T.3: Interesting behaviour of magnetic materials and superconductors in a magnetic field

M. K. Chattopadhyay (maulindu@rrcat.gov.in) and M. A. Manekar

People have been fascinated by magnetism from the ancient times. From about 800 BC, they knew about the attractive power of lodestone. The subject of magnetism has evolved a lot since then. Many varieties of magnetic order are now known. Paramagnetism, ferromagnetism, antiferromagnetism, diamagnetism, ferrimagnetism, mictomagnetism, metamagnetism, asperomagnetism, spin glass, and super-paramagnetism, are only some of them [1]. Superconductivity, on the other hand, is a relatively new subject. The first superconductor was discovered in 1911. It took 45 more years to get the first basic theory of superconductivity proposed by Bardeen, Cooper, and Schrieffer (BCS). However, quite a few superconductors that do not follow the predictions of the BCS theory are already in practical use. Superconducting magnets, made out of Nb-Ti alloys or Nb_3Sn, are regularly used in laboratory equipments, MRI machines, and in the high energy particle accelerators. Kilometer long high temperature superconductor cables have now been developed by SuperPower Inc., USA. They are connected to a grid that is powering homes and businesses places in Albany, New York. Still, the behaviour of magnetic and superconducting materials in the presence of magnetic field is not yet fully understood. In the past, magnetism and superconductivity were considered to be two different subjects. Conventional wisdom would suggest that magnetic order can cause the destruction of superconductivity. However, the recent discovery of magnetic exchange interaction mediated superconductivity has indicated a strong connection between magnetism and superconductivity. Experimental evidences also indicate that the technological application of magnetism and superconductivity would depend significantly on the understanding of the influence of magnetic field on the phase transitions in these materials. The Magnetic and Superconducting Materials Section (MSMS) of RRCAT is deeply involved in experimental research in these fields, and this theme article gives a flavour of this scientific endeavour.

First order magnetic phase transitions and the discovery of a magnetic glass

During a phase-transition, the physical properties of a material undergo an abrupt change, and this naturally draws the interest of the observer. In the case of a first order phase transition, certain physical properties intrinsic to the material, like volume (V), entropy (S), magnetization (M) are expected to change discontinuously. However, if there are impurities or defects in the material, then the physical properties change gradually and the first order phase transition is said to be "broadened". For example, the entire volume of a very pure sample of water, upon cooling, solidifies abruptly at a single temperature. This temperature could be well below 0° C, the thermodynamic transition temperature for water-ice transformation. However, if there are microscopic particles of dirt dispersed in water, then upon cooling, crystals of ice would form around the dirt particles. Slowly these crystals would grow along with the

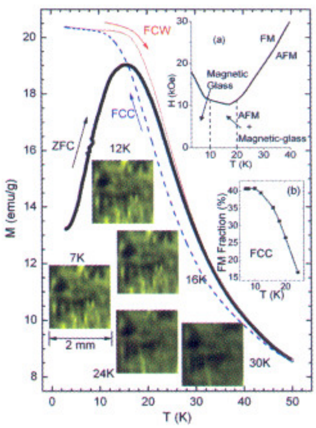

Fig. T.3.1. Temperature dependence of magnetization of Gd_5Ge_4 (H = 10 kOE), along with scanning Hall probe microscopy images recorded at different temperatures in the FCC path. The inset (a) shows the H vs. T phase diagram of Gd_5Ge_4. The inset (b) depicts the evolution of the ferromagnetic fraction in the sample with the lowering of temperature.

formation of newer crystals. In this case, the transition would proceed over a finite width of temperature which is more commonly observed in our daily experience. Such a transition is called as a "disorder broadened transition", during which a "phase co-existence" of water and ice is observed. The phenomenon of cooling water below the thermodynamic transition temperature (0°C) without solidification is known as supercooling. Ice also can be heated slightly above 0°C without melting, which is known as superheating. Both, the supercooled and superheated states are metastable in nature. Phase coexistence and metastability are characteristic features of a disorder influenced first order phase transition, and are expected across the first order magnetic phase transitions as well. Experiments performed in MSMS have shown that such signatures are observed across the first order antiferromagnetic (AFM)-ferromagnetic (FM) transitions in doped $CeFe_2$ aloys [2], Gd_5Ge_4 [3, 4], and FeRh alloys [5]. It was also observed that the nucleation-and-growth dynamics across a first order magnetic phase transition is very similar to that observed during the crystallization of a liquid [6]. This highlights the generality of the transition process.

It has been observed experimentally that if a liquid is cooled very fast, then instead of becoming a crystalline solid, it might form a structure glass (like the glass in the window panes). Upon continuous cooling at a fast rate, the viscosity of the supercooled liquids increases very rapidly. This slows down the molecular motion to such an extent that the molecules cannot rearrange themselves within experimental time scales to form a crystal. The cooling rate required to observe such a glass formation depends on the nature of the liquid. Research in MSMS has shown through magnetization and magnetic relaxation studies that the same dynamics could be observed in the formation of a glass-like magnetic state in $Ce(Fe_{0.96}Ru_{0.04})_2$ [7]. This "magnetic glass" state, as it has been named by MSMS, arises out of a *kinetically arrested* first order FM to AFM phase transition. The term "kinetic arrest" here stands for the viscous retardation of the growth of the low temperature AFM phase out of the supercooled FM phase [7].

The visual evidence of the formation of such a "magnetic glass" was recently obtained in another system, namely Gd_5Ge_4, through scanning Hall probe microscopy experiments, and is shown in Fig.T.3.1. Gd_5Ge_4 orders antiferromagnetically at 128 K and remains in the AFM state down to at least 1.8 K in zero and low applied magnetic fields. However, in the low temperature regime, the system undergoes a field-induced first order AFM to FM transition. To visualize the formation of magnetic glass in Gd_5Ge_4, the sample was subjected to controlled heating and cooling schedules in presence of magnetic field. To achieve this, the experiments were performed using three experimental protocols: The zero-field-cooled (ZFC) warming, field-cooled-cooling (FCC) and field-cooled-warming (FCW). In the ZFC mode, the sample was first cooled to the target temperature (7 K) in zero field, and then a 10 kOe magnetic field was switched on before performing a scanning experiment. In the FCC mode, the field was applied above 80 K (which is above the AFM-FM transition temperature), and the scanning experiments were performed at different temperatures during cooling in the same magnetic field. In the FCW mode, the FCC state at 7 K was prepared first. The scanning measurements were then performed while warming the sample in the presence of the same magnetic field. The M vs T characteristics of Gd_5Ge_4 shown in Fig.T.3.1 is obtained in 10 kOe magnetic field. From the

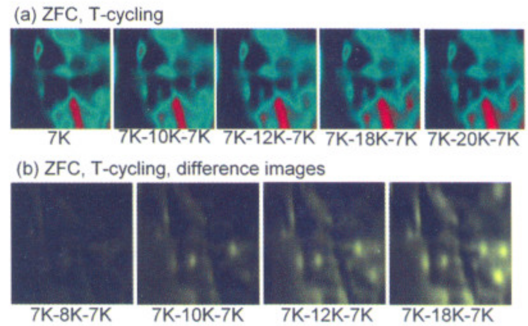

Fig. T.3.2. Scanning Hall probe microscopy images of Gd_5Ge_4 at different temperatures showing the re-crystallization of ferromagnetic clusters as a result of thermal cycling. (a) Black: Antiferromagnetic. Red: Ferromagnetic. Green: Regions producing signals intermediate to black and red. (b) Black: Arrested magnetic glass configuration. Yellow: Released equilibrium ferromagnetic phase.

history dependent magnetization and magnetic relaxation measurements, it was shown that the low-temperature AFM state in Gd_5Ge_4 is not an equilibrium state [8]. According to this understanding [8], the low temperature equilibrium state of Gd_5Ge_4 is FM. The kinetic arrest of the AFM to FM phase transition in zero and low fields, leads to a configuration consisting of a small fraction of equilibrium FM phase in an untransformed non-equilibrium AFM matrix [see the inset (a) of Fig.T.3.1]. The scanning Hall probe microscopy images taken at different temperatures in the FCC path (see Fig.T.3.1) visually show the occurrence of kinetically arrested glass-like state (magnetic glass). Each microscopy image comprises of 256 × 256 pixels, and covers a 2 mm × 2 mm area of sample surface. The images are calibrated to show the AFM regions in the sample in black colour. The yellow regions in the images correspond to higher Hall voltages, and hence to higher local magnetic induction associated with the FM state. The brightness of the spots increases with increasing local magnetic induction. Comparing the images, one can see that relative to the color contrast at 30 K, as the sample is field-cooled, the features become brighter (high magnetization) and new bright spots appear. However, there is very little difference between the images taken at 12 K and 7 K. In order to track the formation of FM regions with the lowering of temperature, the FM fraction in the sample was calculated from the integrated moments of the images. Inset (b) of Fig.T.3.1 shows the growth of the FM fraction. The evolution of the FM phase is completely arrested below 10 K, resulting in a heterogeneous 'magnetic glass'.

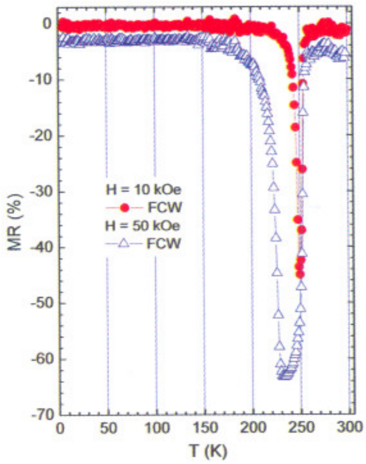

Fig. T.3.3 Temperature dependence of magneto-resistance (MR) of $Ni_{50}Mn_{34}In_{16}$ alloy in different constant magnetic fields.

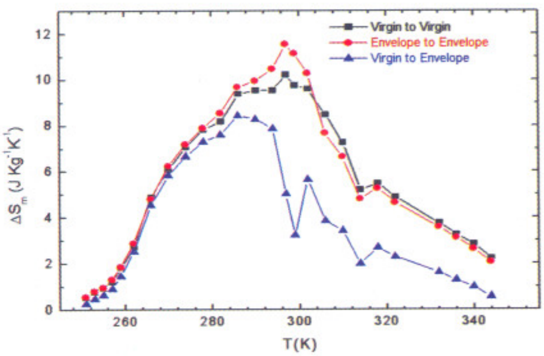

Fig. T.3.4 Temperature dependence of MCE (change in entropy) for various field histories. A reproducible MCE can be achieved by choosing the envelope magnetization curve for magnetizing the material.

A structure glass re-crystallizes if it is exposed to energy fluctuations. It was shown in MSMS through magnetization and magnetic relaxation measurements that the re-crystallization or de-vitrification of magnetic glass is also possible exactly in the same way as structure glass [9]. The visual evidence of such re-crystallization of magnetic glass was obtained through scanning Hall probe microscopy and these results are presented in Fig.T.3.2. In the ZFC state reached by cooling to 7 K, energy fluctuations were introduced by cycling temperature in the presence of 10 kOe magnetic field. This was done by raising the temperature to a point T_1 (> 7 K) and then cooling down back to 7 K. Scanning experiments were performed at different values of T_1, viz. 8 K, 10 K, 12 K, 18 K, 20 K, and the resulting images are shown in Fig.T.3.2(a). In this figure, black colour corresponds to the AFM phase defined as before, red to the FM phase, and green corresponds to signals intermediate to black and red. The emergence of new bright spots, and the growth of bright regions are clearly observed during cycling to 10, 12, and 18 K. The effect is more clearly shown in Fig.T.3.2(b). Here, the ZFC image at T = 7 K taken in 10 kOe magnetic field is subtracted from the images obtained at 7 K after temperature cycling (at 7 K, ZFC, in a 10 kOe magnetic field, the bulk of the sample is AFM). The resulting images are indeed very interesting. Bright yellow spots in the subtracted images represent microscopic regions of high magnetic moment. Thus, it was observed that FM clusters are released out of the arrested glass-like AFM matrix when energy fluctuations are introduced in the system. The FM phase is the equilibrium state at 7 K. The energy fluctuations naturally shift the system towards equilibrium. The nucleation of FM phase is akin to re-crystallization of glass. An increasing number of FM regions are released with the introduction of larger energy fluctuations. Apart from $CeFe_2$ and Gd_5Ge_4, the researchers in MSMS have also observed the formation of magnetic glass in Ni-Mn based Heusler alloys [10].

The physics of glass has been drawing the interest of researchers for many decades. Accordingly, experimentalists have been studying the liquid-solid transitions regularly, using temperature (T) and pressure (P) as the control variables. Pressure is quite difficult to control during an experiment. The studies done in MSMS have shown that an easier way of understanding the glass transitions is to study the magnetic glass where the magnetic field (H) becomes an additional control variable which plays a role akin to pressure. Accurate control of magnetic field is much easier to achieve than that of pressure.

Functional properties related to magnetic phase transitions

In recent times, three kinds of functional properties have been in the focus of global research. These are, (1) giant magneto-resistance, (2) ferromagnetic shape memory effect, and (3) giant magneto-caloric effect. The research in MSMS has contributed immensely in developing the understanding that there is an underlying physics that interconnects these functional properties. A disorder broadened first order phase transition and the associated phase co-existence can explain these functional properties, and it also provides a basis for tuning them for practical use [11].

Magnetoresistance: It is the change of electrical resistance of a material because of applied magnetic field, and its widespread use is in the form of "read heads" for the computer hard disk drives. Materials showing large magnetoresistance near room temperature are extremely important technologically. It was recently found in MSMS [12] that the first order field induced magnetic phase transition in the off-stoichiometric Heusler alloy $Ni_{50}Mn_{34}In_{16}$ is associated with a very large magnetoresistance (MR = $[\rho(H) - \rho(0)] / \rho(0)]$, where ρ stands for electrical resistivity). For H = 10 kOe, an MR of about 46% is obtained at 250 K, and for 50 kOe magnetic field, 64% MR is observed at 230 K (see Fig.T.3.3). On increasing the applied magnetic field to 100 kOe, MR increases to 75% at 180 K .

Ferromagnetic shape memory effect: Research on the shape memory alloys started from early 1930's. These materials are such that if their previously defined shape is deformed due to mechanical forces during usage, their shape can be recovered by heating them above a characteristic temperature. The effect is caused by a "thermo-elastic martensitic transition", which is a reversible phase transition between two different crystal structures (austenite and martensite). The shape memory alloys have a wide range of applications in the aeronautics, defense-artillery, robotics, and in the form of artificial limbs and implants in the bio-medicals. The recovery of shape through heating is a slow process, and often the material needs to be removed from the application-site. In the ferromagnetic shape memory alloys the recovery of shape is achieved with the help of magnetic field. Magnetic field is easier to control and gives faster response. The signature of field induced shape memory effect has been observed in MSMS in the off-stoichiometric Heusler alloy $Ni_{50}Mn_{34}In_{16}$ in the electrical transport measurements [12]. This has been further supported by magnetostriction results which show history effects similar to those discussed earlier in the context of first order transitions.

Magneto-caloric effect: The temperature change in a material because of a change in the applied magnetic field is called magneto-caloric effect (MCE). The effect was discovered in the early 1920's, and cooling cycles based on this effect (then called adiabatic de-magnetization) is being used in the laboratories for several decades to reach milli-kelvin temperatures. Applied magnetic field aligns the spins in a magnetic material and reduces the spin entropy. The spin-system in the material dumps this extra energy into the lattice. This heat is removed from the system by connecting it to a heat-sink. Now if the system is thermally isolated from the surroundings and the magnetic field is switched off, its spin entropy increases back to its zero field value. The spin system needs extra energy for this, which it takes from the lattice. As a result, the system is cooled down. The magnetic cooling cycles are much more energy efficient (70%) as compared to the conventional refrigeration cycles (less than 30% efficiency). Moreover, these cycles use magnetic materials as the working substance and thus avoid the conventional environment-degrading Freon gases altogether. The research on field induced first order magnetic transitions has added a new dimension to the subject of magnetic cooling. A structural transition is often an essential part of a first order magnetic transition. In many cases, this involves a large change of lattice entropy along with the change of magnetic entropy across the field-induced first order phase transition, resulting in a huge MCE. One such material which undergoes a first order magnetic transition coupled to a structural transition is the Fe-Rh alloy. This first order transition occurs close to room temperature (300 K) and was thought to be the cause behind a wide range of its very interesting functional properties like giant magneto-caloric effect, giant elasto-caloric effect (change in temperature by the application of stress), giant volume magnetostriction (change in volume by application of magnetic field) and giant magnetoresistance. However, the initial interest in this alloy system died away quickly because it was seen that the functional properties, especially the magneto-caloric effect, vanish after the first field cycle. Through the systematic study of field dependent magnetization measurements at various temperatures, MSMS has shown that the magnetization of Fe-Rh depends on the thermal and field history experienced by the sample [5]. The virgin magnetization curve (i.e. the M-H curve obtained for a case where the sample has not been subjected to any previous field history) at a particular temperature was shown to lie outside the envelope curve (the M-H curve arising during subsequent field cycles). This fact led to a general belief that since the magnetization does not show a reproducible behaviour, the material would not be suitable for technological applications. Using the understanding on thermo-magnetic history effects, it was shown in MSMS that such history effects arise due to phase coexistence and are general to any first order transition. Once the cause behind these history effects was understood, a solution of this long standing problem of vanishing MCE could be found. A new combination of isothermal and adiabatic field variation cycles was proposed which leads to a reproducible MCE close to room temperature. A large effective refrigerant capacity (ability to carry away heat from the hot end to cold end of the refrigerator) of about 324 J/kg could be achieved by properly choosing the starting point of the experimental cycle in the H-T phase space [13]. Apart from FeRh, the $Ni_{50}Mn_{34}In_{16}$ alloy sample described earlier also exhibits a very large MCE [14]. An effective refrigerant capacity of 220 J/kg was recorded in this material between 214 and 242 K.

The C15 Laves phase doped $CeFe_2$ alloys have been used in MSMS for several years as the test bed materials to study the first order magnetic transition [2] and the formation of magnetic glass [7]. The experiments revealed [15] that the doped $CeFe_2$ alloys are potential giant magneto-resistive materials. Further investigations showed that the doped $CeFe_2$ alloys also exhibit a large MCE, and the temperature, magnitude and sign of this MCE can be tuned by controlling the first order magnetic phase transition with the help of doping [16]. Again, different compositions of Ni-Mn based off-stoichiometric Heusler alloys have been studied in MSMS. It was found that not all the members of a particular family of Heusler alloys exhibit signatures of ferromagnetic shape memory effect. On the other hand, it was found that the composition that exhibits the signatures of ferromagnetic shape memory effect also exhibits giant MR and large MCE. The onset and completion of the first order magnetic phase transformation and the associated MR in such an alloy (viz. $Ni_{50}Mn_{34}In_{16}$) could be tuned with the help of magnetic field [12]. The MR and MCE in $Ni_{50}Mn_{34}In_{16}$ were shown to depend on the thermal history of the sample [12, 17]. Gd_5Ge_4 is a parent compound of the $Gd_5(Ge\text{-}Si)_4$ family of alloys known for giant MCE. The signatures of phase co-existence and metastability across the first order magnetic phase transition and the formation of magnetic glass have been observed in this compound [4]. The cubic Fe-Rh alloys exhibit phase coexistence and metastability across the first order AFM to FM phase transition and the giant MCE exhibited across this phase transition depends on the field-temperature history of the material [5, 13]. All these findings in different classes of materials provide clear evidence of the role of first order magnetic phase transitions in the three different functional properties described above, viz., giant MR, giant MCE, and ferromagnetic shape memory effect. Coexistence of different magnetic phases across a first order magnetic transition is caused by the influence of "quenched" (or static) disorder- including local lattice distortion and a random mixture of doped impurity ions. The disorder produces a distribution of the onset temperatures across the bulk of the samples and leads to the co-existence of different magnetic phases across a first order magnetic transition. An applied magnetic field affects the spin configurations in the coexisting magnetic phases in different ways and leads to further spin disorder giving rise to a large change of the configurational entropy. This results in large MCE and MR across the first order magnetic phase transitions. The field dependence of the nucleation and growth dynamics of phases and the kinetics of partially arrested transitions play crucial role in the ferromagnetic shape memory effect observed in various alloys. Thus, studying of the first order magnetic transitions is the key for understanding the above functionalities and for tuning them towards technologically important H-T regimes.

Superconductors in magnetic fields

Most of the applications of a superconductor are related to its bulk-current carrying capability with zero resistance. Such bulk dissipation-less currents are possible only in type-II superconductors, where the magnetic field can penetrate the material in the superconducting state in form of vortices. These vortices need to be pinned if a dissipation-less current is desired. Disorder in the material in form of point defects, dislocations, and grain boundaries, provides a mechanism to pin these vortices. The relation between one of the fundamental length scales of the superconductor, the coherence length ξ, and the length scale of the pinning centres, dictates the maximum current that can flow through the material in the superconducting state. Interesting situation can arise if the average grain size of the superconductor is also of the order of ξ, the length scale over which the superconducting order develops (typically a few nano-metres). A nano-crystalline superconductor would thus provide an interesting platform to study the response of a superconductor to magnetic fields and also the behaviour of the critical current at small length scales. The detailed magnetization of a nanocrystalline Nb_3Al compound embedded in a matrix of Nb-Al solid solution has been studied recently in MSMS [18]. The grain size of Nb_3Al was found to be about 35 nm, as inferred from x-ray diffraction measurements. Transmission electron microscopy later on confirmed the nano-crystalline nature of the Nb_3Al phase. By fitting the field dependent magnetization curves with the well known models used for the estimation of critical current density, it was shown that a flow of bulk current is possible in the nanocrystalline Nb_3Al sample. The typical length scale of field variation inside the sample was found to be about a fraction of milli metres, which is quite anamolous when compared to the typical size of the superconducting grains, which is of the order of a few nanometres. This shows that the superconducting properties of such small grains are well correlated much beyond their physical sizes through the intermediate matrix, thus making the study of pinning properties of a material even more important. The role of flux pinning in the superconductors was also found to be quite significant in flux-line penetration across the lower critical field H_{C1} in various bulk samples of Nb to be used for fabrication of superconducting RF cavities. It is to be noted here that the transition from Meissner state to type-II or mixed state, is a first order phase transition, and the quenched disorder present in the samples is expected to play an influential role on this transition. It was shown that the chemical processes carried out for cleaning the surface of Nb can alter the pinning properties and the field for first penetration quite significantly and can result in the large Q-drop of the cavities at high fields [19].

The above studies on the response of superconductors in external magnetic fields highlight the fact that the basic understanding of various physical processes is absolutely essential for building successful technology using such materials.

Looking at the future

It is now understood that the tuning of the phase coexistence regime (and thus the influence of disorder) across the first order magnetic phase transitions in different systems would lead to important functionalities like giant MCE and MR, and magnetic shape memory effect. Disorder also plays a major role in dictating the response of superconductors to magnetic fields. One way of tuning these properties is to apply physical pressure on the materials or to apply the pressure chemically. Chemical pressure is applied by choosing constituent atoms of different atomic sizes, i.e., by doping the materials or by making newer alloy compositions. Magnetization and magneto-transport measurements under physical pressure would provide a guideline for choosing the appropriate dopants needed for achieving a desired functionality. The pressure dependent studies would also provide a better scope of exploring two other interesting areas of research: the onset of ferromagnetism in a non-magnetic system, and the onset of superconductivity in a magnetic system. The experience on the studies of phase transitions in MSMS should provide a path for future research and for building new technologies related to these areas.

References

1. C. M. Hurd, Contemp. Phys. **23**, 469 (1982).
2. S. B. Roy, G. K. Perkins, M. K. Chattopadhyay, A. K. Nigam, K. J. Singh, P. Chaddah, A. D. Caplin, and L. F. Cohen, Phys. Rev. Lett. **92**, 147203 (2004), and references therein.
3. M. K. Chattopadhyay, M. A. Manekar, A. O. Pecharsky, V. K. Pecharsky, K. A. Gschneidner Jr., J. Moore, G. K. Perkins, Y. V. Bugoslavsky, S. B. Roy, P. Chaddah, and L. F. Cohen, Phys. Rev. B **70**, 214421 (2004).
4. M. K. Chattopadhyay, S. B. Roy, K. Morrison, J. D. Moore, G. K. Perkins, L. F. Cohen, K. A. Gschneidner Jr., and V. K. Pecharsky, Europhys. Lett. **83**, 57006 (2008), and references therein.
5. M. Manekar and S. B. Roy, Eur. Phys. J. B **64**, 19 (2008).
6. M. Manekar and S. B. Roy, J. Phys.: Condens. Mater **20**, 325208 (2008).
7. M. K. Chattopadhyay, S. B. Roy and P. Chaddah Phys. Rev. B **72**, 180401(R) (2005), and references therein.
8. S. B. Roy, M. K. Chattopadhyay, P. Chaddah, J. D. Moore, G. K. Perkins, L. F. Cohen, K. A. Gschneidner Jr., and, V. K. Pecharsky, Phys. Rev. B **74**, 012403 (2006).
9. S. B. Roy, M. K. Chattopadhyay, A. Banerjee, P. Chaddah, J. D. Moore, G. K. Perkins, L. F. Cohen, K. A. Gschneidner Jr., and V. K. Pecharsky, Phys. Rev. B **75**, 184410 (2007).
10. V. K. Sharma et. al, Phys. Rev. B. 76, 140401(R) (2007).
11. S. B. Roy, M. K. Chattopadhyay, M. A. Manekar, K. J. S. Sokhey, and P. Chaddah, Bull. Mater. Sci. **29**, 623 (2006)
12. V. K. Sharma, M. K. Chattopadhyay, K. H. B. Shaeb, A. Chouhan, S. B. Roy, Appl. Phys. Lett. **89**, 222509 (2006).
13. M. Manekar and S. B. Roy, J. Phys. D: Appl. Phys. **41**, 192004 (2008).
14. V. K. Sharma, M. K. Chattopadhyay, and S. B. Roy, J. Phys. D: Appl. Phys. **40**, 1869 (2007).
15. M. A. Manekar, S. Chaudhary, M. K. Chattopadhyay, K. J. Singh, S. B. Roy, and P. Chaddah, Phys. Rev. B **64**, 104416 (2001). See also K. J. Singh, S. Chaudhary, M. K. Chattopadhyay, M. A. Manekar, S. B. Roy, and P. Chaddah, Phys. Rev. B **65**, 094419 (2002).
16. M. K. Chattopadhyay, M. Manekar and S. B. Roy, J. Phys. D: Appl. Phys. **39**, 1006 (2006).
17. M. K. Chattopadhyay, V. K. Sharma and S. B. Roy, Appl. Phys. Lett. **92**, 022503 (2008).
18. P. Mondal, M. Manekar and S. B. Roy, Appl. Phys. Lett. **92**, 052507 (2008).
19. S. B. Roy, G. R. Myneni and V. C. Sahni, Supercond. Sci. Tech. **21**, 065002 (2008)