Novel dynamical effects and glassy response in strongly correlated electronic system

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We find an unconventional nucleation of low temperature paramagnetic metal (PMM) phase with monoclinic structure from the matrix of high-temperature antiferromagnetic insulator (AFI) phase with tetragonal structure in strongly correlated electronic system BaCo$_{0.9}Ni_{0.1}S_{1.1}$ and BaNi$_{0.9}Co_{0.1}S_{1.9}$. Such unconventional nucleation leads to a decrease in resistivity by several orders with relaxation at a fixed temperature without external perturbation. 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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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[2, 5] as the subject of electron-electron interactions has become a central topic in understanding the metal-insulator transition (MIT) in two dimensions[5]. Such glass behavior is believed to be associated with the interplay between disorder and strong electronic correlations[6]. Phase separation widely observed in strongly correlated electronic system[10, 11] provides the possibility for appearance of locally metastable states, giving rise to the self-organized inhomogeneities (disorders). Phase separation (PS) 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[6], especially in phase separation region. Indeed, a pronounced glassy response[12] and a memory effect have been 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 deserves 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 $T_c$ cuprates. Such quasi-two dimensional system $BaCoS_2$ with $CoS$ 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 a antiferromagnetic insulator (AFI) to a paramagnetic metal (PMM) upon cooling at $T_c$ for the sample $BaCo_{0.9}Ni_{0.1}S_{1.1}$[15]. Such AFI-PMM phase transition is associated with a structural change from high-temperature tetragonal (HTT) phase to low-temperature monoclinic (LTM) phase[16].

In this letter, we report a novel dynamical process for the MIT transition due to the interplay of strong electronic correlations and disorder in $BaCo_{0.9}Ni_{0.1}S_{1.1}$ close to the composition with MIT. In novel dynamical process, the competition of strain fields, Coulomb interactions, magnetic correlations and disorder in this correlated electronic system frustrates the nucleation, giving rise to a slow, nonexponential relaxation and "physical aging" behavior.

Figure 1 shows temperature dependence of resistivity measured in two different sequences of cooling and warming cycles with starting temperature of 400 K and 300 K for the sample $BaCo_{0.9}Ni_{0.1}S_{1.1}$, respectively. In the first round of the first sequence, resistivity was measured with cooling the sample from 400 to 5 K, subsequently warmed to 400 K. The sample shows an insulating behavior with a kink at $T_s \sim 65 K$ upon cooling. Such kink, referred to a first-order AFI-I’ transition, has been observed in 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 between curves recorded upon cooling and subsequent heating. Continuous, resistivity was measured in the second round of 400K to 5K to 300K. The resistivity obtained on cooling in the second round is nearly the same as that in first round, but the hysteresis becomes larger. The sample was continuously measured in the third round from 300K to 5K to 220K. Upon cooling, the resistivity shows the similar behavior to the second round, but the resistivity below 120 K is less than that in the first and second round with much larger hysteresis. Striking feature is that a first-order phase transi-
tion at $T_c \sim 140\,\text{K}$ from insulator to metal with hysteresis occurs in the fourth round of $220\,\text{K} \rightarrow 5\,\text{K} \rightarrow 220\,\text{K}$. It is similar to the AFI-PMM transition observed in the sample with large sulphur deficiency. In the fifth round from $220\,\text{K} \rightarrow 5\,\text{K} \rightarrow 400\,\text{K}$, 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 resistivity is strongly dependent on cooling and warming cycles. The hysteresis becomes larger with cooling and warming cycles, consequently the first-order phase transition from AFI with HTT structure to PMM with LTM structure is induced. It indicates that an irreversible and memory behavior occurs in cooling and warming cycles. After the fifth round, another intriguing behavior is observed with cooling the sample from $400\,\text{K}$ to $5\,\text{K}$, the first-order phase transition from AFI with HTT structure to PMM with LTM structure is gone and the resistivity re-exhibits an insulating behavior. Disappearance of the phase transition with cooling sample from $400\,\text{K}$ suggests that the temperature of $400\,\text{K}$ can remove the memory effect, so that effect of cooling and warming cycle on resistivity is gone.

In order to further understand the effect of $400\,\text{K}$ on resistivity, resistivity was measured in the second sequence with starting temperature of $300\,\text{K}$ after keeping the sample at room temperature for more than ten days. As shown in Fig.1, the resistivity measured with cooling sample from $300\,\text{K}$ in the second sequence exhibits an insulating behavior with the AFI-I’ transition, being similar to that observed in the first sequence. But resistivity obtained with cooling sample from $300\,\text{K}$ is less than that from $400\,\text{K}$ below $120\,\text{K}$ (much less than one order of magnitude at $5\,\text{K}$). The hysteresis obtained in the first round of second sequence is much larger than that in the first round of the first sequence. Continuously, resistivity was measured in the second round of $220\,\text{K} \rightarrow 5\,\text{K} \rightarrow 220\,\text{K}$, a first-order phase transition similar to that observed in the first sequence takes place at $\sim 140\,\text{K}$. The common feature shared in the two sequences is that the phase transition can be only observed after the cooling and warming cycle of $300\,\text{K} \rightarrow 5\,\text{K} \rightarrow 220\,\text{K}$. As shown in Fig.1, the resistivity at $5\,\text{K}$ obtained with the different cooling and warming experience of the sample can change by more than four orders of magnitude. It suggests that an insulating phase and a metallic phase coexist in the sample at low temperature, and a nucleation of the metallic phase from the insulating matrix occurs with cooling and warming cycles. Therefore, a phase separation occurs in $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.97}$ as observed in manganites.

Magnetic properties were systematically studied with cooling and warming cycles as the second sequence in resistivity measurement. Temperature dependence of magnetization is shown in Fig.2 under magnetic field (H) of $5000\,\text{Oe}$. Figure 2 shows an antiferromagnetic transition at $T_N \sim 270\,\text{K}$ and a sharp change around $T_s$ on cooling from $300\,\text{K} \rightarrow 5\,\text{K} \rightarrow 220\,\text{K}$. The sharp change around $T_s$ could arise from spin-state change of Co ions from high-spin to low-spin. Neutron diffraction data have shown that the Co ions of $\text{BaCo}_2\text{S}_2$ have a localized high-spin configuration with $s=3/2$. Pressure can induce a spin state transition from the localized high-spin to low-spin configuration. Therefore, the kink at $T_s$ observed in resistivity is associated with spin-state change. Upon warming, another sharp change of magnetization is observed at $T_{s1} \sim 89\,\text{K}$, which corresponds to the

![FIG. 1: Temperature dependence of resistivity measured with different cooling and warming cycles in the two sequences in $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.97}$ close to the phase boundary between an AFI at lower sulphur deficiency and a PMM at higher sulphur deficiency. Through all measurements, the rate of cooling and warming was kept constant (3 K/min).](image1)

![FIG. 2: Temperature dependence of magnetization measured with cooling and warming cycles under the magnetic field of 5000 Oe for the sample $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{1.97}$.](image2)
sharp change in resistivity measured on warming in the first round of the second sequence as shown in Fig.1. It indicates that the resistivity behavior is closely related to the magnetic property. Being consistent with resistivity results, the first-order transition at \( \sim 140K \) is also observed in magnetization in the second round from \( 220K \rightarrow 5K \rightarrow 220K \), but is gone in the continuous measurement with cooling the sample from 400 K. It further indicates that the "400 K" plays an "annealing" role and remove 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 change at \( T_s \) can be observed only in the sample \( BaCo_{0.9}Ni_{0.1}S_{2-\delta} \) with narrow sulphur deficiency around \( \delta \sim 0.03 \) close to the phase boundary between an AFI at lower sulphur deficiency and a PMM at higher sulphur deficiency.

In order to understand the anomalous evolution of resistivity and magnetization with the cooling and warming cycles, a systematic study of the relaxation (i.e. time dependence) was carried out. As shown in Fig.3 and Fig.4, the relaxation of resistivity and magnetization at 80 K and 100 K was studied after the sample was warmed from 300 K to the desired temperature with the same cooling rate, respectively. It should be pointed out that the sample must have the exact same experience before relaxation measurement because the properties of the sample are strongly dependent on the experience history and what temperature the sample was cooled from as shown in Fig.1 and Fig.2. Therefore, the sample was warmed up to room temperature and kept for a long time (more than ten days) to make sure that the sample has the same behavior before cooling to the next desired temperature after relaxation study at one temperature. Fig.3 and Fig.4 show that the isothermal 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 a AFI host. Such nonstationary behavior has been described as "physical aging" and is widely observed in the glass system. The plots of resistivity and magnetization at 80 K and 100 K as a function of time show a slow, nonexponential relaxation in both of resistivity and magnetization, which is 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. In contrast to all relaxations observed so far, the resistivity and magnetization nearly keep unchanged with a relaxation time of about 100 minutes. After that, the resistivity and magnetization decrease remarkably, but do not follow the exponential relaxation behavior. The resistivity decreases by one and half order of magnitude at 100 K with relaxation time of about 2000 minutes, finally reaches nearly the same value as that in PMM phase as shown in Fig.1. It suggests that the change in both resistivity and magnetization with relaxation at fixed temperature arises from a spontaneous phase transformation from the AFI with HTT structure to PMM with LTM structure without external perturbation. This is confirmed by x-ray diffraction measurements. X-ray diffraction indicates that the structure of the sample changes with relaxation at 100 K from tetragonal to monoclinic structure.

The relaxation behavior of resistivity and magnetization shown in Fig.3 and Fig.4 is qualitatively similar to the nucleation process of crystals \[20\]. It further indicates that the striking feature observed in Fig.1 and Fig.2 arises from the nucleation of PMM in the AFI ma-

![FIG. 3: (a): Temperature dependence of resistivity measured at cooling rate of 3 K/min with an intermediate relaxation at 80 K and 100 K for sample \( BaCo_{0.9}Ni_{0.1}S_{1.97} \), respectively (solid); (b): The same data at 80 K and 100 K are plotted as a function of time (open).](image1)

![FIG. 4: (a): Temperature dependence of magnetization measured at cooling rate of 3 K/min with an intermediate relaxation at 80 K and 100 K under 5000 Oe for the sample \( BaCo_{0.9}Ni_{0.1}S_{1.97} \), respectively (solid); (b): The same data at 80 K and 100 K are plotted as a function of time (open).](image2)
matrix. For the nucleation, a period of time usually elapses between achievement of supersaturation or supercooling and appearance of crystals. This time lag is generally referred to an "induction period". Generally, the physical properties do not change detectably in the induction period. Therefore, the time spent before apparent change of resistivity and magnetization shown in Fig.3 and Fig.4 can be referred to the induction time. But it should be pointed out that the induction time is normally very short (few seconds)\cite{20}. However, the induction period in current material is extremely long (about 100 minutes). Which is very unusual, and may be the reason why the striking behaviors shown in Fig.1 and Fig.2 occur.

The intriguing phenomena observed above can be understood by the anomalous nucleation of the PMM phase with LTM in the AFI matrix with HTT. 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 $T_c$ and $T_c$. Theoretical work by Alin et al.\cite{21} 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\cite{12}. The phase separation occurred in BaCo$_{0.9}$Ni$_{0.1}$S$_{1-0.97}$ should follow this mechanism. This is confirmed with the suppression of AFI-PMM transition by pressure\cite{17}. Phase conversion within the admixture involves 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$_{1-0.97}$. This naturally give rise to glassy dynamics, and a slow, nonexponential relaxation and "physical aging" behavior\cite{22}.

Below $T_c$, the PMM regions with LTM structure 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. In the case, the existence of a hierarchy of energy barriers is revealed by the response of the hysteresis in resistivity and magnetization shown in Fig.1 and Fig.2 to the cooling and warming cycles. The cooling in the cycles lowers the free energy of PMM phase with respect to the AFI phase, and the interphase domain walls that separate the PMM and AFI regions in the mixed phase feel an effective force. Pinning sites up to a certain strength are then overcome and effectively eliminated, and the walls move irreversibly into a new configuration. This pinning behavior arises from the competition of strain fields, Coulomb interactions, magnetic correlations, and disorder in strongly correlated electronic system. These pinning sites can completely be removed only at $\sim 400$ K. This is the reason why effect of 400 K on resistivity and magnetization occurs. Such dynamical process produces aging and memory effects in resistivity and magnetization. Such anomalous relaxation observed here without external perturbation is quite different from the normal relaxation which can be only observed after driving the system out-of-equilibrium with external field.

In conclusion, we found an unusual, and extremely slow and nonexponential relaxation of resistivity and magnetization in BaCo$_{0.9}$Ni$_{0.1}$S$_{1-0.97}$. Another unusual feature is that the induction time for the PMM nucleation in AFI matrix is extremely long in contrast to normal nucleation. All intriguing phenomena arise from the strong cross-couplings between the different degrees of freedom and competition of strain fields, Coulomb interactions, magnetic correlations and disorders, leading to complicated and slow relaxation. Similar phenomena should be expected in other strongly correlated electronic system in phase separation region around MIT.

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