Concentration dependence in kinetic arrest of the first-order magnetic transition in Ta doped HfFe₂

R Rawat¹, P Chaddah¹, Pallab Bag¹, P D Babu² and V Siruguri²

¹UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India
²UGC-DAE Consortium for Scientific Research Mumbai Centre, R-5 Shed, BARC, Mumbai-400085, India

E-mail: rrawat@csr.res.in

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Abstract
Magnetic behavior of the pseudo-binary alloy Hf₁−ₓTaₓFe₂ has been studied, for which the zero-field ferromagnetic (FM) to antiferromagnetic (AFM) transition temperature is tuned near to \( T = 0 \) K. Our studies show that such composition lies around \( x = 0.230 \). Detailed magnetization studies on \( x = 0.225, 0.230 \) and \( 0.235 \) show thermomagnetic irreversibility at low temperature due to kinetic arrest of the first-order AFM–FM transition. All three compositions studied show a reentrant transition in the zero-field-cooled warming curve and non-monotonic variation of the upper critical field. The region in \( H–T \) space where these features of kinetic arrest manifest themselves increases with increasing Ta concentration.

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

1. Introduction
The compound HfFe₂ has been reported to show polymorphism with one of the phases crystallizing in MgZn₂ type hexagonal structure (space group \( P6₃/mmc \)) [1, 2]. This hexagonal phase is reported to be ferromagnetic (FM) at room temperature [3]. Magnetism in this system arises mainly due to Fe, which has two inequivalent sites: 6h and 2a. With Ta substitution for Hf, this phase becomes antiferromagnetic (AFM) at room temperature and shows an AFM to FM transition at lower temperatures [2]. With increasing Ta concentration, the zero-field first-order AFM–FM transition temperature decreases and is found to be absent for more than 25% Ta substitution [2, 4]. Beyond 70% Ta substitution, this system is reported to be a Pauli paramagnet. The first-order AFM–FM transition for less than 25% Ta substitution is accompanied by a large change in lattice volume. Interestingly, the low-temperature FM state has a higher volume compared to the high-temperature AFM state [4, 5]. Morellon et al [5] have observed a volume magnetostriction of 0.6% at low temperature in Hf₁₋ₓTaₓFe₂₋ᵧ with \( x = 0.15 \), 0.17 and \( y = 0.2 \). The Mossbauer studies of Nishihara et al [2] on Hf₁₋ₓTaₓFe₂ (\( x = 0–0.7 \)) showed a discontinuous change in the hyperfine field of Fe across the first-order AFM–FM transition. The hyperfine fields on 6h and 2a Fe sites are of comparable value in the FM state, whereas they are reduced drastically in the AFM state. Their estimates showed that Fe moments at 6h and 2a sites are 1 \( \mu_B \) each in the FM state, and 0.7 and 0, respectively, in the AFM state. A neutron diffraction study of Duijn et al [6] confirmed the magnetic moment of 1 \( \mu_B \) in the FM state but with a moment direction lying within the basal plane. The magnetic structure in the AFM state is considered to be similar to isostructural TiFe₂, which consists of a sublattice of ferromagnetic Fe (6h) layers aligned antiparallel to each other along the c-axis with no moment on the 2a site [2, 6]. Delyagin et al [7] have proposed a canted ferromagnetic structure to interpret their Mossbauer studies on Ti-doped HfFe₂. However, studies related to the determination of magnetic structure in these system are far from complete. The first-order AFM–FM transition in this system appeared to be similar to that observed in the FeRh system, e.g., a large volume change across the first-order transition and vanishing of the Rh moment in the AFM state [8, 9]. However, in the case of HfFe₂, the higher volume...
FM state is the low-temperature state whereas for FeRh, the lower volume AFM state is the ground state. In contrast to the extensively investigated FeRh system, there have been few studies on first-order transition in the Ta-doped HfFe$_2$ system. Nishihara et al [2] applied the model of itinerant electron magnetism and found a qualitative agreement with it. Wada et al [10] also used this framework to explain the higher linear contribution to specific heat at low temperature in the antiferromagnetic system. This analysis indicates the comparable strength of FM and AFM interactions and measurement under pressure and magnetic field shows that the transition temperature can be varied over a wide temperature range [4, 5].

Such first-order magnetic transitions where transition temperature can be shifted to lower temperature are of interest due to the possibility of observing glass-like arrest of kinetics, see e.g. [11, 12]. Recently, Chaddah and Banerjee [13] have proposed that magnetic glasses form in these systems when magnetic latent heat is weakly coupled to a thermal conduction process. In Hf$_{1-x}$Ta$_x$Fe$_2$, the first-order transformation is accompanied by significant latent heat [10] and the first-order transition depends sensitively on Ta content [2]. In contrast to magnetic coupling, the conduction electron mediated coupling is not expected to change much, as the lattice structure remains unchanged with small variations in lattice parameter. Therefore, the arrest of kinetics is expected to dominate with increasing $x$. Here, we present our results on Ta-doped HfFe$_2$, for which first-order transition temperature is tuned to near $T = 0$ K. Earlier studies have shown that such a composition lies in the range of $x = 0.20$ and 0.25 in Hf$_{1-x}$Ta$_x$Fe$_2$ [2, 4]. Therefore, we prepared samples with Ta concentration ($x$) varying from 0.15 to 0.30. We find that lattice parameters $a$ and $c$ decrease linearly by about 0.5% over this range, in accordance with Vegard’s law. Detailed studies for $x = 0.225, 0.230$ and 0.235 compositions show thermomagnetic irreversibility and non-ergodic magnetic states. Using CHUF (cooling and heating in unequal magnetic field) measurements, we show that the AFM state is the non-equilibrium state even though the first-order transition to FM state is absent in these systems for zero-field cooling. The lattice structure for all the studied compositions does not change and there is a slight contraction of less than 0.03%, allowing us to speculate in the discussion that the observed changes can be understood as arising from a change in density.

2. Experimental details

Polycrystalline samples of Hf$_{1-x}$Ta$_x$Fe$_2$ ($x = 0.225, 0.230$ and 0.235) were prepared by arc melting the constituent elements under an inert argon gas atmosphere. The purity of Fe and Ta was better than 99.99% and Hf purity was 99.9% (with ≈2% of Zr). As-prepared samples were cut using a slow-speed diamond saw for x-ray diffraction and magnetic measurements. Powder x-ray diffraction patterns of these samples were analyzed using FullProf refinement [14]. Obtained x-ray powder diffraction patterns (symbol) along with fitted patterns (line) are shown in figure 1 for these compositions. The refinement shows that these alloys crystallize in the $P6_3/mmc$ hexagonal structure and are single phase. Magnetization measurements were performed using a 7 T SQUID-VSM and a 9 T PPMS-VSM, both from Quantum Design, USA.

3. Results

Figure 2(a) shows the unit cell parameters $a$ and $c$ obtained from FullProf refinement of powder XRD patterns. As expected, the obtained lattice parameters decrease monotonically with increasing Ta content, following Vegard’s law. The inset highlights the variation of lattice parameters for compositions which will be investigated in detail in this paper. Figure 2(b) shows the isothermal $MH$ curve at 75 K, which shows that all the three samples are in the AFM state at zero field and become FM with the application of a magnetic field. The higher the Ta content, the higher is the magnetic field required for AFM–FM transition. This monotonic increase of critical field with increasing Ta content is consistent with the existing understanding that AFM state becomes more favorable with $x$.

Figure 3 shows the temperature dependence of magnetization ($M$) for $x = 0.225, 0.230$ and 0.235 in the presence of the labeled magnetic field. For each of these field values, the magnetic field is applied isothermally at 5 K after zero-field cooling and measurement is performed during warming up to 150 K (ZFCW) followed by cooling (FCC). The warming and cooling curves show a hysteretic first-order AFM–FM transition for all the three samples. It is to be noted here that, for higher $x$, the applied magnetic field...
Figure 2. (a) Unit cell parameters \(a\) and \(c\) for Hf\(_{1-x}\)Ta\(_x\)Fe\(_2\). Inset highlights the lattice parameter variation for compositions presented here. (b) Isothermal magnetization at \(T = 75\) K.

Figure 3. Temperature dependence of magnetization measured under labeled magnetic fields for Hf\(_{1-x}\)Ta\(_x\)Fe\(_2\). For each field value, there are two curves: ZFCW and FCC. These curves highlight multivalued \(M\) well below the transition region of the corresponding FCC curve, and reentrant transition in ZFCW.

is higher, which is consistent with \(MH\) curves shown in figure 2. The transition temperature increases with increasing magnetic field, as expected for a first-order transition from the low-temperature FM to the high-temperature AFM state. The ZFCW curve shows a reentrant transition in that at the low-\(T\) state has a low \(M\), which increases with rising \(T\) and again decreases at a much higher \(T\). This entire behavior is very similar to the behavior that has been observed in Gd\(_5\)Ge\(_4\) [15], La\(_2/8\)Pr\(_1/8\)Ca\(_3/8\)MnO\(_3\) [16] and Pr\(_0.5\)Ca\(_0.5\)MnO\(_3\) [17]. Such non-ergodic states and reentrant transitions have been a hallmark of glass-like magnetic states which have been shown to arise due to arrested kinetics of the first-order transition at low temperature [18, 15, 17, 19–23]. Banerjee et al [23] have shown that, by following the CHUF (cooling and heating in unequal magnetic field) protocol, one can determine which of the two states is the equilibrium state. Though not shown here, we also measured the \(M-T\) curve during warming after cooling in a higher field, and such curves showed only one transition. Therefore, as reentrant transition is observed during warming, only when the cooling field is lower, it shows that the low-field state (here, AFM) is the non-ergodic arrested state and the equilibrium state obtained on de-arrest is the FM state. The difference between the ZFCW and FCW curves decreases for higher field values due to the AFM to FM transition induced by magnetic field at 5 K, resulting in a higher FM phase fraction at 5 K for the ZFCW curve.

The regions whose kinetic arrest lines are encountered at lower field are transformed, whereas the remaining regions remain arrested. Such regions will show devitrification on warming. Since at higher field values the devitrification curve merges with the FCW curve at lower temperature and vice versa, it shows that regions which remain arrested at higher field show de-arrest at lower temperature. This conforms to anticorrelated kinetic arrest and supercooling bands [21].

For a given composition, it can be seen that magnetization below the hysteresis region of the first-order transition (in FCC) is higher for a higher applied field, e.g. for \(x = 0.230\) and 5 K it is 1.8, 2.5 and 2.8 \(\mu_B/\text{f.u.}\) for 2.5, 3 and 4 T applied magnetic fields, respectively. This could arise either due to an increasing FM phase fraction or due to the susceptibility of the ferromagnetic phase. To verify this, we measured isothermal magnetization at various temperatures. For these measurements, the sample is cooled to the measurement temperature and \(MH\) is measured during the increasing and decreasing field cycles, i.e. 0–7–0 T. These curves are shown in figure 4—to highlight the critical field (field required for AFM to FM and FM to AFM transition) variation with temperature, data is shown for some representative temperatures only. The critical field (which we have taken as the magnetic field at which \(M\) reaches half the value at 7 T for the respective temperature) required for the AFM to FM transition \(H_{up}\) is higher for higher Ta content for a given temperature. For example, at 5 K, it is observed to
be 1.48, 3.48 and 5.06 T for \(x = 0.225, 0.230\) and 0.235, respectively. Extrapolation of these critical field values is in good agreement with an earlier study [4]. The return curve (7–0 T) varies smoothly without any clear signature of a FM to AFM transition and becomes zero at zero field. This decrease in \(M\) at low field could be due to the soft ferromagnetic nature of the FM phase or due to transformation of the FM phase back to the AFM phase. To check these possibilities, we measured \(MH\) in a subsequent third cycle (0–7 T) to obtain an envelope hysteresis curve at 5 K. In all the three cases, the virgin curve lies outside the envelope curve (not presented here for the sake of clarity), showing that the FM phase is retained down to zero field. This also rules out the magnetocrystalline anisotropy as the probable cause for the increase in \(M\) for the ZFCW curve shown in figure 3. At higher temperature, the return curves (7–0 T) move to higher \(H\), which is expected for a first-order transition from the low-temperature ferromagnetic state to the high-temperature antiferromagnetic state. For such cases, the transition temperature (critical field) increases with increasing magnetic field (temperature). In contrast, forward curves (0–7 T) show anomalous behavior, i.e., they shift to lower \(H\) with increasing temperature, and above 25–35 K they start to shift to higher \(H\). Such an anomalous shift in the \(MH\) curve with temperature has been observed in the return curve of \(MH\) in \(Nd_{0.5}Sr_{0.5}MnO_3\) [24] and the RH curve of \(Pd\) doped \(FeRh\) [18] and has been attributed to kinetic arrest of the first-order transition at low temperature. This anomalous feature becomes more obvious when we draw a phase diagram using these isothermal \(MH\) measurements.

The phase diagram based on these isothermal \(M–H\) measurements is shown in figure 5. It shows that, with increasing \(Ta\) content, the FM region shifts to lower temperature and higher field. The lower critical field (\(H_{dn}\)) increases monotonically with increasing temperature, whereas the upper critical field (\(H_{up}\)) shows a non-monotonic variation for all the compositions, with minima around 25–35 K. Such a non-monotonic variation in critical field has been shown to be a consequence of interplay between the kinetic arrest line and the supercooling line [24]. At low temperature, kinetics dominate, whereas at high temperature, thermodynamics takes over. In the case of \(Gd_3Ge_4\) [15] and \(La_{2/3}Pr_{1/3}Ca_{2/3}MnO_3\) [16] also, a similar non-monotonic variation of \(H_{up}\) has been shown to give rise to a glass-like AFM state at low temperature and field. The low-temperature (below \(\approx 25\ K\)) side of \(H_{up}\) is its field space then represents a kinetic arrest (\(H_{K}, T_{K}\)) band, below which the AFM to FM transition is hindered on experimental time scales. In contrast, the high-temperature side represents the supercooling band. Since these two bands have opposite slope, there is a minimum in \(H_{up}\) at intermediate temperatures.

These phase diagrams also explain the reentrant transition observed in the ZFCW curve, as shown in figure 3. For lower field values, the kinetic arrest line is crossed after crossing the supercooling line and, therefore, the system remains in the
AFM state. When the magnetic field is applied after zero-field cooling, it partly or completely transforms to the AFM state. The part transformation occurs due to quenched disorder broadening of the first-order transition line, where different regions on the length scale of the correlation length can have different transition temperatures. On warming in the presence of a field when the \((H_K, T_K)\) line is crossed for the remaining AFM phase, it transforms to the FM state. Therefore, the AFM to FM transformation for the ZFCW curve occurs across the kinetic arrest line. From these devitrification curves, the kinetic arrest temperature is estimated as the temperature at which the magnetization value reaches half of the saturation magnetization value. These points, shown by black stars in the phase diagram (figure 5), coincide with the rising part of the \(T_{K}\) curve at low temperature.

The monotonic rise in \(H_K\) as \(x\) varies from 0.225 to 0.235, shows that the formation of a magnetic glass becomes more favorable with increasing \(x\). As noted earlier, the lattice parameters decrease monotonically as \(x\) increases. This would favor a direct exchange magnetic coupling, as the wavefunction overlap would rise exponentially, over a conduction electron mediated coupling (that would not vary much with interatomic spacing). Therefore, our results could be relevant to the proposal of Chaddah and Banerjee [13] that a magnetic glass is formed when the magnetic latent heat is weakly coupled (cf the sample specific heat) to the thermal conduction process.

4. Conclusions

To conclude, we prepared and studied the magnetic behavior of the pseudo-binary alloys \(Hf_{1-x}Ta_xFe_2\) for which transition temperature is tuned to near \(T = 0\) K. These alloys showed anomalous thermomagnetic irreversibility at low temperature due to kinetic arrest of the first-order AFM–FM transition. All the three studied compositions showed reentrant transition in ZFCW, anomalous variation of forward curve in isothermal magnetization and non-monotonic variation of upper critical field. With increasing Ta concentration, the AFM state is stabilized and a higher magnetic field is required to induce the FM state isothermally. These measurements clearly show that for lower \(x\) values, the ground state is FM even though the zero-field cooled state is AFM. Due to the interplay of kinetic arrest and supercooling, tunable fractions of AFM and FM phases can be obtained for the same temperature and magnetic field values. Such contrasting magnetic states for the same thermodynamic parameters will be helpful to understand the magnetic structure of these systems. This understanding can provide further insight into the first-order AFM–FM transition in the FeRh system, where the transition is found to be sensitive to particle size [25], strain [26] etc. Whereas, in the case of Ta-doped \(HfFe_2\), the first-order transition is observed even in powder samples, as is evident from the cited Mossbauer studies in these systems.

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References

[1] Nishihara Y and Yamaguchi Y 1982 J. Phys. Soc. Japan 51 1333
[2] Nishihara Y and Yamaguchi Y 1983 J. Phys. Soc. Japan 52 3630
[3] Belosevic-Cavor J, Koteski V, Novakovic N, Concas G, Congiu F and Spano G 2006 Eur. Phys. J. B 50 425
[4] Kido G, Tadakuma Y, Nakagawa Y, Nishihara Y and Yamaguchi Y 1986 J. Magn. Magn. Mater. 54–57 885
[5] Morellon L, Algarabel P A, Ibarra M A, Arnold Z and Kamarad J 1996 J. Appl. Phys. 80 6911
[6] Dujin H G M, Bruck E, Menovsky A A, Buschow K H J, de Boer F R, Coehoorn R, Winkelmann M and Siemensmeyer K 1997 J. Appl. Phys. 81 4218
[7] Delyagin N E, Erzinkyan A L, Parfenova V P, Rozantsev I N and Rysas G K 2008 J. Magn. Magn. Mater. 320 1853
[8] Shirane G, Chen C W, Flinn P A and Nathans R 1963 J. Appl. Phys. 34 1044
[9] Shirane G, Nathans R and Chen C W 1964 Phys. Rev. 134 A1547
[10] Moruzzi V L and Marcus P M 1992 Phys. Rev. B 46 2864
[11] Wada H, Shimamura N and Shiga M 1993 Phys. Rev. B 48 10221
[12] Roy S B, Chaddah P, Pecharsky V K and Gschneidner K A Jr 2008 Acta Mater. 56 5895
[13] Chaddah P and Banerjee A 2011 arXiv:1107.0125v1
[14] Rodriguez-Carvajal J 1993 Physica B 192 55
[15] Roy S B, Chattopadhyay M K, Chaddah P, Moore J D, Perkins G K, Cohen L F, Gschneidner K A Jr and Pecharsky V K 2006 Phys. Rev. B 74 012403
[16] Wu W, Israel C, Hur N, Soonyong P, Cheong S W and de Lozanne A 2006 Nature Mater. 5 881
[17] Banerjee A, Mukherjee K, Kumar K and Chaddah P 2006 Phys. Rev. B 74 224445
[18] Kushwaha P, Lakhani A, Rawat R and Chaddah P 2009 Phys. Rev. B 80 174413
[19] Manekar M A et al 2001 Phys. Rev. B 64 104416
[20] Chattopadhyay M K, Roy S B and Chaddah P 2005 Phys. Rev. B 72 180401
[21] Kumar K, Pramanik A K, Banerjee A, Chaddah P, Roy S B, Park S, Zhang C L and Cheong S W 2006 Phys. Rev. B 73 184435
[22] Kushwaha P, Rawat R and Chaddah P 2008 J. Phys.: Condens. Matter 20 022004
[23] Banerjee A, Pramanik A K, Kumar K and Chaddah P 2006 J. Phys.: Condens. Matter 18 L605
[24] Banerjee A, Kumar K and Chaddah P 2009 J. Phys.: Condens. Matter 21 026002
[25] Rawat R, Mukherjee K, Kumar K, Banerjee A and Chaddah P 2007 J. Phys.: Condens. Matter 19 256211
[26] Navarro E, Multigner M, Yavari A R and Hernando A 1996 Europhys. Lett. 35 307
[26] Fan R et al 2010 Phys. Rev. B 82 184418
[27] Bordel C et al 2012 Phys. Rev. Lett. 109 117201