First order transition from antiferromagnetism to ferromagnetism
in Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$

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Abstract

Results of dc magnetization study are presented showing interesting thermomagnetic history effects across the antiferromagnetic to ferromagnetic transition in Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$. Specifically, we observe (i) ZFC/FC irreversibility rising with increasing field; (ii) virgin curve lying outside the envelope M-H curve. We argue that these effects are quite different from the characteristics seen in spin-glasses or in hard ferromagnets; they can be understood as metastabilities associated with a first order magnetic phase transition.
I. INTRODUCTION

The C15-Laves phase ferromagnetic compound CeFe$_2$, with its relatively low Curie temperature ($T_C \approx 230$K) and reduced magnetic moment ($\approx 2.3\mu_B/f.u.$), is an unusual member of the RFe$_2$ (R= rare earth) family. It is also known for quite some time that CeFe$_2$ is on the verge of a magnetic instability. With small but suitable change in electronic structure on doping with elements like Co, Al, Ru, Ir, Os and Re at the Fe-site of CeFe$_2$ (Ref.4), the higher temperature ferromagnetism readily gives in to a lower temperature antiferromagnetic phase, and after certain concentration of dopants (usually 5 to 10%) the antiferromagnetic (AFM) phase replaces the ferromagnetic (FM) phase altogether. A recent neutron measurement has now confirmed the presence of antiferromagnetic fluctuations in the FM ordered state of pure CeFe$_2$ itself. This in turn suggests the existence of strong competition between the FM and AFM ground state in pure CeFe$_2$ with the AFM ground state being stabilized on doping.

With the initial debate, whether the low temperature ground state of the doped CeFe$_2$ compounds is re-entrant spin-glass or antiferromagnet, being settled in favour of antiferromagnet, the more recent experimental efforts are mainly focussed on understanding the cause of this magnetic instability. The question being asked now whether the observed magnetic properties are linked to the instability of cerium electronic state and/or the peculiarity of the 3d-4f hybridization, and a clear cut model explaining the interesting electromagnetic properties of CeFe$_2$ and its pseudobinary alloys is yet to be established. There is one other aspect of the observed magnetic properties which needs proper attention and the information on which will be important for any future model, is the exact nature of the FM to AFM transition. Although it is generally believed that this transition is of first order in nature, no detail study exists in this regard. We have recently addressed this problem in Ru and Ir-doped CeFe$_2$ alloys. In this letter we shall focus on Al-doped CeFe$_2$ system. In contrast to the quite sharp FM-AFM transition in Ru, Co, Ir doped CeFe$_2$ alloys, this transition in Al-doped CeFe$_2$ alloys is relatively gradual in nature. We report
here interesting thermomagnetic properties of magnetization for a Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$ alloy. These thermomagnetic properties are distinctly different from those observed in spin-glasses and hard ferromagnets. We argue that these thermomagnetic history effects in the present system arise due to the first order nature of the FM-AFM transition. Such effects may be treated as characteristic signatures of a first order FM-AFM transition in general.

The sample used in the present study belongs to the same batch of samples used earlier in the study of bulk magnetic and transport properties, and neutron measurements. The details of the preparation and characterization of the sample can be found in Ref.8. We have used SQUID-magnetometer (Quantum Design-MPMS5) for measuring magnetization (M) as a function of temperature (T) and applied magnetic field (H). We have checked the results varying scan length from 2 to 4 cm and no qualitative dependence on the scan length is found. Before each experimental cycle the sample chamber was flushed with helium gas after heating it to 200K. This is to get rid of any residual oxygen leaking in the sample chamber over a period of time.

In Fig.1 we present M vs T curves, obtained both in the zero-field-cooled (ZFC) and field cooled (FC) mode, at various applied H. A sharp rise in M as a function of decreasing T indicates the transition from paramagnetic (PM) to FM state. This is followed by a sharp drop in M at a lower T indicating the onset of the AFM transition. The PM to FM transition temperature ($T_C \approx 200$K) and FM to AFM transition temperature ($T_N \approx 95$K) obtained from the low field (20 Oe) M-T curve (see Fig. 1(a)), agree well with those obtained earlier from ac-susceptibility measurements. With the increase in H there is a marked decrease in $T_N$, and a relatively slow rise in $T_C$. A distinct thermomagnetic irreversibility (TMI)(i.e. $M_{ZFC} \neq M_{FC}$) is observed in the M-T curves with H=20 and 100 Oe (see Fig. 1(a)) starting well inside the FM regime. This kind of TMI is widely associated in literature with spin-glass transition, but can occur in a ferromagnet also if the measuring field H is of the order of the coercivity field. With the measured coercivity in the FM regime of our present sample being about 100 Oe, we attribute the observed TMI for $H \leq 100$ Oe to the residual domain related pinning effects. In consonance with this conjecture, the TMI in the FM regime
vanishes with the further increase in $H$ (see Fig. 1(a) and (b)).

While the TMI in the FM region vanishes for $H > 100$ Oe, a distinct TMI emerges in the AFM region. In contrast with the TMI in the FM regime this increases in strength with the increasing $H$ (see Fig. 1(a) and (b)). This is quite anomalous in comparison with the TMI associated with nonergodic behaviour of spin response in spin-glasses and hindrance of domain rotation and/or domain wall pinning in the ferromagnets. In both of these cases the TMI is known to reduce with the increase in the applied field.

The anomalous field dependence of TMI above 1 kOe, we believe, is not associated with pinning/hindered motions of the spins or magnetic domains, but can be understood as due to metastabilities associated with FM-AFM transition being first order in nature. While cooling from the FM state to the AFM state, the FM state will continue to exist as supercooled metastable state below $T_N$ down to a certain metastability temperature $T^*$. Between $T_N$ and $T^*$ fluctuations will help in the formation of droplets of the stable AFM state, and at $T^*$ an infinitesimal fluctuation will drive the whole system to the stable AFM state. While lowering $T$ towards $T^*$ although the amount of metastable FM state will go on decreasing, the spin alignment and hence magnetization within the FM state will increase. These combined effects can give rise to nonmonotonic behaviour in the temperature dependence of $M$ below $T_N$. This is quite evident in the higher field ($H > 10$ kOe) $M$-$T$ curves obtained in the FC mode (see Fig. 1(b)). In the ZFC mode the measurement always starts in the low temperature AFM state, and hence there is no contribution to $M$ from the supercooled FM state. The implicit assumptions in the above arguments are: (a) the existence of a $H$ dependent $T^*(H)$ and (b) widening of the difference between $T_N(H)$ and $T^*(H)$ as a function of $H$. It is worth mentioning here that a distinct hysteresis is observed also in the temperature dependence of resistivity of the same sample around $T_N$ measured in the absence of any magnetic external field. Some support for FM-AFM phase coexistence across $T_N$ does exist from existing neutron studies on Ce(Fe,Al)$_2$ alloys. A detailed neutron measurement in presence of applied magnetic field will be very illuminating in this regard.

More support for the first order nature of the FM-AFM transition is obtained from the
history effects we have observed in the isothermal field dependence of M. In Fig. 2 we plot M-H plots for Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$ at various T. It is apparent from Fig.1 that FM order exists for $T \geq 100$K and $H \geq 20$ Oe, and the behaviour of M vs H at $T=100$K (see inset of Fig. 2(a)) is consistent with this picture. The technical saturation of M is reached quite early by $H \approx 3$ kOe and the magnetization is quite reversible with coercivity field of $\approx 100$ Oe. With lowering in T the nature of M-H curve changes drastically with the appearance of a hysteresis bubble. This hysteresis along with the observed cubic to rhombohedral transition, have been associated earlier as possible signatures of the field induced first order metamagnetic transition from AFM to FM in Co-doped CeFe$_2$ alloys. We shall now elaborate more on this issue and argue that these hysteretic field dependence of magnetization is indeed associated with a first order phase transition.

Concentrating on the M-H curve at $T=5$K we find that if the field excursion is confined to $H_M = \pm 30$ kOe, the M-H curve remains perfectly reversible. In this field regime the sample remains in the AFM state. The observed non-linearity in the low field ($\leq 5$ kOe) regime is due to a parasitic weak ferromagnetism leading to a canted spin state. When the applied H crosses the critical value $H_M$, M rises rapidly and upon reversal of H hysteresis is observed. $H_M$ is identified as the metamagnetic field for the onset of the FM order. The hysteresis loop, however, collapses before H is reduced to zero, and reappears again on the third quadrant on reversal of H from beyond $H_M$ in the negative direction, giving rise to distinct double loop structure. Qualitatively similar behaviour is observed at $T=50$K as well (see Fig. 2(b)). In ferroelectric materials such double loop hysteresis is taken as the decisive evidence for a first order ferroelectric transition. We are unaware of similar emphatic arguments in the field of magnetic materials, although a field induced transition accompanied by hysteresis is often quoted to be a first order transition.

While discussing the double loop hysteresis polarization curve in ferroelectrics, it was argued that such field induced first order transition can be explained in terms free energy curves obtained by expanding in a power series in polarization (P) and retaining only terms with even powers in P up to sixth order (Ref.25). The first inspection at the free energy curve
thus obtained (see Fig. 8-16 of Ref.25), does not, however, provide a clear cut explanation of the hysteresis. This situation becomes more clear if we take recourse to a more modern treatment of such free energy curve (Fig. 4.6.1 of Ref.21). Phase coexistence and metastability across the first order transition, and hence hysteresis can be explained naturally from such a free energy curve. In our present magnetic material, on reduction of the field from field values above $H_M$, the high field FM state remains as a metastable state even in the low H regime, and this, we believe, is the cause of hysteresis. The residual ferromagnetic state remains even on reversal of the direction of H, leading to an anomalous situation where the virgin curve lies outside the envelope curve. (The virgin curve in the reverse direction is obtained after zero field cooling the sample from above $T_C$ followed by unidirectional increase of H in the negative direction). This anomalous behaviour of the envelope curve lying above the virgin curve remains on reversal of H through zero in the positive direction. Virgin curve and the envelope curve overlap in the high H regime above $H_M$ (see Fig. 2(c) and inset of Fig. 2(b)). Such anomalous relation between the virgin and envelope curve is uncommon in magnetic materials, except for some recent reports in granular magnetic systems\(^{26}\). However, in those materials the virgin curve goes outside the return envelope curve only after certain applied H and after that they do not seem to merge again. In these materials this anomalous behaviour is tentatively attributed to the prominent contribution from surface magnetism since such behaviour is observed only below a certain grain size\(^{26}\). This is unlikely to be the case in our present bulk magnetic system, since the surface to volume ratio cannot be that high as in those granular magnetic materials.

In conclusion, the results of our present bulk magnetization studies showing distinct thermomagnetic history effects, in conjunction with the existing information of structural distortion across the FM-AFM transition\(^{11}\), strongly claim that the FM-AFM transition in the Ce(Fe,Al)\(_2\) system is of first order in nature. No thermomagnetic history effect is observed across the PM-FM transition\(^{27}\), and the various features from the present as well as previous studies\(^{8,11}\) indicate this transition to be a second order transition. These information will be important in formulation of the theoretical model to explain the interesting
magnetic properties of CeFe$_2$ and its pseudobinaries. We also present through our present study certain thermomagnetic properties which can be used to identify a first order ferromagnetic to antiferromagnetic transition in magnetic materials in general. We now propose a (H,T) path dependent (i.e. FC/ZFC mode) neutron measurement across the FM-AFM transition in Ce(Fe,Al)$_2$ system, which should be able to prove or disprove our claim of the existence of supercooled FM phase across $T_N$, hence the first order nature of the transition.
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27 The TMI inside the ferromagnetic regime (see Fig. 1(a)) is observed only below a characteristic temperature $T_{irr}(H)$, which is distinctly separated from the PM-FM transition temperature.
FIGURES

FIG. 1. Magnetization vs temperature plots at various applied H, obtained both in the ZFC and FC mode. Note that in the M-T curves with H=20 Oe and 100 Oe (Fig.1(a) the TMI extends well inside the FM regime. In Fig. 1(b) lines serve as guide to the eyes.

FIG. 2. Magnetization vs field plots at various temperatures. Note that in Fig. 2(b) (see the inset) and in Fig. 2(c) the virgin curve lies outside the envelope hysteresis curve.
Fig 1(a)

- ■ 20 Oe ZFC
- □ 20 Oe FC
- ● 100 Oe ZFC
- ○ 100 Oe FC
- △ 1 kOe ZFC
- × 1 kOe FC

$M$ (emu/g) vs. $T$ (K)
Fig 1(b)

- ■ 10 kOe ZFC
- □ 10 kOe Fc
- ○ 20 kOe ZFC
- ● 20 kOe FC
- ▲ 30 kOe ZFC
- △ 30 kOe FC
- ▼ 50 kOe ZFC
- ▽ 50 kOe FC

M (emu/g)

T (K)
Fig. 2(a)

$T = 80K$
- ■ field increasing
- □ field decreasing

$T = 100K$
- ● field increasing
- ○ field decreasing
Fig. 2(b)

$T = 50K$

$M$ (emu/g) vs. $H$ (kOe)

- Virgin curve
- Envelope curve
Fig. 2(c) 

$T = 5\text{K}$

- $M$ (emu/g)
- $H$ (kOe)

- Virgin curve
- Envelope curve