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Disorder influenced magnetic phase transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy

M K Chattopadhyay and S B Roy

Magnetic and Superconducting Materials Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India

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Abstract

We have studied a 10% Ru-doped $CeFe_2$ alloy, $Ce(Fe_{0.9}Ru_{0.1})_2$, through magnetization, magnetotransport, and heat capacity measurements. This study shows that, while this alloy is antiferromagnetic at low temperatures and paramagnetic at high temperatures, there exists evidence of ferromagnetic ordering in the intermediate temperature regime. We show here that with 10% Ru doping the first order magnetic transition observed in the $Ce(Fe_{1-x}Ru_x)_2$ alloys with $x < 0.08$ is reduced to a quasi-continuous phase transition. The characteristic thermomagnetic history effects associated with the ferromagnetic–antiferromagnetic phase transition in the $Ce(Fe_{1-x}Ru_x)_2$ alloys with $x < 0.08$ are not observed in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy. This alloy continues to exhibit the large magnetoresistance and large magnetocaloric effect associated with this first order magnetic transition in the alloys with smaller Ru concentration, but it does not show any energy loss due to thermomagnetic hysteresis. The present work thus shows how the introduction of quenched disorder due to alloying effects may be used to tune the first order magnetic transition in a material for more efficient functional use.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The magnetic properties of $Ce(Fe_{1-x}R_x)_2$ (R = Al, Ru, Ir, Os, Re etc) pseudobinary compounds, which first drew attention in the late 1980s [1–4], continue to be a subject of considerable interest [5–8]. $CeFe_2$ is a cubic Laves phase ferromagnet (Curie temperature $\approx$ 230 K [1, 2]), where a partial substitution of selected elements in the Fe site can induce a low temperature antiferromagnetic state [1–4]. This ferromagnetic to antiferromagnetic transition (and the associated structural transition) in the pseudobinary $CeFe_2$ alloys has been studied with various experimental techniques including neutron scattering [1–4, 9]. It is now established that this phase transition is of first order nature, which can be induced both by temperature and magnetic field [10–16]. The substitutional elements also introduce quenched disorder in these pseudobinary $Ce(Fe_{1-x}R_x)_2$ alloys. In a classic paper in the late 1970s, Imry and Wortis carried out detailed theoretical studies on the influence of microscopic random quenched disorder on the first order phase transition [17]. Certain generic features associated with such disorder influenced first order transitions [17] have been experimentally observed in $Ce(Fe_{1-x}R_x)_2$ alloys [11, 13–15]. Within the Imry–Wortis picture, a first order transition gets broadened and ultimately becomes a continuous transition with the increase in the amount of quenched disorder [17]. In the case of the $Ce(Fe_{1-x}R_x)_2$ alloys, it is known that with the increase in x there is a decrease (an increase) in the paramagnetic (ferromagnetic) to ferromagnetic (antiferromagnetic) transition temperature, and for $x \geqslant 0.08$ the low temperature magnetic phase is reported to be antiferromagnetic in nature [4, 5, 9]. However, the amount of random quenched disorder in these doped $CeFe_2$ alloys is also expected to increase with the increase in x. In the light of this information the following questions arise for the alloys with $x \geqslant 0.08$:

(i) What is the actual nature of the paramagnetic to antiferromagnetic phase transition?
(ii) Is the low temperature magnetic state truly antiferromagnetic in nature?

Motivated by these questions we have now investigated the magnetic phase transition in the Ru-doped $CeFe_2$ alloys, focusing on a case where the extent of disorder is relatively large. We show here that with 10% Ru doping (composition: $Ce(Fe_{0.9}Ru_{0.1})_2$) the first order magnetic transition (observed in $Ce(Fe_{1-x}R_x)_2$ alloys with $x < 0.08$) is reduced to

a quasi-continuous phase transition. The characteristic thermomagnetic history effects associated with ferromagnetic–antiferromagnetic transition in $Ce(Fe_{1-x}R_x)_2$ alloys with $x < 0.8$ are not observed in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy. Furthermore, while the lowest temperature magnetic state in $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is antiferromagnetic in nature, a trace of ferromagnetism still exists in a finite temperature regime sandwiched between the low temperature antiferromagnetic state and the high temperature paramagnetic state.

There is a practical implication of the continuous nature of the magnetic transition in $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy. This alloy exhibits large magnetoresistance and large magnetocaloric effect associated with the magnetic transition, but does not show any energy loss due to hysteresis in temperature and magnetic field. The present work thus shows an example of how the first order magnetostructural transition in a material may be tuned for more efficient functional use through the introduction of quenched disorder.

2. Experimental details

The polycrystalline $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy sample used in the present work was prepared by arc melting of high purity constituent elements under inert (argon) atmosphere, and was characterized subsequently with optical metallography and x-ray diffraction [4]. The same sample was used in our previous studies [4, 18]. Magnetization measurements reported here were performed using a SQUID magnetometer (MPMS-5, Quantum Design). A scan length of 4 cm and a 32 point curve fitting procedure were adopted for these measurements. Electrical resistance was measured using the standard four probe configuration, in a physical property measurement system (PPMS, Quantum Design) in the temperature range 2–300 K and in magnetic fields up to 90 kOe. The heat capacity measurements were also made in the same PPMS machine in the temperature range 2–220 K using the two τ relaxation technique.

3. Results and discussion

Figure 1 shows the temperature (T) dependence of magnetization (M) measured while warming up the sample in low magnetic field ($H = 100$ Oe), both after cooling the sample in zero field (the zero field cooled (ZFC) protocol) and in the presence of magnetic field (the field cooled (FC) protocol). Magnetization exhibits a sharp cusp at 137.5 K, which is somewhat similar to that indicated by a paramagnetic to antiferromagnetic phase transition [19]. Above this temperature magnetization falls with increasing temperature, but the magnetic susceptibility does not strictly follow the Curie–Weiss law. This is clearly seen from the temperature dependence of the inverse of magnetic susceptibility (χ^{-1}) shown in the inset to figure 1. A straight line can somehow be fitted to the χ^{-1} versus T data only in the narrow temperature regime between 137.5 and 170 K. The paramagnetic Curie temperature (θ_P) determined from the extrapolation of this straight line turns out to be 21 K approximately. A positive

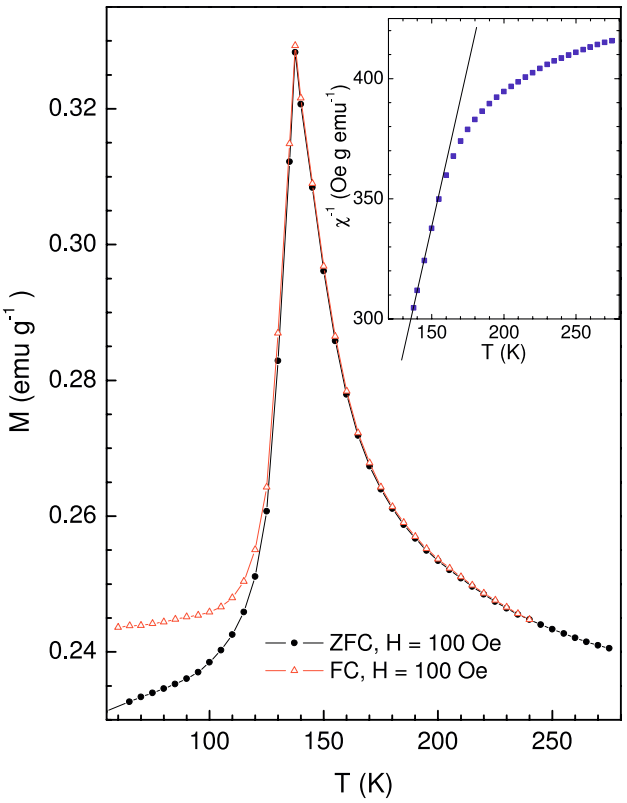

Figure 1. Main panel: the temperature dependence of magnetization of $Ce(Fe_{0.9}Ru_{0.1})_2$ in low magnetic field (100 Oe). Inset: the temperature dependence of the inverse of magnetic susceptibility of $Ce(Fe_{0.9}Ru_{0.1})_2$.

θ_P indicates the presence of ferromagnetic correlations in the material [19].

Figure 2 shows the M versus T curves of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy for 5 and 50 kOe magnetic fields respectively. The transition temperature earlier observed in 100 Oe magnetic field (figure 1) is clearly suppressed with the application of magnetic field. This indicates the presence of a field induced magnetic phase transition in the alloy. Moreover, the cusp in the temperature dependence of magnetization loses its sharpness and takes the form of a relatively broad peak. The difference between the zero field cooled and field cooled magnetization is also erased in the presence of high magnetic field. The shape of the M versus T curve above this broad peak is affected by the applied magnetic field. A close inspection of figure 2(b) reveals that there is an inflection point on the M versus T curve obtained in 50 kOe magnetic field, close to 140 K, which is well separated from the maximum on this curve. The derivative of this curve (inset to figure 2(b)) shows a clear minimum just below 140 K. We conjecture that this inflection point (and the minimum observed on the dM/dT versus T curve) corresponds to a paramagnetic to ferromagnetic transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy with the lowering of temperature. Such an inflection point is also observed in 20 and 40 kOe magnetic fields (data not shown here), but is not observed in 100 Oe or 5 kOe (figures 1 and 2(a)). Probably, the peak in the M versus T curve arises due to the combined effect of two

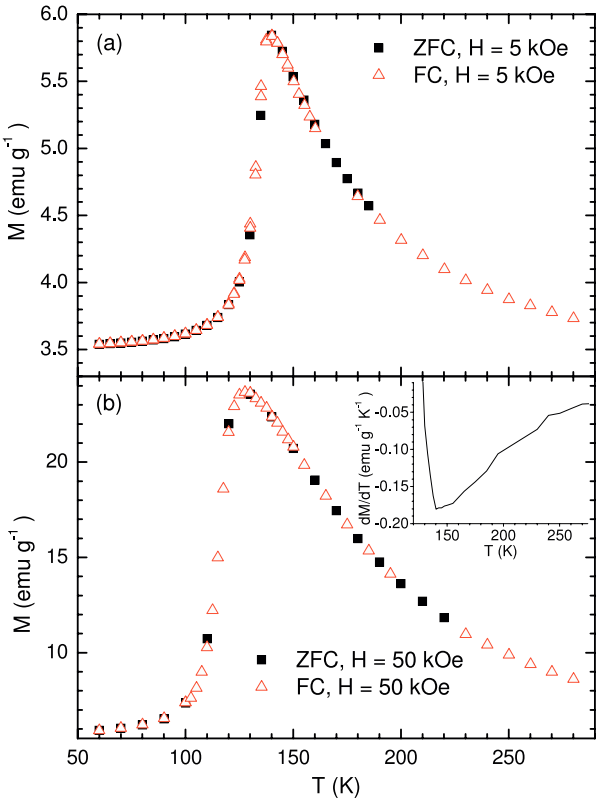

Figure 2. Main panels: the temperature dependence of magnetization of $Ce(Fe_{0.9}Ru_{0.1})_2$ (a) in 5 kOe and (b) in 50 kOe magnetic field. Inset to (b): the temperature derivative of magnetization showing the position of the inflection point on the M versus T curve obtained at 50 kOe.

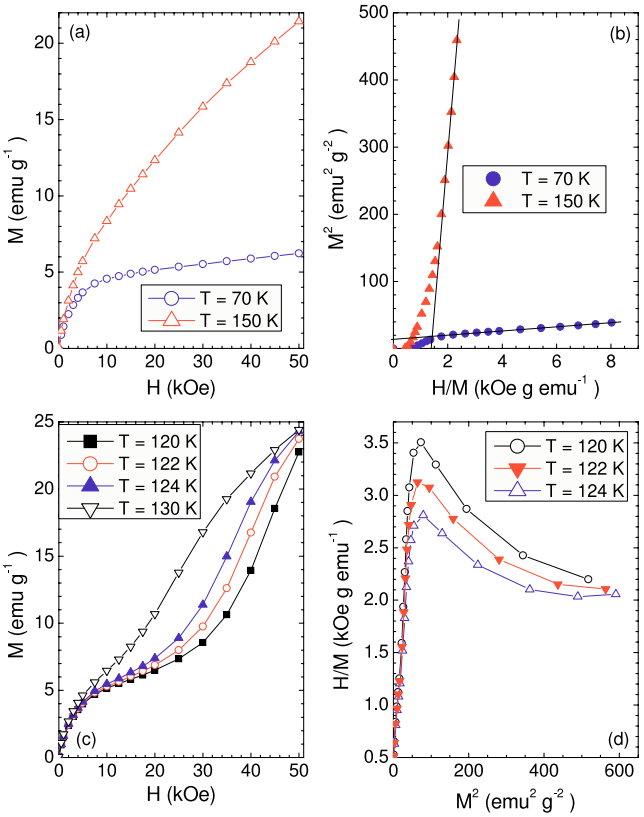

Figure 3. (a) The field dependence of magnetization of $Ce(Fe_{0.9}Ru_{0.1})_2$ at 70 and 150 K. (b) The Arrott plots for 70 and 150 K for the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy. (c) The field dependence of magnetization in the temperature regime of the magnetic field induced phase transition in $Ce(Fe_{0.9}Ru_{0.1})_2$. (d) The inverted Arrott plots showing the first order nature of the field induced transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy.

different magnetic transitions.

(i) With the lowering of temperature below 140 K, the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy undergoes a paramagnetic to ferromagnetic transition, with a transition temperature which is not affected appreciably by applied magnetic field.

(ii) With further lowering of temperature, the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy undergoes another magnetic transition, and this transition shifts towards lower temperature in the presence of high magnetic fields. Thus it is this latter transition that exhibits a field induced character.

Because of the close proximity of the two transitions, it is difficult to resolve them in low magnetic field. As the second transition shifts to lower temperature in high magnetic field, the two transitions may be identified clearly. This also provides an explanation for the apparent broadening of the cusp observed in the temperature dependence of magnetization in the presence of high magnetic fields.

Figure 3(a) shows the field dependence of magnetization of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy at 70 and 150 K, obtained after cooling the sample down to these temperatures in zero field. The $M(H)$ curve obtained at 70 K shows a clear signature of technical saturation above 4 kOe magnetic field. The extrapolation of the high field portion of the Arrott plot [20] (see figure 3(b)) obtained from these data gives a spontaneous magnetization [21] of 3.37 emu g^{-1} at 70 K. On the other hand, no signature of a saturation of magnetization is observed at 150 K (see figure 3(a)). The Arrott plot obtained from the M versus H data recorded at $T = 150$ K confirms that the alloy is paramagnetic at 150 K (see figure 3(b)). However, the M versus H curve obtained at 150 K also exhibits appreciable nonlinearity in low magnetic fields ($H < 8$ kOe). This indicates the presence of short range magnetic correlations in the paramagnetic state of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy. This result is consistent with the nonlinearity (deviation from Curie–Weiss law) observed in the χ^{-1} versus T curve (inset to figure 1) of the present alloy.

Figure 3(c) shows the M versus H curves obtained in the temperature region just below the cusp observed in the low field M versus T curve (figure 1). The $M(H)$ curves in figure 3(c) show the clear signature of a field induced or metamagnetic transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy. The M versus H characteristics of the present alloy are very similar to the M versus H curves corresponding to the antiferromagnetic to ferromagnetic phase transition observed in other doped $CeFe_2$ alloys [11, 13–16, 22]. The M versus H curves corresponding to $T = 124$ K (figure 3(c)), 126 K (figure 4) and 130 K (figure 3(c)) indicate that there could be a magnetic saturation at these temperatures in fields higher than

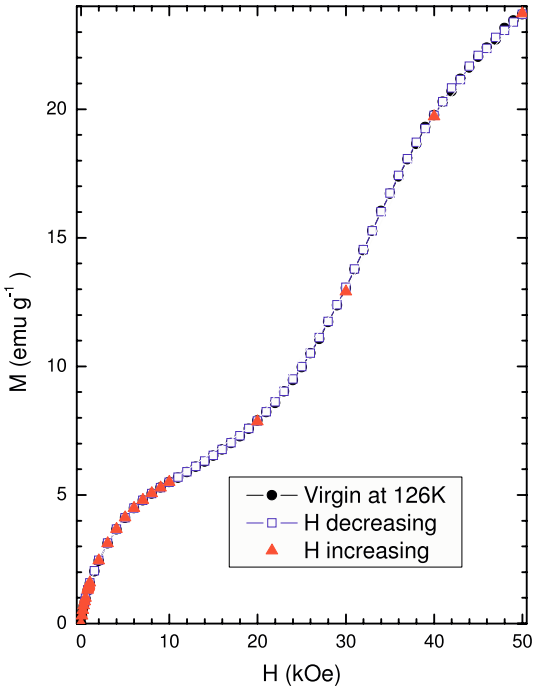

Figure 4. The magnetic field dependence of magnetization of $Ce(Fe_{0.9}Ru_{0.1})_2$ showing the absence of hysteresis effects in the alloy.

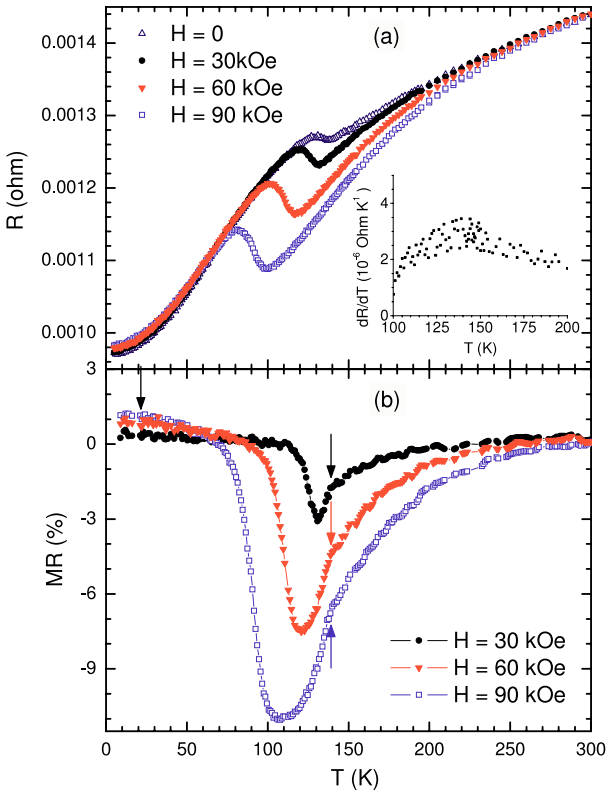

Figure 5. Main panels: the temperature dependence of (a) electrical resistance and (b) magnetoresistance of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy for different applied magnetic fields. Inset to (a): the temperature derivative of electrical resistance, showing the change of slope in the temperature dependence of electrical resistivity close to 140 K for $H = 90$ kOe. The significance of the arrowheads in (b) is explained in the text.

50 kOe. This clearly indicates the possibility of a field induced ferromagnetic phase in $Ce(Fe_{0.9}Ru_{0.1})_2$.

To investigate the order of the field induced phase transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy, we construct the so called inverted Arrott plots [23] from the M versus H curves for a few representative temperatures (120, 122, 124 K). The slopes of the inverted Arrott plots or the H/M versus M^2 plots (figure 3(d)) have been used to find the order of a magnetic phase transition [24]. The negative slope of the H/M versus M^2 curves seen in figure 3(d) indicates that the field induced phase transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is of first order nature [23, 24]. However, the transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is quite broad as compared to the first order antiferromagnetic to ferromagnetic transition observed in many other doped $CeFe_2$ alloys [11, 13–16, 22], and does not exhibit any hysteresis detectable within the resolution of our magnetometer. The absence of hysteresis in the magnetic field dependence of magnetization in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is shown clearly in figure 4: the virgin magnetization curve (measured while increasing H from a zero field cooled state) matches completely with the H-increasing and H-decreasing envelope magnetization curves. On the other hand, it is well known that hysteresis is a generic feature of a first order phase transition [25]. A distinct hysteresis in temperature and magnetic field has been observed across the first order antiferromagnetic to ferromagnetic phase transition in the doped $CeFe_2$ alloys studied earlier [11, 13–16, 22]. To confirm the absence of hysteresis in the present case, and to study the metamagnetic transition in more detail, we have performed measurements on another observable, namely electrical resistance. These results are presented below.

Figure 5(a) shows the temperature dependence of electrical resistance (R) of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy in the presence of different constant magnetic fields. The alloy exhibits a temperature dependence of electrical resistance typically observed in metallic systems, except in an intermediate temperature region where the alloy also exhibits a steep rise of electrical resistance with decreasing temperature. This rise of electrical resistance indicates the occurrence of a magnetic phase transition, which is pushed further below in temperature in the presence of applied magnetic field. The application of magnetic field decreases the electrical resistance at temperatures above 70 K (approximately, as seen from figure 5(a)), and gives rise to a negative magnetoresistance (MR). Here, the magnetoresistance is defined as $\mathrm{MR} = \frac{R(H)-R(0)}{R(0)} \times 100$ (see figure 5(b)). The MR is enhanced significantly across the phase transition referred above, and reaches a maximum magnitude of 11% approximately at a temperature close to 104 K in the presence of 90 kOe magnetic field. It is understood from figures 5(a) and (b) that this enhancement of MR is because of the field induced nature of the phase transition. The effect of magnetic field on the electrical resistance of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy in the phase transition regime look qualitatively very similar to those observed in the other doped $CeFe_2$ alloys showing first order antiferromagnetic to ferromagnetic phase

transition [11, 12, 14, 26]. A major difference of the present results from those of the other doped $CeFe_2$ alloys, however, is that no thermal hysteresis is observed in the temperature dependence of electrical resistance of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy in any field. The warming and cooling curves overlap completely.

We now take a closer look at figures 5(a) and (b). The MR of $Ce(Fe_{0.9}Ru_{0.1})_2$ is negative in the entire paramagnetic regime (at temperatures above 140 K, as per our conjecture, which is also supported by the field dependence of magnetization) up to 300 K, in all the applied magnetic fields. In general, a paramagnetic metal is expected to exhibit a Kohler-type positive magnetoresistance arising out of the orbital motion of the conduction electrons in a magnetic field. A negative magnetoresistance, on the other hand, might result from the reduction of spin disorder scattering due to the ordering of magnetic moments by applied magnetic field [27]. A negative magnetoresistance in the paramagnetic phase of $Ce(Fe_{0.9}Ru_{0.1})_2$ could therefore arise because of the existence of short range ferromagnetic order in this temperature regime. This argument is also consistent with the results on the temperature and field dependence of magnetization presented here. In the low temperature regime (below 115, 90, and 70 K approximately for $H = 30$, 60, and 90 kOe respectively), the magnetoresistance is found to be positive (figure 5(b)) in all the applied magnetic fields. It is worthwhile to note here that a positive magnetoresistance has been reported in various ordered antiferromagnetic compounds [28], and in ferromagnetic compounds with hints of antiferromagnetic fluctuations [29]. Yamada and Takada [30] and Balberg [31] have theoretically discussed the possibility of positive MR in systems with antiferromagnetic correlations. We argue that the positive MR in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is indicative of antiferromagnetic order at low temperatures. It may be observed in figure 5(b) that MR is independent of temperature (within the experimental resolution) below 20 K (approximately, indicated by an arrowhead on the figure) for all applied magnetic fields. Between 20 and 115 K (depending on the applied field), the (positive) MR is a function of temperature. Again, a close scrutiny of figure 5(b) reveals that the MR versus T curves for all measured magnetic fields exhibit a shoulder approximately at 140 K (indicated by arrowheads on the figure 5(b)). We recall once again that the high field M versus T curve has an inflection point at this temperature (see the inset to figure 2(a)). We had conjectured that this inflection point corresponds to a paramagnetic to ferromagnetic transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy with the lowering of temperature. To confirm that the shoulder in the magnetoresistance curves (figure 5(a)) corresponds to the same transition, we have taken the derivatives of the R versus T curves presented in figure 5(a). The dR/dT versus T data for $H = 90$ kOe are shown in the inset to figure 5(a). A clear peak is observed in these data close to 140 K. Similar peaks near 140 K are also observed in the dR/dT versus T data (not shown here) for $H = 60$ and 30 kOe. But the dR/dT versus T data for $H = 0$ does not exhibit a peak. Thus our magnetoresistance results also support our earlier conjecture of the presence of a paramagnetic to ferromagnetic transition close to 140 K. The suppression of spin disorder scattering by applied magnetic field is enhanced in the ferromagnetic phase. The magnitude of MR therefore increases more rapidly with decreasing temperature in the ferromagnetic phase, giving rise to the shoulder structure observed in the MR versus T curves. We believe that the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is ferromagnetic in the temperature regime between this shoulder and the maximum (in magnitude) observed in the temperature dependence of MR. This belief is supported by our analysis of the magnetoresistance results presented below. We first recall that there is an indication of a ferromagnetic saturation of magnetization in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy in the high field parts of the M versus H curves obtained in the temperature regime just below the cusp in the low field (100 Oe) M versus T curve. In our argument, the maximum (in magnitude) in the temperature dependence of MR approximately indicates the onset of the ferromagnetic to antiferromagnetic phase transition with decreasing temperature. This transition is pushed towards lower temperature in the presence of high magnetic fields, and thus the paramagnetic to ferromagnetic and ferromagnetic to antiferromagnetic transitions can be resolved in this condition. With the onset of the ferromagnetic to antiferromagnetic transition with decreasing temperature, the magnitude of the MR decreases because of the competition between the positive MR contributed by the antiferromagnetic phase fraction (by volume) and the negative MR contributed by the ferromagnetic phase fraction (by volume) in the alloy. This results in the formation of the peak in the MR versus T curve. The magnitude of MR keeps decreasing with the increasing volume fraction of the antiferromagnetic phase. When the volume fraction of the antiferromagnetic phase is substantial, the MR becomes positive. But the alloy still contains a finite volume fraction of the ferromagnetic phase, which keeps decreasing with the lowering of temperature. This gives rise to the temperature dependent positive MR at low temperatures. When the alloy is completely antiferromagnetic (below 20 K approximately) the MR is nearly independent of temperature. Thus, we believe that the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy goes to a state of spatial coexistence of antiferromagnetic and ferromagnetic phases in the temperature regime approximately between 20 K and the temperature where a maximum (in magnitude) is observed in the temperature dependence of magnetoresistance. This maximum, on the other hand, indicates both the onset temperature of the ferromagnetic to antiferromagnetic phase transition while cooling and the temperature of completion of the antiferromagnetic to ferromagnetic phase transition while warming as there is no hysteresis across this transition. The indication of the onset temperature of the antiferromagnetic to ferromagnetic transition while warming, or the completion of the ferromagnetic to the antiferromagnetic transition while cooling (~20 K), appears to be rather weak in the magnetoresistance results. This may be related to the combined influences of the excess quenched disorder in the system [13], and the low magnitude of magnetoresistance within the antiferromagnetic phase. We now recall the low value of spontaneous magnetization obtained from the Arrott plot at 70 K. This low value could be related to the scale of spatial distribution of antiferromagnetic and ferromagnetic

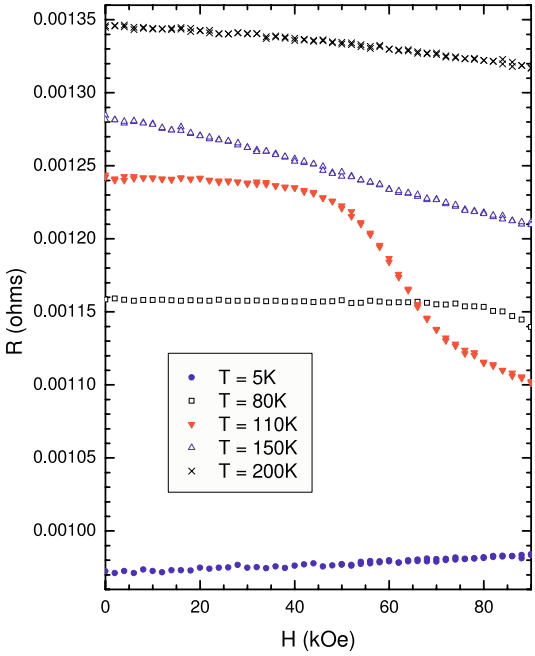

Figure 6. Isothermal magnetic field dependence of electrical resistance in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy.

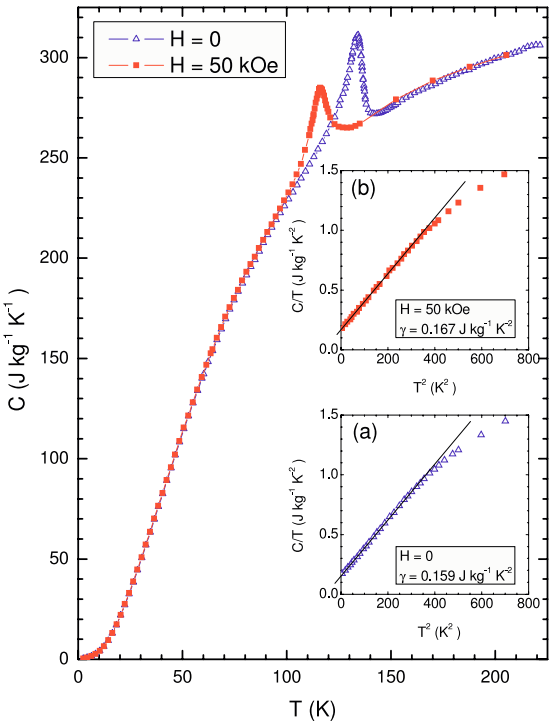

Figure 7. Main panel: the temperature dependence of heat capacity of $Ce(Fe_{0.9}Ru_{0.1})_2$ in different applied magnetic fields. The insets show the C/T versus T^2 curves for the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy drawn at low temperatures in different magnetic fields for the determination of γ.

phases in the alloy and the small total volume fraction of the ferromagnetic phase.

Figure 6 shows the magnetic field dependence of electrical resistance of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy obtained at different constant temperatures both in increasing and decreasing magnetic fields. While the R versus H curve at 80 K shows only the hint of a metamagnetic transition, the curve at 110 K shows a clear signature of the same. The sign and magnitude of the large MR observed in figure 5(b) is further confirmed in the R versus H results. The R versus H curve obtained at 5 K shows that MR is small and positive, and there is no hint of any field induced transition at this temperature up to the highest applied field of the present measurements. This is also in agreement with figure 5(b). No field hysteresis is observed in the alloy at any temperature. The signature of the magnetic phase transition observed in the field dependence of electrical resistance of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is qualitatively very similar to that observed in other doped $CeFe_2$ alloys, except the absence of field hysteresis across the transition [11, 12, 26]. Thus the absence of hysteresis observed in the magnetization results is confirmed in the temperature and magnetic field dependence of the electrical resistance as well.

Hysteresis in varying temperature and/or magnetic field and the coexistence of phases are generic features of disorder influenced first order magnetic phase transitions, and have been observed in many other systems, including Ni–Mn–In Heusler alloys [32], Gd_5Ge_4 [33], manganites [34], and vortex matter [35], apart from the doped $CeFe_2$ alloy family [10–15] that we have used as a test bed materials system to study the characteristics of a disorder influenced first order phase transition. In our present results we indeed have the evidence of coexistence of ferromagnetic and antiferromagnetic phase, but we do not see any hysteresis. To shed further light on the nature of the temperature and magnetic field induced phase transitions in the present $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy, we have measured the temperature dependence of the heat capacity (C) of the alloy both in zero field and in the presence of 50 kOe magnetic field. The main panel of figure 7 shows these results. The magnetic phase transition in the alloy is indicated by a peak in the temperature dependence of heat capacity. The peak shifts towards lower temperature in the presence of applied magnetic field indicating the field induced character of the phase transition. The peak in the temperature dependence of heat capacity of $Ce(Fe_{0.9}Ru_{0.1})_2$ is quite broad, both in zero and applied magnetic field, and does not give any clear indication of the order of the phase transition [25, 36]. The temperature dependence of entropy (S) of $Ce(Fe_{0.9}Ru_{0.1})_2$ is calculated using the equation (originating from the definition of entropy)

$$S = \int_0^T \frac{C}{T} \mathrm{d}T. \quad (1)$$

The main panel of figure 8 shows the temperature dependence of entropy of the alloy obtained in zero field. A first order phase transition is expected to exhibit a discontinuity on the S versus T curve at the transition point [36]. No such discontinuity is observed on the S versus T curve of $Ce(Fe_{0.9}Ru_{0.1})_2$ both in zero (figure 8, main panel) and applied magnetic field (data not shown here). This is consistent with the results of the magnetization and electrical resistance measurements and indicates a continuous nature of the phase transition. The transition may be further analysed by finding the critical

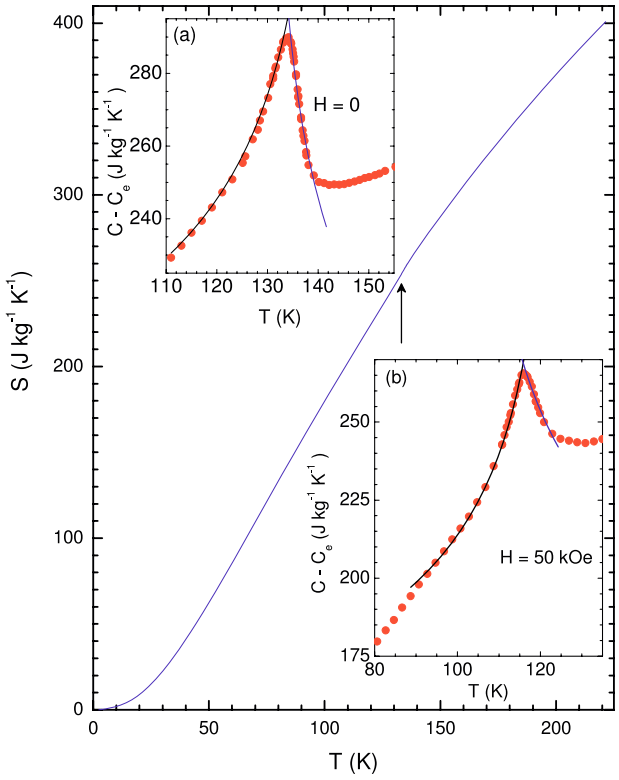

Figure 8. Main panel: the temperature dependence of entropy of $Ce(Fe_{0.9}Ru_{0.1})_2$ in zero field. The arrowhead shows the position of the magnetic phase transition that gives rise to a peak in the heat capacity. The insets show the curve fitting done for the determination of critical exponents of $Ce(Fe_{0.9}Ru_{0.1})_2$ in different applied magnetic fields (see text for details).

exponents [25, 36] from the temperature dependence of heat capacity. To do the same we first separate out the electronic contribution to the heat capacity of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy. In general, the heat capacity of a non-magnetic material consists of electronic and lattice contributions. At temperatures much below the Debye temperature (the Debye temperature of the doped $CeFe_2$ alloys is reported to be higher than 200 K [37]), the temperature dependence of heat capacity of a non-magnetic material may be expressed by the following relation:

$$C(T) = \gamma T + \beta T^3. \tag{2}$$

The term linear in T in equation (2) denotes the electronic contribution to heat capacity, and the cubic term gives the lattice contribution to heat capacity below Debye temperature. Interestingly, the temperature dependence of the heat capacity of an antiferromagnet *is of the same form as the lattice* heat capacity and it is reported that *it is virtually impossible to separate the lattice and magnetic terms correctly* [38]. Therefore, if in accordance with our magnetoresistance results $Ce(Fe_{0.9}Ru_{0.1})_2$ is antiferromagnetic at low temperatures, the C versus T curves of the alloy should follow equation (2) in this temperature regime. In that case β in equation (2) should represent both the lattice and antiferromagnetic contributions. The electronic specific heat coefficient γ for the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is determined by fitting a straight line to the low temperature portion of the C/T versus T^2 curves obtained in zero and 50 kOe magnetic field. Such a method has been used earlier to find the γ in the antiferromagnetic phase of Co-doped $CeFe_2$ alloys [37]. These fittings are shown in the insets (a) and (b) to figure 7. Clearly, equation (2) fits the experimental data quite well below 20 K, and this actually supports our argument that the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is antiferromagnetic at low temperatures (below 20 K). The electronic specific heat coefficient γ determined from this fitting turns out to be 0.159 J kg^{-1} K^{-2} (41.48 mJ mol^{-1} K^{-2}) in zero field and 0.167 J kg^{-1} K^{-2} (43.56 mJ mol^{-1} K^{-2}) in 50 kOe magnetic field. Similar values of γ in the doped $CeFe_2$ alloys in the absence and presence of magnetic field were reported earlier [37]. It was found earlier in Co-doped $CeFe_2$ alloys that γ in the ferromagnetic phase decreases with increasing magnetic field. The suppression of spin fluctuations because of applied magnetic field in the ferromagnetic state was thought to be the reason behind such an observation [37]. In the present sample, however, γ is found to increase with the application of magnetic field in the antiferromagnetic phase. We are not sure whether this could be related to any kind of spin fluctuation that might be present in the system in the antiferromagnetic phase at low temperatures. Irrespective of the reason behind this magnetic field dependence of γ, the electronic contribution to the heat capacity ($C_e = \gamma \cdot T$) may be subtracted from the measured heat capacity (for the respective applied magnetic field) and the following equation [25, 39] may be fitted to the subtracted data in the region close to the peak observed in heat capacity:

$$(C - C_e)^{\pm} = \frac{A^{\pm}}{\alpha} |t|^{-\alpha} + b. \tag{3}$$

This equation describes the critical behaviour of a material, where $t = (T–T_{tr})/T_{tr}$ is the reduced temperature, T_{tr} is the transition temperature, b is a temperature independent background contribution, and the plus (minus) refers to temperatures for which $t > 0$ ($t < 0$). The curve fitting is shown in the insets to figure 8. In zero magnetic field, a good fit is obtained with $\alpha = 0.18$ below and $\alpha = 0.21$ above the peak observed in the $(C–C_e)$ versus T curve. In the presence of 50 kOe magnetic field a good fit is obtained with $\alpha = 0.21$ both above and below the peak. The T_{tr} obtained from this curve fitting exercise are respectively 133 K and 116 K respectively for $H = 0$ and 50 kOe. We relate this value of T_{tr} to the maximum (in magnitude) observed in the temperature dependence of magnetoresistance, and thus to the onset of the ferromagnetic to antiferromagnetic phase transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy with the lowering of temperature. The signature of the ferromagnetic to paramagnetic transition in heat capacity is probably too small as compared to our experimental resolution. This is consistent with our R versus T results, where the change of slope across the ferromagnetic to paramagnetic transition is not observed clearly (the signature of this transition is observed only in the derivatives, and the magnetoresistance curves). A strong presence of spin fluctuations, as has been inferred earlier, might be a reason behind the suppression of the signature of this phase transition in the above experimental observables. The difference in the

value of α above and below T_{tr} in zero field may be related to the close proximity of the antiferromagnetic to ferromagnetic and ferromagnetic to paramagnetic phase transitions in the alloy in this field. The fitting is better when these transitions move apart on the temperature scale in the presence of high magnetic field. For a comparison of the value of critical exponents, it is observed that the present value of $\alpha = 0.21$ is close to that (0.24) for a chiral 3D Heisenberg system [39].

In the case of $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy, it is expected that the entropy of the material (calculated from the measured heat capacity) would have lattice, electronic, and magnetic contributions. The total entropy of $Ce(Fe_{0.9}Ru_{0.1})_2$ in the presence and absence of magnetic field were earlier calculated using equation (1). The isothermal entropy change (ΔS) in $Ce(Fe_{0.9}Ru_{0.1})_2$ due to the application or change of magnetic field, can be calculated using a related relationship originating from equation (1) [40]:

$$\Delta S(T)_{\Delta H} = \int_0^T \frac{C(T)_{H_2} - C(T)_{H_1}}{T} \mathrm{d}T. \qquad (4)$$

The temperature dependence of ΔS in $Ce(Fe_{0.9}Ru_{0.1})_2$ for 50 kOe magnetic field is shown in figure 9(a) with the help of (blue) open triangles. The (red) filled squares show the isothermal change of magnetic entropy (ΔS_M) in $Ce(Fe_{0.9}Ru_{0.1})_2$ due to the application of magnetic field (50 kOe). This curve is taken from [18], where ΔS_M was calculated from the magnetization results using the Maxwell's relation:

$$\left(\frac{\partial S_M(T,H)}{\partial H}\right)_T = \left(\frac{\partial M(T,H)}{\partial T}\right)_H. \qquad (5)$$

Here S_M represents magnetic entropy. It is observed in figure 9(a) that while ΔS exhibits a maximum of 4.3 J kg^{-1} K^{-1} at 122.7 K, ΔS_M shows a maximum of only 2.6 J kg^{-1} K^{-1} at 121 K. The width of the peak in ΔS is also much larger than that of ΔS_M, and in fact the temperature dependences of ΔS and ΔS_M are quite different qualitatively, i.e., $\Delta S \neq \Delta S_M$. This implies that, apart from the magnetic contribution indicated by ΔS_M, either or both of the lattice and electronic contributions to the total entropy (or heat capacity) undergo isothermal changes due to the application of magnetic field. The change in γ due to the application of magnetic field, as determined above, appears to be quite small. However, the isothermal change in the electronic contribution to the entropy (ΔS_e), calculated using a formula similar to equation (4), turns out to be quite appreciable. The temperature dependence of ΔS_e is shown as a dotted (black) line in figure 9(a). It is easily seen in this figure that ΔS_e does account for a large part of the difference observed between ΔS and ΔS_M. However, we still observe that $\Delta S > (\Delta S_M + \Delta S_e)$. Thus, there could possibly be a change (increase) of γ across the antiferromagnetic to ferromagnetic phase transition in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy; or there could possibly be a change of lattice structure as well associated with this phase transition, as is observed in the lesser doped $CeFe_2$ alloys [9]. It is worthwhile to note that an increase of γ across the antiferromagnetic to ferromagnetic phase transition in the Co-doped $CeFe_2$ alloys has been inferred earlier [37].

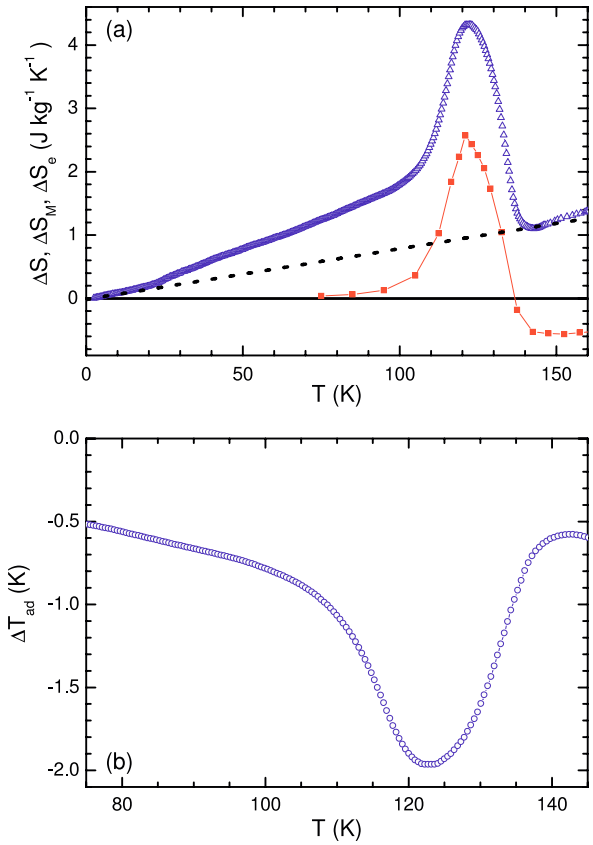

Figure 9. (a) The temperature dependence of isothermal change of entropy in $Ce(Fe_{0.9}Ru_{0.1})_2$ because of applied magnetic field. (b) Adiabatic temperature change in $Ce(Fe_{0.9}Ru_{0.1})_2$ because of applied magnetic field.

We have seen here that the magnitude of magnetocaloric effect (MCE) observed in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is considerably larger than what we had reported earlier [18]. We therefore estimate the magnitudes of the other measures of MCE as well. The adiabatic temperature rise (ΔT_{ad}) in the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy, due to the application of magnetic field, is calculated using the following relationship:

$$\Delta T_{ad}(T)_{\Delta H} = [T(S)_{H_2} - T(S)_{H_1}]_S. \qquad (6)$$

This is done with the help of the S versus T curves obtained using equation (1). The temperature dependence of ΔT_{ad} for 50 kOe magnetic field is shown in figure 9(b). It shows a maximum of 2 K (approximately) close to 123 K, which is quite appreciable. The refrigerant capacity of the $Ce(Fe_{0.9}Ru_{0.1})_2$ alloy is estimated using the $\Delta S(T)$ curve obtained from the heat capacity data, to find the cooling power of the alloy and the temperature range where it could be applicable as a potential magnetic refrigerant. The refrigerant capacity (RC) is defined as the heat transferred between the hot and cold reservoirs in one ideal thermodynamic refrigeration cycle [41]. It is expressed as

$$\mathrm{RC} = \int_{T_{cold}}^{T_{hot}} [\Delta S(T)]_{\Delta H} \mathrm{d}T \qquad (7)$$

where T_{cold} and T_{hot} are the temperatures corresponding to the full width at half maximum in the $\Delta S_M(T)$ curve. The

value of RC is found to be 94.5 J kg^{-1}, for T_{cold} = 107 K and T_{hot} = 134 K. This value of RC is much higher than that calculated using the $\Delta S_M(T)$ versus T curve (figure 9(a)) obtained from the magnetization results [18]. Interestingly, a large part of this enhancement of RC seems to be because of the small increase of γ due to the application of magnetic field. Generally, materials exhibiting magnetic phase transitions are taken as potential candidates for large MCE applications [40]. The present study shows that researchers could also look for materials having field dependent γ over and above the magnetic phase transitions.

4. Summary and conclusion

The Ru-doped $CeFe_2$ alloy $Ce(Fe_{0.9}Ru_{0.1})_2$ was studied through magnetization, magnetotransport, and heat capacity measurements. The studies revealed that the alloy has an antiferromagnetic order at low temperatures below 20 K, but undergoes antiferromagnetic to ferromagnetic and ferromagnetic to paramagnetic phase transitions at higher temperatures. The results show that the antiferromagnetic to ferromagnetic phase transition in $Ce(Fe_{0.9}Ru_{0.1})_2$ could be induced by both temperature and applied magnetic field. Though different characteristics of this phase transition resemble the first order magnetostructural phase transition observed in the lesser doped $CeFe_2$ alloys, the transition in the present alloy shows no hysteresis in temperature and magnetic field and actually bears some second order characteristics. Thus the present results may be considered to be an example of the case where the first order nature of a magnetic phase transition is on the verge of being changed to second order nature due to the influence of increased quenched disorder. This change in nature of the phase transition is consistent with the theoretical work of Imry and Wortis [17]. In contrast to the earlier suggestions [4, 9], the present study observes that the ferromagnetism of $CeFe_2$ is not completely replaced by antiferromagnetism in the $Ce(Fe_{1-x}Ru_x)_2$ alloys with high Ru concentrations. While the lowest temperature state of $Ce(Fe_{0.9}Ru_{0.1})_2$ is antiferromagnetic in nature, ferromagnetism in some form survives in a finite temperature regime. From the point of view of application the important finding of the present study is that the substantial quenched disorder in the material could suppress the hysteresis losses related to the first order phase transitions, while retaining the functional properties of the material like large magnetocaloric effect and large magnetoresistance. The present results also indicate that, apart from the magnetic phase transitions, the magnetic field dependence of the electronic coefficient of heat capacity can play an important role in applications related to the large magnetocaloric effect.

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