)$. It is well fitted by Eq. (2), assuming a constant electron-lattice relaxation rate δ_{el}, where B can be expressed as $B = A/(1-x)$ with a constant parameter A. The resulting Korringa rate $b = 10$ Oe/K is typical for usual metals and related intermetallic compounds (e.g. $LaCu_2Si_2$ [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 co-workers during the last 15 years [17–19]. They found that the ESR behavior 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 $GdPd_2Ge_2$ a value of 2.0 Oe/K was found, [18] which is enhanced in comparison to 1.2 Oe/K for Gd_2PdSi_3 (Fig. 3). This result is in agreement with regard to the relative Gd concentration, which is higher in the latter compound.

The increase in the resonance linewidth and the shift of the resonance field towards lower temperatures on approaching magnetic order is a common feature of intermetallic compounds containing rare-earth ions like Gd as reported in the experimental review by Taylor and Coles [21,22]. Generally, for antiferromagnetic 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_3Gd and $EuAl_4$, however, show an ESR signal also below T_N, which has been attributed as common to materials which undergo metamagnetic transitions in magnetic fields comparable to the resonance field [21,22]. Exactly such a behavior has been reported for Gd_2PdSi_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 (Fig. 3) for $x \leq 0.5$, we conclude that our system belongs to the same peculiar class of intermetallics as Pd_3Gd 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 $(Gd_{1-x}Y_x)_2PdSi_3$ at low temperatures in more detail, we remind the MR effects, which indicate the importance 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 $EuAl_4$ [21,22] and

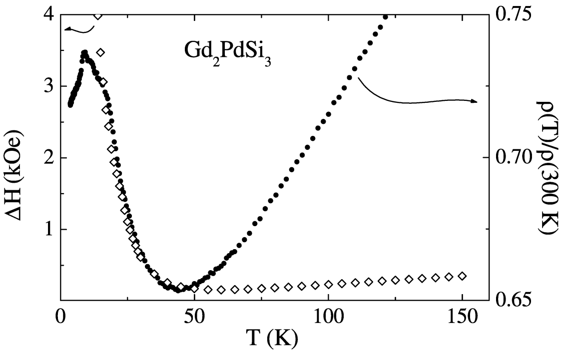

Fig. 6. Temperature dependencies of ESR linewidth (◇) and resistivity (●, taken from Ref. [4]) in Gd_2PdSi_3.

Pd_3Gd making it difficult to judge unambiguously, whether a correlation between linewidth and resistivity could be another common property of those materials. To date, the origin of such a behavior cannot easily be explained, but due to the fact that the Gd 4f level in Gd_2PdSi_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 in the linewidth is attributed to spin fluctuations, which could also give rise to the resistivity behavior. Another system where a correlation between ESR linewidth and resistivity has been observed is Fe doped $La_{2-x}Sr_xCuO_{4+\delta}$ [23], 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 $(Gd_{1-x}Y_x)_2PdSi_3$ [4]. Very recently, Eremin et al. [1] gave an explanation for the MR effects of another Gd alloy, namely GdI_2, which orders ferromagnetically close to room temperature [2,3]. The concomitant anomalous peak in the resistivity has been attributed to scattering of the 5d conduction electrons by localized $4f^7$ 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 $(Gd_{1-x}Y_x)_2PdSi_3$.

4. Conclusion

We have performed ESR measurements in $(Gd_{1-x}Y_x)_2PdSi_3$. 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 behavior 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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