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LETTER TO THE EDITOR

First-order transition from ferromagnetism to antiferromagnetism in $CeFe_2$-based pseudobinary alloys

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Abstract. We present the results of alternating-current susceptibility measurements highlighting the presence of thermal hysteresis and phase coexistence across the ferromagnetic-to-antiferromagnetic transition in various $CeFe_2$-based pseudobinary systems. These results indicate that the ferromagnetic-to-antiferromagnetic transition in these systems is first order in nature.

The C15-Laves-phase compound $CeFe_2$ stands out amongst the members of the RFe_2 family (where R = Y, Zr and heavy rare-earth elements). First, the magnetic moment of $CeFe_2$ per formula unit ($\approx 2.4\ \mu_B$) is distinctly smaller than those found for other RFe_2 compounds [1]. Second, its Curie temperature T_C ($\approx$235 K) is relatively small in comparison to those of other RFe_2 compounds [1]. However, short-range magnetic order is detected in its paramagnetic state even in the temperature regime up to four times T_C [2]. All of these aspects have drawn the attention of experimentalists during the last thirty years, and amongst other things the role of Ce in the magnetic properties of $CeFe_2$ has been a subject of both theoretical [3] and experimental investigation [4, 5]; this in turn led to the discovery of newer interesting properties [6]. The most recent neutron measurements on a single-crystal sample of pure $CeFe_2$ have now revealed the presence of low-temperature antiferromagnetic fluctuation in this otherwise ferromagnetic compound [6]. From the study of doped $CeFe_2$, it has already been known for quite some time that the ferromagnetism of $CeFe_2$ is quite fragile in nature and a low-temperature antiferromagnetic state can be established easily with small amounts of doping with elements like Al, Co, Ru, Ir, Re, Os [7–13]. It should be noted, however, that the destabilization of the ferromagnetism in $CeFe_2$ is not a simple disorder-induced one, since doping with other elements like Ni, Mn, Rh, Pd leads to simple dilution of the ferromagnetism [8, 10].

Most of the early experimental activities relating to $CeFe_2$ were focused on establishing the exact nature of the low-temperature magnetic phase—whether it is a re-entrant spin-glass state [14, 15] or an antiferromagnetic state [9, 10, 16, 17]—and, except in a few cases [17, 18], not much emphasis was given to the exact nature of this phase transition. With the antiferromagnetic nature of the low-temperature state being more or less established [16, 17], in the present work we shall specifically address the following question: What is the nature of this ferromagnetic-to-antiferromagnetic transition? While there exists no complete theory (to our knowledge) that can explain the interesting magnetic properties of $CeFe_2$, a phenomenological model dealing with itinerant-electron systems [19] has often been invoked to explain the paramagnetic-to-ferromagnetic-to-antiferromagnetic transition in the doped pseudobinary alloys of $CeFe_2$. This phenomenological model of Moriya and Usami predicted that the ferromagnetic-to-antiferromagnetic transition would be a first-order transition, while the paramagnetic-to-ferromagnetic transition would be a second-order transition [19]. On the basis of our high-resolution ac susceptibility measurement across this ferromagnetic-to-antiferromagnetic transition for two doped samples of $CeFe_2$, we shall report characteristics which are typically associated with a first-order transition. On the other hand, the higher-temperature paramagnetic-to-ferromagnetic transition can be characterized as a standard second-order phase transition. We believe that such a clear-cut characterization of the various phase transitions in $CeFe_2$-based pseudobinaries is necessary, either for an appropriate extension of the Moriya–Usami model [19] or for the development of a newer theory for the proper understanding of the magnetic properties of $CeFe_2$.

The two samples—$Ce(Fe, 5\%\ Ir)_2$ and $Ce(Fe, 7\%\ Ru)_2$—used in the present study were prepared by argon arc melting from metals of at least 99.99% purity. Details of the sample preparation, heat treatment and characterization can be found in reference [10]. The same samples were used earlier in some other studies [13, 20, 21].

The ac susceptibility set-up consists of a coil system having a primary solenoid and two oppositely wound secondaries each consisting of 1500 turns. The coil is dipped in liquid nitrogen to ensure that the temperature of the coil remains constant throughout the entire experiment to avoid drifts in the value of the applied field. The sample is mounted in a double-walled quartz insert and its temperature is raised by heating the exchange gas with a heater wound on a separate Teflon mounting. A temperature controller (Lake Shore DRC-91CA) is used for controlling the temperature. A copper–constantan thermocouple is used in differential

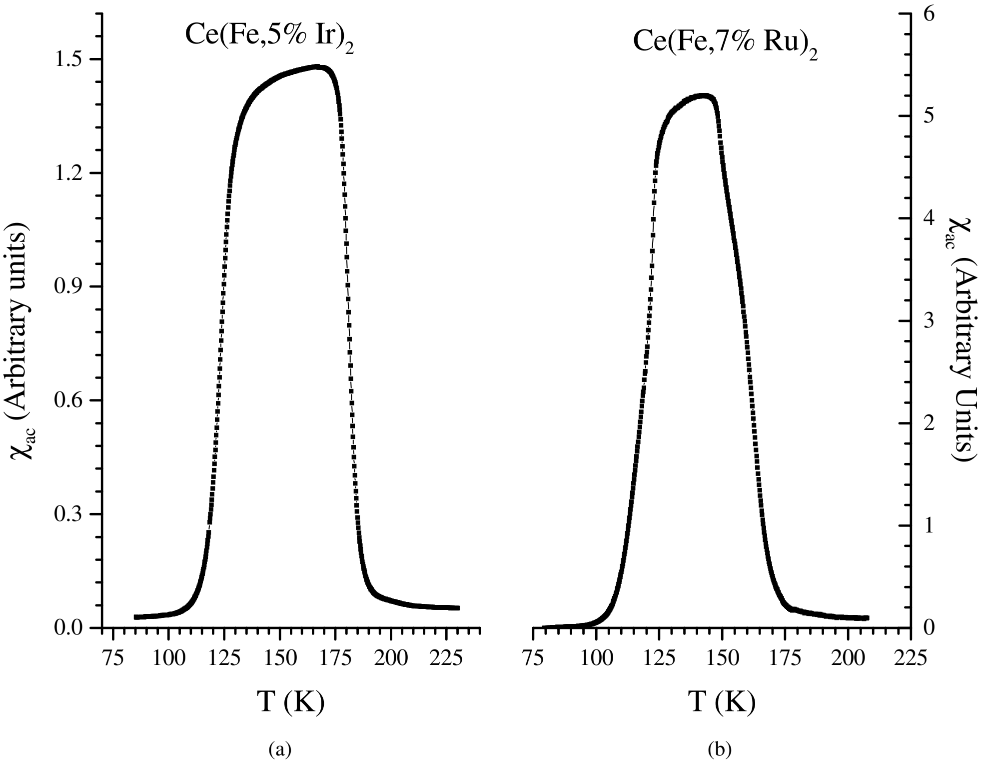


Figure 1. Plots of the ac susceptibility (χ) versus temperature (T) for (a) $Ce(Fe, 5\%\ Ir)_2$ and for (b) $Ce(Fe, 7\%\ Ru)_2$.

mode to monitor the small temperature lag between the sample and the sensor. The sinusoidal output of a lock-in amplifier (Stanford Research SR830) is supplied to a voltage-to-current converter which drives the current through the coil to generate the necessary ac magnetic field. The signal from the pick-up coil which is proportional to the susceptibility is measured by the same lock-in amplifier. The field and frequency values were 4 Oe rms and 333 Hz respectively.

Figure 1 shows the ac susceptibility (χ) as a function of temperature (T) for both Ce(Fe, 5% Ir)$_2$ and Ce(Fe, 7% Ru)$_2$. The paramagnetic-to-ferromagnetic transition is characterized by a sharp increase in susceptibility (χ) with the decrease in T at $T_{Curie} \approx 185$ K in the 5% Ir-doped sample and $T_{Curie} \approx 165$ K in the 7% Ru-doped sample. Below T_{Curie} the susceptibility more or less flattens out for both samples, before decreasing sharply at around 135 K in Ce(Fe, 5% Ir)$_2$ and at around 125 K in Ce(Fe, 7% Ru)$_2$. This low-temperature decrease in χ was earlier taken as a signature of ferromagnetic-to-antiferromagnetic transition [10, 13, 20], and the transition temperatures (T_N) estimated from our present study agree well with the existing literature [10, 13, 20].

Our aim now is to find out the exact nature of these two magnetic transitions observed in CeFe$_2$-based pseudobinaries. Experimentally, the indication of a first-order transition usually comes via a hysteretic behaviour of various properties, not necessarily thermodynamic ones. As an example, the first indication of a first-order melting transition from elastic solid to vortex liquid in vortex matter comes from a distinct hysteresis observed in transport property measurements [22, 23]. The confirmatory tests of the first-order nature of a transition of course involve the detection of discontinuous change in thermodynamic observables and the

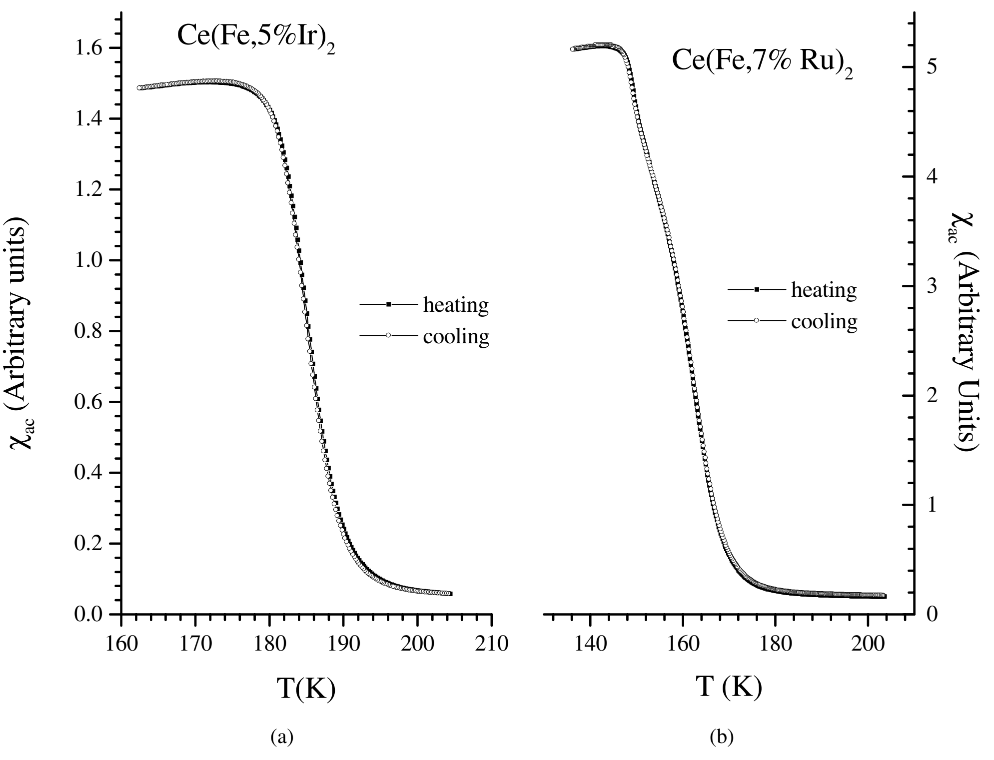
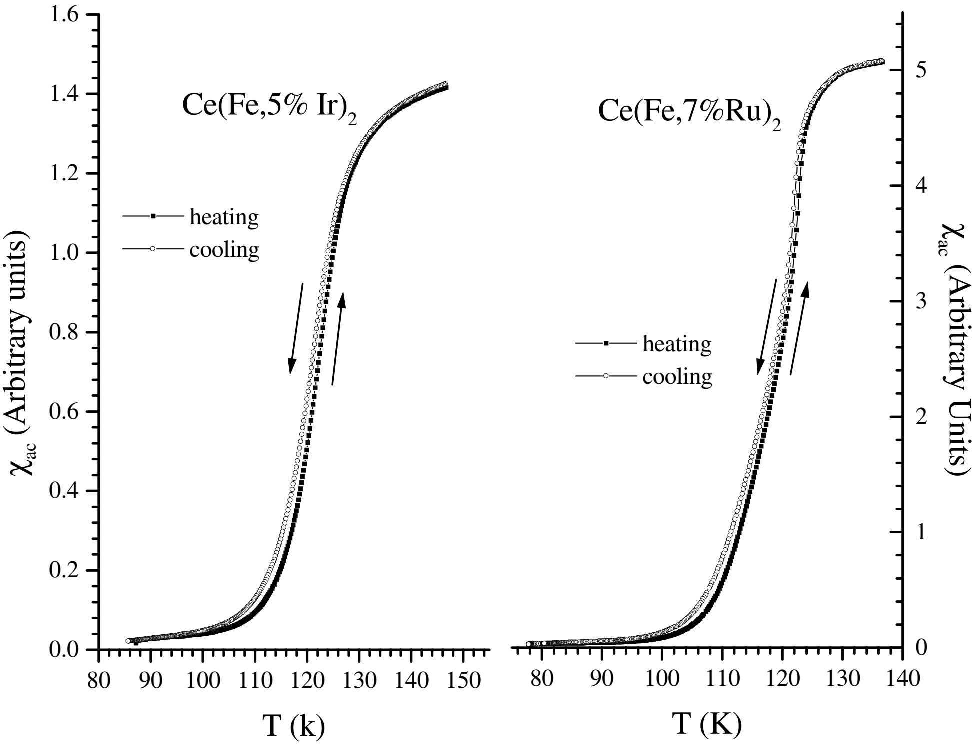


Figure 2. A χ-versus-T plot highlighting the thermal reversibility of the paramagnetic-to-ferromagnetic transition in (a) Ce(Fe, 5% Ir)$_2$ and (b) Ce(Fe, 7% Ru)$_2$.

estimation of latent heat, and this has subsequently been achieved for vortex lattice melting in vortex matter [24,25]. There also exists a less rigorous class of experimental tests which involve the study of phase inhomogeneity and phase coexistence across a first-order transition. This kind of experiment has also turned out to be fairly informative for the melting transition [26] as well as the transition from ordered solid to disordered solid [27, 28] in vortex matter. In our present study we shall use hysteresis and phase coexistence to investigate the nature of the magnetic transitions in $CeFe_2$-based systems; our observable will be the ac susceptibility (χ).

In order to observe the hysteresis in the transition, if there is any, we have chosen to sweep the temperature at a slow rate (0.006 K s^{-1} typically, and slower when needed) instead of stabilizing at each temperature. This was done to ensure that the temperature is varied unidirectionally during both the heating and cooling cycles. The signal was measured at temperature intervals of 0.2 K. The time constant of the low-pass filter of the lock-in amplifier was chosen such that the temperature changes negligibly (compared to our temperature step) within a time interval of 10 times the time constant. The temperature difference between the sensor and the sample, as monitored by the differential thermocouple, was always less than 1% of the sensor temperature and is used to obtain the correct value of the sample temperature.

First, we show the effect of temperature cycling on the paramagnetic-to-ferromagnetic transition in figure 2. In the case of $Ce(Fe, 5\%\ Ir)_2$ the transition is reversible within an error of 0.15 K to 0.2 K. In the case of $Ce(Fe, 7\%\ Ru)_2$ the reversibility is even better. The lack of hysteresis in the paramagnetic-to-ferromagnetic transition within an error bar smaller than our



(a) (b)

Figure 3. A χ-versus-T plot highlighting the thermal irreversibility of the ferromagnetic-to-antiferromagnetic transition in (a) $Ce(Fe, 5\%\ Ir)_2$ and (b) $Ce(Fe, 7\%\ Ru)_2$.

temperature step is indicative of a second-order phase transition.

We then focus our attention on the ferromagnetic-to-antiferromagnetic transition which has been shown to be associated with a structural distortion from cubic to rhombohedral [16,17], hinting at a first-order transition. The same protocol of sweeping the temperature and measuring the signal at closely spaced temperature values is followed during this measurement also.

Figure 3 shows the result of our measurements on both 5% Ir-doped and 7% Ru-doped $CeFe_2$ samples. Both the samples show a distinct thermal hysteresis in the ac susceptibility across the ferromagnetic-to-antiferromagnetic transition. The width of the hysteresis is about 2 K which is well beyond the error in our measurements.

To study the phase coexistence we use the technique of minor hysteresis loops (MHLs) [29]. We first define the 'envelope curve' as the curve enclosing the thermally hysteretic susceptibility between the lower- and higher-temperature reversible regions (see figure 3). We can produce a MHL during the heating cycle, i.e. start heating and increase T from the lower-temperature reversible (antiferromagnetic) region and then reverse the direction of the temperature change before reaching the higher-temperature reversible (ferromagnetic) region. We can also produce a MHL in the cooling cycle, i.e. start cooling from the reversible ferromagnetic region and reverse the direction of the temperature change before reaching the lower-temperature reversible antiferromagnetic region. If the heating is reversed at sufficiently 'low' temperature, the minor loop does not coincide with the cooling part of the 'envelope curve'. Here in the lower part of the hysteretic regime the high-temperature ferromagnetic

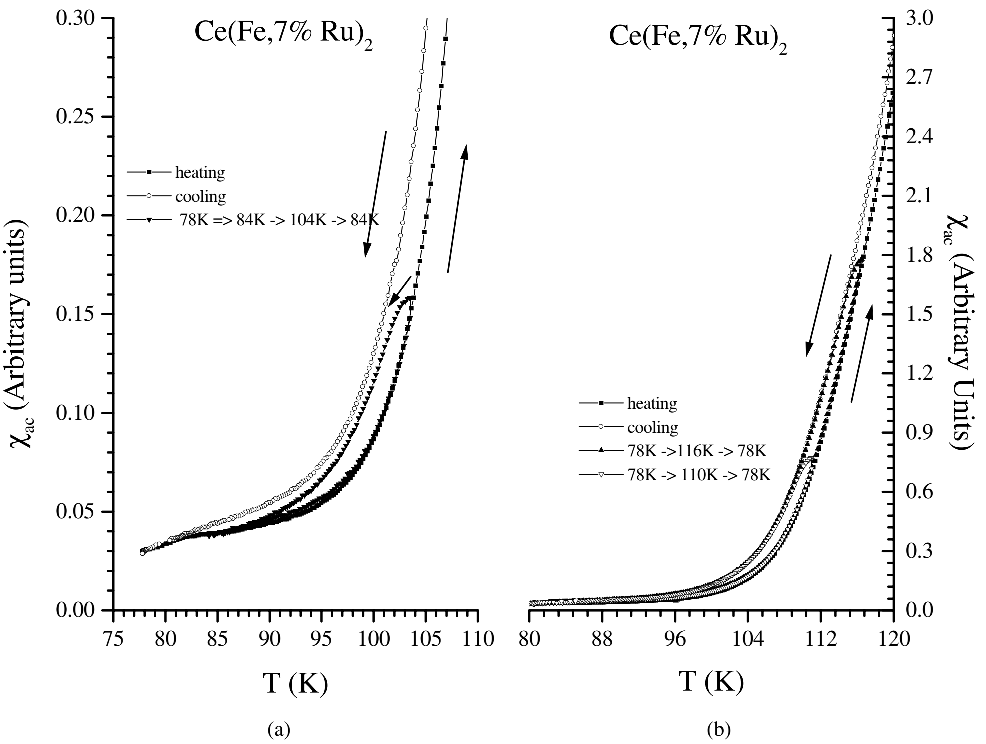


Figure 4. Minor hysteresis loops (MHLs) in χ-versus-T plots highlighting phase coexistence in Ce(Fe, 7% Ru)$_2$: (a) a representative MHL initiated from the lower part of the hysteretic regime and (b) representative MHLs initiated from well inside the hysteretic regime. See the text for details.

phase is not formed in sufficient quantities; so when the temperature is decreased, the curve does not fall on the cooling part of the envelope curve which represents the curve along which the high-temperature phase is supercooled. The MHLs initiated from temperatures well inside the hysteretic regime coincide with the cooling part of envelope curve, indicating that the high-temperature phase has formed in sufficient quantities. In figures 4 and 5 we present some representative MHLs for both the Ce(Fe, 5% Ir)$_2$ and Ce(Fe, 7% Ru)$_2$ alloys. We have produced similar MHLs from the cooling branch of the envelope curve, which are not shown here for the sake of clarity and conciseness. We have reproduced this behaviour of the MHLs over many experimental cycles. The presence of these MHLs clearly suggests the existence of phase coexistence across the ferromagnetic-to-antiferromagnetic transition. Had there been no phase coexistence, we would have followed the cooling part of the envelope curve reversibly on increasing T. A very similar MHL technique has been used to study the phase coexistence associated with first-order metal–insulator transitions in $PrNiO_3$ [30].

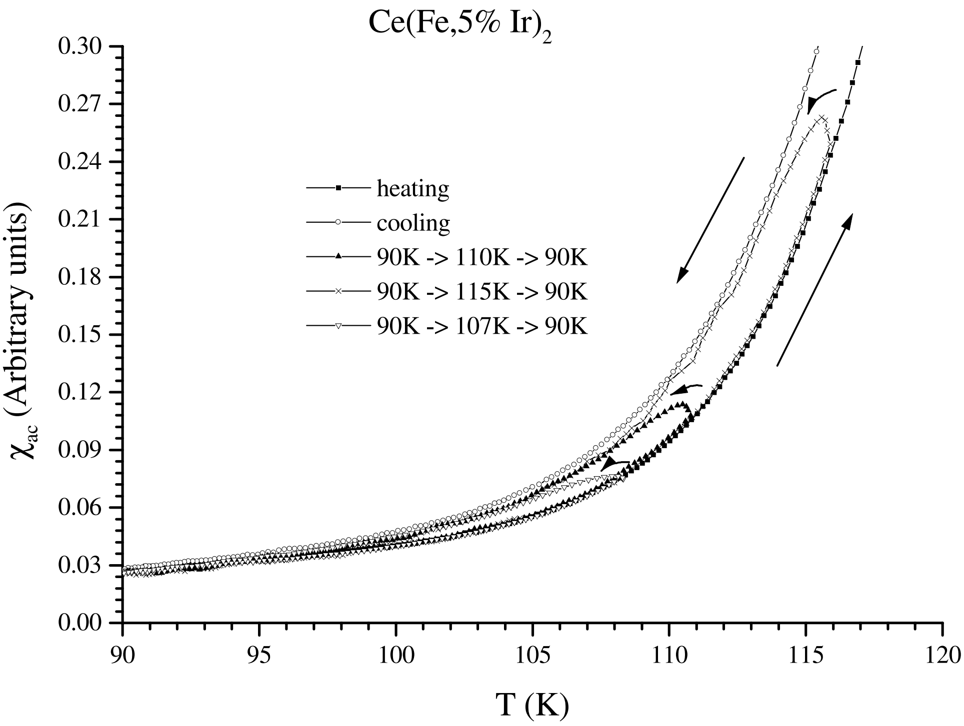


Figure 5. Minor hysteresis loops (MHLs) in a χ-versus-T plot highlighting phase coexistence in Ce(Fe, 5% Ir)$_2$.

It should be noted here that the pinning of solitons (domain walls) by lattice defects can also give rise to a thermal hysteresis [31] in magnetic measurements. However, the observed thermal hysteresis in our present study is confined to a relatively narrow temperature window and this argues against such a possibility.

In conclusion, we have shown that the ferromagnetic-to-antiferromagnetic transition in the compounds Ce(Fe, 5% Ir)$_2$ and Ce(Fe, 7% Ru)$_2$ is accompanied by distinct thermal hysteresis as well as signatures of phase coexistence. We argue that these observations are indicative of the first-order nature of the phase transition concerned. The higher-temperature paramagnetic-to-ferromagnetic transition appears to be a typical second-order phase transition. These results support the applicability of the Moriya–Usami model [19] in explaining the double magnetic transitions in various $CeFe_2$-based pseudobinary systems. A calorimetric study is now required to confirm the conjecture that this ferromagnetic-to-antiferromagnetic transition is first order in nature. However, it should be noted that in the case of small latent heats it might be difficult to distinguish a first-order transition through calorimetric studies [32]; in such cases the observed hysteresis and phase coexistence would remain useful tools for identification of a first-order transition.

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