Novel Dynamical Effects and Glassy Response in a Strongly Correlated Electronic System

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We find an *unconventional* nucleation of a low-temperature paramagnetic metal phase with a monoclinic structure from the matrix of a high-temperature antiferromagnetic insulator phase with a tetragonal structure in a strongly correlated electronic system $BaCo_{0.9}Ni_{0.1}S_{1.97}$. Such unconventional nucleation leads to a decrease in resistivity by several orders with relaxation at a fixed temperature. The novel dynamical process could arise from the competition of strain fields, Coulomb interactions, magnetic correlations, and disorders. Such competition may frustrate the nucleation, giving rise to a slow, nonexponential relaxation and ''physical aging'' behavior.

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Glassy behavior was first seen and is currently studied in structural glass systems. Slow, nonexponential relaxations of glassy dynamics have been widely observed in doped semiconductors [1], strongly disordered indium-oxide films [2], and various granular metals [3,4]. Such nonergodic behavior is very interesting because one normally expects electron systems to relax rather rapidly. Many glassy systems exhibit a nonstationary behavior that has been described as ''physical aging'' [5]. Recently, the electron glass has received renewed interest [6,7] as the subject of electron-electron interactions has become a central topic in understanding the metal-insulator transition (MIT) in two dimensions [8]. Such glass behavior is believed to be associated with the interplay between disorder and strong electronic correlations [9]. The phase separation widely observed in a strongly correlated electronic system [10,11] provides the possibility for the appearance of locally metastable states, giving rise to the self-organized inhomogeneities (disorders). The phase separation scenario appears as particularly favorable for the existence of out-of-equilibrium features. Therefore, it is expected that the glass behavior occurs in the strongly correlated electronic system due to interplay between disorder and strong electronic correlations [9], especially in phase separation region. Indeed, a pronounced glassy response [12] and a memory effect have been recently observed in phase separated manganites [13]. The interplay of strong electronic correlations and disorder is believed to be responsible for many new phenomena occurring in complex materials in the MIT region [14]. Therefore, novel findings in complex materials with strongly electronic correlations in the MIT region clearly deserve further study.

$BaCoS_2$ is a Mott-Hubbard insulator having Co_2S_2 layers with spin-1/2 Co ions that order antiferromagnetically at 310 K and properties shared by members of the high-temperature superconducting cuprates. Such a quasi-two-dimensional system, $BaCoS_2$ with Co_2S_2 conducting planes separated by insulating BaS rocksalt sheets, is structurally analogous to the high-T_c cuprates [15]. Substitution of Ni for Co leads to a first-order transition from antiferromagnetic insulator (AFI) to paramagnetic metal (PMM) upon cooling at T_c in a $BaCo_{0.9}Ni_{0.1}S_{2-y}$ system for $0.05 \leq y \leq 0.20$ [15]. Such an AFI-PMM phase transition is associated with a structural change from a high-temperature tetragonal (HTT) phase to a low-temperature monoclinic (LTM) phase [16]. In this Letter, we report a novel dynamical process for the MIT due to the interplay of strong electronic correlations and disorder in $BaCo_{0.9}Ni_{0.1}S_{1.97}$ close to the composition with the MIT. In the novel dynamical process, the competition of strain fields, Coulomb interactions, magnetic correlations, and disorder in this correlated electronic system could frustrate the nucleation, giving rise to a slow, nonexponential relaxation of glassy dynamics and ''physical aging'' behavior.

Polycrystalline samples of $BaCo_{0.9}Ni_{0.1}S_2$ were prepared by a conventional solid-state reaction. To introduce the sulfur vacancy y in $BaCo_{0.9}Ni_{0.1}S_{2-y}$, the samples with $y = 0$ were sealed in a quartz tube at a pressure of 10^{-4} Torr, heated to 900 °C, and kept for 12–24 h, producing a sulfur deficiency of $y = 0.03$. The sulfur deficiency was determined by a standard atomic-emission spectrum. Figure 1 shows the temperature dependence of the resistivity measured by an ac method with a fixed excitation voltage of 6 mV (the current in the measurement changes from 3 mA to about 30 nA) in two different sequences of cooling and warming cycles with starting temperatures of 400 and 300 K, respectively. Through all measurements, the rate of cooling and warming is always kept at 3 K/min. In the first round, resistivity was measured by cooling the sample from 400 to 5 K and subsequently warming to 400 K. The sample shows an insulating behavior with a kink at $T_s \sim 65$ K upon cooling. Such a kink, referred to as a first-order AFI-I' transition, has been observed in the sample $BaCo_{0.9}Ni_{0.1}S_{1.9}$ after complete suppression of the AFI-PMM transition by pressure [17]. A hysteresis is observed in the cooling and warming measurement. Continuously, resistivity was measured in the second round of 400 K → 5 K → 300 K and in the third round from 300 K → 5 K → 220 K. The resistivity shows

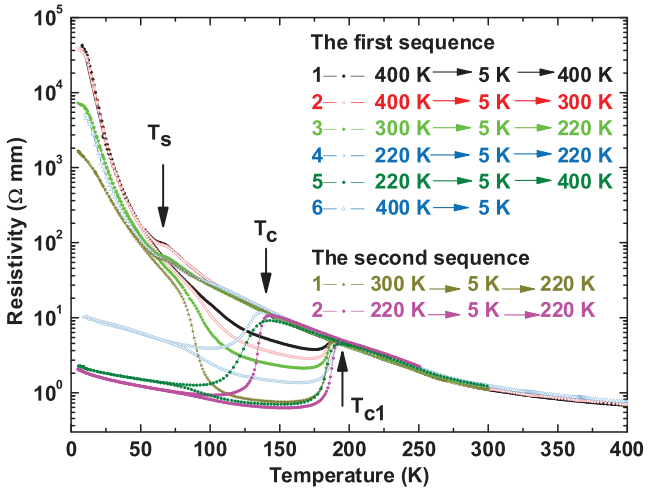

FIG. 1 (color). Temperature dependence of the resistivity measured with different cooling and warming cycles in the two sequences in $BaCo_{0.9}Ni_{0.1}S_{1.97}$ close to the phase boundary between an AFI at lower sulfur deficiency and a PMM at higher sulfur deficiency.

similar behavior to that in the first round, but the hysteresis becomes larger.

A striking feature is that a first-order phase transition at $T_c \sim 140$ K from insulator to metal occurs in the fourth round of 220 K → 5 K → 220 K. It is similar to the AFI-PMM transition observed in the sample with a large sulfur deficiency [15]. In the fifth round from 220 K → 5 K → 400 K, the resistivity shows similar behavior to that in the fourth round except that the transition is sharper with a larger reduction of resistivity. These results indicate that the resistivity is strongly dependent on cooling and warming cycles. The hysteresis becomes larger, and consequently the first-order phase transition from AFI to PMM is induced. It indicates that an irreversible memory behavior occurs in the cooling and warming cycles. After the fifth round, another intriguing behavior is observed with cooling the sample from 400 to 5 K: the first-order phase transition from AFI to PMM is gone, and the resistivity reexhibits an insulating behavior. The disappearance of the phase transition with cooling the sample from 400 K suggests that 400 K can remove the memory effect, so that the effect of the cooling and warming cycle on resistivity is gone.

To understand the effect of 400 K, the resistivity was measured in the second sequence by cooling from 300 K after keeping the sample at room temperature for more than ten days. As shown in Fig. 1, the resistivity exhibits an insulating behavior with the AFI-I' transition being similar to that observed in the first sequence. But the resistivity is less than that from 400 below 120 K. The hysteresis is much larger than that in the first sequence. Continuously, the resistivity was measured in the second round of 220 K → 5 K → 220 K; the phase transition from AFI to PMM takes place at ~140 K. The common feature shared in the two sequences is that the phase transition can be only observed after the cooling and warming cycle of 300 K → 5 K → 220 K. The resistivity at 5 K changes with more than 4 orders of magnitude in the cooling and warming cycle. It suggests that a *nucleation* of the metallic phase from the insulating matrix occurs with cooling and warming cycles.

Magnetic properties were systematically studied with the cooling and warming cycles as the second sequence in the resistivity measurement. The temperature dependence of the magnetization is shown in Fig. 2 under a magnetic field (H) of 5000 Oe. Figure 2 shows an antiferromagnetic transition at $T_N \sim 270$ K and a sharp change around T_s on cooling from 300 K → 5 K → 220 K. The sharp change around T_s arises from a spin-state change of Co ions from high spin to low spin. Neutron diffraction data have shown that the Co ions of $BaCoS_2$ have a localized high-spin configuration with $s = 3/2$ [18]. Pressure can induce a spin-state transition from the localized high-spin ($s = 3/2$) to low-spin ($s = 1/2$) configuration [19]. Therefore, the kink at T_s observed in the resistivity is associated with spin-state change. Upon warming, another sharp change of magnetization is observed at $T_{s1} \sim 89$ K, which seems to coincide with the sharp change in resistivity observed on warming in the first round of the second sequence. T_{s1} is also observed in the round of 400 K → 5 K → 220 K, but only a minor change in resistivity at T_{s1} is observed upon warming. At this moment, we do not know why T_{s1} happens. The first-order transition at 140 K is observed in both the magnetization and the resistivity in the cooling and warming cycle from 220 K → 5 K → 220 K, but is gone in the continuous measurement with cooling from 400 K. It further indicates that the "400 K" plays an "annealing" role and produces a removal of the memory effect. It should be pointed out that the intriguing phenomena are directly related to the change in resistivity and magnetization at T_s. Such a change at T_s can be observed only in the sample $BaCo_{0.9}Ni_{0.1}S_{2-\delta}$ with a narrow sulfur deficiency around $\delta \sim 0.03$. A "Curie tail"

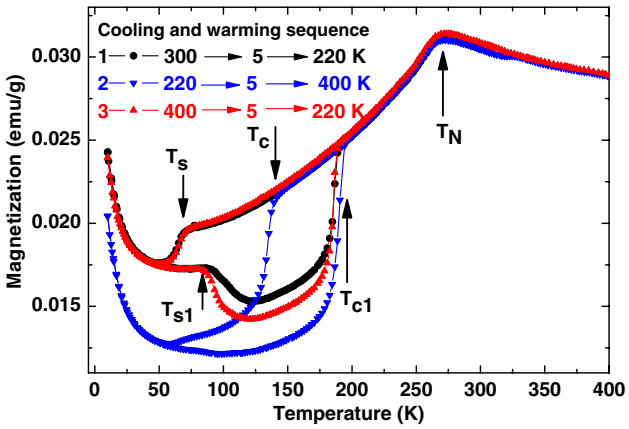

FIG. 2 (color online). Temperature dependence of the magnetization measured with cooling and warming cycles under a magnetic field of 5000 Oe for the sample $BaCo_{0.9}Ni_{0.1}S_{1.97}$.

below 30 K is observed in Fig. 2. The "Curie tail" could be from the sulfur vacancies or the impurity Ba_2CoS_3. However, the susceptibility of $BaCo_{0.9}Ni_{0.1}S_{1.97}$ is 2 orders of magnitude larger than that of Ba_2CoS_3. Therefore, the contribution to the susceptibility from an impurity phase is ignored, and the vacancies are the cause of the "Curie tail." To estimate the vacancy density, the Curie-Weiss law was used to fit the "Curie tail" assuming $s = 1/2$. The estimated density of spin-1/2 sites is about 0.014 f. u. This is consistent with the vacancy number per unit cell.

The relaxation of the resistivity and the magnetization at 80 and 100 K were studied, respectively. It should be pointed out that the sample must have the exact same experience before the relaxation measurement because the properties are strongly dependent on the experience history and what temperature the sample was cooled from, as shown in Figs. 1 and 2. Therefore, the sample was warmed up to room temperature and kept for a long time (about 10 h) to make sure that the sample has the same behavior on relaxation. Figure 3(a) shows that the resistivity and magnetization at 80 and 100 K decrease apparently with relaxation time. Both relaxations are consistent with the isothermal growth of PMM regions embedded in an AFI host. Such nonstationary behavior has been described as "physical aging" and is widely observed in the glass system [5]. Figure 3 shows a slow, nonexponential relaxation, which is the typical relaxation characteristic of glass dynamics. Such glass behavior is not like that of a glass consisting purely of spin or charge, but a cross-coupled variable. The resistivity and magnetization keep nearly unchanged with a relaxation time of about 100 min; this is different from other relaxation behaviors observed so far, that the physical properties change in the beginning of relaxation. After that, the resistivity and magnetization decrease remarkably, but do not follow the exponential relaxation behavior. The resistivity decreases by 1.5 orders of magnitude at 100 K with a relaxation time of about 2000 min, and finally reaches nearly the same value as that in the PMM phase as shown in Fig. 1. As shown in Fig. 3(b), similar relaxation behavior is also observed in single crystal $BaCo_{0.9}Ni_{0.1}S_{1.97}$ except that the resistivity

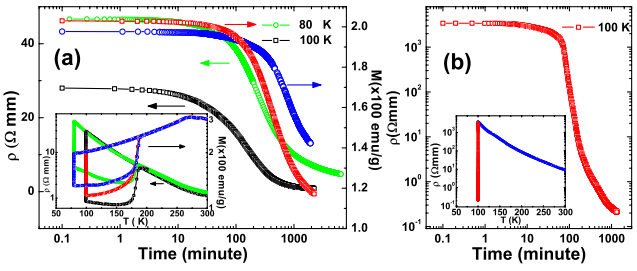

FIG. 3 (color online). (a) Resistivity and magnetization as a function of time at 80 K (circles) and 100 K (squares) for polycrystalline $BaCo_{0.9}Ni_{0.1}S_{1.97}$. Inset: Temperature dependence of the resistivity and magnetization with intermediate relaxation at 80 and 100 K. (b) Resistivity relaxation at 100 K on single crystal $BaCo_{0.9}Ni_{0.1}S_{1.97}$.

of a single crystal changes by 4 orders of magnitude at 100 K with relaxation, versus 1.5 orders of magnitude for the polycrystalline sample. The results observed in a single crystal indicate that the intriguing phenomena are not only observed in polycrystalline samples explicitly, indicating that the behavior is intrinsic. This is confirmed by x-ray diffraction (XRD) measurements. As shown in Fig. 4, the XRD pattern obtained as soon as the sample was cooled to 100 K can be indexed with a tetragonal structure, similar to the structure reported for $BaCo_{0.9}Ni_{0.1}S_{2-\delta}$ at room temperature [20]. After keeping the sample at 100 K for 10 h, the XRD pattern is different. The apparent difference can be observed around 2θ of 28° and 57.5°. As shown in the inset, the two peaks are observed for the tetragonal structure around 2θ of 28°, while three peaks show up in the XRD pattern at 100 K for 10 h. The three peaks around the 2θ of 28° are characteristic of a monoclinic structure [20]. The XRD pattern at 100 K for 3 h looks like a mixture of the tetragonal and monoclinic structure. It definitely indicates spontaneous nucleation of the PMM phase with LTM structure from the matrix of the AFI phase with HTT structure. To clearly show the difference between the LTM and HTT phases, the model XRD patterns for the LTM and HTT phases are also plotted in Fig. 4.

The relaxation behavior of the resistivity and magnetization is qualitatively similar to the nucleation process of crystals [21]. It indicates that the striking feature observed in Figs. 1 and 2 arises from the nucleation of PMM in the AFI matrix. For the nucleation, a period of time usually elapses between the achievement of supersaturation or supercooling and the appearance of crystals. This time lag is referred to as an "induction period." Generally, the physical properties do not change detectably in the induc-

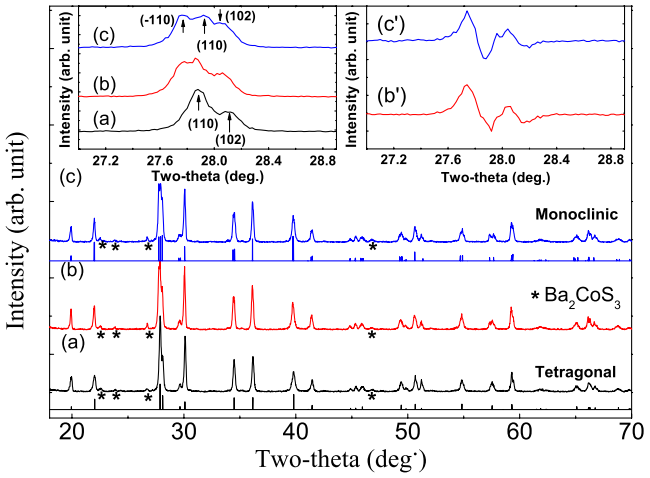

FIG. 4 (color online). XRD patterns at 100 K for polycrystalline sample $BaCo_{0.9}Ni_{0.1}S_{1.97}$. (a) taken as soon as the sample was cooled to 100 K with 90 min; (b) taken after the sample was kept at 100 K for 3 h; (c) taken after the sample was kept at 100 K for 10 h. The inset shows the XRD pattern (left) in the two-theta range from 27° to 29°, and the intensity difference between $t = 3$ h/10 h and $t = 90$ min (right).

tion period. Therefore, the time spent before the apparent change of the resistivity and magnetization can be referred as to the induction time. But it should be pointed out that the induction time is normally very short (a few seconds) [21]. However, the induction period in the current material is *extremely long* (about 100 min). This is very *unusual*, and may be the reason why the striking behaviors shown in Figs. 1 and 2 occur.

The intriguing phenomena can be understood by the anomalous nucleation of the PMM phase with LTM structure in the AFI matrix with HTT structure. The nucleation leads to enhancement of the PMM phase with respect to the AFI phase, and the resistivity and magnetization vary with the motion of the domain boundaries separating the coexisting phases. The metastable state consisting of PMM clusters and an AFI matrix results in a slow relaxation dynamics of the resistivity and magnetization between T_s and T_{c1}. Theoretical work by Ahn *et al.* [22] has indicated that the combined effects of long-range strain field and local intrinsic disorder naturally give rise to the phase separation and a metastable landscape with hierarchical energy barriers for relieving the strain, which can explain the phase separation in manganites [12]. The phase separation that occurred in $BaCo_{0.9}Ni_{0.1}S_{1.97}$ should follow this mechanism. This is confirmed with the suppression of the AFI-PMM transition by pressure [17]. Phase conversion within the admixture involves the rearrangement of many coupled degrees of freedom spanning all relevant length scales. The presence of competing strain fields, Coulomb interactions, magnetic correlations, and disorder may *frustrate the nucleation*, giving rise to the complex free energy landscape with hierarchical energy barriers in $BaCo_{0.9}Ni_{0.1}S_{1.97}$. This naturally gives rise to glassy dynamics, a slow, nonexponential relaxation, and ''physical aging'' behavior [23].

Below T_c, the PMM regions start to grow against the host material with the equilibrium size of the clusters increasing as T is lowered. The dynamical process followed by the clusters to reach their equilibrium size can be thought of as a stepwise movement of the phase boundaries through energy barriers. Existence of a hierarchy of energy barriers is revealed by the response of the hysteresis in resistivity and magnetization to the cooling and warming cycles. The cooling in the cycles lowers the free energy of the PMM phase with respect to the AFI phase, and the interphase domain walls feel an effective force, so that the pinning barriers are overcome and the walls move irreversibly into a new configuration. Such an explanation has been proposed for the glass response to an external field in manganites [12]. This pinning behavior could arise from the competition of strain fields, Coulomb interactions, magnetic correlations, and disorder in strongly correlated electronic systems. The removal of these pinning sites at $\sim$400 K could be because the sulfur vacancies are mobile at such a high temperature. This is the reason why the effect of 400 K on the resistivity and magnetization occurs.

In conclusion, we find *an unusual, and extremely slow and nonexponential* relaxation of the resistivity and magnetization in $BaCo_{0.9}Ni_{0.1}S_{1.97}$. Another *unusual* feature is that the induction time for the PMM nucleation in the AFI matrix is extremely long in contrast to normal nucleation. All intriguing phenomena may arise from the strong cross couplings among the different degrees of freedom and competition of strain fields, Coulomb interactions, magnetic correlations, and disorders, leading to a complicated and slow relaxation. Similar phenomena should be expected in other strongly correlated electronic systems in the phase separation region around the MIT.

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