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Field-induced first-order magnetic phase transition in an intermetallic compound Nd_7Rh_3: Evidence for kinetic hindrance, phase coexistence, and percolative electrical conduction

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The compound Nd_7Rh_3, crystallizing in the Th_7Fe_3-type hexagonal structure, was previously known to exhibit two magnetic transitions, one at 32 K and the other at 10 K (in a zero magnetic field). Here we report the existence of a field-induced first-order antiferromagnetic-to-ferromagnetic transition at 1.8 K in this compound. On the basis of the measurements of isothermal magnetization and magnetoresistance, we provide evidence for the occurrence of kinetic hindrance, proposed in the recent literature, resulting in phase coexistence (supercooled ferromagnetic+antiferromagnetic) and percolative electrical conduction in this stoichiometric intermetallic compound. A point of emphasis, as inferred from ac susceptibility data, is that such a coexisting phase is different from spin glasses thereby clarifying a question raised in the field of phase separation.

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The phenomenon of electronic phase separation turned out to be one of the most fascinating aspects in the field of giant magnetoresistive manganites,[1,2] particularly across the first-order metal-semiconductor transition induced either by temperature (T) or magnetic field (H), resulting in percolative electrical conduction through ferromagnetic metallic clusters dispersed in nonmetallic antiferromagnetic clusters. Dagotto *et al.*[1] raised a question whether such mixed phases and spin glasses are in the same class. These authors also pointed out that such mixed-phase tendencies and percolative conduction should be more general even among other classes of materials exhibiting disorder-influenced first-order phase transitions (FOPT). However, such reports are uncommon for magnetic-to-magnetic transitions among intermetallics, except perhaps exhaustive investigations made on the doped-$CeFe_2$ alloys.[3–6] In particular, such studies on stoichiometric compounds are scarce, except the one[7] on Gd_5Ge_4. It is therefore of interest to search for compounds exhibiting first-order magnetic transitions among stoichiometric compounds as well as to look for the above characteristic features and also to clarify the question raised by Dagotto *et al.*[1] In this paper we present the results of isothermal magnetization (M), electrical resistivity (ρ), and magnetoresistance (MR) measurements for a compound, Nd_7Rh_3 (Ref. 8), crystallizing in the Th_7Fe_3-type hexagonal structure (space group: $P6_3mc$), at low temperatures, as a continuation of our work in this family of compounds.[9] We show the existence of a magnetic-field induced first-order magnetic transition at 1.8 K with all the characteristic features, including the ones attributable to kinetic hindrance[3] and phase co-existence in this compound. The results firmly establish that such a mixed phase is different from spin glasses.

The compound Nd_7Rh_3 in the polycrystalline form was prepared by melting together stoichiometric amounts of high purity Nd (>99.9%) and Rh (99.99%). The molten ingot was annealed in an evacuated sealed quartz tube at 300 °C for 50 h. The sample thus obtained was found to be single phase by x-ray diffraction. Temperature dependent (1.8–300 K) dc susceptibility (χ) measurements in the presence of 100 Oe were performed for the zero-field cooled (ZFC) condition of the specimen employing a commercial (Quantum Design) superconducting quantum interference device (SQUID) as well as by a vibrating sample magnetometer (VSM, Oxford Instruments). The same magnetometers were employed to perform isothermal M measurements at desired temperatures and the rate of variation of H with the VSM is 4 kOe min unless otherwise stated. Further details of the measurements will be mentioned while presenting the results. ac $\chi(T)$ behavior (1.8–50 K) was tracked at several frequencies (ν=1, 10, 100, 1000 Hz) employing the above SQUID magnetometer (H_{ac}=1 Oe). The $\rho(H)$ behavior was obtained with the help of a Physical Property Measurements System (PPMS, Quantum Design).

The observed behavior of dc $\chi(T)$ and $\rho(T)$ is qualitatively the same as that reported in Ref. 8; we show the data below 50 K only in the insets of Fig. 1 to highlight the existence of at least two prominent magnetic transitions, one at 32 K and the other at 10 K. We have performed isothermal M measurements at selected temperatures (1.8, 5, 15 and 25 K) to address the nature of these two transitions (see Fig. 1). Though Fig. 1 shows $M(H)$ data for different field cycling, for this purpose we consider the "virgin curve" only, that is, the one obtained while increasing the field from 0 to 30 kOe after zero-field cooling from 50 K. The results reveal that there is a sudden increase in M at a certain value of H in the virgin curve as though there is a spin reorientation, not only above 10 K, but also below 10 K. This transition occurs (in the data shown in this figure) at about 5, 5, 3, and 10 kOe for 25, 15, 5 and 1.8 K, respectively. This finding reveals that the zero-field state is of an antiferromagnetic (AF) type in the entire T range of measurement below 32 K. However, the nature of the curves (also see further discussions below) is different in these two temperature ranges (below and above 10 K). That is, for T=15 and 25 K, the $M(H)$ curves are very weakly hysteretic, whereas for T =1.8 and 5 K there is a significant irreversibility behavior while reversing H. Thus there is a transformation from one type of magnetic structure (which we label as AF1 for the purpose of our present discussion) to another type of magnetic structure (which we label as AF2) as T is decreased

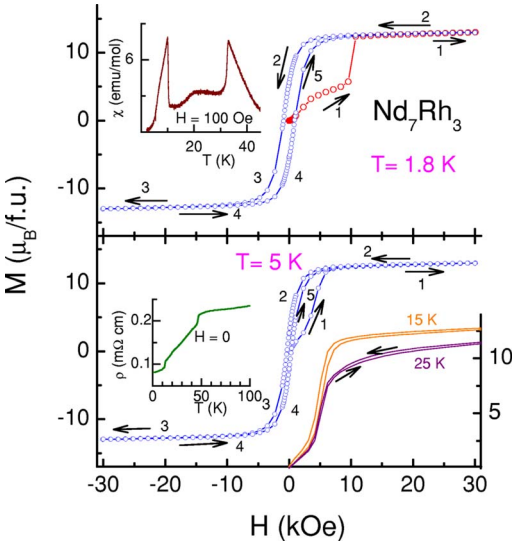

FIG. 1. (Color online) Isothermal magnetization behavior for Nd_7Rh_3 at various temperatures obtained with a SQUID magnetometer. The paths are: 1, 0 to 30 kOe (virgin curve); 2, 30 to 0 kOe; 3, 0 to −30 kOe; 4, −30 to 0 kOe; 5, 0 to 30 kOe. Before measurements at each temperature the specimen was zero-field cooled from 50 K. In the insets the temperature dependencies of magnetic susceptibility (χ), for the zero-field-cooled state of the specimen and electrical resistivity (ρ) are shown to highlight the existence of the magnetic transitions at 10 and 32 K.

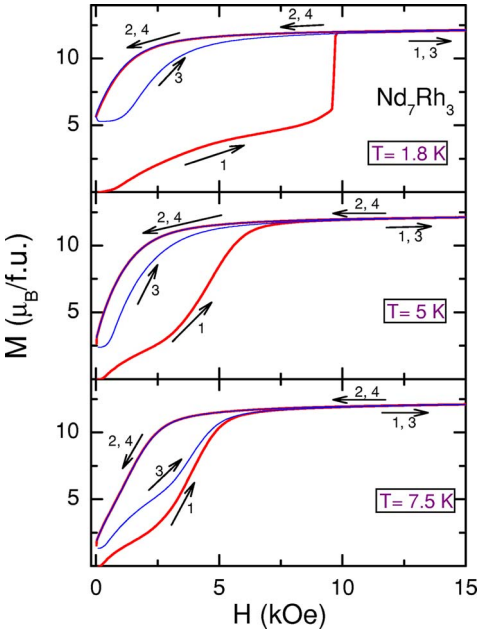

FIG. 2. (Color online) Isothermal magnetization behavior for Nd_7Rh_3 (with a VSM) at 1.8, 5 and 7.5 K for the field excursion: 1, 0 to 30 kOe; 2, 30 to 0 kOe; 3, 0 to 30 kOe; 4, 30 to 0 kOe without any break between these paths. Before measurements at each temperature the specimen was zero-field cooled from 50 K.

across 10 K. We do not find any further spin-reorientation effect beyond 10 kOe until 120 kOe, and the increase of M beyond 10 kOe was found to be very weak. The saturation magnetization of close to $1.7\mu_\beta$ per Nd is nearly half of the theoretically expected value, which is attributable to crystal-field effects.

The most important observation which we would like to stress is that the field-induced ferromagnetism at 1.8 K, occurring around 10 kOe, is very sharp as though there is a first-order metamagnetic transition. This transition apparently broadens as one approaches the AF1 phase, as indicated by the 5 K data. The rest of the discussion in this paper will be focused on probing the characteristics[3–7] of the field-induced first-order magnetic-to-magnetic transition at 1.8 K. At this juncture, we should mention that this transition as reported in Ref. 8 is very broad. One can easily miss the sharpness of the feature as we find that its appearance is very sensitive to a history of measurements as well as to the rate of change of H. For instance, for a rate of increase of H of 1 kOe min, the transition appears at about 14 kOe with a significantly reduced jump; if we wait in the AF1 phase at 20 K for a long time (let us say 30 min) while zero-field cooling, we are able to reproduce the broad transition reported in Ref. 8. Thus, the FOPT is influenced by energy fluctuations. It is therefore not surprising that Tsuotaka *et al.*[8] missed this first-order transition.

It is clear from the data shown in Fig. 1 that the sharp discontinuity is absent while reversing the field to zero (that is, path 2). The FOPT cannot be seen for the field excursion, 0 to −30 to +30 kOe, which means that any kind of field cycling destroys this transition. Thus, there is an irreversibility of $M(H)$ behavior following first-order transition. The high-field ferromagnetic (F) state is partially retained (see below) even when H is reduced to zero, which implies a supercooling effect characteristic of disorder-influenced FOPT. As a signature of the existence of an F component, there is a distinct hysteresis loop in the $M(H)$ plot. The FOPT can be restored only if the specimen is warmed up and cooled again from the paramagnetic state (let us say from 50 K).

The question that now arises is whether the magnetic state attained after reversing the field to zero (path 2) is purely ferromagnetic in character. We have performed additional isothermal M measurements (with a VSM with a field excursion different from that in Fig. 1) at a few temperatures (1.8, 5 and 7.5 K), which are shown in Fig. 2. For measurements at each temperature, we cooled from 50 K. Paths 1, 2, 3 and 4 represent continuous field variations 0 to 30, 30 to 0, 0 to 30 kOe, and 30 to 0 kOe, respectively (to ensure a negligible time delay between these paths, which is possible with the VSM employed). The points to be noted are as follows: When the H is reduced to zero (path 2 or 4), the value of M, called $M(0)^{\text{mixed}}$, stays below that obtained from high-field linear extrapolation. The same value of $M(0)^{\text{mixed}}$ is attained after any number of rounds of field cycling. If the value of $M(0)^{\text{mixed}}$ is of any indication then it is clear that the entire specimen is not ferromagnetic in the zero field after field cycling and that the fraction of the F-component keeps decreasing with increasing temperature, let us say from 1.8 to 7.5 K. (Note that above 10 K, the M value is reduced to a value close to zero in the reverse H cycle; see the data for 15 and 25 K in Fig. 1.) When path 3 in Fig. 2 is followed there is a distinct step at low fields, which clearly indicates

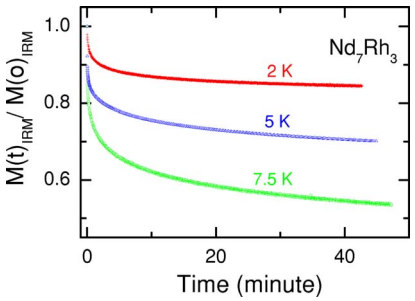

FIG. 3. (Color online) Time (t) dependence of isothermal remanent magnetization normalized to the value at $t=0$ (defined as the time at which H becomes zero in this measurement) for Nd_7Rh_3 (with a VSM) at various temperatures. Before measurements at each temperature the specimen was zero-field cooled from 50 K.

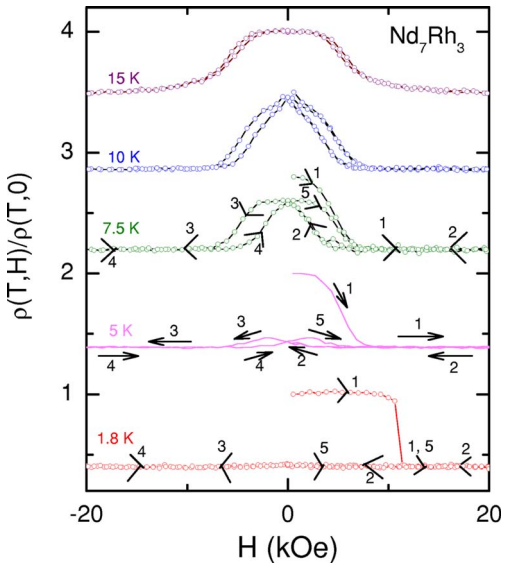

FIG. 4. (Color online) Electrical resistivity (normalized to respective zero-field values in the virgin curve) as a function of magnetic field for Nd_7Rh_3. The paths denoted are the same as described in Fig. 1, though the data are shown in the range −20 to 20 kOe only. The curve for each temperature is shifted along the y axis for the sake of clarity.

that an AF component is definitely present after path 2. These results establish that the magnetic state in the zero field after field cycling is a mixture of AF and F phases. It is thus interesting that despite the fact that this is a stoichiometric compound there is distinct evidence for "phase-coexistence," which then has to be attributed to crystallographic imperfections.

We now address the question of stability of the zero-field phase after field cycling by performing time-dependent isothermal remanent magnetization (M_{IRM}) measurements as a function of time (t) at 2, 5, and 7.5 K. For this purpose, we cooled the sample in the zero field from 50 K to the desired temperature, switched on a field of 5 kOe for 5 min, and the value of M was measured as a function of t after switching off the field. The results thus obtained (Fig. 3) reveal that there is a steep decrease of M_{IRM} for an initial few minutes and the rate of decay gets smaller thereafter as though the transformation of the high-field magnetic phase to a zero-field state is gradually slowing down. The features are qualitatively the same even if the starting field is 15 kOe (instead of 5 kOe). We take this as an evidence for the kinetic slowdown proposed in Ref. 3. As another signature[3,7] of kinetic arrest, the virgin $M(H)$ curves at 1.8 and 5 K in Fig. 1 lie outside the envelope curve and such behavior has been known among manganites as well.[10] The decay of M_{IRM} with t is nearly logarithmic and we would like to stress here that this cannot be attributed to spin-glass behavior in this case (see the discussion below).

In order to see how the metastability, kinetic hindrance, and phase-coexistence influence the transport behavior of this compound, we have performed ρ measurements as a function H at several temperatures in the magnetically ordered state, and for each temperature the virginity of the specimen was ensured before collecting data. The results are shown in Fig. 4 and the excursion of H is described in the caption. Needless to mention that there is a sharp jump in ρ near $H=10$ kOe in the virgin path for $T=1.8$ K. At 15 K, in the low-field range (<about 3 kOe), ρ is nearly constant and there is a sudden decrease of ρ around 5 kOe due to spin-reorientation effects, inferred from $M(H)$ data as well. The ρ behavior is reversible for any field cycling, that is from 0−30 to −30−30 kOe. As T is decreased to 10 K, as in the $M(H)$ curves, the virgin curve (path 1) tends to lie outside the envelope curve and a butterfly-like hysteresis loop starts appearing with the $\rho(0)$ value after the excursion, called $\rho(0)^{mixed}$, being marginally lower than the initial or virgin $\rho(0)$ value. After a further decrease of T to 7.5 K or 5 K, the above-described virgin curve and butterfly behavior get very prominent. The value of $\rho(0)^{mixed}$ undergoes gradual reduction compared to respective virgin $\rho(0)$ values, as a result of which for $T=5$ K the size of the butterfly loop becomes smaller compared to that at 7.5 K. It is fascinating that at 1.8 K, the butterfly behavior is totally absent and the high-field ρ value is retained even in the zero field. Such a high-field memory of ρ was actually known earlier for some manganites.[11,12] It is interesting to note that any additional cycling of field (let us say, +30 to −30 to +30, ----), the value of ρ does not vary at all with H. A point to be stressed here is that at 1.8 K, while the $M(H)$ data discussed above establish the presence of both F and AF phases in zero H after field cycling the presence of the AF component is not felt in the transport process. This establishes the existence of percolative transport, as the F state is less resistive than the AF phase. Evidence in favor of kinetic hindrance is the fact that the values of $\rho(0)^{mixed}$ (after completion of path 5) does not vary with time at all (unlike M_{IRM}), and, in this sense, the transport behavior is markedly different from that reported for a manganite.[12] This can be consistently understood with the idea of percolative conduction. The gradual increase in the value of $\rho(0)^{mixed}$ towards virgin $\rho(0)$ with increasing T (see Fig. 4) implies an increase in the fraction of the AF component at the expense of the F component supporting the observation made from the $M(H)$ data.

We have performed ac χ measurements at several frequencies in the T region of interest (1.8–50 K), mainly to understand the question raised by Dagotto *et al.*[1] as stated in

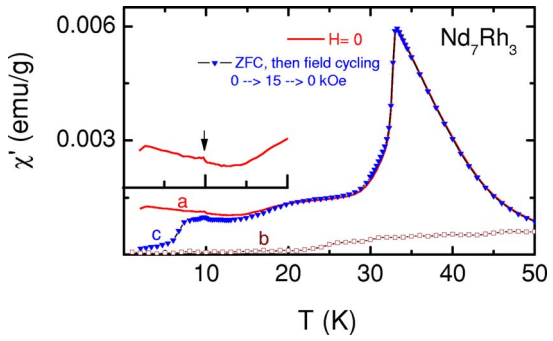

FIG. 5. (Color online) Real part of the ac magnetic susceptibility as a function of temperature for Nd_7Rh_3. The curves *a*, *b*, and *c* are described in the text. To show the presence of a weak feature (marked by vertical arrow), the data below 20 K for curve *a* are also shown in an expanded form. Since the curves for all frequencies overlap, the data for only frequency are plotted.

our opening remarks. The measurements were performed with increasing temperature for three sample-history conditions (see Fig. 5 for the real part): (i) The sample was cooled from 50 K in zero dc H (curve *a*) following which the data were collected to make sure that there is no spin-glass freezing in the zero field; (ii) after cooling in the zero field to 1.8 K, the data were taken (curve *b*) in the presence of a dc H of 15 kOe to see the response of the high-field F state to ac χ; and (iii) ZFC to 1.8 K, dc H of 15 kOe was switched on to attain a high-field ferromagnetic state, and then switched off H, following which the data were taken, as this curve is expected to yield information about the nature of the mixed phase (curve *c*). There is a distinct peak in curve *a* at 32 K arising from the transition from paramagnetism to AF1, but the curve shows a very weak peak only at the 10 K transition. No ν dependence of the peak position (or of the values of ac χ) could be observed and the signal from the imaginary part is negligible; therefore, spin-glass freezing in zero dc H should be ruled out. An application of a dc H of 15 kOe, apart from reducing the absolute values of ac χ, broadens the 32 K feature (see curve *b*) and this curve serves as a reference for the response from the high-field F phase. For the experimental condition of curve *c*, it is to be emphasized that the values at low temperatures, let us say at 1.8 K, are rather close to those in curve *b*, as though the F phase is the dominating one with a small admixture of the AF2 phase. A look at curve *c* reveals that this F/AF2 phase ratio undergoes a gradual, but slow, decrease with increasing *T* until about 7 K, and at this temperature there is a sudden decrease of this ratio towards curve *a*. These findings offer another evidence for the mixed phase nature of the nonvirgin specimen (i.e., the one in zero dc H attained after high-field cycling) below 10 K, and 7 K is the characteristic temperature marking the dominance of kinetic arrest. Another important observation is that there is no ν dependence in the *T* range of interval for curve *c*, thereby revealing that the mixed phase does not behave like a spin glass. This work thus directly supports the belief[5] that the coexisting phases are different from spin glasses, clarifying the question posed by Dagotto *et al.*[1] Therefore, "magnetic glass"[5,7] may be a better term to describe such mixed phases considering that such as field-cycled state also shows certain glassy features, such as irreversibility.

To conclude, we have established the existence of a magnetic-field-induced first-order magnetic-to-magnetic transition at 1.8 K for the compound Nd_7Rh_3. Several features characterizing first-order transitions—supercooling, irreversibility, metastability, and phase co-existence—are seen distinctly in the data, clearly bringing out the role played by crystallographic defects for such a stoichiometric intermetallic compound. In addition, the data provide distinct evidence for the concept of kinetic hindrance[3] in the zero field after the field cycling across the first-order transition regime. Thus, the behavior observed for doped $CeFe_2$ and Gd_5Ge_4 should be more general even among stoichiometric compounds for quenched disorder-influenced first-order magnetic transitions at which two phases are in competition. The electrical resistivity data as a function of dc H provide evidence for percolative transport in the mixed-phases interestingly resulting in the "memory" of high-field resistivity when the field is reduced to zero. Above all, the ac χ data conclusively establish that the coexisting phases obtained by field cycling across such a FOPT are different from spin glasses, thereby clarifying a question raised by Dagotto *et al.*[1] While the characteristics of compound are interesting, the question remains whether the first-order magnetic transition is driven by a simultaneous structural transition as in doped $CeFe_2$ and Gd_5Ge_4. If not, the underlying physics of the present compound could be distinctly different from these two compounds. Therefore, careful neutron and x-ray diffraction studies[13] as a function of temperature and magnetic field will be quite rewarding.

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