NMR in Laves Phase Alloy System GdPt$_x$—
Analysis of Nonstoichiometry in Intermetallic Compounds

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NMR is applied to ferromagnetic Laves phase compounds Gd$_{1-x}$A$_x$Pt$_2$ (A = Sc, La) and GdPt$_x$ (2 ≤ x ≤ 3). The different hyperfine field contributions are analyzed. Neighbour contributions to the Gd hyperfine field and strength of ferromagnetic coupling are compared. It is found that there is a strong predominance of the nearest neighbour contribution (92 %) to the Pt hyperfine field. We show that the Pt NMR allows to derive the deviation in occupation number of Gd atoms on Gd sites in nonstoichiometric compounds with about 4 % accuracy.

I. Introduction

Since many years it is recognized that for compounds belonging to the group of magnetic semiconductors —like the rare earth monochalcogenides— stoichiometry plays a crucial role in the determination of their physical characteristics such as electrical resistivity or magnetic properties [1]. Only more recently, though, one realized that the influence of nonstoichiometry in intermetallic compounds can be drastic as well. For instance, the magnetic anisotropy and coercivity of cobalt-rich rare earth (RE) compounds like SmCo$_5$ or YCo$_5$ depend strongly on the degree in which RE atoms are replaced by Co dumbbell pairs in the CaCu$_5$ basic structure [2a, b]. We have shown before for Y$_2$Co$_{17}$ that the NMR technique — at least in special cases — can be superior to X-ray analysis in detecting changes in layer stacking in a given direction leading to regions of insufficient long range periodicity in that direction [3]. In the present investigation we will analyze to what extent NMR can be used to reveal nonstoichiometry in simple intermetallic compounds. As an example, we use a rather exceptional intermetallic compound for which nonstoichiometry has been reported to be rather pronounced and seems to be the rule and not the exception — the Laves phase alloy system GdPt$_x$.

Harris et al. [4a, b] have shown that the cubic MgCu$_2$-C15-type structure is stable in argon-arc molten Gd-Pt alloys for Gd concentrations between 23 and 33 atomic percent. In order to explain the unusually large extent of this stability range studied by means of X-ray diffraction, electrical resistance, magnetic susceptibility and electron spin resonance, they propose a model in which Pt atoms substitute progressively on Gd sites [4b]: at the stoichiometric composition, GdPt$_2$, vacancies are believed to occur on both sites whereas in Gd$_{23}$Pt$_{75}$ all Pt and two of eight Gd sites in the C15-type unit cell are supposed to be occupied by Pt. We report here on our NMR results of ferromagnetic Gd$_{1-x}$A$_x$Pt$_2$ (A = Sc, La) and GdPt$_x$ with 2 ≤ x ≤ 3 ($T_c ≈ 30$ K). The Gd$^{157}$, Gd$^{155}$ and Pt$^{195}$ resonances of GdPt$_2$ are analyzed first. Then the replacement of Gd by Sc and La is used to derive the influence of lacking Gd moments in GdPt$_2$ on its NMR spectrum. Finally, the NMR spectra of different compositions of GdPt$_x$ are compared. In this entire analysis, Pt$^{195}$ proves to be a very useful probe since its nuclear spin $I = \frac{1}{2}$ does not react on the electric field gradients arising at perturbed lattice sites. Furthermore, its gyromagnetic ratio and hyperfine coupling constant are large enough to have the Pt$^{195}$ resonance lines at sufficiently high frequencies, well separated from the Gd, La or Sc resonances. In the course of the following analysis we also show that

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the NMR results on GdPt$_2$ agree favourably with the picture of magnetic interactions and hyperfine fields which we have derived in the past for a variety of different intermetallic compounds of Gd with non-magnetic partners [5].

II. Experimental Details

The samples used for the present measurements \{Gd$_{1-x}$A$_x$Pt$_2$ (A=Sc, La; 0$\leq$x$\leq$0.3), Gd$_{31.4}$Pt$_{68.5}$, Gd$_{28}$Pt$_{72}$ and Gd$_{25}$Pt$_{75}$\} were prepared by argon arc melting of appropriate amounts of at least 99.9% pure starting materials. No subsequent annealing treatment was applied, in conformity with the results of the investigation of Harris et al. [4a]. X-ray diffraction analysis indicates that all the samples are of the cubic Laves phase structure.

The results of magnetic measurements on the non-stoichiometric compounds GdPt$_x$ (2$\leq$x$\leq$3.2) were already reported by Taylor et al. [4b], so we restricted our analysis mainly to the compounds of the type Gd$_{1-x}$La$_x$Pt$_2$. The magnetic susceptibility $\gamma$ of the samples in the paramagnetic region was measured on a Curie balance. The effective moment $\mu_{\text{eff}}$ and the paramagnetic Curie temperature $\theta_p$ were derived from the temperature dependence of the reciprocal susceptibility. In the magnetically ordered regime we used an adaption of the Faraday method to derive the magnetization $\sigma$. The saturation magnetization was estimated from the magnetization $\sigma$ measured at 4.2 K in applied fields up to $H_{\text{max}}$=30 kOe. The ferromagnetic Curie temperatures $T_c$ were obtained by extrapolation of $\sigma^2$ versus temperature curves.

NMR measurements were performed at 4.2 K on powdered material (particle size 70 $\mu$m and below) immersed in silicon oil, mostly in zero applied field. For measurements in the frequency range 16 to 62 MHz a Bruker BKR 322 spin echo spectrometer was used; echos were excited by two pulses of 2 and 3 $\mu$s duration and 20 $\mu$s delay in between. For the range 60–186 MHz the frequency extension Bruker BKR 323 was employed which works with the fourth and sixth harmonic of the fundamental frequency of the unit BKR 322. Exploitation of the twelfth harmonic allowed to reach 210 MHz, the frequency limit of our present setup. The spin echos in the upper frequency range were excited by two pulses of 4 and 6 $\mu$s duration (to reach maximal echo height with the pulse power available).

The value of the rf field $H_1$ was optimized at the main resonance line and then kept roughly constant throughout the frequency range for each isotope. With the exception of a superimposed wall signal on the Pt$^{195}$ domain resonance in GdPt$_2$ which will be discussed in Section IIIIB, no unusually rapid variation of the $H_1$ enhancement factor was observed. By comparison with 90° pulses for protons, $H_1$ enhancement factors of about 150 were derived for the Gd$^{155}$-signals (22.7 MHz) and the Pt$^{195}$-domain signals (192 MHz) in GdPt$_2$, or $H_2$ enhancement factors of about 100 for the Pt$^{195}$ resonances (at about 150 MHz) in the non-stoichiometric samples. From the small values of the enhancement factors and from the observed dependence of the signal intensity on applied external magnetic fields it is inferred that we observed mainly nuclei within domains.

The spin echo signals were detected in phase sensitive mode; the variation of the spectrometer's sensitivity was controlled with the help of a Rohde and Schwarz Polyskop and calibrated with a sample of protons. The echo heights given in Figures 1–5 are consequently already corrected for the Boltzmann factor, not so, however, for the possible influence of the frequency-dependent skin depth and variations in signal enhancement factors. Most of the spectra shown in the figures are normalized to the largest echo of a given sample in the frequency range represented. In Figures 1 and 5, however, we have plotted the signals of different samples on a scale relative to the respective Gd$^{155}$ and Pt$^{195}$ resonance maxima of GdPt$_2$; this type of data representation allows to see that the signals observed for different sample compositions stem from corresponding nuclear sites; the comparison of absolute intensities of different samples is less reliable because in addition to the signal enhancement also the filling factor (grain size) can introduce errors.

The NMR spectra were analyzed as follows. The resonance field is given by

$$H_{\text{res}}=H_{\text{hf}}+H_{\text{dip}}+H_{\text{ext}}-NM(H)+4\pi M_{s}/3$$

(1)

where $M(H)$ represents the field-dependent magnetization, $M_s$ the saturation magnetization and $N$ the demagnetization factor. For multidomain powder particles of approximately spherical shape $N \cdot M(H)$ equals zero in zero external field. Also in the presence of an external field the values of $N \cdot M$ and $H_{\text{ext}}$ cancel until $H_{\text{ext}}=4\pi M_{s}/3$ so that in both cases $H_{\text{hf}}+H_{\text{dip}}=H_{\text{res}}-4\pi M_{s}/3$. To obtain the sign of the hyperfine field we applied external fields larger than $4\pi M_{s}/3$ and measured the shift of $H_{\text{res}}$. (For GdPt$_2$, with $\mu_s=7 \mu_B/$Gd atom, we calculate $4\pi M_{s}/3=4.9$ kOe.) For some samples (e.g. GdPt$_2$, Fig. 3) we used external fields also in order to eliminate signals not originating from nuclei in domains.

III. Results and Discussion

A. Known Data

We premise a short summary of what we already know of the electronic structure, the magnetic interactions