Defects and magnetic hyperfine fields in ZrFe$_2$ investigated using perturbed-angular-correlation spectroscopy

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We have measured the temperature dependence of the electric and magnetic hyperfine interactions at $^{181}$Ta nuclei substituted into the Zr site in the Laves-phase compound ZrFe$_2$, using the perturbed angular correlation of $\gamma$ rays emitted after the $\beta^-$ decays of $^{180}$Hf probe nuclei. Although the overall crystal structure is cubic, a weak strongly damped electric-quadrupole interaction is observed, which shows no significant temperature dependence over the investigated temperature range from 290–1300 K. Thus below the magnetic ordering temperature $T_C$ of 631(2) K we observe combined magnetic-dipole and electric-quadrupole hyperfine interactions. Two separate magnetic components characterize the magnetic-dipole interactions. For the interaction at the primary site, which is occupied by 70–80% of the probes, the Larmor frequency measured at temperature has a value of $\omega_L=407(1)$ Mrad sec$^{-1}$. The secondary site is populated by the remaining 20–30% of the probes, for which the corresponding Larmor frequency has a room temperature value of $\omega_L=579(3)$ Mrad sec$^{-1}$. We attribute the primary interaction to the “perfect-crystal” probe environment at the Zr site, whereas we ascribe the secondary interaction to the enhancement of the transferred hyperfine field by the presence of Fe antisite defects near the Zr site. At temperatures below but very close to $T_C$, those frequencies cannot be determined for either interaction, because the magnetic-hyperfine and the electric-quadrupole frequencies converge to comparable values.

I. INTRODUCTION

Intermetallic compounds, such as the Laves-phase ZrFe$_2$, differ fundamentally from ordinary alloys of metals, because the constituent metal atoms exhibit long-range structural order in the crystal. Binary intermetallic compounds consist therefore of crystals that have two distinct sublattices. If one or both constituent atoms have either $d$ or $f$ electrons that can order via the exchange interaction, then both structural and magnetic ordering characterize the intermetallic crystal. Defects, dopants, and impurities affect the properties of intermetallic compound by breaking the symmetry of the crystal structure. This reduction in symmetry may affect only the local environment of a defect; or, alternatively, this reduction may modify the long-range magnetic ordering in the crystal. The fundamental purpose of this investigation therefore is to understand the effects of defects and magnetism that take place on a nanometer scale in the context of the macroscopic structural and magnetic properties of the crystal.

For this purpose, we use perturbed-angular-correlation (PAC) spectroscopy, because with it we can observe local structural changes that point defects produce via the nuclear electric-quadrupole interaction and concurrently the long-range effects that magnetic ordering produce via the nuclear magnetic-dipole interaction. The PAC technique is based on substituting a relatively low concentration of a radioactive probe atom, in this case, $^{181}$Hf$\rightarrow^{181}$Ta, into a well-defined site in a crystal. Because the chemistries of Hf and Zr are very similar, the probe $^{181}$Hf$\rightarrow^{181}$Ta substitutes into the Zr site in ZrFe$_2$. This probe can be added at relatively low levels, $\leq 0.1$ at. % Hf, so that it does not measurably alter the global properties of the crystal. Because of this sensitivity, PAC spectroscopy provides a unique means to investigate the nanometer-scale effects of local crystal and magnetic fields at the Zr site in ZrFe$_2$. At the probe site, the former generate electric-field gradients (EFG’s), when the site symmetry is lower than cubic; and the latter generate magnetic hyperfine fields (MHF’s), which can be measured below the magnetic ordering temperature $T_C$ (i.e., the Curie temperature). Specifically, we measured EFG’s and MHF’s in the compounds (Zr$_{1-x}$Hf$_x$) Fe$_{2+y}$, temperatures ranging from 290–1300 K, for values of $x$ varying from 0.003–0.05, and for values of $y$ varying from 0–0.1. Experiments were repeated several times, and were performed while both increasing and decreasing the temperature.

The compound ZrFe$_2$ crystallizes in the C15 MgCu$_2$-type Laves-phase structure. The stoichiometry corresponding to the C15 structure ranges approximately from 66–72 at. % Fe. Thus we can take advantage of the range of composition over which the C15 structure is stable. By increasing the Fe concentration to slightly greater than 66 at. %, we can cause

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The formation of Fe antisite defects (Fe atoms that reside on Zr sites).

Because the local symmetry at the Fe site is lower than cubic, EFG's are present at the Fe site. When the crystal orders magnetically, the Fe sites, which are crystallographically equivalent above the magnetic ordering temperature, separate into two magnetically nonequivalent Fe sites, which have a population ratio of 3–1. However, the PAC technique probes only the sites where the probes are. Figure 1 presents a schematic diagram of the nearest-neighbor environment of a Zr site, where the Hf probes are located. Four Zr atoms and 12 Fe atoms are located in the nearest-neighbor environment of the Zr site. The crystal contains only one crystallographic site for Zr, and the local symmetry at the Zr site is cubic. Based on this information, for Hf probes at the Zr site, we would expect to observe no EFG's and one single well-defined magnetic-dipole interaction below $T_C$, and a nonperturbed correlation above $T_C$.

However, earlier measurements on this compound (reviewed below) using a variety of techniques, indicate that these expectations do not correspond to reality. Instead, weak EFG's and two well-defined MHF's characterize hyperfine interactions at the Zr site in ZrFe$_2$. These measurements provide little detailed information about the origins of the unexpected weak EFG's and the nature of these MHF's. Therefore we have investigated in detail the magnetic-ordering phase transition by measuring the dependence of the MHF's temperatures up to $T_C$. In this context, we have determined that the primary MHF arises from a "perfect-crystal" surrounding coordination of Fe and Zr atoms and the secondary MHF arises from a local environment that contains an antisite defect. The reproducibility and consistency of measurements performed on a variety of samples suggests strongly that the thermodynamically stable crystal structure crystallizes with a small amount of disorder.

II. EARLIER RELATED INVESTIGATIONS

The history of measuring hyperfine interactions and related quantities in this Laves phase is long. For this reason, we briefly mention the earlier investigations related to this work. Pieger and Craig$^7$ used magnetization measurements to determine that the magnetic moment at the Fe site in ZrFe$_2$ is 1.62$\mu_B$ and that ZrFe$_2$ is ferromagnetic below 628 K. They note that the magnetic moment in the ZrFe$_2$ is reduced from the corresponding value of 2.2$\mu_B$ observed in pure Fe. To explain this difference, they state that the Zr atoms donate electrons to the Fe atoms, creating a more nearly filled d shell in the compound.

In the initial measurements of Fe site hyperfine interactions using $^{57}$Fe-Mössbauer-effect spectroscopy, Wertheim, Jaccarino, and Wernick$^8$ observed two combined electric-quadrupole and magnetic-dipole interactions below a magnetic ordering temperature $T_C = 586$ K, in the proportion 3:1. In ZrFe$_2$, the direction of easy magnetization is (111). When the sample is magnetized, at one of the sites, the direction of the EFG is aligned with this direction of easy magnetization; but, at the other site, the direction of the EFG lies at an angle of 70.3° to the direction of easy magnetization. Thus the two different interactions arise because the Fe atoms occupy crystallographically identical but magnetically different sites. Amaral, Livi, and Gomes$^6$ confirmed this interpretation.

Bruckner, Kleinstick, and Schulze$^8$ investigated the dependence of the lattice parameter on deviations from stoichiometry. They found that the lattice parameter does not change for Fe compositions slightly below 66 at. % but that it decreases for Fe compositions between 66 and 72 at. %. According to the authors, this effect arises because crystals having excess Zr are not stable and because excess Fe can be accommodated in the structure up to 72 at. %. To determine how this Fe excess is accommodated in the structure, the authors exclude the possibility that Fe atoms could fit into interstitial sites by noting that the space filling in this structure is 71 at. %. So no interstitial sites are available in the structure that have a size comparable to that of an Fe atom. They analyzed their diffraction data using a least-squares fitting method, and found that the best fit was obtained by assuming that the departure from stoichiometry was accommodated by Fe antisite defects in the Zr sites (rather than vacancies or Fe tetrahedra in Zr sites).

Based on observations of a low value of the electronic specific-heat coefficient $\gamma$ and small high-field susceptibility $\chi_{hf}$, Muraoka, Shiga, and Nakamura$^9$ give strong evidence for ferromagnetism in ZrFe$_2$. They also note that excess Fe atoms increase the Curie temperature $T_C$ and magnetization, because, when those atoms are accommodated as antisite defects, they are surrounded by other Fe atoms as nearest neighbors. This configuration creates a more stable local magnetic moment. They report $T_C = 630$ K and that the direction of easy magnetization is (111), which changes to (100) when 20 at. % Co is substituted for Fe. These authors and others$^{10}$ report that it is very difficult to make ZrFe$_2$ without some amount of antisite defects.

Livi, Amaral, and Fries$^{11}$ measured the dependence of the Zr-site MHF on Hf concentration in (Zr$_{1-x}$Hf$_x$)Fe$_2$ for $x = 0.01, 0.03, 0.1, \text{ and } 0.25$ using PAC spectroscopy. Although Hf is very similar chemically to Zr and should substitute exclusively onto the Zr site, Livi, Amaral, and Fries measured two magnetic hyperfine fields, with values of 62.5 and 92 kOe at laboratory temperature, for the composition $x = 0.01$. They attributed the lower value to Hf atoms on Zr...
sites in a perfect-crystal environment and the higher value to Hf atoms on Zr sites, where another Hf atom is located in one of the nearest-neighbor Zr sites. They also found that increasing the Hf concentration decreased the magnitude of the Zr-site hyperfine fields. Wiesinger and co-workers used Mössbauer-effect and nuclear-magnetic-resonance (NMR) spectroscopies to investigate the magnetic properties of Zr(Fe$_{1-x}$Co$_x$)$_2$. Although their Mössbauer-effect results agree generally with those of Wertheim, Jaccarino, and Wernick, they found additional features in the Mössbauer-effect spectra measured on the stoichiometric ZrFe$_2$ compound. They could only accurately fit the Mössbauer spectra by assuming an additional Fe spectrum, which corresponds to a direction of easy magnetization along [110]. Thus, their model includes two interactions, one corresponding to magnetization along [111] and one along [110]. The authors associate the magnetization along [110] to the presence of Fe antisite defects on Zr sites. Their NMR measurements of the hyperfine field of the $^{91}$Zr in ZrFe$_2$ agree with the results of Betsuyaki and Komura, who report a hyperfine field of 135 kOe. They noted that the line shapes of the zero-field spin-echo spectra of $^{91}$Zr are asymmetric, an unusual occurrence in a crystal site with cubic symmetry.

Mohn and Schwarz have recently performed self-consistent spin-polarized energy-band calculations for ZrFe$_2$, which predict that a small negative magnetic moment of $-0.56\mu_B$ resides at the Zr site. Their calculations show a magnetic moment of 1.90$\mu_B$ for the Fe atoms, resulting in a net moment of 1.62$\mu_B$ per Fe atom, once the contribution from the Zr is deducted. According to these calculations, ZrFe$_2$ should be considered as a ferrimagnetic rather than ferromagnetic compound. The pressure dependence of the magnetization of ZrFe$_2$ measured by Dumelow et al. and Armitage et al. provide support for this interpretation.

Luck and Wang recently performed heat-capacity measurements on ZrFe$_2$ using differential scanning calorimetry. They found a discontinuity in the heat-capacity curve at 586 K, which they ascribe to the critical temperature for magnetic ordering. They determined that $T_C=586$ K, in agreement with the measurements of Wertheim, Jaccarino, and Wernick and Komura and Shikazono in disagreement with the measurements of most other researchers noted above. Arias and Abriata suggest that Komura and Shikazono may have obtained this last result because they used a ZrFe$_2$ sample that contained excess Fe.

In summary, a variety of spectroscopic and macroscopic techniques have been used to investigate the magnetic properties of ZrFe$_2$ in contexts that involve the effects of defects and dopants. For the most part, these reports do not present clear connections between magnetic effects and effects of defects. We present results that give a clear connection between measured MHF’s and a prevalent defect type in ZrFe$_2$, namely, Fe antisite defects.

### III. EXPERIMENTAL TECHNIQUES

Intermetallic alloys were prepared by arc melting the pure constituents within an Ar atmosphere. The purity of the starting materials was 99.8% Zr, 99.995% Fe, and 97% Hf (most of the impurity content in Zr is Hf and vice versa). Before melting, a Hf wire was irradiated with thermal neutrons in the Penn State Breazeale Reactor to produce the $^{181}$Hf radioactivity via the $^{180}$Hf($n,\gamma$) nuclear reaction. The Zr and Hf pieces (containing radioactive $^{181}$Hf and stable carrier $^{180}$Hf) were first melted together to help ensure a homogeneous Zr-Hf solid solution, and then the Zr and Hf pieces were mixed with Fe to produce buttons of (Zr$_{1-x}$Hf$_x$)$_2$Fe$_{2+y}$. Samples were usually melted three times, turning the sample after each melting to help achieve homogeneity. We measured the weight of the samples before and after melting and found negligible mass loss. Visual inspection of the samples indicated that the samples had a bright, shiny appearance. This observation strongly suggests that significant amounts of oxygen were not incorporated into the bulk samples during melting. This observation is supported by previous studies using Mössbauer effect techniques, and which did not detect any evidence of oxygen contamination in similar samples. To form the ZrFe$_2$ phase requires no special heat treatment after melting. The x-ray-diffraction patterns measured on the as-melted radioactive ZrFe$_2$ samples could be indexed in accord with the C15 Laves-phase structure and indicated phase purity to within a few percent. For the PAC measurements, samples were sealed under Ar in a fused-silica tube prior to measurement.

The PAC spectrometers used in this study are equipped with four (BaF or CsF) scintillation detectors that give a nominal time resolution of 0.8–1.0 nsec full width at half maximum for the gamma rays emitted in the decays of $^{181}$Hf. On one of the spectrometers we have designed and built a furnace and a very-high-precision temperature-control system, which can maintain a sample temperature to within ±0.03 K at the set point for a measurement period of up to 24 h. This apparatus gives us the capability to investigate magnetic ordering phase transitions at temperatures very close to $T_C$.

For a polycrystalline sample and for the spin $I=\frac{1}{2}$ intermediate level of $^{181}$Ta, the measured angular correlation function is given by

$$W(\theta,t)\equiv \exp(-t/\tau_N)[1 + A_{22}G_{22}(t)P_2(\cos \theta)].$$

(1)

where $\theta$ and $t$ are the angle between emission directions of the cascade $\gamma$ rays, and the time between emission of the first and second $\gamma$ rays, respectively. $\tau_N$ represents the lifetime of the intermediate level of the $^{181}$Ta probe nucleus, and $A_{22}$ represents the corresponding anisotropy of the angular correlation. The perturbation function,

$$G_{22}(t) = S_0 + \sum_i S_i \cos(\omega_i t) \exp(-\delta \omega_i t),$$

(2)

represents the extranuclear hyperfine interaction, where the parameter $\delta$ is a measure of the width of the Lorentzian distribution of the hyperfine frequencies about their mean values. The frequencies $\omega_i$ and their amplitudes $S_i$ are related to the hyperfine splitting of the intermediate nuclear level. Above $T_C$ where no MHF is present, three interaction frequencies $\omega_i$ are observable, related to the nuclear electric-quadrupole interaction (NQI) frequency $\omega_0 = eQV_{zz}/2I(2I - 1)\hbar$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where the $V_{ii}$ are the elements of the EFG tensor in its principal axis system. Below $T_C$, the frequencies $\omega_i$ are obtained by diagonalizing the hyperfine interaction matrix resulting
from the combination of the NQI with the MHF represented by the magnetic frequency $\omega_L = -g_1 \mu_B B/\hbar$, in which $B$ represents the MHF, $g_1$ represents the nuclear $g$ factor [$g_1 = 1.30(3)$], and $\mu_N$ represents the nuclear magneton. Because of the lifting of the degeneracy of the NQI by the addition of the MHF, the number of allowable $\omega_2$ is increased from 3 to (in principle) 15. The hyperfine parameters were extracted from the measured perturbation functions $A_{22}G_{22}(t)$ using the DEPACK program developed by Lindgren.

In the present set of experiments, we consider two distinct cases, experimental perturbation functions measured at temperatures below and above $T_C$. At temperatures above $T_C$, the perturbation functions for stoichiometric samples of ZrFe$_2$ show very weak nuclear electric-quadrupole interactions (NQI's) that represent broad distributions of EFG's and, correspondingly, interaction frequencies. The aforementioned model of an NQI does not provide a unique set of parameters that gives an accurate representation of the experimental measurement. Instead, adequate representations could be achieved by assuming one, two, or several distinct interaction sites. For the nonstoichiometric samples, the above-$T_C$ perturbation functions show stronger NQI's than those for the stoichiometric samples, and these perturbation functions also represent broad distributions of interaction frequencies. To achieve an accurate representation of these perturbation functions requires assuming at least two interaction sites.

At temperatures well below $T_C$, the perturbation functions show two components. Each of these components corresponds to a strong magnetic-dipole interaction perturbed by a weak electric-quadrupole interaction. Generally, for the stoichiometric samples, one of the two combined interactions dominates, representing 70–80% of the probes. The other, higher-frequency interaction represents the remainder of the probes. To represent these perturbation functions accurately requires using the (aforementioned) model of combined magnetic and quadrupole interactions. At temperatures very
near but below $T_c$, the effects of the two magnetic-dipole interactions cannot be separated, because the corresponding interaction frequencies approach each other in magnitude. In addition, the distributions associated with these frequencies become broader and comparable in magnitude to the frequencies that arise from the NQI.

**IV. RESULTS**

Figure 2 presents perturbation functions and corresponding Fourier transforms for a stoichiometric sample of ZrFe$_2$ (top and second-from-top figures), an Fe-rich sample having composition Zr$_{0.32}$Fe$_{0.68}$ (third-from-top figure), and an Fe-rich sample having composition Zr$_{0.30}$Fe$_{0.70}$ (bottom figure), show line broadening that increases as the Fe concentration increases.

FIG. 3. Perturbation functions and corresponding Fourier transforms, measured at laboratory temperature on (1) a stoichiometric sample of ZrFe$_2$ (top and second-from-top figures), (2) an Fe-rich sample having composition Zr$_{0.32}$Fe$_{0.68}$ (third-from-top figure), and (3) an Fe-rich sample having composition Zr$_{0.30}$Fe$_{0.70}$ (bottom figure), show line broadening that increases as the Fe concentration increases.

a pure magnetic-dipole interaction in a polycrystalline sample, the amplitudes of the two components for frequencies $\omega_L$ and $2\omega_L$ should be equal. Thus the broadening of the peaks indicates the effect of the weak, poorly-defined NQI, which is operative over the entire investigated temperature range. At temperatures approaching $T_c$, the peaks in the Fourier transforms become difficult to resolve. At laboratory temperature (290 K), we consistently obtained $\omega_L=407(1)$ Mrad sec$^{-1}$ and $\omega_L=579(3)$ Mrad sec$^{-1}$, and the ratio of these two values is 1.42(1), which corresponds to magnetic hyperfine fields of 93.0(0.5) kOe and 65.4(0.2) kOe. These values correspond quite well to the ratio of 1.413 and values of the hyperfine field 92 and 62.5 kOe obtained by Livi, Amaral, and Fries$^{11}$ on similar samples. In Fig. 3 we present several laboratory-temperature perturbation functions and corresponding Fourier transforms that show the effects produced by changing the Fe composi-
FIG. 4. Perturbation functions, which were measured at a series of elevated temperatures on an Fe-rich sample having composition \(Zr_{0.3} Fe_{0.7}\), show more line broadening than in the corresponding case of stoichiometric samples, which Fig. 3 shows. The fits to the measured functions represent a model of two NQI’s, which broad distributions of frequencies characterize.

V. DISCUSSION
As discussed above, based on the crystal structure and on the local symmetry at the Zr site in the ZrFe\(_2\), we would expect to observe no nuclear electric-quadrupole interaction at the Zr site. Above the magnetic ordering temperature \(T_C\), we would expect the \(\gamma-\gamma\) angular correlation to show no perturbations; and, below \(T_C\), in the \(\gamma-\gamma\) angular correlation, we would expect to observe a single well-defined magnetic-dipole interaction. However, both the results of this work and the previous work of other researchers\(^{11}\) show that weak EFG’s and two MHF’s characterize the hyperfine interactions at the Zr site in ZrFe\(_2\) below \(T_C\).

defects generate. The latter represents the effects of fluctuating EFG’s. Unfortunately, the effects of prompt coincidences obscure the information in the perturbation functions at times less than two or three nanoseconds. In principle, this information could be used to determine which of these two models gives a more accurate physical representation, because the curvature of \(G_{22}(t)\) for small values of \(t\) differs for the two models. Moreover, if fluctuating EFG’s were operative, their fluctuation rates would be insufficiently fast, in order to reduce the anisotropy to zero within the experimental time scale of \(\approx 40\) nsec. Hence distinguishing between static and time-varying EFG’s in this case is problematical.

Figure 5 presents perturbation functions for a stoichiometric sample of ZrFe\(_2\) measured at a series of temperatures very close to \(T_C\) and at two temperatures above \(T_C\) (633.0 and 1300 K). The two perturbation functions measured at a temperature very close to but above \(T_C\) and a temperature well above \(T_C\) show no discernible temperature dependence, which is consistent with the source of the interaction being immobile point defects. These two perturbation functions are representative of many that we measured at temperatures above \(T_C\). This series of measurements performed below \(T_C\) shows the gradual evolution of the interaction frequencies and line shapes, which characterizes the ferromagnetic-to-paramagnetic transition. As the temperature increases, the frequencies decrease in magnitude and the line shapes broaden, which, for temperatures within \(\approx 20\) K of \(T_C\), makes the separation of the components indeterminate. Likewise, we are unable to determine the power-law dependence of \(\omega_T\) on reduced temperature \([\omega_T = \omega_T(0) T^\beta, \quad T \rightarrow 0- T/T_C\)] at temperatures very close to \(T_C\) (however, from about 500–600 K both MHF’s show a power-law exponent \(\beta = 0.3\)).

We can, however, estimate \(T_C\) by visual inspection. The perturbation function measured at 633 K shows the evolution to the high-temperature shape, which remains invariant over several hundred degrees, whereas, the function measured at 629 K shows qualitatively a stronger perturbation. Therefore \(T_C\) must lie between these two temperatures, \(T_C = 631(2)\) K. Figure 6 presents the temperature dependence of the Larmor frequencies for the two MHF’s. The temperature dependence of the primary interaction confirms the determination of \(T_C\). In one series of measurements, the temperature was increased in successive steps; and in another series, temperature was decreased successively. We cannot resolve differences in the temperature dependence of the frequencies that represent the two series. Therefore we observe no hysteresis, within the experimental accuracy.
To explain these observations, we consider the fractions of probes corresponding to the two magnetic-dipole interactions, which are 70–80% for the lower-frequency interaction (majority interaction) and approximately 20–30% for the higher-frequency interaction (minority interaction). We made several samples of ZrFe$_2$, and observed that these site fractions fluctuated about the aforementioned values by about 5%. At a Zr site in ZrFe$_2$, a Zr atom has four Zr-atom next-nearest neighbors. If some type of point defect were present in relatively high concentrations of a few percent and randomly distributed in the crystal, then the probability that, at a given Zr atom, a point defect is located in either coordination sphere would be approximately 0.2–0.3. Therefore the observed probe site fractions, which correspond to the two magnetic-dipole interactions, are consistent with the hypothesis that the origin of the frequency increase in the interaction corresponding to the ~20% fraction is a point defect and that concomitantly the origin of the ~80% fraction is a defect-free “perfect-crystal” probe environment.

We consider further the hypothesis that primarily a single type of point defect causes the minority higher-frequency magnetic-dipole interaction. Although this hypothesis implies a relatively high defect concentration, Muraoka, Shiga, and Nakamura, Yamada and Ohira, and Wiesinger, Oppelt, and Buschow observed that Fe antisite defects, i.e., Fe atoms that reside on Zr sites, arise commonly even for stoichiometric samples in the ZrFe$_2$ crystal. Additionally, probe-defect interactions could cause the distribution of defects to be not completely random. This effect would lead to a higher minority interaction site occupancy at lower global defect concentrations.

In addition to changing the observed MHF below $T_C$, the
antisite defects are also likely to contribute to the NQI. This is because the lattice distortion associated with the antisite defect breaks the cubic symmetry around the Zr site. The resulting NQI, combined with those caused by other defects that might be present in the compound can lead to the observed quadrupole interaction above and below $T_C$.

Moreover, as Fig. 3 indicates, the site fraction for the minority interaction (high-frequency MHF) increases as the concentration of excess Fe increases. The associated line broadening, which also increases with the excess Fe concentration, corresponds to changes in the magnetic hyperfine interactions from the existence of different types of defects at higher concentrations. Measurements, which we performed above $T_C$ on the Fe-rich sample and which Fig. 4 shows, also indicate that the addition of excess Fe gives rise to a stronger NQI, which a broad distribution of frequencies characterizes. An increased concentration of defects associated with the departure from stoichiometry could cause this stronger NQI. The line broadening could be caused by the existence of different types of different NQI’s that accompany higher defect concentrations.

To test this hypothesis further, we asked Legoas and co-workers to calculate MHF’s and the corresponding Larmor frequencies $\omega_L$ at the Zr site for several types of defects in the ZrFe$_2$ structure. They used the real-space, linear muffin-tin orbital atomic sphere approximation (RS-LMTO-ASA) method. They performed these calculations for a Ta atom at a Zr site for four different situations: (1) a perfect crystal, (2) an antisite defect Fe–Zr in a nearest-neighbor Zr site, (3) a vacancy in a nearest-neighbor Fe site, and (4) a vacancy in a nearest-neighbor Zr site. The ratio of the value of the hyperfine field with the corresponding defect present, cases 2, 3, and 4, and the value of the perfect-crystal hyperfine field, case 1, yield: 1.8 for case 2, the antisite defect Fe in a nearest-neighbor Zr site; 1.5 for case 3, a nearest-neighbor Fe vacancy; and 2.6 for case 4, a nearest-neighbor Zr vacancy. The measured ratio of the higher-frequency (minority) MHF to the lower-frequency (majority) MHF is 1.42. The ratios for cases 2 and 3 are sufficiently close to the experimental ratio, given the uncertainties in the calculations and the experiments, that we cannot rule out either possibility. However, we can rule out case 4, a vacancy in a nearest-neighbor Zr site, because the calculated ratio of 2.6 deviates sufficiently from the experimental ratio of 1.42. Therefore to identify the origin of the minority MHF, these model calculations do not uniquely allow us to distinguish between the Fe antisite defect and the nearest-neighbor Fe-site vacancy.

According to the model calculations, the observed probe site fractions, corresponding to the two magnetic-dipole interactions, are consistent with the hypothesis that the difference (from the majority interaction) in the interaction magnitude corresponding to minority interaction arises from an Fe antisite point defect and that concomitantly the origin of the majority interaction is a “perfect-crystal” probe environment. We base this conclusion on (1) the correlation between excess Fe concentration and the minority site fraction, (2) the line shapes corresponding to the NQI’s and the related broadening of the lines corresponding to the magnetic-dipole interactions, and (3) empirical evidence obtained from other measurements for Fe antisite defects in ZrFe$_2$.

Additionally, from sample to sample, we varied the Hf concentration in $(Zr_{1-x},Hf_x)Fe_{2+y}$, from $x = 0.003–0.04$, and we observed no strong dependence of these site fractions on this concentration. Therefore the point defect in question is not related to the Hf doping and is an indigenous defect. Moreover, we observe only two well-defined MHF’s. We assign the majority interaction to a near “perfect-crystal” environment located in the vicinity of the probe atoms. The minority interaction, we ascribe to the alteration of the transferred spin density produced by an Fe atom that lies on a nearest-neighbor Zr site. We observe no other magnetic-dipole interactions. Therefore we conclude that the defects, which provide stoichiometric compensation for the envisioned Fe antisite defects, are not localized with respect to the probe atoms. The accommodation of the stoichiometry variation could occur through extended defects, such as antiphase boundaries, or through the existence of small amounts of an undetected Zr-rich second phase. The reproducibility and consistency of measurements performed on a variety of samples suggests strongly that perfect order does not characterize the thermodynamically stable crystal structure. Instead the stable structure crystallizes with a small amount of disorder.

VI. CONCLUSIONS

We have measured the temperature dependence of a primary MHF, a secondary MHF, and a weak EFG at the Zr-site in several samples of ZrFe$_2$. Using experimental and theoretical information, we have identified the sources of the two MHF’s. The primary, lower-frequency MHF represents a nearly “perfect-crystal” Zr-site probe environment, in which the transfer of spin density from Fe $d$ orbitals polarizes the $^{181}$Ta nuclei. The secondary, higher-frequency MHF represents a probe environment in which a nearest-neighbor Fe antisite defect in a Zr site augments the transferred hyperfine field. Calculations of the MHF’s performed using the RS-LMTO-ASA method are consistent with this interpretation. At temperatures very close to but below $T_C$, the frequencies corresponding to the two Zr-site MHF’s approach each other in value. For this reason, we cannot resolve the power-law dependence of either MHF at temperatures very close to $T_C$.

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23) S. B. Legoas and S. Frota-Pessôa (unpublished).