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Pressure effect on magnetic and transport properties of $FeCr_2S_4$

Y.M. Xie [a], R. Tong [b], Z.R. Yang [b,*]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China

[b] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

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ABSTRACT

In this paper, the influence of chemical pressure caused by Se substituting and hydrostatic pressure on magnetic and transport properties of $FeCr_2S_4$ have been investigated. In addition to a large irreversibility between zero-field-cooled (ZFC) and field-cooled (FC) magnetization under low magnetic field, $FeCr_2S_4$ polycrystalline sample also shows a cusp-like anomaly around 70 K and a step-like transition around 9 K. With increasing Se content, ferrimagnetic transition temperature decreases, irreversibility between ZFC and FC magnetization increases. At the same time, both the step-like transition and the cusp-like anomaly in magnetization shift to a lower temperature and disappears gradually. All the above effects caused by Se substituting are in accord with the effects caused by applying hydrostatic pressure. Furthermore, we found magnetoresistance increases with increasing Se content, and attributed it to the stabilization of magnetic polarons.

Chalcogenide chromium spinel compounds with the general formula ACr_2X_4 (A=Fe, Cd, Zn, Hg; X=S, Se) has attracted special interest due to a variety of exotic phenomena such as large magnetostriction [1], colossal magnetocapacitance [2], gigantic Kerr rotation [3], magnetostructural transition [4] and so on. Among these compounds, $FeCr_2S_4$ is a typical strongly correlated electron system. Due to the strong interplay of spin, charge, orbital and lattice degrees of freedom, $FeCr_2S_4$ shows complex magnetic behaviors [5,6] and multiple orbital state [7,8]. The temperature dependence of low-field magnetization shows a cusp-like anomaly around 70 K for polycrystalline and single-crystal sample, and a step-like transition around 9 K for polycrystalline sample indicating orbital-order transition. Below the first anomaly temperature around 70 K, transmission electron microscopy studies on single-crystal sample revealed a cubic-to-triclinic structural transition within crystallographic domains [9]. However, high-resolution X-ray powder diffraction on polycrystalline sample did not find structural transition [10]. At low temperature, single-crystal (SC) is orbital glass, while polycrystalline (PC) is orbital ordering [11]. It was also reported that a structural anomaly accompanies with orbital-order transition due to a static cooperative Jahn–Teller effect [10]. A different orbital state between PC and SC samples, implies that the ground state is delicately modulated by finely balancing different interactions.

The above phenomena reflects that lattice degrees of freedom and other degrees of freedom in $FeCr_2S_4$ are strongly coupled. The change of lattice degrees of freedom is normally accompanied by the variation of other degrees of freedom. Previously, $FeCr_2S_4$ has been studied by substituting Fe^{2+} or Cr^{3+} [12–15]. This would mainly change spin degrees of freedom, but would not change lattice degrees of freedom greatly. In this paper, we study the influence of lattice degrees of freedom on system's physical properties. This can be studied by substituting S with Se for the following reasons. The radius of Se^{2-} is much larger than that of S^{2-}, so substituting S with Se will cause the expansion of lattice; Anion is nonmagnetic, so substituting S does not change spin degrees of freedom greatly. The experimental results show that, with increasing Se content, ferrimagnetic transition temperature decreases, irreversibility between ZFC and FC magnetization increases, both the step-like transition and the cusp-like anomaly in magnetization shift to lower temperatures and disappear gradually, magnetoresistance increases. We also investigate the magnetic properties of $FeCr_2S_4$ sample under different hydrostatic pressure. All the effects caused by applying hydrostatic pressure are in accord with the effects caused by Se substituting.

The polycrystalline samples of $FeCr_2Se_xS_{4-x}$ $(0 \le x \le 1)$ were prepared by the solid-state reaction method [12]. The structure was characterized by X-ray diffraction (XRD) measurement. The magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer. The application of pressure was performed in a pressure cell (easyLab Mcell). The resistivity was measured using a standard four-probe method in physical properties measurement system (PPMS).

The XRD patterns shown in Fig. 1 reveal that all samples have

* Corresponding author.
E-mail address: zryang@issp.ac.cn (Z.R. Yang).

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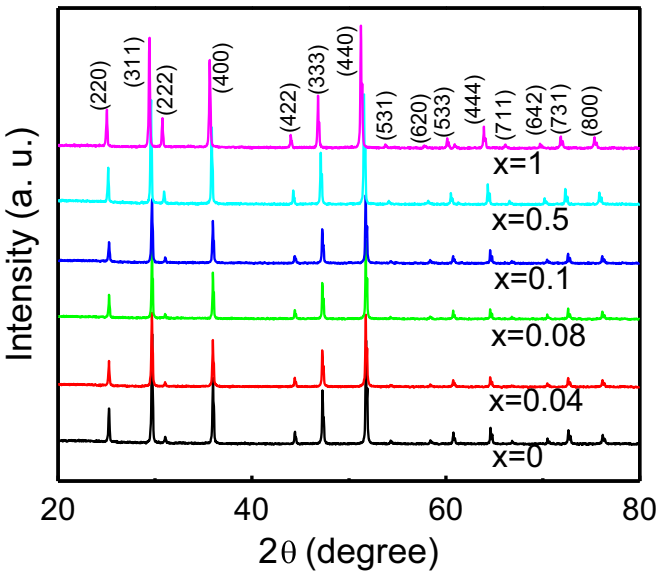

Fig. 1. XRD patterns for $FeCr_2Se_xS_{4-x}$ (x=0–1).

Table 1
Characteristic parameter of $FeCr_2Se_xS_{4-x}$.

x	0	0.04	0.08	0.1	0.5	1
a(Å)	9.9861	9.9881	9.9884	9.9904	10.0235	10.0802
T_c(K)	168	168	167	165	158	147
T_p(K)	69	66	63			
T_{oo}(K)	9.1	7.7	6.2			

single phase with spinel structure. The lattice parameter was computed by means of a weighted least-squares fitting, as shown in Table 1. With increasing selenium content, the lattice parameter increases, implying that selenium atoms substitute sulfur atoms effectively.

Fig. 2 displays the temperature dependence of magnetization in zero-field-cooled (ZFC) and field-cooled (FC) processes with H=50 Oe for $FeCr_2Se_xS_{4-x}$ ($0 \le x \le 1$) samples. Curie Temperature T_c is defined as the temperature corresponding to maximum of $|dM/dT|$. For $FeCr_2S_4$ sample, as shown in Fig. 2(a), with decreasing temperature, the magnetization increases sharply around T_c due to paramagnetic-ferrimagnetic transition. With further decreasing temperature, it shows irreversibility between ZFC and FC magnetization. A cusp-like anomaly in FC magnetization appears around $T_p \sim 70$ K. A step-like decrease (increase) in the ZFC (FC) magnetization with cooling appears at $T_{oo} \sim 9$ K, which is related to orbital-ordering transition.

For $x < 0.1$ samples, with increasing x, T_c decreases gradually as shown in Table 1, both the cusp-like anomaly and the step-like transition shift to lower temperatures as seen from Fig. 2(a), (b), (c) and Table 1. When x is increased further ($x \ge 0.1$), T_c continues to decrease, the discrepancy between ZFC and FC magnetization becomes more and more distinct, both cusp-like anomaly and step-like transition disappear gradually, as seen from Fig. 2(d), (e), (f). It can be known from Table 1 that, Se content has much more great influence on T_p and T_{oo} than on T_c. It was reported that there are structural anomalies around T_p and T_{oo} [10], reflecting that these two characteristic temperatures are strongly correlated with lattice degrees of freedom. Thus the change of lattice degrees of freedom influence T_p and T_{oo} greatly.

Previously, the irreversible behavior between ZFC and FC magnetization in $FeCr_2S_4$ has been attributed to large magnetic anisotropy by the study of coercitivity [16]. The large coercitivity in $FeCr_2S_4$ is a reflection of the large magnetic anisotropy. The coercitivity decreases with increasing temperature. Since no magnetic field is applied in ZFC case while cooling sample, the magnetic domains are locked in random directions. When a small field is applied at the lowest temperature, the magnetization is small due to a high coercitivity. During FC process, sample is cooled in the presence of a magnetic field, the magnetic domains will be locked in a particular direction depending on the strength of the applied field, so FC magnetization is larger than ZFC magnetization and irreversibility occurs. We selected x=1 sample to measure magnetic hysteresis loop at different temperatures. The coercitivity of this sample is much larger than that of $FeCr_2S_4$ sample [16], so irreversibility between ZFC and FC magnetization in this sample is more obvious than that in $FeCr_2S_4$ sample.

In $FeCr_2S_4$, antiferromagnetic Fe–S–Cr superexchange is the

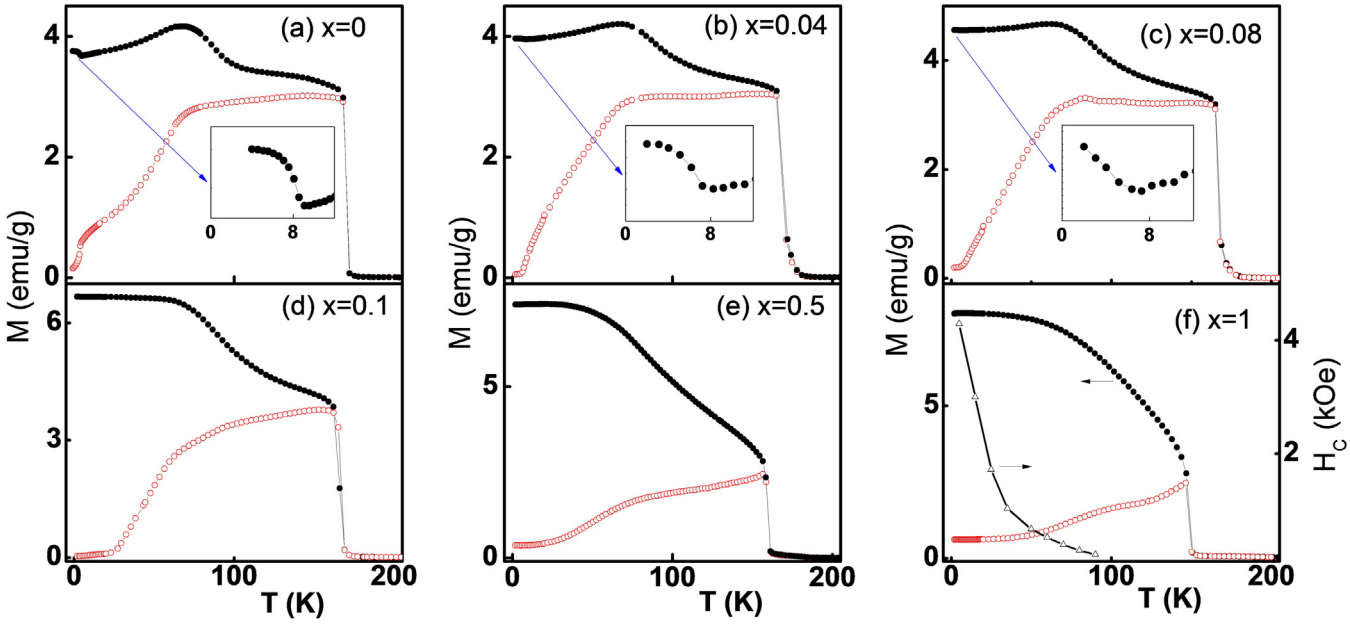

Fig. 2. ZFC (close black circle) and FC (open red circle) magnetization at 50 Oe. The inset of (a)–(c) is the magnification of FC at low temperature. The right scale of (*f*) is the coercitivity of x=1 sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

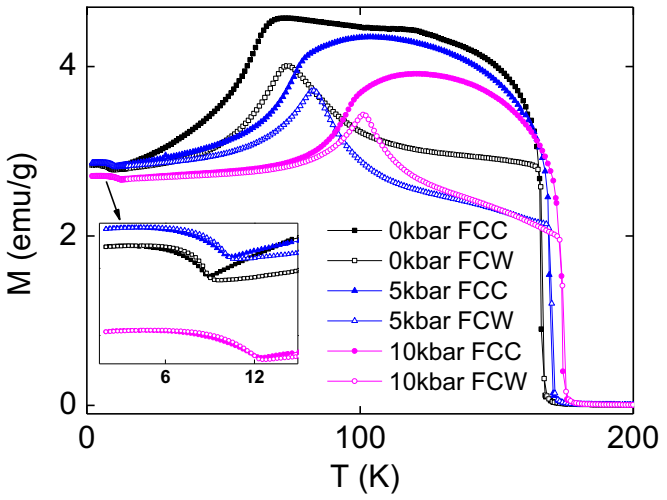

Fig. 3. FCC (close symbols) and FCW (open symbols) magnetization at 50 Oe under different hydrostatic pressure for $FeCr_2S_4$ sample. The inset is the magnification at low temperature.

dominating exchange interaction [17]. T_c is mainly determined by this interaction. From the fact that T_c decreases with increasing Se content, we can deduced that Se substitution can weaken Fe–S–Cr superexchange.

To further confirm that Se substitution effect on magnetic properties is equivalent to pressure effect, we measured the temperature dependence of magnetization in FCC (field-cooled and measure during cooling) and FCW (field-cooled and measure during warming) process under different hydrostatic pressures for $FeCr_2S_4$ sample, as shown in Fig. 3. Similar with the irreversibility between ZFC and FC magnetization, the irreversibility between FCC and FCW magnetization is also associated with magnetic anisotropy [18]. It has been explained qualitatively by considering spin-reorientation due to the increase of magnetic anisotropy upon cooling [18]. When the hydrostatic pressure increases, T_c, T_p (the temperature at which the FCW magnetization shows a cusp-like anomaly) and T_{oo} increases, the irreversibility on magnetization between FCC and FCW decreases. All these effects are in accord with the effects caused by Se substituting.

Fig. 4 gives out the temperature dependence of resistivity (ρ) under 0 T and 5 T and corresponding magnetoresistance (MR=(ρ(0 T)−ρ(5 T))/ρ(0 T)) for $x=0.5$ and $x=1$ samples. The zero-field resistivity first increases with decreasing temperature. After reaching up to a peak near T_c, the resistivity decreases. Upon further cooling, the resistivity increases again. External magnetic field makes the resistivity peak shift to a higher temperature. This is similar to $FeCr_2S_4$ sample [19]. We can also find that ρ increases with increasing Se content. This is in accord with the result under different hydrostatic pressure [20]. For $x=0.5$ and $x=1$ samples, the maximum of MR is 18% and 22%, respectively. For $FeCr_2S_4$ sample, the maximum of MR is 16% [19]. It can be found that the maximum of MR increases with increasing Se content. For the resistivity at 0 T, at the high temperature range and the low temperature range, the curves of $\ln\rho \sim 1000/T$ can be fitted with the formula $\rho=\rho_0 \exp(E/k_BT)$. The activation energy in these two temperature range is defined as E_H and E_L, respectively. E_H for $x=0.5$ and $x=1$ sample is 56 meV and 72 meV respectively, while E_L is 28 meV and 31 meV respectively.

For $FeCr_2S_4$ sample, E_H and E_L is 47 meV and 26 meV, respectively [19]. The value of E_L for these sample with different Se content is nearly equal, which means the band structure is nearly unchanged. The discrepancy between E_L and E_H is due to the presence of magnetic polarons [19]. With increasing Se content, E_H increases which means magnetic polarons is more stable. The stabilization of magnetic polarons is the main reason why magnetoresistance increases with increasing Se content.

In summary, through Se substituting or hydrostatic pressure, we have modified lattice degree of freedom and studied its influence on magnetic and transport properties of $FeCr_2S_4$. With increasing Se content, T_c decreases, irreversibility between ZFC and FC magnetization increases, both the step-like transition and the cusp-like anomaly in magnetization shift to a low temperature and disappears gradually. All these effects caused by Se substituting are in accord with effects caused by applying hydrostatic pressure. We also found magnetoresistance increases with increasing Se content, and attributed it to the stabilization of magnetic polarons.

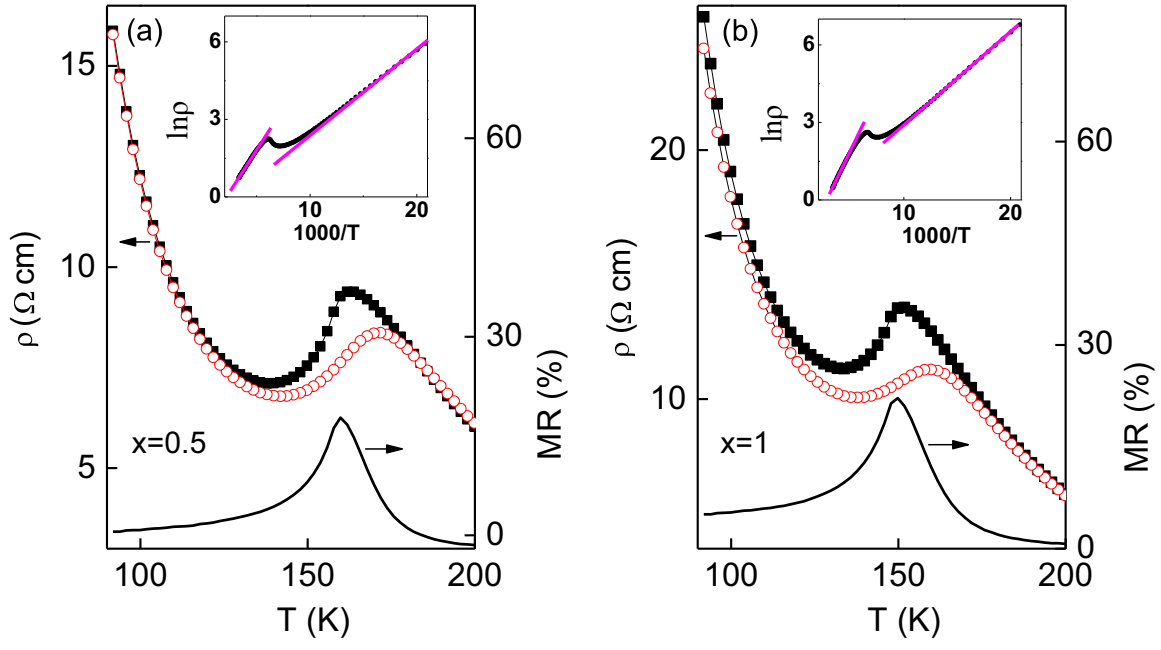

Fig. 4. Temperature dependence of resistivity under 0 T (close black square) and 5 T (open red circle) and corresponding magnetoresistance for (a) $x=0.5$ and (b) $x=1$ samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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