

Perturbed angular correlation study of static and dynamic hyperfine interactions at ^{181}Ta in the Laves-phase hydrides ErFe_2H_x

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The static magnetic hyperfine interaction and the hydrogen-induced dynamic electric quadrupole interaction (QI) at the nuclear probe ^{181}Ta on cubic Er sites in magnetically ordered *C15* Laves-phase hydrides ErFe_2H_x have been investigated by perturbed angular correlation (PAC) spectroscopy as a function of temperature ($10\text{ K} \leq T \leq 600\text{ K}$) and hydrogen concentration ($0 \leq x \leq 3.2$). At room temperature and concentrations $x < 2$, the PAC spectra, supported by x-ray diffraction measurements, indicate the coexistence of two hydride phases ErFe_2H_x with $x \leq 0.1$ and $x \sim 1.6\text{--}1.7$, respectively, and a linear increase of the fraction of the high-concentration phase with increasing x . At low temperatures the PAC spectra of the high-concentration hydride reflect a broad distribution of strong static hyperfine interactions. The dynamic QI caused by rapidly diffusing H atoms becomes observable at $T > 400\text{ K}$. The resulting ^{181}Ta nuclear quadrupole relaxation rates show an Arrhenius behavior with an activation energy of $E_a = 0.39(3)\text{ eV}$ for $x = 1.5$ and 2.0 and permit an estimate of the effective charge associated with the diffusing H atom of $Z' e \approx 0.095e$. The vanishing time average of the nuclear quadrupole interaction in the fast-fluctuation region allows the separation of the magnetic and electric hyperfine interactions and the determination of the ^{181}Ta magnetic hyperfine field B_{hf} as a function of temperature and H concentration. At a given temperature $T \geq 450\text{ K}$ in the fast-fluctuation region, B_{hf} decreases with increasing x , indicating a decrease of the *s* conduction electron polarization at the probe site. The temperature dependence of B_{hf} in the fast-fluctuation region is also affected by the hydrogen concentration: at $x = 1.1$, B_{hf} was found to decrease, at $x = 1.5$ and 2.0 to increase with increasing T . Irreversible changes of the PAC spectra indicate that the thermal stability of crystalline ErFe_2H_2 encapsulated under vacuum is limited to $T \leq 550\text{ K}$. ErH_2 was identified by x-ray diffraction as one of the dissociation products, but there was no evidence for the precipitation of elemental Fe and a hydrogen-induced amorphization step.

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I. INTRODUCTION

The perturbed angular correlation (PAC) technique has been established in recent years as a useful tool for the investigation of metal-hydrogen systems (for a review see Ref. 1). In particular, PAC spectroscopy has been used to study the hydrogen motion in a number of H absorbing pure metals^{2,3} and intermetallic compounds.^{4,5} Similar to NMR, PAC spectroscopy allows the observation of the nuclear spin relaxation caused by time-dependent hyperfine interactions (HFI's), which may provide information on the activation energy and other parameters of a diffusion process. In PAC studies of hydrogen diffusion, the relevant interaction is usually the dynamic quadrupole interaction (QI) between the quadrupole moment of the PAC nucleus and the fluctuating electric-field gradient (EFG) caused by the moving H charge. The nuclear spin relaxation caused by the nuclear magnetic dipole moment of the moving hydrogen is much weaker than the quadrupole relaxation and even for nuclei with zero quadrupole moment it is difficult to detect within the time window of most PAC probes. In the past PAC spectroscopy has been applied to diamagnetic and paramagnetic metal-hydrogen systems. In this paper we extend the PAC technique to magnetically ordered hydrogen absorbing intermetallic compounds. In a magnetically ordered host the PAC probe is subject to a static magnetic hyperfine field related to the spin polarization at the probe site. Charging the host with hydrogen produces an electric-field gradient at the probe

nucleus which—relative to the PAC time window—is static at low temperatures and fluctuating at high temperatures. We were interested in the question whether the resulting dynamic QI can be detected in the presence of a strong static magnetic hyperfine field. A positive answer to this question—which to our knowledge has not yet been studied—would open the way for PAC investigations of the hydrogen motion in numerous magnetically ordered hydrides. Another interesting aspect motivating the present study is the hydrogen-induced change of the static magnetic hyperfine field and its temperature dependence. Furthermore, measurements of hyperfine interactions may provide information on the thermal stability of intermetallic hydrides.

The investigation was carried with the *C15* Laves-phase hydride ErFe_2H_x as host and ^{181}Ta as PAC nucleus. This host-probe combination was chosen for the following reasons: (i) The *C15* Laves phases $R\text{Fe}_2$ ($R =$ rare earths) are magnetically ordered with Curie temperatures up to 800 K and may under certain conditions absorb large quantities of hydrogen maintaining their lattice structure.⁶ Among these compounds, the properties of ErFe_2H_x are particularly well documented and hyperfine interactions in ErFe_2H_x have previously been investigated by ^{166}Er and ^{57}Fe Mössbauer spectroscopy.^{7,8} (ii) For most solid-state applications of PAC spectroscopy it is desirable that the probe atom, which in most cases is an impurity in the investigated compound, occupies a regular site of the host lattice. The nuclei ^{111}Cd and ^{181}Ta are usually considered as the most convenient PAC

probes. The site location of these impurity atoms in the C15 Laves phases $R\text{Fe}_2$ has been extensively investigated by Komissarova *et al.*^{9,10} and Sorokin *et al.*^{11,12} Their work has shown that both probes mainly reside on the cubic R site of $R\text{Fe}_2$; in the case of ^{111}Cd , however, a high-pressure synthesis is required, whereas for ^{181}Ta standard alloying is sufficient. The magnetic hyperfine field at ^{181}Ta in $R\text{Fe}_2$ increases with increasing R atomic number and reaches a value of about 20 T at the end of the $4f$ series, which also favored the choice of ErFe_2H_x for the present study.

ErFe_2 orders ferrimagnetically with antiparallel Er and Fe moments below $T_c = 573$ K. The structural changes of $R\text{Fe}_2$ in a hydrogen atmosphere have been extensively investigated. As a rule, several different phases are formed as temperature is increased.^{13,14} At low temperature ($T \sim 400$ K) hydrogen is absorbed mainly into $R_2\text{Fe}_2$ interstices to form crystalline (c -) $R\text{Fe}_2\text{H}_x$. The next reaction step is the hydrogen-induced amorphization (HIA) which in a high-pressure H_2 atmosphere occurs at $T \sim 500$ – 600 K. Then the precipitation of RH_2 and finally the decomposition into RH_2 and α -Fe are observed between 650 K and 800 K.

In this paper we are concerned with crystalline hydrides ErFe_2H_x with $0 < x \leq 3.2$. In this concentration range a single-phase hydride can be produced only for $x > 1.2$ – 1.6 .^{15–17} Up to $x = 3.2$ the cubic C15 structure is retained, with the lattice expanding with increasing H concentration. At lower concentrations, the coexistence of two phases has been reported. One has a lattice parameter ($a \sim 7.28$ Å) close to that of uncharged ErFe_2 ; the other one corresponds to ErFe_2H_x with $x \sim 1.5$. The H site occupation has been studied by neutron diffraction of c - ErFe_2D_x .¹⁸ At $x = 2$ the hydrogen atoms are exclusively located on the $R_2\text{Fe}_2$ interstitial sites of the C15 structure. At higher concentrations some occupation of the $R\text{Fe}_3$ interstitials is to be expected, as shown, e.g., by magnetic aftereffect spectroscopy of DyFe_2H_x .¹⁹

The magnetic properties of ErFe_2 change significantly upon hydrogenation. Deryagin *et al.*²⁰ have reported a substantial decrease of the bulk Curie temperature T_C with increasing lattice expansion, i.e., H concentration for all $R\text{Fe}_2\text{H}_x$. Neutron scattering studies of the effect of deuterium on the Er and Fe sublattice magnetizations have been carried out by Fish *et al.*²¹ for $\text{ErFe}_2\text{D}_{3.5}$ as a function of temperature and by Shashikala *et al.*¹⁷ for different concentrations at 10 K. While the Fe moment was found to remain identical to that of ErFe_2 , the saturation magnetic moment of Er is drastically reduced with increasing concentration x . Furthermore, the Er sublattice magnetization decreases strongly with increasing temperature and the Er sublattice becomes completely disordered well below the bulk Curie temperature.¹⁶ ^{166}Er Mössbauer measurements,⁷ however, have established that the local magnetic moment of Er in ErFe_2H_x is close to the free ion value. The pronounced reduction of the Er sublattice magnetization as seen by neutron scattering is therefore attributed to an increasing noncollinearity of the Er moments (“fanning”) caused by the random distribution of the H atoms in the C15 structure.

II. EXPERIMENTAL DETAILS

A. Sample preparation and equipment

The PAC measurements were carried out with the 133-482 keV $\gamma\gamma$ cascade of ^{181}Ta populated in the β decay of the 42 d isotope ^{181}Hf , which can be produced by thermal neutron irradiation of natural Hf. Samples of ErFe_2 were doped with about 0.1 at. % of radioactive Hf by arc melting of the metallic constituents Er and Fe with neutron-irradiated Hf metal in an argon atmosphere. Radioactive and inactive hydrides ErFe_2H_x were produced by first activating the parent compound at about 1000 °C in a quartz tube in high vacuum. A known quantity of H_2 gas admitted into the calibrated quartz volume while the switched-off furnace was cooling down and the concentration of the absorbed hydrogen was determined from the final H_2 pressure. Radioactive ErFe_2H_x hydrides were prepared for the concentrations $x = 0.6, 1.1, 1.5, 2.0,$ and 3.2 and investigated by PAC spectroscopy in the temperature range $10 \text{ K} \leq T \leq 600 \text{ K}$. For structural and stability information inactive hydrides with similar concentrations were studied by x-ray diffraction at room temperature (using Co $K\alpha$ radiation with $\lambda = 1.7902$ Å) after different thermal treatments.

For PAC measurements at $T \geq 290$ K the radioactive hydrides were sealed under vacuum into small quartz tubes. For measurements at $T < 290$ K a closed-cycle He refrigerator was used. The PAC spectra were taken with a standard four-detector setup equipped with fast BaF_2 detectors of conical shape. This shape allows to reduce the source-detector distance to about 15 mm and leads to a solid angle of almost 90°. As a consequence the solid angle attenuation of the angular correlation coefficient A_{44} is much stronger than that of the coefficient A_{22} and the coefficient A_{44} can be neglected in the data analysis.

B. Data analysis

The angular correlation theory of two successive γ rays of a $\gamma\gamma$ cascade, expressed by angular correlation coefficients A_{kk} ($k = 2, 4$), may be modulated in time by hyperfine interactions in the intermediate state of the cascade. For polycrystalline samples this modulation can be described by the perturbation factor $G_{kk}(t)$ which depends on the multipole order, the symmetry and time dependence of the interaction, and on the spin of the intermediate state (for details see, e.g., Frauenfelder and Steffen²²).

For static hyperfine interactions in polycrystalline samples the perturbation factor can be written as a sum of oscillatory terms:

$$G_{kk}(t) = s_{k0} + \sum_n s_{kn} \cos(\omega_n t). \quad (1)$$

The frequencies ω_n are the transition frequencies between the hyperfine levels into which a nuclear state is split by the hyperfine interaction. These frequencies and the amplitudes s_{kn} have to be determined by diagonalization of the interaction Hamiltonian. The number of terms in Eq. (1) depends on the spin I of the intermediate state. In favorable cases the

perturbation factor can be expressed in analytical form. For a pure magnetic interaction with Larmor frequency $\omega_m = 2\pi\nu_m = g\mu_N B_{hf}/\hbar$ one has

$$G_{22}(t) = \frac{1}{5} + \frac{2}{5} \sum_{n=1,2} \cos(n\omega_m t). \quad (2)$$

If the ensemble of the probe nuclei is subject to a distribution rather than a unique hyperfine interaction, the nuclear spins of the ensemble no longer precess all with the same frequency and an attenuation of the oscillation amplitudes results which is the stronger the broader the distribution. The effect of a Lorentzian HFI distribution of relative width δ on the angular correlation can be approximated by

$$G_{kk}(t) = s_{k0} + \sum_n s_{kn} \cos(\omega_n t) e^{-\delta n \omega_n t}. \quad (3)$$

Frequently, several fractions of nuclei subject to different HFI's are found in the same sample. The effective perturbation factor is then given by

$$G_{kk}(t) = \sum_i f_i G_{kk}^i(t), \quad (4)$$

where f_i (with $\sum_i f_i = 1$) is the relative intensity of the i th fraction.

As shown below, the PAC spectrum of ^{181}Ta on regular sites of the uncharged parent compound ErFe_2 is well described by a pure magnetic hyperfine interaction [Eq. (2)]. For probe nuclei in the hydrides ErFe_2H_x , however, the situation is much more complex. Here we expect in addition to the magnetic interaction perturbations by the nuclear electric QI between the nuclear quadrupole moment Q of the intermediate state of the cascade and the EFG produced by the H charge.

This combined hyperfine interaction is described by five parameters: the magnetic frequency ν_m , the quadrupole frequency $\nu_q = eQV_{zz}/h$, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ where V_{ii} are the principal-axis components of the EFG tensor with $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, and the Euler angles β, γ which describe the relative orientation of the magnetic hyperfine field and the EFG tensor.

In the present case—depending on temperature—this combined interaction will be either static or time dependent. At low temperatures the H atoms are “frozen,” each PAC probe will see a different configuration of H atoms and thus experience a different EFG tensor (ν_q, η) with different orientation (β, γ) relative to the magnetic hyperfine field. Consequently the ensemble of probes is subject to a distribution of static hyperfine interactions, even if all probes experience the same magnetic field. Qualitatively, the PAC spectrum will have the form given by Eq. (3); i.e., one expects attenuated or—depending on the width of the distribution and the relative strengths of the magnetic and the electric interactions—completely wiped-out oscillations. Quantitatively, the analysis may at best provide the ensemble average of the hyperfine frequencies ω_n . A separation of the parameters $\nu_m, \nu_q, \eta, \beta, \gamma$ and the determination of their distri-

butions from the ensemble-averaged hyperfine frequencies, however, appears not possible.

When hydrogen diffusion sets in at higher temperatures, the moving H atoms produce fluctuations of the QI. The effect of the resulting nuclear spin relaxation on the angular correlation depends on the fluctuation rate w . Slow fluctuations ($w \ll \nu^0$; $\nu^0 =$ center of the static distribution of hyperfine frequencies) at low temperatures lead to an additional attenuation of the angular correlation which becomes observable when the residence time τ_R between hydrogen jumps is of the same order of magnitude as the PAC time window ($\sim 10\tau_N, \tau_N =$ lifetime of the nuclear state). With increasing fluctuation rate w the nuclear spin relaxation increases. The resulting attenuation of the angular correlation first increases towards a maximum at $w \approx \nu^0$ and then—in the fast-fluctuation region with $w > \nu^0$ —decreases again, analogous to the motional narrowing of a NMR signal. Qualitatively, the PAC signature of a dynamic process therefore is a temperature-dependent, reversible attenuation of the angular correlation which passes through a maximum as one moves from the slow to the fast-fluctuation regime.

Quantitatively, the effect of the nuclear spin relaxation caused by jumping H atoms on the angular correlation is most appropriately described by Blume's stochastic theory^{23,24} which, however, is very difficult to apply to the complex situation of a substoichiometric hydride where the hydrogen motion leads to fluctuations of the orientation, strength, and symmetry of the quadrupole interaction. The analysis of experimental data in this case is therefore usually based on an approximation of the Blume theory with a single relaxation parameter λ_k :

$$G_{kk}(t) = \Gamma_{kk}(t) e^{-\lambda_k t}. \quad (5)$$

The validity of this approximation is discussed in Refs. 25 and 26. For slow fluctuations ($w \ll \nu^0$ the function $\Gamma_{kk}(t)$ is given by the perturbation factor of a static distribution of HFI's [Eq. (3)]) and the relaxation parameter λ_k is proportional to the jump rate w . In the case of over-barrier diffusion with an Arrhenius relation of the jump rate $w = w_0 e^{-E_a/kT}$ ($E_a =$ activation energy), for slow fluctuations the relaxation parameter therefore increases with increasing temperature, $\lambda_k \propto e^{-E_a/kT}$.

Fast fluctuations are adequately described by Eq. (5) if several jumps occur within one spin precession period ($w \geq 5\nu^0$). In the fast-fluctuation regime the function $\Gamma_{kk}(t)$ depends on the time average of the interaction. In nonmagnetic hydrides [e.g., $\text{HfH}_{1.6}$ (Ref. 5)] one frequently finds a vanishing time average of the QI. In this case one has $\Gamma_{kk}(t) = 1$. In the present case of ErFe_2H_x the time average is a pure magnetic interaction (see below) and $\Gamma_{kk}(t)$ is given by Eq. (2). The relaxation parameter λ_k corresponds to the Abragam-Pound spin relaxation constant²⁷ which for the case of a fluctuating QI of strength ν_q^f , residence time $\tau_R = 1/w$, and nuclear spin I is given by

$$\lambda_k = \left(\frac{3\pi^2}{5} \right) (\nu_q^f)^2 \tau_R k(k+1) \frac{[4I(I+1) - k(k+1) - 1]}{[2I(2I-1)]^2}. \quad (6)$$

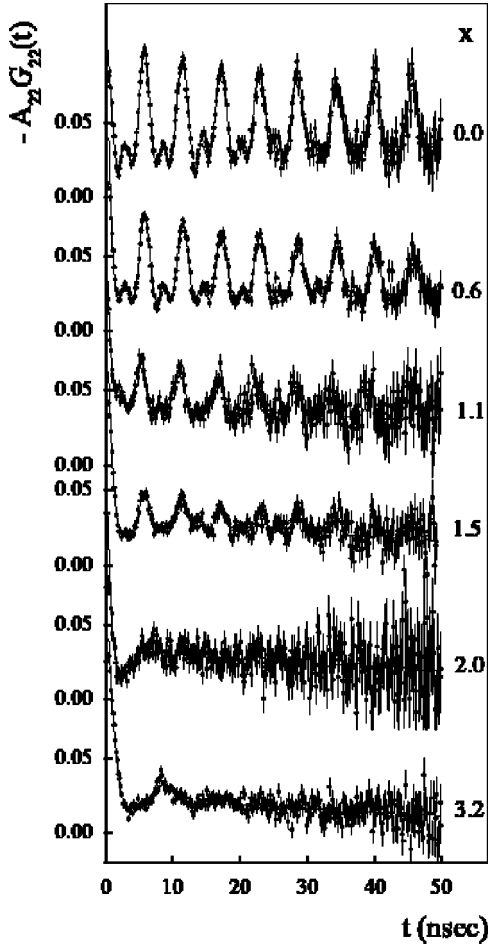


FIG. 1. PAC spectra of ^{181}Ta in ErFe_2H_x at 290 K for different H concentrations x .

In the fast-fluctuation regime the relaxation parameter therefore decreases with increasing temperature according to $\lambda_k \propto e^{(E_a/kT)}$.

III. MEASUREMENTS AND RESULTS

A. ^{181}Ta PAC in ErFe_2 in the temperature range $10 \text{ K} \leq T \leq 600 \text{ K}$

The hyperfine interaction of ^{181}Ta in the parent compound ErFe_2 was investigated in the temperature range $10 \text{ K} \leq T \leq 600 \text{ K}$. As a typical example the PAC spectrum of $^{181}\text{Ta}:\text{ErFe}_2$ measured at 290 K is shown in the topmost section of Fig. 1. The spectrum shows the periodic oscillation of the anisotropy characteristic for a pure magnetic HFI in polycrystalline samples [Eq. (2)]. The observation of a pure magnetic interaction implies that ^{181}Ta resides on the cubic Er site of ErFe_2 . For ^{181}Ta on the noncubic Fe site one should observe a well-defined combined magnetic and electric HFI.

The amplitude of the magnetic precession amounts to about 50% of the anisotropy (after solid angle correction) of the 133–482 keV $\gamma\gamma$ cascade of ^{181}Ta . A second oscillatory component accounting for the other 50% of the anisotropy, however, is not observed. From this one may conclude that

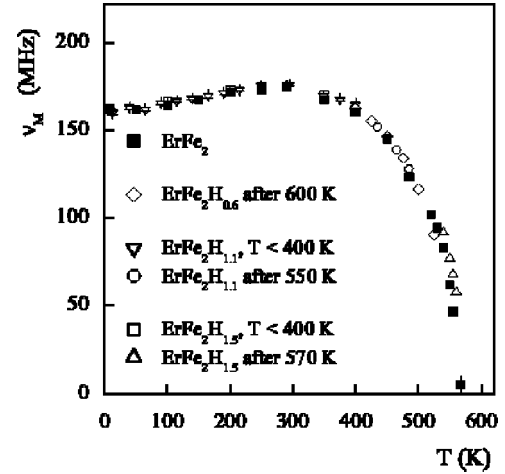


FIG. 2. The magnetic interaction frequency ν_m of ^{181}Ta in ErFe_2 and the hydrides ErFe_2H_x with $x=0.6, 1.1, 1.5$ as a function of temperature. The hydride frequencies measured before reaching $T=400 \text{ K}$ and after heating to $T \geq 550 \text{ K}$, respectively, are shown.

only about 50% of the probes are on the cubic Er sites of ErFe_2 while the rest must be subject to a broad distribution of strong HFI's. The PAC spectra of $^{181}\text{Ta}:\text{RFe}_2$ reported by Komissarova and co-workers^{10–12} show a similar reduced cubic site fraction. Our data were therefore analyzed with a two-site model, assuming a fraction of probes subject to a well-defined magnetic hyperfine field (regular site fraction) and a fraction characterized by a broad frequency distribution (irregular site fraction). The magnetic hyperfine frequency of ^{181}Ta on the regular cubic Er sites (relative intensity $f_{reg} \sim 0.5$) at 290 K is $\nu_m = 175.2(2) \text{ MHz}$, showing a slight Lorentzian distribution with relative width $\delta \sim 0.02$. The temperature dependence of the cubic site frequency ν_m is shown in Fig. 2. The frequency distribution of the irregular site has a center frequency of the order 150 MHz and a large relative width of $\delta \sim 0.7$. Most probably, both magnetic and electric hyperfine interactions contribute to this frequency distribution; an unambiguous separation of the different contributions, however, is not possible.

B. ^{181}Ta PAC in ErFe_2H_x at 290 K as a function of the H concentration $0.6 \leq x \leq 3.2$

Figure 1 illustrates the changes of the PAC spectra of $^{181}\text{Ta}:\text{ErFe}_2\text{H}_x$ caused by hydrogenation to different H concentrations at a given temperature. The PAC spectra measured at 290 K and nominal H concentrations $x=0.6, 1.1, 1.5, 2.0,$ and 3.2 are shown. At small H concentrations x one observes the same periodic oscillation characterizing the cubic site fraction of the uncharged compound, but the amplitude of this precession decreases continuously with increasing x and for $x \geq 2$ the PAC spectra only show the strong damping typical for a perturbation by a broad HFI distribution. Again, two fractions or components are required for a description of the spectra, the regular site fraction showing the periodic precession and an irregular site characterized by a broad frequency distribution. One expects two contributions to the frequency distribution, one coming from the ir-

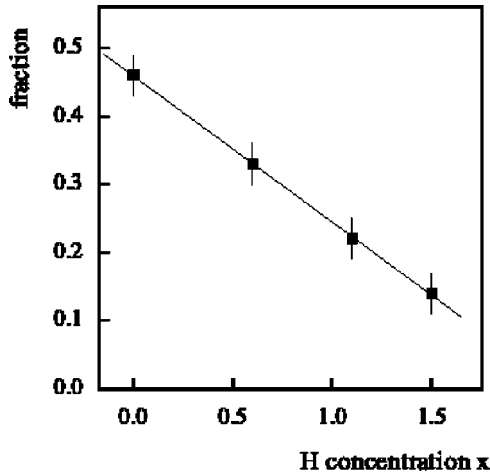


FIG. 3. The “regular site” fraction in the PAC spectra of $^{181}\text{Ta}:\text{ErFe}_2\text{H}_x$ at 290 K for different H concentrations x . This fraction represents the amount of $\alpha\text{-ErFe}_2\text{H}_x$ with $x \leq 0.1$ found in a ErFe_2 hydride charged to nominal concentration x .

regular site fraction already found in the parent compound ErFe_2 , the other one due to different static H environments of the cubic R sites. A separation of these two irregular site components is not possible. In the analysis we have assumed that the irregular site fraction of the parent compound is not affected by the presence of H and in the following we only consider the changes in the regular site fraction ($f_{reg} \approx 0.5$) in the parent compound by the H absorption.

The main results of the analysis, based on this two-site model, are the following: (i) the room-temperature regular site fraction is a linear function of the hydrogen concentration (see Fig. 3): $f_{reg} \approx 0.5 - 0.25(4)x$; (ii) the regular site frequency ν_m at 290 K is independent of the H concentration and identical to that of the uncharged parent compound ErFe_2 .

C. ^{181}Ta PAC in ErFe_2H_x as a function of temperature at concentrations $0.6 \leq x \leq 3.2$

The influence of temperature on the PAC spectra of $^{181}\text{Ta}:\text{ErFe}_2\text{H}_x$ was studied between 10 K and 600 K for the H concentrations $0.6 \leq x \leq 3.2$. Typical spectra are shown in Fig. 4 for the case of $x = 1.5$. For concentrations $0.6 \leq x \leq 2$ three temperature ranges with pronounced differences of the perturbation factor can be distinguished.

(i) In the range $10 \text{ K} \leq T \leq 350 \text{ K}$, the form of the spectra and the regular site fraction remain practically unchanged, only the regular site frequency ν_m varies with temperature following exactly the $\nu_m(T)$ curve of uncharged ErFe_2 (see Fig. 2).

(ii) In the range $350 \text{ K} < T \leq 525 \text{ K}$ the PAC spectra show the characteristic features of a perturbation by a fluctuating HFI: As temperature is raised beyond 350 K, the amplitude of the regular site oscillation starts to decrease and this decrease is the stronger the larger the H concentration: For $x = 1.5$ the oscillations are completely wiped out at $T \approx 400 \text{ K}$ (see Fig. 4) while for $x < 1.5$ at the same temperature some oscillations of reduced amplitude still remain vis-

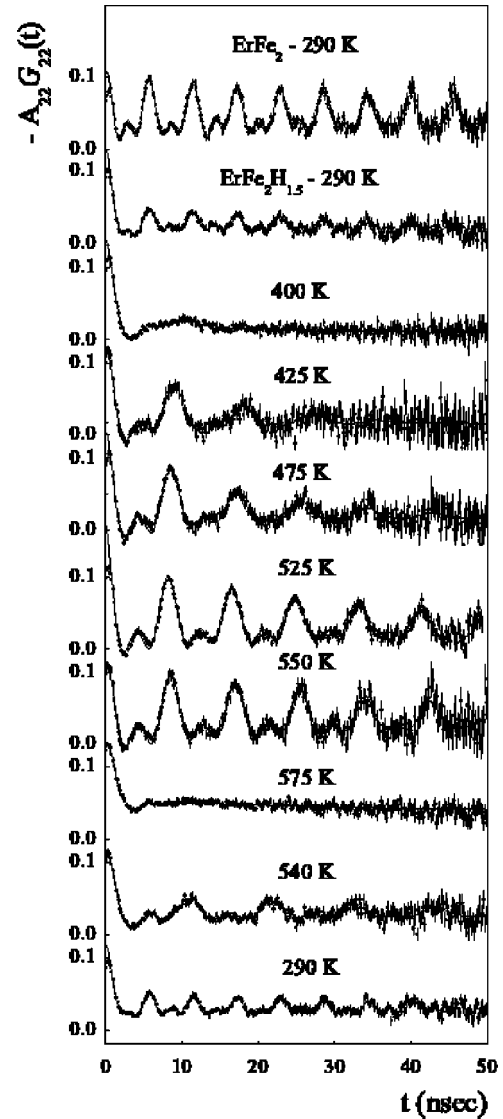


FIG. 4. PAC spectra of ^{181}Ta in ferromagnetic $\text{ErFe}_2\text{H}_{1.5}$ at different temperatures. Magnetic order is lost at $T \geq 575 \text{ K}$. For comparison, the spectrum of uncharged ErFe_2 at 290 K is shown in the topmost section.

ible. Upon further increase of temperature, however, a new periodic modulation appears, also for $x = 2.0$ which shows no oscillations at $T = 290 \text{ K}$. This new modulation has the same amplitude as the cubic site fraction of uncharged ErFe_2 (compare Figs. 1 and 4), but a considerably smaller frequency. Initially, the oscillations are damped—the stronger the higher the H concentration—but with increasing temperature the attenuation decreases and the perturbation factor evolves towards the periodic pattern of static, pure magnetic perturbation. Up to $\sim 525 \text{ K}$, these changes are fully reversible.

The attenuation maximum and the high-temperature recovery towards the pattern of a static magnetic interaction constitute clear evidence for a dynamic perturbation. The spectra for $T > 400 \text{ K}$ were therefore analyzed with the approximation [Eq. (5)] of the Blume theory, using Eq. (2) for the function $\Gamma_{kk}(t)$. The analysis then yields the temperature

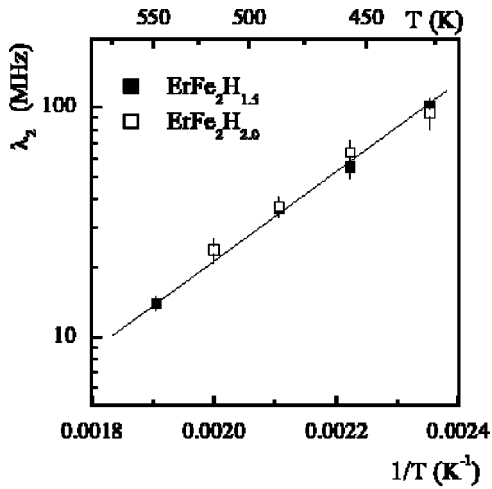


FIG. 5. The relaxation parameter λ_2 of ^{181}Ta in the hydrides ErFe_2H_x , $x = 1.5$ and 2.0 , as a function of the inverse temperature.

dependence of the relaxation parameter λ_2 and of the magnetic frequency ν_m which describes the time-averaged effect of rapidly diffusing H on the magnetic interaction. The analysis was restricted to the fast-fluctuation region $T \geq 400$ K because—as discussed in detail in Ref. 26—in the slow-fluctuation region the approximation of the Blume theory by a single relaxation parameter [Eq. (5)] tends to overestimate the activation energy, in particular if in the low-temperature limit the spectra show a broad static frequency distribution. Additional complications for the analysis of the low-temperature spectra come from the phase coexistence and from the presence of the irregular site of the uncharged parent compound.

In Fig. 5 the relaxation parameter λ_2 for $x = 1.5$ and 2.0 is displayed as a function of the inverse temperature. For the concentration $x = 0.6$ and 1.1 the relaxation rates are smaller

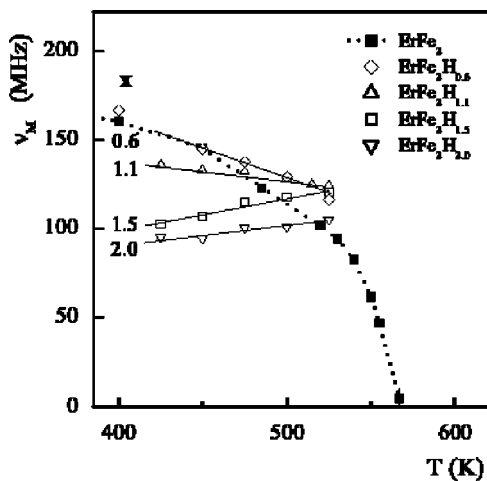


FIG. 6. The magnetic interaction frequency ν_m of ^{181}Ta in ErFe_2 and in the hydrides ErFe_2H_x with $x = 0.6, 1.1, 1.5,$ and 2.0 as a function of temperature in the fast-fluctuation region which starts at $T \sim 400$ K and extends to $T \sim 550$ K. Upon heating beyond $T \sim 550$ K the hydride frequencies change irreversibly to those of uncharged ErFe_2 .

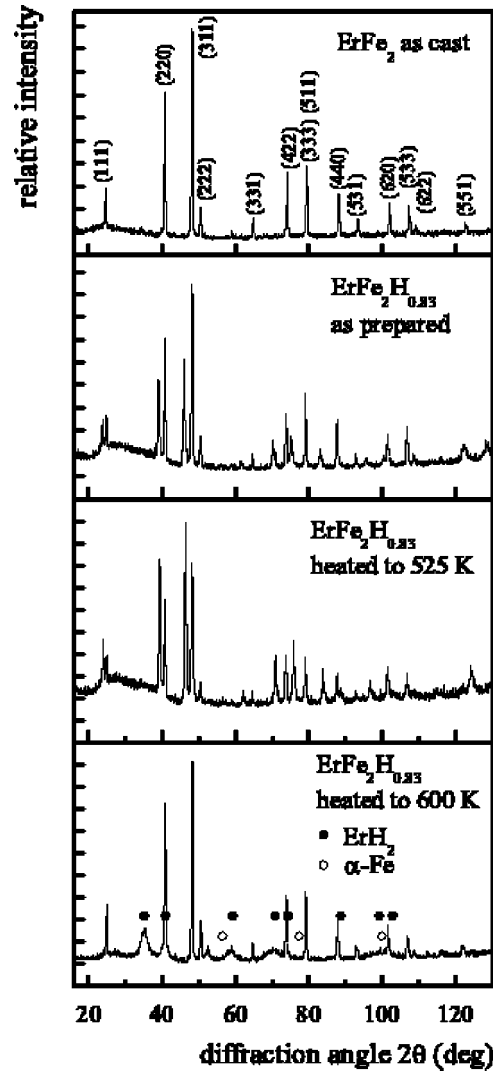


FIG. 7. X-ray diffraction spectra of ErFe_2 (topmost spectrum) and of $\text{ErFe}_2\text{H}_{0.83}$ after different thermal treatments (taken with $\text{Co K}\alpha$ radiation, $\lambda = 1.7902$ Å).

and the ratio of the dynamic to the static interaction unfavorable²⁶ for a precise determination of their temperature dependence. Figure 6 compares the temperature dependence of the magnetic frequency ν_m for the concentrations $0.6 \leq x \leq 2$ to that of the uncharged compound ErFe_2 in the temperature range $400 \text{ K} \leq T \leq 525 \text{ K}$.

(iii) $T > 550$ K: Irreversible changes of the perturbation factor occur when the samples are heated beyond 550 K. The amplitude of the oscillations is strongly reduced (compare 550 K and subsequent 540 K in Fig. 4) and at all temperatures the frequency ν_m is now identical to that of uncharged ErFe_2 (see Fig. 6). This indicates the decomposition of ErFe_2H_x at $T > 550$ K and identifies ErFe_2 as one of the decomposition products. At $T = 570$ K the compound is in the paramagnetic phase and the magnetic precession has disappeared. For the concentration $x = 3.2$ the spectra showed a broad frequency distribution up to the highest temperature investigated. There is some evidence for a dynamic QI at high temperatures; a magnetic precession, however, was not observed.

D. X-ray diffraction measurements

The PAC study of ErFe_2H_x has been accompanied by x-ray diffraction measurements of inactive samples of ErFe_2H_x with concentrations $0 \leq x \leq 3.6$. Figure 7 shows the diffraction pattern of the parent compound ErFe_2 (topmost spectrum) and of the hydride $\text{ErFe}_2\text{H}_{0.83}$ after different heat treatments (taken with Co $K\alpha$ radiation, $\lambda = 1.7902 \text{ \AA}$). A single-phase $C15$ diffraction pattern was found for the parent compound ErFe_2 (lattice parameter $a = 7.27 \text{ \AA}$) and for hydrides with $x > 1.6$ (lattice parameters $a = 7.62, 7.65, 7.72,$ and 7.85 \AA for $x = 1.92, 2.0, 2.54,$ and $3.6,$ respectively). This concentration dependence of the lattice parameter is in agreement with the result of de Saxcé *et al.*¹⁶

The x-ray pattern of $\text{ErFe}_2\text{H}_{0.83}$ in the as-prepared state shows the superposition of two phases with lattice parameters $a = 7.33 \text{ \AA}$ and 7.65 \AA , respectively. To gain more information on the decomposition process indicated by the irreversible changes in the PAC spectra at $T > 550 \text{ K}$, room-temperature x-ray spectra of $\text{ErFe}_2\text{H}_{0.83}$ heated to 525 K and 600 K were taken. After 525 K only the relative intensity of the two phases has changed, with the $a = 7.65 \text{ \AA}$ component being now dominant. After 600 K , however, the $a = 7.65 \text{ \AA}$ component has disappeared and new broad lines corresponding to ErH_2 (solid points in the bottommost section of Fig. 7) are observed. Lines corresponding to $\alpha\text{-Fe}$ (expected positions marked by the open points in Fig. 7) were not found. Apparently, under the low- H_2 -pressure conditions of our experiment crystalline ErFe_2H_x decomposes into ErFe_2 and ErH_2 without passing through the H-induced amorphization usually observed at higher H_2 pressures.¹⁴

IV. DISCUSSION

A. Magnetic hyperfine field of ^{181}Ta in ErFe_2

Our measurement of the magnetic hyperfine interaction of ^{181}Ta in uncharged ErFe_2 confirms the previous results of Komissarova *et al.*¹⁰ and extends the temperature dependence of ν_m down to 10 K . Rather than decreasing continuously with increasing temperature, the magnetic frequency passes through a maximum at $T \sim 300 \text{ K}$. This behavior of $\nu_m(T)$ which is observed for ^{181}Ta in all $R\text{Fe}_2$ compounds except in LuFe_2 with $\mu_{4f}(\text{Lu}) = 0$ (Ref. 28) is a consequence of the antiparallel coupling of Er and Fe and implies that the contributions of the Er and the Fe sublattice to the hyperfine field have different temperature dependences. The magnetic frequency $\nu_m(10 \text{ K}) = 162.0(5) \text{ MHz}$ corresponds to a magnetic hyperfine field of $B_{hf} = 16.16(5) \text{ T}$. The R dependence of the ^{181}Ta hyperfine field in the $R\text{Fe}_2$ series is discussed in detail in Refs. 10 and 11.

Only about 50% of the ^{181}Ta probes in $R\text{Fe}_2$ resides on cubic R sites; the rest is subject to a broad frequency distribution (see Sec. III A and Refs. 9–12). Among the possible reasons for this reduced cubic site fraction is the trapping of light impurities by ^{181}Hf , the mother isotope of the PAC nucleus. Metallic Hf is known to be an excellent getter which readily traps O and other light impurities such as C and N and R metals even of high purity may contain considerable concentrations of such nonmetallic elements. As the trapping

of an impurity strongly affects the hyperfine interaction seen by the PAC probe, the formation of different probe-impurity complexes will lead to a broad frequency distribution and thus reduce the number of probes subject to a well defined HFI. This impurity trapping has been shown to be responsible for a strong reduction of the regular site fraction of ^{181}Ta in Dy (Ref. 3) and Y (Ref. 29) metal.

B. Phase coexistence in ErFe_2H_x

For nominal H concentrations $x < 2$ and room temperature, both the x-ray diffraction and the PAC measurements indicate the coexistence of two phases (see Secs. III B and III D), in agreement with previous investigations.^{15–17} One has a lattice parameter ($a = 7.33 \text{ \AA}$) slightly larger than that of uncharged ErFe_2 ($a = 7.28 \text{ \AA}$) which according to Andreyev *et al.*¹⁵ corresponds to the α phase of the $\text{ErFe}_2\text{-H}_2$ system with $x \leq 0.1$. From its lattice parameter of $a = 7.65 \text{ \AA}$ the other phase in the x-ray spectra can be identified as a hydride phase ErFe_2H_x with $x \sim 1.6\text{--}1.7$.^{15,16}

In the PAC spectra the “regular site” fraction—characterized by a well-defined magnetic interaction—decreases linearly with increasing nominal H concentration x (see Fig. 3) and for $x < 2.0$ and $T < 400 \text{ K}$ its magnetic hyperfine frequency is identical to that of the parent compound ErFe_2 (see Fig. 2). This PAC component can therefore be attributed to the α phase of the $\text{ErFe}_2\text{-H}_2$ system with a very small H concentration.

In the high-concentration phase with $x \sim 1.6\text{--}1.7$ the PAC probes are subject to a static QI distribution. This phase therefore contributes to the irregular site fraction. It is, however, difficult to separate from the irregular site contribution of the parent compound.

For concentrations $x = 1.1$ and 1.5 the fraction with the static magnetic frequency of uncharged ErFe_2 which we attribute to the α phase of the $\text{ErFe}_2\text{-H}_2$ system completely disappears at temperatures $T > 400 \text{ K}$ and the PAC spectra are fully described by a single phase with a new magnetic perturbation pattern and the same relative intensity as the regular site fraction of uncharged ErFe_2 (see Sec. III C). Apparently, with increasing temperature the phase boundary of the high-concentration hydride is shifted towards lower concentrations.

C. Dynamic quadrupole interactions in ErFe_2H_x

An important new result of this study is the observation of a dynamic quadrupole interaction in the presence of a strong static hyperfine field in the temperature range $400 \text{ K} < T \leq 525 \text{ K}$ and concentrations $0.6 \leq x \leq 2.0$ (see Sec. III C). Evidence for this dynamic QI is the temperature-dependent attenuation of the new magnetic perturbation pattern appearing at $T \geq 400 \text{ K}$. A damping of the oscillation amplitudes of a PAC pattern may be caused either by a static frequency distribution or a fluctuating hyperfine interaction (see Sec. II B). Static frequency distributions result from some perturbation—chemical or structural—of the periodicity of the compound. Their width may decrease with increasing temperature, but such an annealing effect is usually not re-

versible upon cooling. The attenuation observed in the present case is fully temperature reversible for $T \leq 525$ K and it is not found in uncharged ErFe_2 . Therefore it can be clearly attributed to a fluctuating quadrupole interaction caused by the moving H atoms. It is easily shown that the dynamic magnetic interaction due to the H nuclear magnetic moment is too weak to account for the observed relaxation. The exponential decrease of the relaxation parameter λ_2 with increasing temperature (see Fig. 5) is the signature of the fast fluctuation region; i.e., the average residence time between H jumps is short compared to the precession time of the magnetic interaction and the PAC time window. The effect of slow fluctuations at lower temperatures is difficult to detect in the presence of the regular site fraction with the static magnetic interaction frequency of $\alpha\text{-ErFe}_2\text{H}_x$, $x \leq 0.1$, and the irregular site contribution of the parent compound ErFe_2 .

The observation of a pure magnetic interaction in the high-temperature limit implies a vanishing time average of the fluctuating QI. A rapidly diffusing H ion spends the same amount of time on all equivalent sites of the H lattice, so that in the time average the same charge resides on each of these sites. The time average of the QI is therefore related to the sites occupied by the rapidly diffusing H. The vanishing time average in the present case confirms that up to the concentration $x=2$ the hydrogen atoms are exclusively located on the $R_2\text{Fe}_2$ interstitial sites of the $C15$ structure, since the lattice consisting of identical charges on the $R_2\text{Fe}_2$ interstitials has cubic symmetry and produces a zero EFG at the R site.

The effective charge $Z'e$ associated with the moving H atom can be estimated from the dynamic quadrupole frequency ν_q^f responsible for the nuclear relaxation. According to Refs. 25 and 26, the maximum of the relaxation parameter λ_2^{\max} obtained with the approximation of a single relaxation constant [Eq. (5)] and the frequency ν_q^f of the fluctuating QI are approximately related by $\lambda_2^{\max} \sim \frac{1}{2} \nu_q^f$ from which one may estimate the strength of the dynamic QI without knowledge of the residence time between H jumps. For $x=1.5$ and 2.0 we have $\lambda_2^{\max} \sim 100$ MHz (see Fig. 5) and hence $\nu_q^f \sim 200$ MHz, so the dynamic QI and the static magnetic interaction are of comparable strength. In a point-charge model the quadrupole frequency produced by a charge $Z'e$ at a distance r from a nucleus with quadrupole moment Q is given by

$$\nu_q = 2Z'e^2 Q (1 - \gamma_\infty) \frac{1}{h} \frac{1}{r^3}.$$

Inserting $Q = 2.36$ (5) b (Ref. 30) for the quadrupole moment of the $\frac{5}{2}$ state of ^{181}Ta , $(1 - \gamma_\infty) = 62$ for the Sternheimer correction³¹ of Ta^{5+} and $r = 1.67$ Å for the distance between the Er site and the nearest H on an Er_2Fe_2 interstitial¹⁸ one obtains $\nu_q \sim 2.15Z'e$ (GHz). The comparison with the experimental value $\nu_q^f \sim 200$ MHz leads to an effective charge of $Z'e \sim 0.095e$, similar to the H charge estimated for other metal-hydrogen systems.^{32,33}

The activation energy for H jumps in ErFe_2H_x for $x = 1.5$ and 2.0 , obtained by a fit of the Arrhenius relation λ_k

$\propto e^{(E_a/kT)}$ to the data in Fig. 5, is $E_a = 0.39(3)$ eV, in good agreement with the result of Atsumi *et al.*¹⁹ for the diffusion of H on $R_2\text{Fe}_2$ interstitials in DyFe_2H_x . For the concentration $x = 0.6$ and 1.1 the PAC spectra also show evidence for a dynamic QI, but due to the smaller H concentration, the relaxation rates are smaller and a precise determination of the activation energy is not possible, in particular for $x = 0.6$. For $x = 1.1$ the data suggest a slightly larger value of E_a than for $x = 1.5$ and 2.0 .

D. Effect of hydrogen on the magnetic hyperfine field of ^{181}Ta in ErFe_2H_x

The hydrogen-induced changes of the static magnetic hyperfine field in the fast-fluctuation region are illustrated in Fig. 6, where the magnetic frequencies ν_m measured in ErFe_2H_x for $425 \text{ K} \leq T \leq 525 \text{ K}$ are compared to those of uncharged ErFe_2 . One should note the difference to the room-temperature Mössbauer measurements of Shashikala *et al.*⁸ While our study provides the magnetic hyperfine field of ^{181}Ta on Er sites with—on the time average—all the Er_2Fe_2 interstitials occupied by H with equal probability, Shashikala *et al.*⁸ have determined the effect of a single static H neighbor on the ^{57}Fe hyperfine interaction. Such information cannot be extracted from the low-temperature PAC spectra. Contrary to the Mössbauer spectra, the PAC spectra show one broad static frequency distribution and do not allow one to separate magnetic and electric HFI contributions and thereby identify different H configurations. This is mainly a consequence of the much larger ^{181}Ta quadrupole moment which makes ^{181}Ta more sensitive to quadrupole interactions than ^{57}Fe .

At high temperatures the strong ^{181}Ta QI averages out and the changes of the magnetic hyperfine field become observable. Both the magnitude and the relative temperature dependence of the magnetic field are affected. The magnetic frequency at a given temperature decreases with increasing concentration: at 450 K, e.g., the magnetic hyperfine field decreases from 14.5 T for $x = 0.6$ to 9.5 T for $x = 2$. Between $x = 0$ and $x = 0.6$ the field is practically constant. The temperature dependence of ν_m at small H concentrations is weaker than in uncharged ErFe_2 and at high H concentrations even changes sign, i.e., the frequency increases with increasing T .

It is interesting to relate the drastic decrease of the hyperfine field B_{hf} at 450 K by about 50% from $x = 0.6$ to $x = 2$ to the information on the magnetic properties of $R\text{Fe}_2\text{H}_x$ available from previous studies.

The magnetic hyperfine field of probes with zero orbital angular momentum is due to the Fermi contact term in the magnetic nucleus-electron interaction and reflects the spin polarization of the s conduction electrons at the nuclear site. A finite s -spin polarization at the probe may arise from the polarization of the host conduction electrons and from the polarization of the electron core of the probe by a localized magnetic spin moment.

As discussed in detail by Komissarova *et al.*¹⁰ and Sorokin *et al.*,¹² in the case of ^{181}Ta in $R\text{Fe}_2$ both the core polarization (CP) and the conduction electron polarization

(CEP) are expected to contribute to the magnetic hyperfine field. In $R\text{Fe}_2$ compounds the Stoner criterion for itinerant $3d$ magnetism is fulfilled and Fe carries a $3d$ magnetic moment of the order of $(1.7-1.9)\mu_B$, also for the nonmagnetic R constituents $R = \text{Y, Lu}$.³⁴ The hybridization between the Fe $3d$ and the R $5d$ electrons produces a $5d$ moment at the R site antiparallel to the $3d$ moment and the local $5d-4f(R)$ exchange then leads to the ferrimagnetic coupling of the R $4f$ and the Fe $3d$ moments.³⁵ It can therefore be assumed that the $5d$ element ^{181}Ta on R sites of $R\text{Fe}_2$ also carries a localized $5d$ moment producing a CP contribution which depends on the Fe $3d$ moment and the $5d-4f(R)$ exchange.

A CEP contribution to the hyperfine field is expected both from the $3d$ and the $4f$ sublattice. In a $3d$ transition metal with a wide s band mixed with a narrow spin-polarized $3d$ band the $s-d$ hybridization produces a finite s -electron spin density. The resulting CEP component of the hyperfine field is found to be approximately proportional to the inducing $3d$ moment.^{36,37} In magnetically ordered R metals or R compounds the interaction of the s conduction electrons with the hybridized $4f-5d$ electrons also contributes to the CEP.³⁸ The corresponding hyperfine field component is in a first approximation proportional to the projection $(g-1)J$ of the R spin on the total angular momentum J .^{39,40}

We may therefore write the hyperfine field B_{hf} as a sum of two components, one coming from the $3d$, the other from the $4f$ sublattice:

$$B_{hf} = B_{3d} + B_{4f}. \quad (7)$$

The comparison of B_{hf} of ^{181}Ta in ErFe_2 (17.5 T at 300 K) and in LuFe_2 (20.5 T, Ref. 28)—which because of the complete $4f$ shell of Lu carries no $4f$ magnetic moment—shows that the two terms have opposite sign and that the $4f$ contribution in ErFe_2 amounts to only $\sim 15\%$ of the $3d$ contribution.

For the discussion of the hydrogen induced changes of the magnetic interaction, we assume—based on the above arguments—these contributions to be proportional to the inducing spins of the $3d$ and $4f$ sublattices, respectively, which leads to the relation

$$B_{hf} = \chi_{3d}S_{3d} + \chi_{4f}S_{4f}. \quad (8)$$

Neutron diffraction studies of ErFe_2H_x have shown that the Er sublattice magnetization in ErFe_2 hydrides depends sensitively on temperature and H concentration. The saturation magnetization of the Er sublattice decreases drastically with increasing H concentration which is attributed to an increasing noncollinearity of the Er moments (“fanning”) caused by the random distribution of the H atoms in the $C15$ structure. The Fe moment, however, was found to remain identical to that of ErFe_2 which implies that contrary to the $3d-4f$ coupling the $3d-3d$ exchange is little affected by the H absorption. This is confirmed by our observation of magnetic order up to the decomposition temperature $T \sim 550$ K which shows that for H concentrations $x \leq 2$ the Curie temperature decreases at most by 10%.

For a given temperature one might then at first sight expect the Er contribution to the magnetic hyperfine field to decrease with increasing H concentration and the Fe contribution to remain more or less constant. But in view of the relative magnitude and the opposite sign of the two contributions, these assumptions can obviously not account for the observed 50% decrease of B_{hf} between $x=0.6$ and $x=2.0$ at, e.g., 450 K. With $S_{3d} \approx \text{const}$ and $B_{4f} \ll B_{3d}$, the experimental trend of $B_{hf}(x)$ therefore strongly suggests a decrease of the s -conduction-electron polarization—expressed mainly by the factor χ_{3d} —with increasing H concentration, to which both the lattice expansion upon hydrogen absorption and the electronic state of hydrogen may contribute. In the anionic model of the rare-earth hydrides a hydride anion is formed by the removal of s electrons from the conduction band to more localized states. In the R hydrides RH_2 this decrease of the s -conduction-electron density reduces the magnetic order temperature because the $4f-4f$ coupling is mediated by the conduction electrons. In the present case of RFe_2H_x , however, the magnetic order is mainly determined by $3d-3d$ exchange. A decrease of the s conduction density would therefore have little effect on the order temperature, but strongly reduce the magnetic hyperfine field, in agreement with the experimental observations.

The changes in the temperature dependence of the hyperfine field B_{hf} with the H concentration $B_{hf}(T;x)$ must be related to the concentration dependence of B_{3d} and B_{4f} and to the differences in their temperature dependences. Because of the opposite sign of the two contributions, the temperature decrease of the net magnetization will be slower than that of uncharged ErFe_2 if in the temperature range of interest the magnetization of the Er sublattice decreases faster than that of the Fe sublattice and depending on the relative magnitude of the two components even an increase of the net magnetization with temperature is conceivable. Different temperature dependences of the Er and the Fe sublattice magnetization have been evidenced by the neutron diffraction study of $\text{ErFe}_2\text{D}_{3.5}$.²¹ The magnetization of the Er sublattice decreases much faster with increasing temperature than that of the Fe sublattice and the Er sublattice becomes completely disordered well below the bulk Curie temperature. In addition to the sublattice magnetizations, both the concentration and the temperature dependence of the conduction electron polarization—expressed by χ_{3d} and χ_{4f} —can be expected to contribute to the trend of $B_{hf}(T;x)$. A quantitative interpretation, however, is beyond the scope of this paper.

V. SUMMARY

The hyperfine interaction of ^{181}Ta on Er sites in $C15$ Laves hydrides ErFe_2H_x has been investigated by PAC spectroscopy as a function of H concentration and temperature.

At low temperatures the PAC spectra of the high-concentration hydride fraction reflect a broad distribution of strong static magnetic and electric hyperfine interactions. The dynamic QI caused by rapidly diffusing H atoms becomes observable at $T > 400$ K. The resulting ^{181}Ta nuclear quadrupole relaxation rates show an Arrhenius behavior with an activation energy of $E_a = 0.39(3)$ eV for $x = 1.5$ and 2.0

and permit an estimate of the effective charge associated with the diffusing H atom of $Z'e \approx 0.095e$. In the fast-fluctuation region the magnetic and electric hyperfine interaction can be separated and the ^{181}Ta magnetic hyperfine field B_{hf} was determined as a function of temperature and H concentration. At a given temperature $T \geq 450$ K, B_{hf} decreases with increasing x , reflecting a decrease of the s-conduction-electron polarization at the probe site. The temperature dependence of B_{hf} in the fast-fluctuation region is also affected by the hydrogen concentration: at $x=1.1$, B_{hf}

was found to decrease, at $x=1.5$ and 2.0 to increase with increasing T .

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