Low temperature high magnetic field $^{57}$Fe Mössbauer study of kinetic arrest in Ta doped HfFe$_2$

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Abstract

Low temperature high magnetic field $^{57}$Fe Mössbauer measurements were carried out on the inter-metallic compound Hf$_{0.77}$Ta$_{0.23}$Fe$_2$ by following novel paths in $H$–$T$ space. The ferromagnetic (FM) fraction at 5 K and zero magnetic field is shown to depend on the cooling field, i.e., the higher the field is, the higher the FM fraction is. Mössbauer spectra collected in the presence of a 4 T magnetic field show that the antiferromagnetic (AFM) spins are canted with respect to the applied magnetic field and hence contribute to the total bulk magnetization in this compound. The data also show an induced magnetic moment even at the 2a site of the AFM phase. Mössbauer spectra collected using the CHUF (cooling and heating in un-equal magnetic fields) protocol show a reentrant transition when the sample is cooled in zero field and measured during warming in 4 T, showing the FM state as the equilibrium state. This work is the first microscopic experimental evidence for the de-vitrification of the kinetically arrested magnetic state.

(Some figures may appear in colour only in the online journal)

1. Introduction

The compound HfFe$_2$, which belongs to the Laves phase compounds of RFe$_2$-type where R is transition metal (A = Sc, Ti, Nb, Hf and Ta), has been reported to show polymorphism with one of the phases crystallizing in MgZn$_2$ type hexagonal structure (space group $P6_3/mmc$) and the second one in cubic structure of MgCu$_2$ type [1, 2]. The MgZn$_2$ type hexagonal structure, also known as the C14 structure in the literature, contains two crystallographically inequivalent Fe sites. The structure consists of atomic layers alternating along the hexagonal $c$-axis in the sequence Fe(6h)–R–Fe(2a)–R–Fe(6h) and so on. While the exchange interaction between the Fe(6h) atoms is always ferromagnetic within the same layer, the interaction between the neighboring Fe(6h) layers depends on the type of R atom, and the Fe atoms at the 2a site. Therefore, depending on the type of R atom, these compounds exhibit large changes in the magnetic properties with composition/temperature without any change in the crystal structure and, hence, have been extensively explored [1–4]. For example, the magnetic ground state is reported to change from ferromagnetism (FM) to antiferromagnetism (AFM) at a Ta concentration between $x = 0.2$ and 0.3 in Hf$_{1-x}$Ta$_x$Fe$_2$ [2, 5], whereas in Hf$_{1-x}$Ti$_x$Fe$_2$, this transition is reported to take place in the vicinity of $x = 0.6$ [3]. Irrespective of magnetic ordering, the fraction of Fe occupying 6h and 2a sites is reported to be in the ratio of 3:1 from structural and Mössbauer data as well [1–4]. Apart from bulk magnetization measurements, these compounds have also been studied by Mössbauer and perturbed angular correlation techniques to measure their hyperfine interactions. The Mössbauer studies of Nishihara et al. [2] on Hf$_{1-x}$Ta$_x$Fe$_2$ ($x = 0–0.7$) showed discontinuous change in the internal hyperfine fields ($B_{INT}$) of Fe across first order AFM–FM transition. Such discontinuous change in $B_{INT}$ values through the FM to AFM transition is also observed in the FeRh system and is explained in terms
of the difference of the polarization of conduction electrons to \( B_{\text{INT}} \) in the two states [6]. The \( B_{\text{INT}} \) values on the 6h and 2a sites of Fe in Hf\(_1-x\)Ta\(_x\)Fe\(_2\) compounds are comparable (\( \approx 17 \) T) in the FM state and they reduce drastically in the AFM state (\( \approx 10 \) T for the 6h site and zero for the 2a site of AFM phase) [1–4, 7]. In FM HfFe\(_2\), various contributions to the \( B_{\text{INT}} \) at both Hf and Fe sites are calculated theoretically and are found to match excellently with measured values, and it is reported that the magnetism in HfFe\(_2\) originates mainly from the Fe atomic magnetism [4]. However, only a few reports are seen in the literature dealing with the mechanism of magnetic transition in these compounds and the studies on this aspect are far from complete. For example, Nishihara et al [2] explained their results with the model of itinerant electron magnetism and Delyagin et al [3] invoked the concept of magnetic frustration of Fe(2a) sites which is caused by a non-collinearity of the magnetic moment of the Fe(6h) sublattice.

Recently, Rawat et al [5] have reported bulk magnetization measurements on Hf\(_1-x\)Ta\(_x\)Fe\(_2\) (\( x = 0.225,0.230 \) and 0.235) compounds and observed anomalous theromagnetic irreversibility at low temperatures due to kinetic arrest of the first order AFM–FM transition. They observed that the region of coexisting AFM and FM phases increases in \( H–T \) space with Ta concentration and concluded that due to the interplay of kinetic arrest and supercooling, one can have tunable fractions of AFM and FM phases for the same temperature and magnetic field values. It is to be noted that the phenomena of phase coexistence and kinetic arrest are reported in many compounds such as manganites, shape memory alloys, multiferroics, magnetocaloric materials, other inter-metallics and oxides [8–29]. In compounds such as manganites, there is a huge difference between the resistivities of the AFM and FM states, and therefore resistivity measurements, in conjunction with bulk magnetization measurements, are employed to study such phenomena. However, from such magnetic and transport data, it is difficult to obtain accurate quantitative information about the fraction of FM and AFM phases and their individual responses to the applied magnetic field.

In this work, we have carried out \(^{57}\text{Fe} \) Mössbauer measurements under the application of external magnetic fields to study the phenomena of phase coexistence and kinetic arrest in the Hf\(_{0.77}\)Ta\(_{0.23}\)Fe\(_2\) compound. It is to be noted that, because of the significant difference in the internal hyperfine field (\( B_{\text{INT}} \)) at Fe sites corresponding to the FM and AFM phases of this compound, one can unambiguously estimate these fractions to support the concept of kinetic arrest. The results presented here clearly demonstrate the phenomenon of kinetic arrest in this compound. Also, in contrast to bulk magnetic measurements, which essentially measure the response of the sample as a whole to the applied magnetic field, one can estimate the individual responses of the FM and AFM fractions to the applied magnetic field from the Mössbauer measurements, as discussed below. Finally, because of polarization selection rules with the application of external magnetic fields, the Mössbauer data give unambiguous information regarding the linearity of the magnetic structure, which is expected to give inputs to explain the magnetic phase transition, as proposed by Delyagin et al [3].

2. Experimental details

The studied polycrystalline sample of Hf\(_{0.77}\)Ta\(_{0.23}\)Fe\(_2\) was prepared by arc melting the constituent elements under inert argon gas atmosphere; the details of preparation are reported elsewhere [5]. The prepared sample was found to be single phase from powder x-ray diffraction measurements and the refinement of the diffraction pattern showed that the alloy crystallizes in the \( P6_3/mmc \) hexagonal structure. The ingots were crushed to powder and mixed with silicone grease for \(^{57}\text{Fe} \) Mössbauer measurements, which were carried out in transmission mode with a \(^{57}\text{Co(Rh)} \) radioactive source in constant acceleration mode using a standard PC-based Mössbauer spectrometer equipped with a WissEl velocity drive. Velocity calibration of the spectrometer was carried out with natural iron absorber at room temperature. For low temperature high magnetic field measurements, the sample was placed inside a Janis made superconducting magnet and the external magnetic field was applied parallel to the \( \gamma \)-ray (i.e., longitudinal geometry). The Mössbauer data were analyzed using the NORMOS SITE [30] program for the extraction of hyperfine parameters. Magnetization measurements were performed using a 7 T SQUID-VSM (Quantum Design, USA) on the same sample (powdered and mixed with silicon grease) that was used for Mössbauer measurements.

3. Results and discussion

Figure 1 shows the temperature dependent \(^{57}\text{Fe} \) Mössbauer data at the indicated temperatures. Spectra recorded at 300 K and down to 65 K were fitted with a sextet and a doublet which correspond to Fe at the 6h and 2a sites, respectively, of the AFM phase. To fit 5 K data, an overlap of two sextets and a doublet was considered, where the additional sextet corresponds to the Fe in the ferromagnetic (FM) phase. The observed isomer shifts relative to natural iron are \( -0.11 \pm 0.01 \) and \( -0.07 \pm 0.01 \) mm s\(^{-1}\); the quadrupole splitting values are \( 0.11 \pm 0.01 \) and \( 0.32 \pm 0.02 \) mm s\(^{-1}\) for the 6h and 2a sites of the AFM phase, respectively. As reported in the literature, we have not observed any significant variation of these parameters across the FM–AFM transition [1, 2]. It is the \( B_{\text{INT}} \) values that change drastically across the FM–AFM transition and hence only these parameters including the line width (FWHM), area fraction of different magnetic phases, and area ratio of second and third line intensities (A23) are shown in the obtained hyperfine parameters given in table 1. It is to be noted that the estimated area fraction of Fe in the 6h and 2a sites is always in the ratio of 3:1, which is consistent with the crystallographic data on these compounds [1–4]. The A23 parameter of the sextet was observed to be close to two, which is expected. Since the measurements are carried out on powder samples and in zero external magnetic fields, one would expect an isotropic distribution of angles between the incident \( \gamma \)-ray and the internal hyperfine field corresponding.
Figure 1. Zero field $^{57}$Fe Mössbauer spectra of Hf$_{0.77}$Ta$_{0.23}$Fe$_2$ at the indicated temperatures. The dots are the experimental points and the solid lines are the best fits to the data. The obtained hyperfine parameters are shown in table 1.

Table 1. The obtained hyperfine parameters from the fitting of $^{57}$Fe Mössbauer spectra measured at zero field (shown in figure 1) at the indicated temperatures approached by zero field cooling.

| Temp (K) | FWHM (mm s$^{-1}$) | $B_{\text{INT}}$ (T) | $A_{23}$ (%) | Phase       |
|---------|-------------------|----------------------|-----------|------------|
| 300     | 0.45 ± 0.02       | 6.5 ± 0.06           | 2.00      | 75 AFM(6h) |
|         | 0.36 ± 0.03       | —                    | —         | 25 AFM(2a) |
| 150     | 0.43 ± 0.02       | 10.0 ± 0.06          | 2.00      | 74 AFM(6h) |
|         | 0.33 ± 0.04       | —                    | —         | 26 AFM(2a) |
| 65      | 0.45 ± 0.03       | 10.7 ± 0.07          | 2.00      | 77 AFM(6h) |
|         | 0.34 ± 0.05       | —                    | —         | 23 AFM(2a) |
| 5       | 0.46              | 17.0 ± 0.3           | 2.00      | 8 FM       |
|         | 0.43 ± 0.01       | 11.1 ± 0.03          | 2.00      | 68 AFM(6h) |
|         | 0.46 ± 0.04       | —                    | —         | 24 AFM(2a) |

The spectra are fitted with two sextets and one doublet by keeping all the parameters as free (except in the 5 T remnant data, where the area ratio of AFM 6h and 2a sites is constrained to be equal to 3:1 due to relatively poor statistics). The derived hyperfine field parameters from the fit are shown in table 2. One can clearly see from the data that, as the strength of the cooling magnetic field is increased, the FM fraction increases in intensity. The FM fraction obtained from these measurements as a function of cooling field at 5 K and 0 T is shown in figure 3, which shows a rapid increase in FM phase fraction for cooling field $\pm 3.5$ T, which becomes about 39% for cooling in 5 T. On the other hand, the $M-T$ data of Rawat et al [5] on the same system suggest that cooling in a magnetic field higher than 3 T results in an FM phase fraction close to 100%. The powder sample used in the present study was taken from the same ingot as that used in the earlier studies as reported in [5]. The difference between these two studies could be due to the sample mounting conditions for these two measurements. For the Mössbauer study, a powder sample with silicon grease was used, whereas the earlier magnetization studies were performed on a piece of ingot.
Figure 2. Zero field $^{57}$Fe Mössbauer spectra of Hf$_{0.77}$Ta$_{0.23}$Fe$_2$ measured at 5 K. The sample was cooled from 150 K in the presence of an applied magnetic field ($B_{\text{EXT}}$) as indicated in the figure. The $B_{\text{EXT}}$ was reduced to zero isothermally at 5 K and the spectra were collected in the remnant state. The dots are the experimental points and the solid lines are the best fits to the data. The obtained hyperfine parameters are shown in table 2.

To find the origin of the difference between these two measurements, we performed magnetization measurements on the same powder sample (along with grease) as was used for the Mössbauer measurements. Figure 4(a) shows the $M$–$H$ curve measured after zero field cooling with the magnetic field varied isothermally at 5 K from 0 → 7 → 0 → 7 T. As can be seen from this figure the magnetic field required for AFM to FM transition is distinctly higher than that observed in previous work for the same but bulk ingot sample. Similar measurements on a powder sample but without grease (not shown here) showed that critical field was almost the same as that of the bulk ingot sample. The only difference between the bulk sample and the powder sample without grease was the absence of a jump in $M$ versus $H$ in the virgin curve. From these measurements it was evident that the presence of grease leads to the shift in the critical field required for the AFM to FM transition rather than process of making the measurements in powder form. Since the critical field is higher for the sample mixed with grease we infer that the effect of grease is equivalent to pressure.

The virgin $M$–$H$ curve (first field increasing cycle from 0 → 7 T; curve (i)) measured after zero field cooling to 5 K in figure 4(a) shows an initial increase in $M$ value at low field which can be attributed to domain reorientation of minor FM phase. This is in agreement with the above Mössbauer analysis which suggests the presence of FM phase at 5 K after zero field cooling. Beyond 3 T the magnetization increases sharply indicating a field induced AFM to FM transition. With reducing magnetic field (curve (ii): 7 → 0 T) no visible signature of reverse transformation could be observed. However, for the second field increasing cycle, the initial rise in $M$ at low field is significantly higher than

| Cooling field (T) | FWHM (mm s$^{-1}$) | $B_{\text{EFF}}$ (T) | $A_{23}$ (%) | Phase |
|-------------------|--------------------|----------------------|--------------|-------|
| 3                 | 0.5 ± 0.1          | 16.7 ± 0.2           | 2.00 13 FM   |
| 3.5               | 0.56 ± 0.08        | 16.8 ± 0.2           | 2.00 20 FM   |
| 4                 | 0.46 ± 0.02        | 11.0 ± 0.04          | 2.00 64 AFM(6h) |
| 5                 | 0.40 ± 0.03        | 1.1 ± 0.05           | 2.00 61 AFM(6h) |
| 3                 | 0.45 ± 0.04        | 11.2 ± 0.07          | 2.00 56 AFM(6h) |
| 4                 | 0.36 ± 0.04        | —                    | 2.00 18 AFM(2a) |
| 5                 | 0.47 ± 0.08        | —                    | 2.00 15 AFM(2a) |

Figure 3. Variation of the ferromagnetic (FM) fraction in the remnant state at 5 K as a function of cooling magnetic field obtained from analysis of the $^{57}$Fe Mössbauer spectra shown in figure 2. The solid line is a guide to the eye.
(as evident from the nonsaturating FM fraction compared to that present at 7 T magnetic field. for curves (i) (ii) and (iii). This gives about 7% and 60% 0 T are found to be 0.005, 0.044 and 0.071 emu, respectively by the lines in figure 4(a). The extrapolated values of \(M\) at 0 T are found to be 0.005, 0.044 and 0.071 emu, respectively for curves (i) (ii) and (iii). This gives about 7% and 60% FM fraction compared to that present at 7 T magnetic field. Since the AFM–FM transformation is not completed at 7 T (as evident from the nonsaturating \(M\) and hysteresis at 7 T), these FM fraction estimates are upper limits of the FM phase fraction. Similarly cooling in 4 T gives about 73% FM phase and remnant FM phase of about 60%. The relative invariance of the FM phase fraction on reducing the magnetic field to zero (after cooling in 4 T) is consistent with our M¨ossbauer measurement which shows a remnant phase fraction (26%, table 2) identical to that at 4 T (figure 7, FCC at 5 K).

Figure 4. (a) Magnetization \((M–H)\) of Hf_{0.77}Ta_{0.23}Fe_{2} powder mixed with silicone grease (as used in the Mössbauer experiments). The curve represented by open circles (blue) was measured after cooling in zero field with the magnetic field varied from 0 \(\rightarrow\) 7 \(\rightarrow\) 0 \(\rightarrow\) 7 T (labeled as (i), (ii) and (iii) respectively). The curve represented by red triangles was measured after cooling in 4 T from 150 K with the magnetic field varied from 4 \(\rightarrow\) 0 \(\rightarrow\) 4 T. (b) Temperature dependence of magnetization measured in the presence of 4 T during warming after zero field cooling (ZFCW; 5 \(\rightarrow\) 150 K) and subsequent cooling (FCC; 150 \(\rightarrow\) 5 K). The arrows indicate the temperature and magnetic field sweep directions for the respective curves.

Figure 5. High field (4 T) \(^{57}\)Fe Mössbauer spectra of Hf_{0.77}Ta_{0.23}Fe_{2} measured at (a) 150 K and (b) 5 K. The dots are the experimental points and the solid lines are the best fits to the data. The obtained hyperfine parameters are shown in table 3.

It is to be noted that when the external magnetic field is applied at 5 K (i.e., when the sample is cooled to 5 K in ZFC and the external magnetic field is applied), no enhancement of the FM fraction is observed (figure 6, ZFCW at 5 K) from Mössbauer measurements. This shows that the fraction of FM and AFM states at 5 K depends on the path followed in \(H–T\) space to reach the measurement temperature. Similar path dependent values of magnetization and resistivity at low temperature have been reported for doped CeFe_{2} [26, 29], Gd_{3}Ge_{4} [24, 25, 29], Co doped Mn_{2}Sb [22], Pd doped FeRh [23], manganites [10, 31], etc. In these studies such path dependence has been associated with a path dependent coexisting phase fraction of magnetic states of contrasting nature.

Figure 5(a) shows the M¨ossbauer spectrum measured at 150 K with external magnetic field (4 T). At 150 K, the sample is in a completely AFM state. The in-field Mössbauer data at 150 K are fitted with two sites corresponding to AFM(6h) and AFM(2a). The evolution of the Mössbauer spectrum with the application of magnetic field depends on the nature of the magnetic ordering present in the samples [32]. The width of the lines, the separation of the outer lines and the A_{23} give unambiguous information about the magnetic texture present in the compound. When the Mössbauer spectrum of the AFM sample is measured under the application of high magnetic field, various phenomena, namely, spin-flop, spin-canting and parallel spin alignment, can occur [32], depending on the interplay between the \(B_{\text{INT}}\), anisotropy field \((B_{A})\) and \(B_{\text{EXT}}\). All these transitions can be clearly observed in single crystal AFM samples and often the observed lines are sharp. However, in polycrystalline AFM samples, because the angle between the \(B_{\text{EXT}}\) and the easy axis is evenly.

Figure 7. The arrows show the isothermal \(M\) \((4 T)\) of the virgin curve. This suggests a higher FM fraction at zero field after field cycling (0 \(\rightarrow\) 7 \(\rightarrow\) 0 \(\rightarrow\) 4 T). Figure 4(a) also shows the isothermal \(M–H\) (4 \(\rightarrow\) 0 \(\rightarrow\) 4 T) curve at 5 K, obtained after cooling in the presence of 4 T magnetic field. In this case the sample has higher magnetization for the field reducing cycle (4 \(\rightarrow\) 0 T) than the subsequent field increasing cycle which overlaps with the curve (iii) of the \(M–H\) curve obtained after zero field cooling. This shows that majority of the FM fraction obtained after cooling in 4 T remains in the FM state even when the magnetic field is reduced to zero. Since these measurements were performed with a powder sample mixed with silicon grease, the absolute determination of magnetization and therefore phase fraction is not possible. However, these \(M–H\) curves could provide a relative estimate of ferromagnetic phase fraction. For this we fitted the approximately linear parts of the curves (i) to (iii) of the \(M–H\) curve and extrapolated to zero; these are shown by the lines in figure 4(a). The extrapolated values of \(M\) at 0 T are found to be 0.005, 0.044 and 0.071 emu, respectively for curves (i) (ii) and (iii). This gives about 7% and 60% FM fraction compared to that present at 7 T magnetic field.
distributed between 0 and $\pi$, the experimental signal is then a superposition of all the constituent crystallite signals, and therefore one observes a broadened line with an effective hyperfine field $B_{\text{EFF}} = (B_{\text{INT}} + B_{\text{EXT}})^{1/2}$. The intensity of the lines corresponding to the $\Delta m = 0$ transition gives the information about the spin configuration, which is usually estimated by measuring the $A_{23}$ parameter, whereas for a non-magnetic sample one would observe a hyperfine splitting equal to that of $B_{\text{EXT}}$. However, if any moment is induced with the application of magnetic field then the observed $B_{\text{EFF}}$ would not be exactly equal to $B_{\text{EXT}}$. Since the strength of the hyperfine field and the quadrupole splitting values corresponding to the AFM(2a) site are comparable, the data are fitted with the following Hamiltonian [33] corresponding to this site:

$$H = -g \mu_N I \cdot H + \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1)]$$

where the first part is the magnetic interaction and the second part is the quadrupole interaction.

The area ratio of Fe(6h) and Fe(2a) sites in the AFM state is constrained to be in the ratio of 3:1 respectively (this is adopted for all the high field data in the present work) and all other parameters are kept free. The obtained hyperfine parameters are shown in table 3. As one can see, the hyperfine parameters are shown in table 3. As one can see, the hyperfine parameters are shown in table 3. As one can see, the hyperfine parameters are shown in table 3.

Table 3. The obtained hyperfine parameters from the fitting of $^{57}$Fe Mössbauer spectra measured in the presence of 4 T external magnetic field at the indicated temperatures (shown in figure 5).

| Temp (K) | FWHM (mm s$^{-1}$) | $B_{\text{EFF}}$ (T) | $A_{23}$ (%) | Phase |
|----------|-------------------|---------------------|--------------|-------|
| 150      | 0.74 ± 0.03       | 10.8 ± 0.1          | 3.8 ± 0.3    | 75    | AFM(6h) |
| 0.35 ± 0.03 | 3.5 ± 0.1       | 25                  | AFM(2a)     |
| 5        | 0.46 ± 0.06       | 13.8 ± 0.14         | 0.00         | 24    | FM      |
| (FCC)    | 0.79 ± 0.07       | 12.1 ± 0.4          | 2.7 ± 0.6    | 57    | AFM(6h) |
| 0.59 ± 0.09 | 3.2 ± 0.2        | —                   | 19           | AFM(2a) |

Figure 5(b) shows the Mössbauer spectrum measured at 5 K with external magnetic field (4 T). The temperature 5 K was approached in the field cooled cooling (FCC) condition from 150 K. The high field data for 5 K are fitted with a convolution of three sub-spectra corresponding to the FM and AFM (6h and 2a) sites. For an FM sample, what is observed with the application of $B_{\text{EXT}}$ is that the effective hyperfine field ($b_{\text{EFF}}$) defined as $b_{\text{EFF}} = b_{\text{INT}} + b_{\text{EXT}}$ (neglecting the demagnetizing fields) would either decrease or increase depending on whether the magnetic moment is anti-parallel/parallel to the $b_{\text{INT}}$. Since the FM component is expected to be magnetically soft and aligns with the $b_{\text{EXT}}$, the $A_{23}$ parameter of this sextet is fixed as zero. The obtained hyperfine parameters are shown in table 3. As one can see, the hyperfine field of the FM component is reduced with the application of external field indicating that the moment is anti-parallel to the $b_{\text{INT}}$ similar to most compounds [32]. A magnetic moment ($\mu_{\text{FM}}$) of about 0.03 $\mu_B$ is calculated due to the FM component from the observed $b_{\text{EFF}}$ using the equation $b_{\text{EFF}} = A_{\mu_B}$ where $A$ is a constant, whose value is taken as 9.5 T/$\mu_B$ from the study of Belosevic et al [4].
on this compound. The spectrum corresponding to the AFM phase is similar to that of the 150 K (figure 5(a)) data as discussed above. However, the observed value of the $A_{23}$ parameter corresponding to the AFM(6h) site is drastically different from the 150 K data and the angle ($\theta$) between the external magnetic field ($\gamma$-ray) and the Fe magnetic moment comes out to be about 64°, which indicates that the AFM(6h) site moments are canted with respect to the applied magnetic field. As a result of spin-canting one observes a larger magnetization arising due to the AFM phase ($\mu_{\text{AFM}}$), which is calculated as the cosine component in the direction of $B_{\text{EXT}}$ and has a value of about 0.32 $\mu_B$. Therefore, from the present high field Mössbauer data, we conclude that the contribution of the AFM component at 4 T and 5 K to the total magnetization is almost comparable to that of the FM component. The observed increase in the canting of AFM spins at 5 K as compared to 150 K indicates that there is some sort of magnetic interaction between the FM and AFM components.

To determine the equilibrium state of the system we carried out Mössbauer measurements under the CHUF protocol [31]. The high field (with the application of 4 T field parallel to the gamma rays) Mössbauer measurements were carried out at different temperatures under two protocols, namely, field cooled cooling (FCC) and zero field cooled warming (ZFCW). For the FCC measurements, the $B_{\text{EXT}}$ was applied and the sample was cooled from 150 K to the temperature of interest in the presence of magnetic field. Meanwhile, in the ZFCW protocol, the sample was cooled from 150 to 5 K in zero field, 4 T magnetic field was applied at 5 K and the sample was heated to the temperature of interest in the presence of the magnetic field. In both the FCC and ZFCW protocols, the Mössbauer data are recorded in the presence of an applied magnetic field. Figure 6 shows representative high field Mössbauer data measured at 4 T and different temperatures approached in different protocols, namely, FCC and ZFCW. The fits to the data were carried out in a similar manner to that discussed above to extract the fraction of FM component. Thus, the obtained FM fraction from this analysis is plotted in figure 7 as a function of temperature. For ZFCW in the presence of 4 T, the FM fraction increases to 17% on warming from 5 to 30 K. With further increase in temperature, the FM fraction starts to decrease above 65 K, therefore, showing a reentrant transition. Under the CHUF protocol [31], if a reentrant transition is observed during warming when measured in higher field compared to the field in which the sample is cooled then the high field state will be the equilibrium state. Since we observe a reentrant transition during warming after cooling in a smaller field (here 0 T), the FM state (high field state) is the equilibrium state. The bulk $M$–$T$ measurements also show a reentrant transition during warming for the present sample, as shown in figure 4(b). During FCC in the presence of 4 T, an AFM to FM transition with a sharp increase in FM fraction around 65 K is shown. The FM fraction at 65 K during FCC is found to be identical to that observed at 75 K during ZFCW, thereby giving a hysteresis width of about 10 K for the first order AFM–FM transition. Comparatively, a smaller hysteresis width could be associated with a much longer measurement time (70 h) for Mössbauer measurements as compared to magnetization measurements, which are performed at a rate of 1.5 K min$^{-1}$. These Mössbauer measurements in $H$–$T$ space show that the observed thermomagnetic irreversibility for the studied system arises due to the path dependent coexistence of AFM and FM phases. The observed reentrant transition during warming after cooling in zero field, as shown in figures 4(b) and 7, arises due to a change in the FM and AFM phase fraction and these FM and AFM phases are long range ordered magnetic states. The observed behavior is more akin to de-vitrification of glass to crystal followed by melting on warming. Here the high temperature state (separated from the low temperature state by a first order transition) remained arrested during cooling.

One of the common features of the materials [8–29], which show similar thermomagnetic irreversibility, has been strong coupling between structural and magnetic degrees of freedom. The AFM–FM transition in Ta doped HfFe$_2$ is known to occur with a large volume change of about 1% with zero net magnetic moment at the Fe 2a site in the AFM state. Our in-field Mössbauer data show an induced moment at the Fe 2a site even in the AFM state. Therefore the absence of a net contribution to the magnetization in the absence of an applied magnetic field may be related with the topological frustration at the 2a site. A similar observation has been made by Rechenberg et al for the Fe moment at the 2a site in the AFM state of Hf$_{0.8}$Ta$_{0.2}$Fe$_2$ [7]. In the case of the La–Pr–Ca–Mn–O system Sharma et al related the occurrence of a glass like magnetic state to the mobility of structural interfaces [34]. Manekar et al correlated the formation of magnetic glass in the Ni doped FeRh system to crossover from nucleation to a growth process [35]. Recently, Tang et al using molecular dynamic simulation has attributed the superior glass forming ability of CuZr (as compared to NiAl) alloy to a poorly structured crystal/liquid interface [36]. Our Mössbauer data showed the presence of about 8% FM
phase even in zero field at 5 K. Cooling in higher magnetic field shifts the transition temperature to higher temperature, i.e. away from the glass transition temperature, which in turn can favor nucleation and growth of the FM phase. Our data also showed an increase in the canting of the AFM spin at 5 K, therefore suggesting some sort of magnetic interaction between the FM and AFM components. Whether it is related to AFM–FM interfaces remains to be probed.

4. Conclusions

In conclusion, low temperature high magnetic field (LTHM) $^{57}$Fe Mössbauer measurements were carried out on the inter-metallic compound Hf$_{0.77}$Ta$_{0.23}$Fe$_2$ to provide the microscopic origin of the kinetic arrest and de-vitrification recently reported in this compound using bulk magnetization measurements. It is also observed that, in the presence of a ferromagnetic component, the antiferromagnetic spins are canted with respect to the applied magnetic field and, hence, contribute to the total bulk magnetization in this compound. The remnant FM fraction at 5 K increases with increase in applied magnetic field during cooling. This analysis also showed the presence of about 8% FM phase at 5 K and 0 T for a sample cooled in the absence of applied magnetic field. On warming (after cooling in zero field) in the presence of 4 T magnetic field the FM fraction increases from 8% (at 5 K) to 17% (at 30 K) and shows a reentrant transition to the AFM state above 65 K. Cooling in a 4 T magnetic field shows a temperature hysteresis of about 10 K and about 25% FM contribution to the net magnetization at low temperature therefore arises due to the FM component as well as the AFM component due to spin-canting.

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