Tunable two-phase coexistence in half-doped manganites

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Abstract. We discuss our very interesting experimental observation that the low-temperature two-phase coexistence in half-doped manganites is multi-valued (at any field) in that we can tune the coexisting antiferromagnetic-insulating (AF-I) and the ferromagnetic-metallic (FM-M) phase fractions by following different paths in (H, T) space. We have shown experimentally that the phase fraction, in this two-phase coexistence, can take continuous infinity of values. All but one of these are metastable, and two-phase coexistence is not an equilibrium state.

1. Introduction

First-order phase transitions (FOPT) in vortex matter in superconductors have been studied extensively, and can be caused by varying either temperature T or magnetic field H [1]. Phase transitions observed in vortex matter [1] are broadened by both intrinsic disorder and pinning giving rise to a variation of the local field across the sample. This broadening of a FOPT was established in a very convincing manner by the mesoscopic magnetic images of vortex-lattice melting by Soibel *et al* [2]. These images established that both melting and crystallization occur over a finite range of magnetic field, occurring in different regions at different values of H, and show hysteresis. 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. It was realized that broad first-order phase transitions would not show jump discontinuities in physical properties, and Clausius–Clapeyron relation cannot be invoked for identifying the order of the transition [1]. It was recognized that supercooling and superheating across a first-order phase transition (FOPT) yield metastable states, and the resulting hysteresis can be used to identify whether the transition is first order.

Such broad first-order phase transitions give rise to coexisting phases 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. 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, and thus the transition being broad is intrinsic to the functional materials. The broadening of the FOPT was established in a very convincing manner by the mesoscopic magnetic images of the ferromagnetic (FM) to antiferromagnetic (AFM) transition in doped-CeFe$_2$ by Roy *et al* [4]. These images again established that both forward and back transitions occur over a finite range of magnetic field (or of temperature), occurring in different regions at different values of H (or of T), and show hysteresis. The broadening of the transition was invoked, by Manekar *et al* [5], to broaden the supercooling and superheating spinodal lines in (H, T) space, into spinodal bands. But kinetic hysteresis is also seen when molecules in amorphous solids exhibit arrested kinetics, and equilibrium in this 'glassy' or kinetically arrested state cannot be reached over experimental time-scales. Manekar *et al* [5] had investigated an interplay between kinetic arrest and supercooling in the context of phase coexistence across FOPTs. They used this interplay to explain earlier published data on some half-doped manganites, and tested their ideas through detailed measurements on doped-CeFe$_2$. Our recent work on half-doped manganites builds on those ideas to explain our data showing continuously tunable phase coexistence of FM and AFM states.

Macroscopic hysteresis across transitions is often used to assert their first-order nature, and this has also been done in the case of half-doped manganites [6]. Kuwahara *et al* [7] and Tokura *et al* [8] used hysteresis in isothermal measurements of magnetization (M) vs. H, and of resistance (R) vs. H, to establish that the FM-to-AFM transition is an FOPT. As expected for such multi-component systems with their intrinsic disorder, even these studies on single crystal samples of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ showed a broad transition. The mid-points of the observed hysteretic transitions were plotted, and while the AFM-to-FM transition in increasing H was monotonic as a function of T, the FM-to-AFM transition in decreasing H was non-monotonic. We can easily argue that if the decreasing H transition from FM-to-AFM is taken as occurring at the supercooling spinodal, then this non-monotonicity is counter-intuitive. This is because the free-energy barrier separating the minima corresponding to the AFM and the FM states vanishes as T is lowered, in constant H, to reach the supercooling spinodal (see figure 1). This barrier cannot suddenly reappear as T is monotonically lowered, which is what is required if the decreasing H transition from FM-to-AFM is to be taken as occurring at the supercooling spinodal.

2. Kinetic arrest

Manekar *et al* [5] had found in their isothermal M–H and R–H measurements on doped-CeFe$_2$ that the virgin curve anomalously falls outside the envelope hysteresis curve at low temperature. They attributed this to a glass-like arrest of the kinetics of the FM-AFM transition as T is lowered. This was a new concept, beyond those discussed in vortex-matter transitions, where a transition from one crystalline phase to another was 'frozen in time'. Manekar *et al* [5] made detailed tests of this idea

on measurements on doped-$CeFe_2$, and noted that the results of Kuwahara *et al* [7] and Tokura *et al* [8] could be explained. Measurements to make detailed tests have only been done recently on polycrystalline samples of $Nd_{0.5}Sr_{0.5}MnO_3$ [9]. During these recent studies, the disorder-induced broadening of the 'kinetic arrest' line into a band was explored. Significantly, a detailed study on doped-$CeFe_2$ and a single-crystal manganite sample established that if a region has deeper supercooling then that region has its kinetics arrested at higher temperature [10]. We shall not go further into this remarkable result, which is expected to have implications for the broad field of glass formation.

This talk concentrates on the coexistence of AFM-insulating (AF-I) and FM-metallic (FM-M) phases. These two contrasting long-range magnetic orders are, as outlined above, accepted as connected through a FOPT. These dissimilar phases coexist over a range of control variables like H and T. This observation, by itself, is explainable as a consequence of a disorder-broadened FOPT [11]. However, inhomogeneous phase coexistence has been observed to persist to the lowest temperature in many materials like doped-$CeFe_2$, Gd_5Ge_4 and half-doped manganites. We subscribe to the explanation of ref. [5] that this is arising out of an interplay of a disorder-broadened supercooling band with a disorder-broadened kinetic-arrest band. In this explanation, coexisting phases result because glass-like arrest of dynamics triumphs over thermodynamics. Coexisting phases at lowest temperatures, where hysteresis is not seen on cycling temperature, are not equilibrium states. The observations in half-doped manganites have been variously interpreted as due to a complex equilibrium phase. To settle the question whether coexisting phases in half-doped manganites are or are not equilibrium states, we have studied a number of half-doped manganites by following novel paths in (H, T) space.

Our basic postulate is that below a certain temperature $T_K(H)$ the kinetics of the FM-AFM transformation is hindered and arrested just like in a quenched metallic glass. We would depict this as a (H_K, T_K) line in the two control-variable (H, T) space, which we broaden into a band with the same argument used to replace the other thermodynamic transition lines by a band (see figure 2).

At temperatures below the (H_K, T_K) band, the freezing-in occurs throughout the sample; within the band it occurs in some regions of the sample. If we cool the sample in a field below H_1, then the supercooling spinodal is crossed before the (H_K, T_K) band is encountered, and the high-T FM-M phase is fully converted to the low-T AF-I phase. If the sample is cooled in a field above H_2, then the (H_K, T_K) band lies above the (H^*, T^*) band, and the sample is kinetically arrested in the FM-M phase, and the low-T state again shows no phase coexistence. If the sample is cooled in a field lying between H_1 and H_2, then some fraction of the FM-M phase will transform to the AF-I phase as T is lowered, whereas the remaining will be arrested in the FM-M phase. The field in which the sample is cooled thus dictates the ratio of equilibrium AFM-I and arrested FM-M fractions at low-T.

Since the transformation process is fully arrested at T below the (H_K, T_K) band, we can reach any desired value of H at low-T without changing the fraction of the two coexisting phases. Thus, to have any desired (say x) fraction of AF-I phase at low-T, we cool the sample to the lowest T in the corresponding H, and then vary H isothermally. We can continuously tune the phase fraction x from 0 to 1 by changing the cooling field from H_1 to H_2.
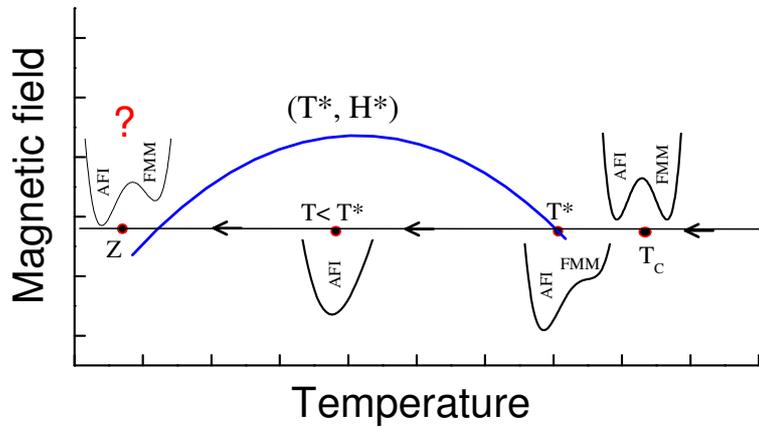
Figure 1. This schematic shows that the minimum corresponding to the FM-M phase becomes shallow as T is lowered below T_C in constant field, but would have to again become deep if the supercooling spinodal is non-monotonic. This is counter-intuitive.
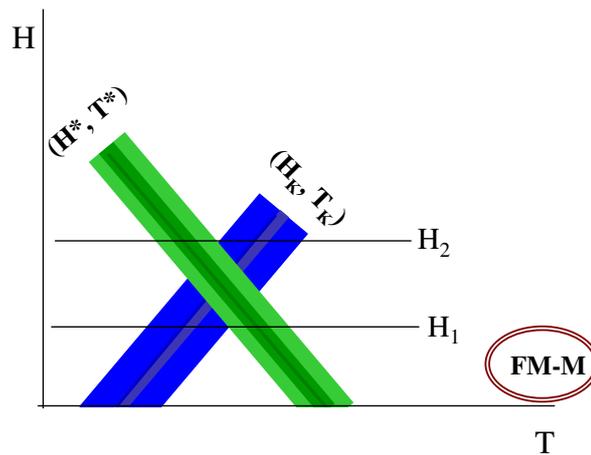

Figure 2. Schematic H–T diagram for the case having AF-I ground state. This depicts that the FOPT from FM-M state by crossing the supercooling (H^*, T^*) band is hindered by the presence of kinetic arrest (H_K, T_K) band. Cooling in fields between H_2 and H_1 gives rise to different amounts of coexisting phase fractions (see ref. [12]).

3. Observation of tunable two-phase coexistence

The data are shown in figure 3 for a half-doped manganite where both magnetization and electrical conductivity are measured for same values of measuring temperature and measuring field. Different cooling fields are used, and the field is changed isothermally to the measuring field of 40 kOe at 5 K. The signatures of H_1 and
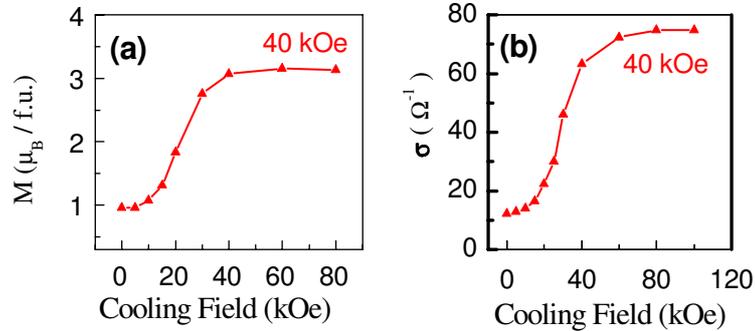
Figure 3. Tunable phase fraction for $Pr_{0.5}Sr_{0.5}MnO_3$. (**a**) The sample is cooled each time from 320 K to 5 K in different cooling fields, and then the magnetization is measured after the field is isothermally changed to 40 kOe (measuring field). (**b**) $Pr_{0.5}Sr_{0.5}MnO_3$ sample is cooled similar to (a) and the electrical conductivity is measured in 40 kOe at 5 K (see ref. [12]).
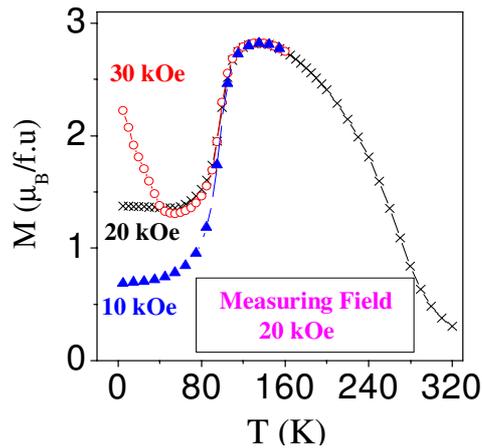

Figure 4. After cooling $Pr_{0.5}Sr_{0.5}MnO_3$ from 320 K to 5 K in 10, 20 and 30 kOe the field is isothermally changed to 20 kOe at 5 K and the magnetization is measured while warming. The magnetization for higher cooling field of 30 kOe shows two sharp changes but the magnetization for the lower cooling field of 10 kOe shows one sharp change only (see ref. [12]).

H_2 are clearly seen in both magnetization and electrical conductivity data. We must mention here that the arguments of the previous section go through if the high-T phase is AF-I and the low-T phase is FM-M. A detailed discussion on this, along with data corresponding to that shown in figure 3, can be found in our recent paper [12].

We have established in these studies [12,13] that the low-T fraction of the two coexisting phases can be continuously controlled, over the entire range from 0 to
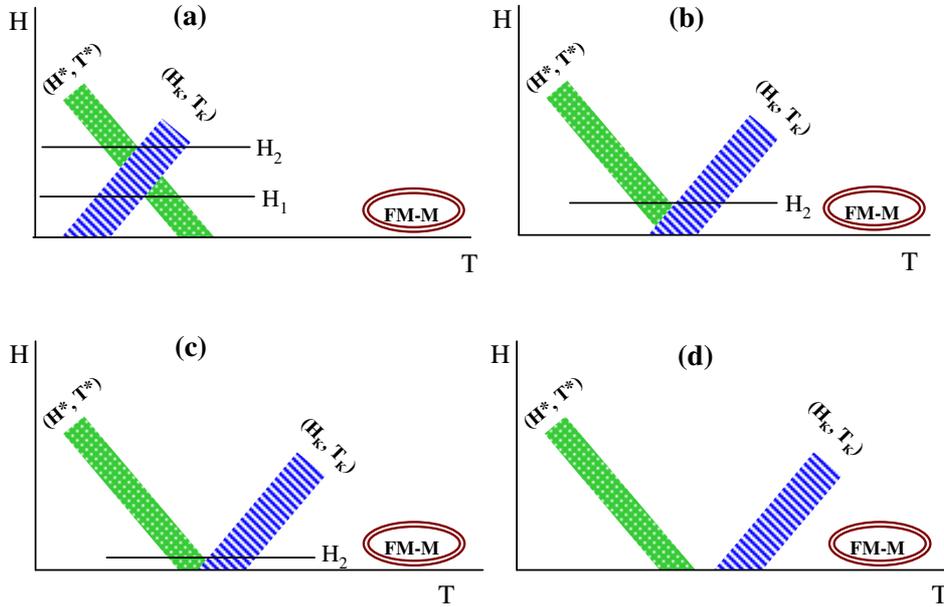
Figure 5. This schematic indicates how the relative positions of the (H^*, T^*) band and the (H_K, T_K) band affect experimental observations. We note that coexisting phases are frozen if field-cooling is done with $H_1 < H < H_2$ (see ref. [12]). This implies that cooling in zero-field will yield coexisting phases in case (c).

1, for various measuring fields. This ability to tune the coexisting phase fractions by following novel paths in (H, T) space is the second significant result of this talk, and is likely to have important ramifications for theories of half-doped manganites. We should note here that similar tunable coexisting phase fractions occur in doped-$CeFe_2$, Gd_5Ge_4 and probably in other materials.

As a failure-test on this idea that two-phase coexistence is due to kinetic arrest, we create different phase fractions at, say, 20 kOe and 5 K. If the cooling field is more than 20 kOe, then our analysis [10] predicts that some of the arrested FM-M fraction will de-arrest on warming; no such de-arrest will be seen if the cooling field is less than the measuring field of 20 kOe. As reported in ref. [12], this was observed in our measurements. If the high-T phase is AF-I and the low-T phase is FM-M, then de-arrest will be observed if the cooling field is less than the measuring field. It will not be observed if the cooling field is more than the measuring field. Detailed data in confirmation of this failure-test [12,13] are shown in figure 4.

4. Discussion

We have discussed here our very interesting experimental observation that two-phase coexistence in half-doped manganites is multi-valued (at any field) in that

we can tune the phase fractions by following different paths in (H, T) space. Since we have a continuous infinity of phase fractions in this two-phase coexistence, all but one of these are metastable. We have argued [12,13] that two-phase coexistence is not an equilibrium state.

We should point out that H_1 can have the value zero, or be negative. We depict this in figure 5. We are shifting the relative positions of the (H_K, T_K) band and the (H^*, T^*) band as we move from figures 5a–5d. H_1 is positive in (a), becomes zero in (b), is negative but small in (c) in that there is some overlap of the two bands at $H = 0$, and is negative and large in (d) in that the (H_K, T_K) band lies entirely above the (H^*, T^*) band. Systems corresponding to case (c) would show two-phase coexistence in zero field and in all fields below H_2 (which may or may not be accessible experimentally). If H_2 is beyond experimental access, then all field-cooled measurements in case (c) would show two-phase coexistence, and pursuit of our 'novel paths in (H, T) space' would be necessary to unravel the equilibrium phase.

Acknowledgements

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