Studies on magnetic-field-induced first-order transitions

P CHADDAH

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 017, India
E-mail: chaddah@csr.ernet.in; director@csr.ernet.in

Abstract. We shall discuss magnetization and transport measurements in materials exhibiting a broad first-order transition. The phase transitions would be caused by varying magnetic field as well as temperature, and we concentrate on ferro- to antiferromagnetic transitions in magnetic materials. We distinguish between metastable supercooled phases and metastable glassy phase.

1. Introduction

First-order phase transitions (FOPT) caused by either varying temperature or by varying H were extensively studied in the context of vortex matter phase transitions [1]. Such phase transitions occur in magnetocaloric materials, colossal magnetoresistance materials, magnetic shape-memory alloys etc. and are also believed to be the cause for the functional properties of these materials [2]. In the absence of disorder, the FOPT occurs at a sharply defined line in the 2-control variable (H, T) space. Many of these functional magnetic materials are multi-component systems whose properties become more interesting under substitution. Such substitutions are an intrinsic source of frozen disorder. Early theoretical arguments of Imry and Wortis [3] showed that such samples would show a disorder-broadened transition, with a spatial distribution of the (H_C, T_C) lines across the sample.

Phase transitions observed in vortex matter [1] are broadened both by intrinsic disorder and by pinning giving rise to a variation of the local field across the sample. It was realized that broad first-order transitions would not show jump discontinuities in physical properties, and Clausius–Clapeyron relation cannot be invoked for identifying the order of the transition [1].

Supercooling and superheating across a first-order transition (FOPT) yield metastable states, resulting in hysteresis. But hysteresis and metastability, by themselves, are arguable signatures of a FOPT. Kinetic hysteresis is also seen when molecules in amorphous solids exhibit arrested kinetics, and equilibrium in this
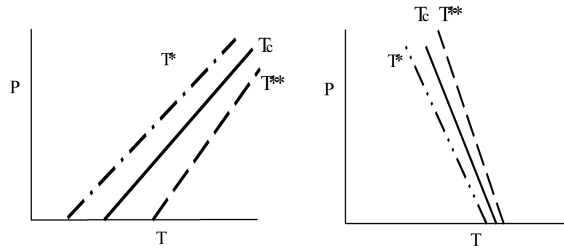
Figure 1. The hysteresis window encompasses smaller T-range with rising density if T_C rises with rising density, and larger T-window if it falls.

glassy state cannot be reached over experimental time scales. Supercooled and 'glassy' states are both metastable states associated with an underlying FOPT. We shall briefly outline some features of hysteresis associated with supercooling, as these were used in establishing the nature of a first-order transition in vortex matter. We shall then look at an interplay between these two phenomenon across disorder-broadened first-order transitions, which have been under active study because these show phase coexistence.

2. Supercooling

Following the standard treatment of supercooling across a first-order transition we considered the case when both T and density are varied to cross the phase boundary [4]. The spinodal or limit for supercooling T^* is the limit above which the supercooled state sits in a local minimum of free energy and is metastable; below this it is unstable and must convert to the ordered state unless kinetics prevents this. A supercooled state is not unstable but sits in a local minimum of the free energy. Similarly, a superheated state is metastable up to a limiting temperature T^{**}. The extent of hysteresis observed, in a constant pressure phase transition, is dictated by the window $\{T^{**} - T^*\}$. We obtained the general result [4], depicted in figure 1, that this window must increase(decrease) with increasing density for transitions in which T_C falls(rises) with increasing density. We also showed that the limit to which one can supercool will be farther if there is no change in density (of vortex matter) during the supercooling process; cooling in constant magnetic field would allow deeper supercooling [4]. We also showed that oscillations in vortex density, caused by oscillations in applied H, would transform the metastable supercooled state into the stable equilibrium state. All these conclusions constituted a verifiable result, and were used for establishing that the transition at the peak-effect in CeRu$_2$ is a first-order transition [5].

3. Glass formation or kinetic arrest

Other than the general definition that 'glass is a noncrystalline solid material that yields broad nearly featureless diffraction pattern', there exists another widely
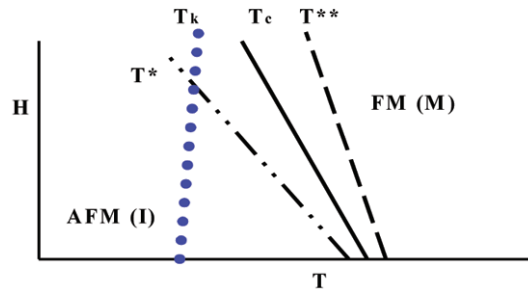
Figure 2. The dotted curve shows the T_K line which falls below T^* at low H (as in a metglass), but lies above it at high H (as in O-terphenyl).

acceptable picture of glass as a liquid where the atomic or molecular motions *or kinetics are arrested.* Within this latter dynamical framework, 'glass is time-held still' [6]. It appears reasonable that kinetic arrest, on experimental time scale, would occur below some T_k. In case glass is formed in a state that is metastable (in terms of free energy) then glass formation can be caused by slow cooling, as in O-terphenyl. If the state in which glass is formed is unstable, then rapid quenching is essential so that kinetics is frozen *before* it can effect a structural change, as in metglasses. In our understanding, what matters is whether it is $T_k < T^*$ (metglass) or $T_k > T^*$ (O-terphenyl). By studying a material in which T_C varies sharply with H, one can hope to go from a metglass-like situation to an O-terphenyl-like situation. This potential situation exists in vortex matter phase transitions, as also in many magnetic materials undergoing a metamagnetic transition. This was recognized by Manekar *et al* [7] in the case of doped $CeFe_2$, and they also speculated that this could also be happening for the charge-ordering transition in some manganites. The schematic in figure 2 shows a situation in which the low-T ground state is antiferromagnetic (AFM) and the high-T equilibrium state is ferromagnetic (FM). This is the situation encountered by Manekar *et al* in doped $CeFe_2$ and in $(Nd,Sr,Sm)MnO_3$. Zero-field-cooling (ZFC) process would produce an AFM state, while field-cooling (FC) in large H would result in a kinetically arrested FM state T because the kinetics is arrested at T_k, and the FM-to-AFM was to occur at the lower T^*.

4. Disorder-broadening

We had started by stating that many functional magnetic materials are multi-component systems whose properties become more interesting under substitutions, which are an intrinsic source of frozen disorder. Such samples would show a disorder-broadened transition, with a spatial distribution of the (H_C, T_C) line across the sample. The spinodal lines corresponding to the limit of supercooling (H^*, T^*) would also be broadened into bands for samples with quenched disorder [7]. Each of these bands correspond to a quasicontinuum of lines; each line represents a region of the disordered sample. Similarly, the disordered system would have a (H_k, T_k) band formed out of the quasi-continuum of (H_k, T_k) lines. Each line in this (H_k, T_k)

band represents a local region of the sample and would have its conjugate in the (H^*, T^*) band. The formation of the supercooling band results in phase coexistence, a phenomenon being reported with increasing frequency, since when T lies within the band some regions of the sample would have transformed and others would not have. The first visual realization of such a phase coexistence was provided by Soibel *et al* [8] for the vortex melting transition. A similar visual realization of such a phase coexistence for an AFM to FM transition, in doped $CeFe_2$, was provided by Roy *et al* [9]. An explanation for these observations is provided in figure 3, adapted from ref. [7]. The results in these two papers correspond to point C and path 2 because the two phases coexisted only over a finite range of fields, and full transformation could be seen in both H-increasing and H-decreasing cases. Similarly, Roy *et al* showed FC measurements for point A since the transformation was completed in both T-increasing and T-decreasing cases. More intriguing data results if one reaches point F following path 2, or point C and then L, following path 1. Specifically, following path 2 at 3 K in doped $CeFe_2$, Manekar *et al* [7] found that even though H is reduced to zero, the starting AFM state is not fully recovered. The data is shown in figure 4a and 4b. To understand this, we look at figure 3 and path 2 leading to point F (which is at $H = 0$). Part of the arrested FM state is converted to AFM, but full de-arrest does not take place. It follows from figure 3 that if the run is repeated at slightly higher T, then the arrested FM fraction will be smaller; the data at 5 K confirmed this [7]. Similar, but less complete, data existed in literature on $(Nd,Sr)MnO_3$, and this was also explained [7]. FC data was also taken in various fields on doped $CeFe_2$, and figure 5 shows data for $H = 0.7$ T [10]. Again, following path 1 leading to points D and E in figure 3, we do not recover the full AFM state obtained in the ZFC case. Points E and L will have the same frozen FM fraction, and this comes out in figure 5. Singh *et al* [10] took data at higher fields and, as expected, the frozen FM fraction was larger. Similar data existed in literature on $(Nd,Sr,Sm)MnO_3$, and this was also explained [10]. Such part-transformations, and frozen coexisting-phases, is a manifestation of disorder-broadened transitions. It is also a strong interplay between supercooled
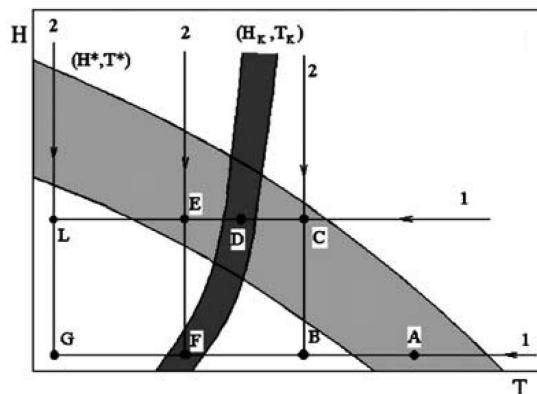

Figure 3. Two phases will be observed at points A, C, D, E and L by paths 1 (FC); and at points C and F by paths 2 (*T*-fixed, lowering *H*), from [7].
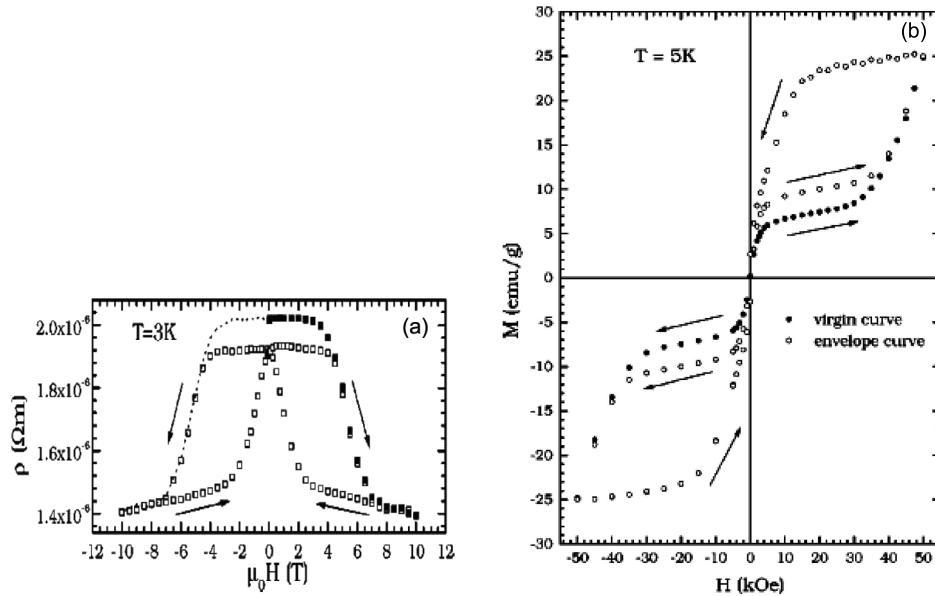
Figure 4. (**a**) Isothermal reduction of field results in only part conversion of FM-to-AFM phase, down to $H = 0$; from [7]. (**b**) The virgin M–H curve lies outside the hysteresis loop, because the virgin ZFC state is AFM, whereas the remanent state at $H = 0$ has some frozen FM [7].
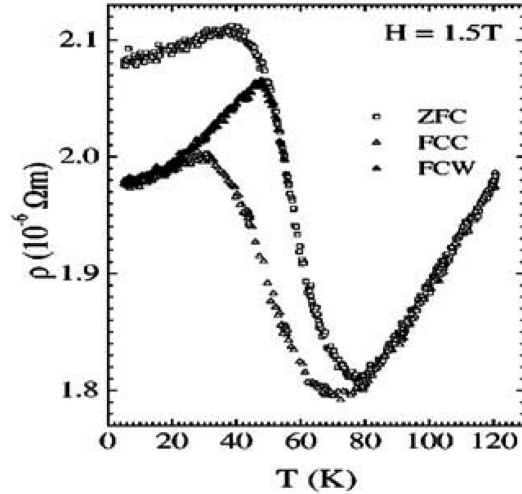

Figure 5. FCC results in part conversion to AFM phase; from [10].

states and kinetically-arrested (or glassy) states. Since both these are *not equilibrium or stable* states, there is an expectation of observable relaxation effects. We now address these possibilities.
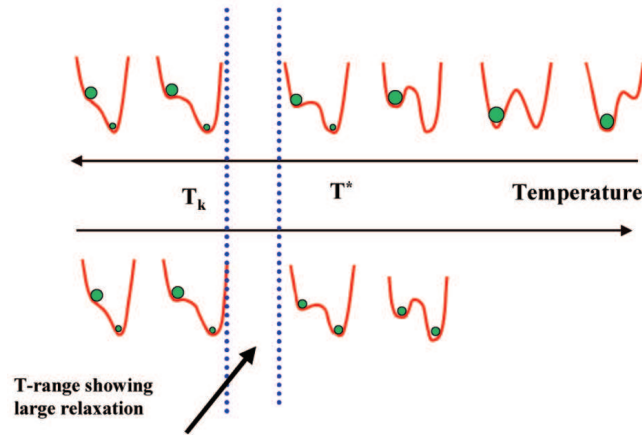
Figure 6. Schematic of close-lying T^* and T_k.

5. Relaxation effects

As discussed earlier, a supercooled state sits in a local minimum of free energy, and the barrier defining this local minimum decreases with falling T. It is thus expected that relaxation effects would *increase* as one lowers T for a supercooled state. A kinetically arrested state, on the other hand, need not be in a local minimum of free energy; its further transformation is inhibited because molecular motions are too slow. It is thus intuitive that these motions would become slower as T is lowered, and relaxation effects here would *decrease* as T is lowered. As indicated in figure 2, for cooling in some particular field value, T^* could lie just above T_k. In this case, relaxation rate would first rise as T is lowered towards T^*, and then fall as one crosses T_k. This is depicted in figure 6. Chattopadhyay *et al* [11] have observed this behaviour in doped CeFe$_2$. Similar behaviour has been observed by Ghivelder and Parisi [12] in LaPrCaMnO$_3$.

6. Discussion

I have discussed two distinct types of metastable states associated with a first-order phase transition. Intrinsic disorder adds newer features because the free energy landscape broadens various transition lines into bands. Features like coexisting phases, commonly observed over regions of T (or H) in many functional magnetic materials, can be understood. We have added to the complexity by adding the concept of kinetic arrest. This adds newer possibilities, which have been confirmed through measurements on the doped CeFe$_2$ system. This has helped in explaining intriguing observations in various manganite systems. Similar observations in the magnetocaloric material Gd$_5$Ge$_4$ have also been explained using these ideas [13]. These ideas have also been recently exploited to explain irreversibilities in another intermetallic Nd$_7$Rh$_3$ [14].

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