Disorder-induced orbital glass state in FeCr$_2$S$_4$
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received 3 November 2009; accepted in final form 17 February 2010

published online 18 March 2010

PACS 71.70.Ej – Spin-orbit coupling Zeeman and Stark splitting, Jahn-Teller effect
PACS 64.70.P– – Glass transitions of specific systems
PACS 71.23.-k – Electronic structure of disordered solids

Abstract – The effect of disorder on the orbital state in the spinel FeCr$_2$S$_4$ has been investigated with the substitution of Cr by Al, Ga, and Fe, respectively. For polycrystalline FeCr$_2$S$_4$, being related to the orbital-ordering transition around 9 K, the temperature dependence of magnetization shows a step-like transition, and the specific heat displays a well-defined $\lambda$-type anomaly correspondingly. However, for single-crystal and doped FeCr$_2$S$_4$ samples, the step-like transition in magnetization disappears, and the $\lambda$-type anomaly of specific heat is replaced by a broad hump. Moreover, the specific heat obeys a $T^2$-dependence at temperatures below 2 K, suggesting the formation of the orbital glass state in these samples. Consistently with different orbital states, the resistivity at low temperature can be better fitted with a thermally activated model for the polycrystalline FeCr$_2$S$_4$ sample, and better described by Mott’s variable-range hopping expression for the others. All these results imply that the disorder induces orbital glass state in FeCr$_2$S$_4$.

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The role of orbital degrees of freedom in determining the physical properties of correlated electron systems has been emphasized in the past few years [1,2]. Being analogous to conventional material phases, the orbital order may form as different states — orbital ordering, orbital liquid and even orbital glass. The effective control of the orbital state by an external field is promising for further applications of orbitronics [1]. Comparing with the orbital-ordering state that is widely under study, the orbital glass state has seldom been investigated and unraveled experimentally [1,2]. Recently, the spinel FeCr$_2$S$_4$ was reported to display the orbital glass state in single-crystal (SC) samples, while it displays orbital ordering in polycrystalline (PC) ones [3,4]. The origin of the discrepancy is still unclear.

FeCr$_2$S$_4$ is a typical strongly correlated electron material. Due to the strong coupling among spin, charge, orbital and lattice degrees of freedom, FeCr$_2$S$_4$ not only shows fascinating physical effects, e.g., colossal magnetoresistance and gigantic Kerr rotation, but also displays abnormal low-field magnetic behavior [5–10]. In FeCr$_2$S$_4$, the Fe$^{2+}$ ion is tetrahedrally coordinated by the sulfur ions. The Fe$^{2+}$ ion, with an electronic configuration $e_g^{4}t_2g^{6}$ and $S = 2$, is Jahn-Teller (JT) active. Hence long-range orbital order might be realized at low temperatures due to the JT effect [1,11]. However, the Fe ions themselves form a diamond lattice which is geometrically frustrated for the orbital degrees of freedom [3,4]. Therefore, concerning the discrepancy of different orbital states in FeCr$_2$S$_4$, two possibilities should be considered as mentioned in ref. [3]. One is that the orbital glass state might be the intrinsic property, which is driven by geometric frustration and broken in the PC due to marginal disorder [3,11]. Alternatively, the orbital ordering might be the ground state as resulting from the JT electron-lattice interaction, and the frozen-in of orbital order in SC is caused by chlorine defects contaminated during the growth process [3]. Clearly, the role of disorder in these two possibilities is different.

In this paper, the influence of disorder on the orbital state has been investigated. For the PC FeCr$_2$S$_4$ sample, being related to the orbital-ordering transition around 9 K, the temperature dependence of low-field magnetization shows a step-like transition, and the specific heat displays a well-defined $\lambda$-type anomaly correspondingly. For the SC sample and polycrystalline samples with element substitution (FeCr$_{1.9}$Al$_{0.1}$S$_4$, FeCr$_{1.95}$Ga$_{0.05}$S$_4$ and FeCr$_{1.95}$S$_4$), the step-like transition in magnetization
FeCr$_2$ cubic cell with space group $\text{Fd}_{\text{3}}$c. Observation of peaks for each sample could be indexed with a cubic cell with space group $Fd\bar{3}m$, which reveals that all the samples have single phase with spinel structure. Upon substitution, no structure change has been observed.

In our previous work, the cation occupation of the substituted Al, Ga, and Fe ions in FeCr$_2$S$_4$ has been studied in detail [12–14]. The introduced Al or Fe is found to substitute for Cr and occupy the octahedral site, which belongs to the normal spinel type [12,14]. However, the Ga ion has a preference to occupy the tetrahedral site and FeCr$_{1.95}$Ga$_{0.05}$S$_4$ belongs to an inverse spinel type [13]. Therefore, the substitution of Al or Fe can be regarded as inducing Cr-site disorder, and the Ga substitution results in disorder in both the Fe-site and the Cr-site.

FeCr$_2$S$_4$ is a simple Néel-type ferrimagnet with antiparallel spin alignment between the Fe and Cr sublattice [15]. Since the magnetic moment of the Cr sublattice is larger than that of the Fe sublattice, the system displays a net magnetization at temperatures below $T_c$. Therefore, different cation distribution for the substituted elements should be reflected in magnetism. The magnetism of these PC, SC and doped PC samples was studied by performing magnetization measurements from 2 to 200 K under applied fields of 0.005 and 1 T, respectively. Figure 2 displays the field-cooled magnetization under 1 T. For FeCr$_{1.9}$Al$_{0.1}$S$_4$, the substitution of nonmagnetic Al ions destroys the magnetism of the Cr sublattice, thereby it weakens the magnetic coupling between the Fe and Cr sublattice. FeCr$_{1.9}$Al$_{0.1}$S$_4$ has a lower $T_c$ and smaller saturation magnetization as compared with FeCr$_2$S$_4$. In contrast, in Fe$_{1.05}$Cr$_{1.95}$S$_4$, the substitution of magnetic Fe$^{3+}$ ions, with larger magnetic moments, in Cr-site has opposite influence on both $T_c$ and the saturation magnetization, see fig. 2. For FeCr$_{1.95}$Ga$_{0.05}$S$_4$, partial Ga ions occupying the Fe-site weaken the magnetism of the Fe sublattice. But on the other hand, the substituted Fe ions replacing in the Cr-site strengthen the magnetism of the Cr sublattice [13]. Accordingly, FeCr$_{1.95}$Ga$_{0.05}$S$_4$ displays higher $T_c$ and larger saturation magnetization with respect to FeCr$_2$S$_4$. The corresponding variation of $T_c$ and the saturation magnetization with the substitution of different ions suggests that these ions enter the lattice as expected.

Figure 3(a) and fig. 4 display the magnetization as a function of temperature obtained in zero-field-cooled (ZFC) and field-cooled (FC) processes with $H = 0.005$ T.
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Fig. 3: (Colour on-line) (a). Zero-field-cooled (open circle) and field-cooled (solid circle) magnetization measured at 0.005 T for PC FeCr$_2$S$_4$. The inset shows an enlarged view of the magnetization at low temperatures. (b). Temperature dependence of the specific heat plotted as $C_p/T$ vs. $T$ for PC FeCr$_2$S$_4$. The inset shows an enlarged view of the specific heat at temperatures below 2 K. (c). Zero-field resistivity curves plotted as $\ln\rho$ vs. $1000/T$ (open triangle) and $\ln(1000/T)^{1/4}$ (solid circle) for PC FeCr$_2$S$_4$. The solid lines are the linear fitting curves, the temperature value shown in the figure marks where the experimental curve starts to deviate from linearity.

All samples display clear anomalies around 65–75 K and irreversibility between ZFC and FC curves. The cusp-like anomaly around 70 K can be correlated with a structural transformation within crystallographic domains [16]. In our previous work, the anomaly and irreversible behavior have been studied and attributed to an abrupt increase of magnetic anisotropy below 70 K [10]. In addition to these anomalies, as seen from the insets of fig. 2 and fig. 3(a), the PC FeCr$_2$S$_4$ displays a step-like decrease (increase) in the ZFC (FC) magnetization around 9 K. However, other samples only show a smooth temperature dependence, see the insets of fig. 4. The step-like transition for PC and smooth temperature dependence for SC are in agreement with the results of the Loidl group, and can be related to the orbital-ordering transition and orbital glass state, respectively [7]. A similar temperature-dependent magnetization between SC and doped PC samples suggests that the orbital order might also be frozen in these samples.

Therefore, in order to investigate the orbital state for different samples, we further performed specific-heat measurements.

Figure 3(b) shows the specific heat plotted as $C_p/T$ vs. $T$ for PC FeCr$_2$S$_4$. In agreement with the step-like transition in magnetization, the PC FeCr$_2$S$_4$ displays a well-defined $\lambda$-type anomaly around 9 K, indicating the orbital-ordering transition [3,4]. For the SC and doped PC samples, as seen from fig. 5, the $\lambda$-type anomaly is completely suppressed and replaced by a broad hump. Especially, with temperature decreasing to low temperatures, the specific heat approaches zero following a strict $T^2$-dependence, see the insets of fig. 5. In contrast, as shown in the inset of fig. 3(b), the pure PC sample shows a clearly different behavior where the curve of $C_p/T$ vs. $T$ is nonlinear at temperatures below 2 K.

At ultra-low temperatures, the phonon and magnon contribution to the specific heat of SC FeCr$_2$S$_4$ is minor as compared to the orbital contribution [3,4]. The $T^2$ law for orbital contribution implies the existence of the orbital glass state in both SC and doped samples, theoretically it has been predicted that the specific heat obeys the $T^2$-dependence if the orbital order is suppressed by random fields [17]. All of the above results clearly show that not only in SC but also in doped PC samples, the orbital degrees of freedom have been frozen into the orbital glass state. For a different orbital state, the orientation of the orbital is coupled to the elastic response of the ionic lattice via electron-phonon interaction and therefore a different orbital state is accompanied by a different
and FeCr

heat obeys a $T^2$-dependence.

charge distribution \[8,11\]. Thus we further examined the charge transport by performing DC resistivity measurements.

FeCr$_2$S$_4$ is a semiconductor, and the conduction comes from the Fe$^{2+}$ narrow band \[18\]. As is known, for semiconductor-like transport behavior, an Arrhenius law, $\rho = \rho_0 \exp(E/(k_B T))$, is generally used to model activated behavior due to a band gap $E$ or a mobility edge. In addition, if the carriers are localized by random potential fluctuations, Mott’s VRH expression $\rho = \rho_0 \exp(T_0/T)^{1/4}$, is appropriate \[19\]. Figure 3(c) and fig. 6 show the zero-field resistivity curves plotted as $\ln\rho$ vs. $1000/T$, and $\ln(1000/T)^{1/4}$, respectively. For PC FeCr$_2$S$_4$, as seen from fig. 3(c), different regions can be clearly discerned, suggesting the variation of the conduction mechanism with temperature. At temperatures below $37\,K$, the curve of $\ln\rho$ vs. $1000/T$ is linear indicating a semiconductor-like behavior. With further increasing temperature, a curvature can be clearly seen. The curvature might be related to the formation of the orbital liquid state or corresponding to a structural transformation \[3,16\]. For the SC and doped PC (fig. 6) samples, the resistivity could be better fitted by $\ln(1000/T)^{1/4}$ at lower temperatures as compared to the thermally activated conduction ($\rho = \rho_0 \exp(E/(k_B T))$), indicating that Mott’s VRH expression, $\rho = \rho_0 \exp(T_0/T)^{1/4}$, is more appropriate. For VRH, the existence of random potential fluctuations is necessary, which can be correlated with the degrees of disorder \[19\]. A similar transport behavior between SC and doped samples suggest that the random potential also dominates in SC, which might be caused by a slight amount of chlorine defects \[3,4\].

Although the possibility of orbital glass formation has been predicted more than twenty years ago, the direct evidence for the orbital glass state is rare and the forming mechanism is still far from being understood \[1,20\]. The orbital glass might be purely driven by frustration as observed in LuFe$_2$O$_4$, or induced by 2D antiferromagnetic fluctuations as reported in Eu$_2$CuO$_4$, or formed by diluting a JT crystal with non-JT ions etc. \[21–24\]. In FeCr$_2$S$_4$, the coexistence of geometrical frustration and strong coupling among different degrees of freedom results in a complex ground state. The presence of geometrical frustration increases the fluctuation of orbital order \[11\]. On the other hand, strong coupling among different degrees of freedom might remove the frustration. A different orbital state between PC and SC samples, implies that the ground state is delicately modulated by finely balancing the frustration and different interactions. For PC samples, it seems that the geometrical frustration is not adequate to result in the orbital glass state, it might be overcome by strong electron-phonon coupling. At temperatures above the orbital-ordering temperatures, the system is in the orbital liquid state characterized by large fluctuations of the orbital order. The presence of disorder in SC and doped samples increases the random potential, which frustrates the orbital interaction further and finally results in the frozen-in of orbital order.
The role of disorder in FeCr$_2$S$_4$ recalls manganese oxides where quenched disorder separates the charge/orbital-ordered insulator and ferromagnetic metal into various sizes ranging from nanometer to micron scales [25–28]. In the manganese oxides, depending on the microstructure and charge carrier density, different kinds of orbital ordering as well as orbital liquid state might be achieved. The transition from orbital liquid to ordering state is similar to the case of PC FeCr$_2$S$_4$ and the structure effect on the orbital occupancy should also work in FeCr$_2$S$_4$ [27,28]. Quenched disorder, like structure distortion and random distribution of doped ions, increases or frustrates the interaction between different phases and results in their coexistence in real space. Clearly, due to the subtle balance among different interactions in these strong correlated systems, minute perturbations such as disorder can trigger gigantic changes in physical properties [26].

In conclusion, the magnetism, specific heat and transport properties of FeCr$_2$S$_4$, Fe$_{1.9}$Al$_{0.1}$S$_4$, FeCr$_{1.95}$Ga$_{0.05}$S$_4$ and Fe$_{1.05}$Cr$_{1.95}$S$_4$ polycrystalline samples as well as the single-crystal FeCr$_2$S$_4$ are studied. The experimental results indicate clearly that the introduction of disorder suppresses the orbital order transition and induces the appearance of the orbital glass state.

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This research was financially supported by the National Key Basic Research of China Grant 2007CB925001, the National Nature Science Foundation of China Grant 10774147, as well as Director’s Fund of Hefei Institutes of Physical Science, Chinese Academy of Sciences.

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