

Colossal magnetoresistance (CMR) effect in (Fe,Cu)Cr₂S₄

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The Colossal magnetoresistance (CMR) effect in Cr-based chalcogenide spinels has been observed. Our results indicate the valence variation of ions in stoichiometric spinel Fe_{1-x}Cu_xCr₂S₄ (x=0, 0.5) is observed. Then, XPS and Moessbauer studies show that Fe²⁺, Fe³⁺ occupy the tetrahedral A-sites. Also, we confirm the formation of the magnetic polaron coupled by short-range magnetic correlation by fitting the resistivity curves. And the decrease of MR is explained by inhibiting the formation of the magnetic polaron.

Key words: colossal magnetoresistance (CMR); Cr-based chalcogenide spinels; magnetic polaron; ferromagnetic semiconductors; triple exchange model

1. INTRODUCTION

Since the colossal magnetoresistance (CMR) effect in hole-doped manganite perovskites epitaxial thin film [1,2] is discovered, special attention has been paid to the transport properties of these compounds, which seems to be explained by the double-exchange (DE) model and Jahn-Teller (JT) distortion [3-6]. However, these understandings cannot be applied to other CMR material such as Cr-based chalcogenide spinel compounds, Fe_{1-x}Cu_xCr₂S₄, since they are chemically, structurally and electronically so different from the manganites [7]. With respect to electrical properties, FeCr₂S₄ (FCS) and Fe_{0.5}Cu_{0.5}Cr₂S₄ (FCCS) show p-type and n-type behavior, respectively, while CuCr₂S₄ is metallic [8].

One of the important issues in the chalcogenide spinel compounds is the valence states of constituent elements. Indeed, the question on the valency of Cu in CuCr₂S₄ has been a long standing problem [8, 9]. If the Cu ion is monovalent in spinels, the valence configurations of the Cr ion in CuCr₂S₄ are expected to be Cu⁺(Cr³⁺Cr⁴⁺)₂S₄, yielding a formal mixed valence of +3.5. The substitution of Cu for Fe leads to a more complex situation with several possible electronic models.

In this paper, magnetic properties and the conduction behavior of Fe_{1-x}Cu_xCr₂S₄ are reported.

2. EXPERIMENT

Synthesis of the polycrystalline Fe_{1-x}Cu_xCr₂S₄ samples was accomplished by the following direct-composition method. High-purity powders of iron (99.9%), copper (99.99%), chromium (99.9%), and sulfur (99.99%) were mixed uniformly according to the stoichiometric ratio and sealed into evacuated quartz tubes. These mixtures was heated at 393K for 12h, at 773K for 24h, and 1273K for 96h, and then cooled down slowly to room temperature at a rate of 10K/h. In order to obtain a homogeneous material, it was necessary to grind the sample after the first firing and press the powder into a pellet before heating it for a second time to 1323K for 99h.

Sample compositions were checked by inductively coupled plasma emission analysis (ICP) and X-ray

photoelectron spectra (XPS). The structure of the samples was confirmed by X-ray diffraction analysis (XRD). Magnetic properties have been studied with a vibrating-sample magnetometer (VSM: Toei Industry 002005). The resistivity measurements were performed using a standard four-probe method under an applied field of 5T. The X-ray photoelectron spectra (XPS) were measured with Quantum-2000 spectrometer with monochromatized Al K_α radiation. The Moessbauer spectra were measured at 80K. The isomer shifts are referred to pure iron metal.

3. RESULTS AND DISCUSSIONS

3.1 Pure phase with spinel structure

Structure and phase purity of FCS (x=0) and FCCS (x=0.5) were examined by XRD measurements, which reveal that both samples are single phased with spinel structure and all observed peaks could be indexed with a cubic cell with a=0.9995nm (FCS), a=0.9991nm (FCCS), and a space group Fd3m.

3.2 Magnetic properties

The ferromagnetic transition temperature for the sample was determined from magnetization data measured in low fields and observed to be 336K for FCCS. The Curie temperature *T_c* is defined as the temperature corresponding to maximum of $|dM/dT|$. The Curie temperature is in satisfactory agreement with previously reported value of 340K [7]. We measured the field dependence of ρ and magnetization at several different fixed temperatures (Fig.1). Due to the saturation of magnetization seen from Fig.1 (a), it is presumed that the magnetic domain wall motion is suppressed at a rather low field. However, the dominant behavior is the large negative MR which does not saturate even at the highest measured fields. Thus it appears that the large MR is not due to only domain wall motion associated with the onset of FM (ferromagnetic) order but something intrinsic for this chalcogenide spinels system. The closer *T* is to *T_c*, the higher *H(T)* saturates.

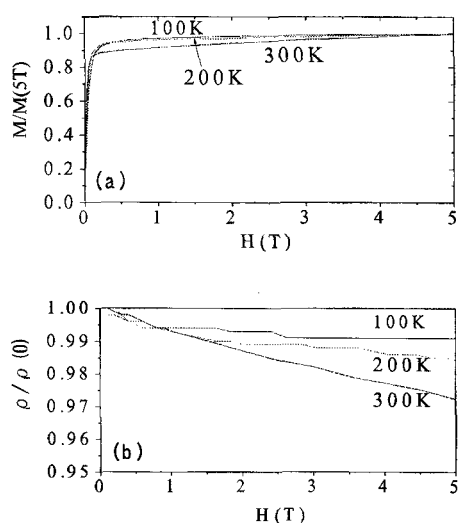


Fig.1 The magnetic field dependence of the magnetization (normalized to the 5T value) at various temperatures for $Fe_{0.5}Cu_{0.5}Cr_2S_4$ (a). The magnetic field dependence of the normalized resistance at various temperatures for $Fe_{0.5}Cu_{0.5}Cr_2S_4$ (b).

3.3 Magnetoresistance

The resistivity ρ and magnetoresistance MR_5 ($=[\rho(0) - \rho(5)]/\rho(0)$), as functions of temperature are shown in Fig.2. Both ρ and MR_5 display a peak near T_c . It is clear that the resistivity shows a point of inflection near T_c , the CMR effect occurs at the temperature range and the semiconductor-metal transition occurs at T_c . The large MR at low temperature (at about 20K) is observed. But, in FCS and FCCS single crystals, this large anomaly at low temperature was not observed [10]. The large change at low temperature has been speculated to arise from the orientation of spontaneous magnetization of each crystal grain and not from the double-exchange (DE) model. These points lead to the assumption that the MR in polycrystalline sample at low temperature is dominated by transport across grain boundaries that is extremely sensitive to an applied magnetic field.

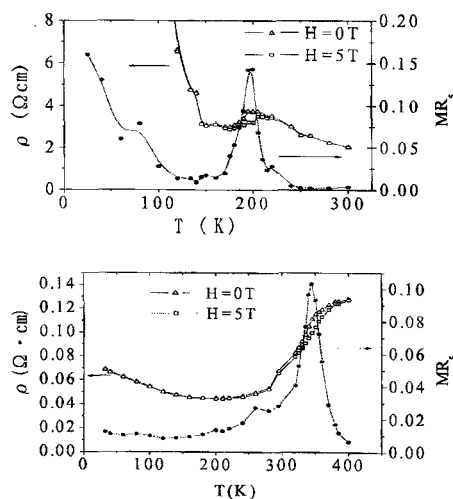


Fig.2 Resistivity and magnetoresistance (MR) versus temperature for $FeCr_2S_4$ (upper) and $Fe_{0.5}Cu_{0.5}Cr_2S_4$ (lower).

3.4 Chemical states

From our results, it can be seen that with the substitution of Cu, the resistivity and magnetoresistance decrease. In order to check the chemical state, the X-ray photoelectron spectra (XPS) has been performed. XPS measurements were carried out only at room temperature, however, no change has been observed in the ferromagnetic and paramagnetic states on sulfides, so the results are expected also the represented the low temperature state. [11]

All samples in this study were found to contain only divalent S.

One of the most striking results of our study is that the Cu 3s spectrum consists only of a single non-splitting line (Binding energy: 932.3eV), which indicates the diamagnetic $3d^{10}$ configuration of the Cu ions in FCCS. A similar conclusion was drawn in [12] by comparing the Cu 2p spectra of the $Fe_{1-x}Cu_xCr_2S_4$ crystals with several copper oxides. It is worth noticing, however, that the typical features of the 2p spectra for the monovalent and divalent copper ions in oxides [13] were not observed in copper chalcogenides. We believe that our finding directly confirms the monovalent copper in FCCS.

The valence distribution for Fe and Cr in the range $0 \leq x \leq 0.5$ has been supposed to be $Fe_{1-2x}^{2+}Fe_x^{3+}Cu_x^{1+}Cr_2^{3+}S_4^{2-}$ [14]. However, our results disagree with this model. The quantitative results and parameters of the fit (Fe2p) are listed in Table.1. Even from $x=0$, about 10% of the iron atoms are in the Fe^{3+} , and the remaining 90% are Fe^{2+} . For $x=0.5$, equal amounts of Fe^{2+} and Fe^{3+} exists.

And it is concluded that the chromium presented in these samples is mainly in Cr^{3+} valence state and a portion of the Cr^{2+} , Cr^{4+} is very small.

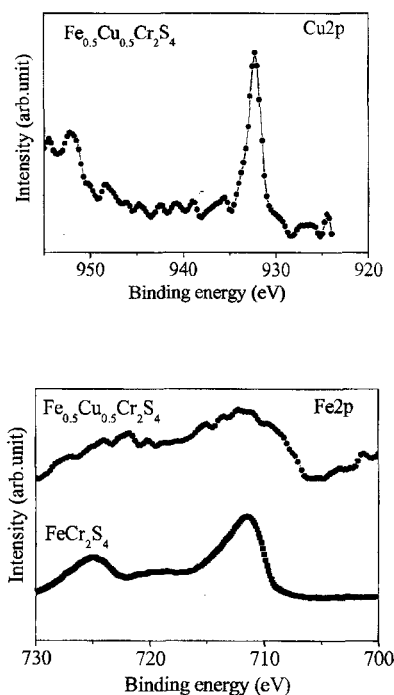


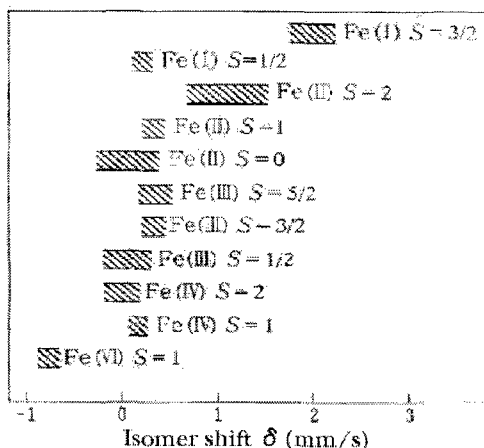
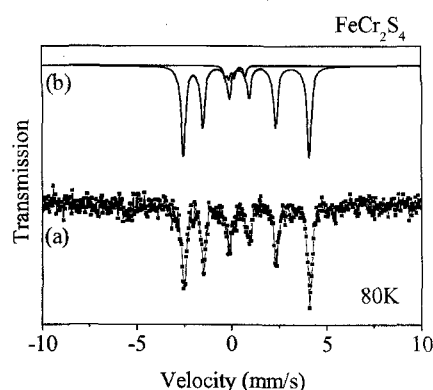
Fig.3 Intensity of Cu2p (upper), Fe2p (lower) peak of $FeCr_2S_4$ and $Fe_{0.5}Cu_{0.5}Cr_2S_4$

Table.1 XPS data from multiplet fitting of Fe2p spectra for FeCr_2S_4 and $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{S}_4$

Sample	Fe2p(3/2)	Atomic	Oxidation state
	BE(eV)	percentage ^a (%)	assignment
FeCr_2S_4	711.32	88.4	+2
	714.74	11.6	+3
$\text{Fe}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{S}_4$	710.4	21.8	+2
	713.82	28.2	+3

^a Percentage of the fitted peak areas of each valence component vs. the whole area of spectrum

The valence distribution for Fe (FCS) is in accordance with our experimental data of Moessbauer spectra analysis. Isomer shift δ for the valence distribution for Fe is listed in Fig.4 [15, 16]. The Moessbauer spectra of FCS were measured at 80K (Fig.5). Moessbauer studies show that there is little deviation from cubic symmetry at the tetrahedral A-sites that are occupied by Fe. The evidence for this conclusion is the appearance of about zero quadrupole splitting. The spectra are well resolved two Zeeman sextets from Fe^{2+} ($S=2$) and Fe^{3+} ($S=5/2$). And it is found that there is not a mixed valence of Cr in FCS. Table.2 shows intensity of the parameters used for the calculations of the spectra in Fig.5.

Fig. 4 Isomer shift δ for the valence distribution for FeFig.5 The Moessbauer spectra of FeCr_2S_4 (a)The observed spectrum. (b)The calculated spectrum. Positions of Zeeman sextets from Fe^{2+} and Fe^{3+} are shown.Table.2 Isomer shift δ and Intensity of the spectra for FeCr_2S_4

	Fe(+2)	Fe(+3)
Isomer shift δ (mm/s)	0.61	0.14
Quadrupole splitting	0.38	0.39
$1/2eQV_{zz}$ (mm/s)		
Intensity (%)	90.6	9.4

As a conduction mechanism, Palmer and Greaves [17] proposed a triple-exchange model for $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($x \leq 0.5$). In this model the electrical conduction is established via hopping between Fe^{2+} and Fe^{3+} . Substituting Fe with Cu empties the $\text{Fe}^{2+} e_g$ spin-up band and thus, destroys the band splitting, which explains the strong decrease of the resistivity by a triple exchange model.

3.5 The conduction mechanism

As is known, for semiconductorlike transport behavior, there are four models; (a) 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; (b) nearest-neighbor hopping of small polarons, $\rho = \rho_0 T^{1/2} \exp(E_{SP}/k_B T)$; (c) large polaron hopping model, $\rho = \rho_0 T \exp(E_{LP}/k_B T)$; (d) if the carriers are localized by random potential fluctuations, Mott's Variable-range hopping (VRH) expression $\rho = \rho_0 \exp(T_0/T)^{1/4}$ is appropriate. Thus in order to understand the transport mechanism in the $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ system, it is necessary to fit the resistivity curves based on these four descriptions. Figure.6 and 7 show the zero-field resistivity curves replotted as $\ln \rho - 1/T$, $\ln(\rho/T^{1/2}) - 1/T$, $\ln(\rho/T) - 1/T$, $\ln \rho - 1/T^{1/4}$ for FCS and FCCS, respectively. For both samples, the curve of $\ln \rho$ versus $1000/T$ is linear both at $T > T_c$ and at temperature far below T_c , indicating a semiconductorlike behavior in two regions. The activation energy E obtained from the fits to $\rho = \rho_0 \exp(E/k_B T)$ reads $E_H = 35.0 \text{ meV}$ and $E_L = 11.9 \text{ meV}$, respectively. The discrepancy between E_L and E_H for FeCr_2S_4 has been discussed in detail and has been attributed to magnetic-polaron conduction [18]. As we know, a magnetic polaron is a carrier coupled by short-range magnetic correlation within a magnetic cluster at temperatures above T_c . This magnetic polaron may be the small quantity of the Fe^{3+} ions (3.4)

Accordingly, the effective mass of a magnetic polaron increases greatly with respect to that of a naked carrier, and the magnetic polaron has a lower mobility and requires a higher activated energy. The formation of a magnetic polaron will become impossible if the system is in an ideal ferromagnetic or ferrimagnetic order, which explains the rapid fall off in resistivity observed near T_c . Likewise, an external magnetic field will increase the magnetic order and inhibit the formation of the magnetic polaron, thus CMR occurs [19-20].

As can be seen from Fig.6, for FCS, the resistivity can be described by the VRH expression at low temperature range, and can be better fitted by small polaron hopping conduction at high temperature range, respectively. For FCCS (Fig.7), the resistivity could be well described by VRH at high temperature range.

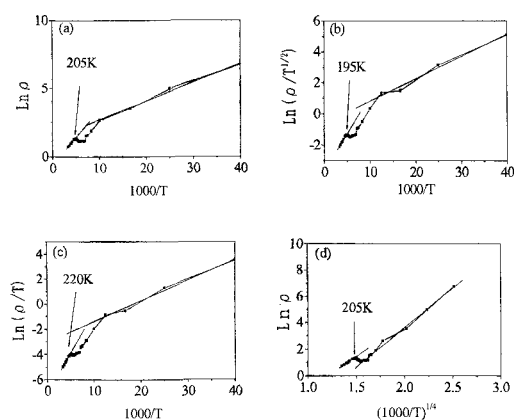


Fig.6 Zero-field resistivity curves for $FeCr_2S_4$. The solid lines are the linear curves.

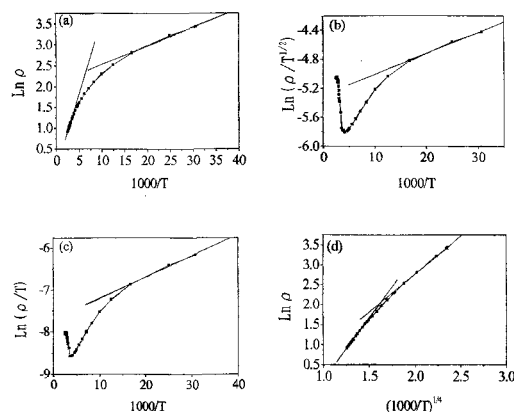


Fig.7 Zero-field resistivity curves for $Fe_{0.5}Cu_{0.5}Cr_2S_4$. The solid lines are the linear curves.

At lower temperatures, the thermal energy is not great enough to allow electrons to hop to their nearest neighbors. In this case it is more favorable for the electrons to hop farther to find a smaller potential difference. At high temperature, because of the increase of phonon energy, nearest-neighbor hopping can contribute significantly to the transport. At temperature above T_c , the presence of magnetic disorder will influence the conduction, which leads to the carrier further localization. Thus the carrier at $T > T_c$ become more localized. Then nearest-neighbor hopping process with high activation energy may transform into VRH when the available phonon energy is so small as to make longer-ranged hops occur. As a consequence, VRH dominates the conduction at the temperature above T_c .

The results suggest that the transport mechanism changes from small polaron transport to VRH with substituting Cu. With substituting Cu, accompanying the introduction of Coulomb potential fluctuations, the contribution of magnetic disorder becomes less important; then the carrier may be mainly localized by the Coulomb potential fluctuation for FCCS. Naturally, it can be deduced that an applied field may have less influence on the localization of carrier upon Cu substitution; thus the value of the MR decreases.

4. CONCLUSIONS

In conclusion, the large MR at low temperature in polycrystalline FCS and FCCS occur in the orientation of spontaneous magnetization of each crystal grain. Secondly, XPS and Moessbauer studies show that there is a mixed valence of Fe^{2+} , Fe^{3+} in FCS. Substituting Cu empties the $Fe^{2+} e_g$ spin-up state, which explains the decrease of the resistivity by triple exchange model. Next, we confirm the formation of the magnetic polaron (a carrier coupled by short-range magnetic correlation) in $Fe_{1-x}Cu_xCr_2S_4$. And the decrease of MR is explained by the decrease of the effect of magnetic disorder and inhibiting the formation of the magnetic polaron. But the formation of the magnetic polaron may inhibit triple exchange model. Since the origin of this unusual feature is still unclear, further investigations in $Fe_{1-x}Cu_xCr_2S_4$ are needed and are a promising challenge for future.

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References

- [1] S. Jin, T. H. Tiefel, M. McCormack, R.A Fastnacht, R. Ramesh, L. H. Chen, *Science* 264 (1994) 413.
- [2] M. McCormack, S. Jin, T.H. Tiefel, R.M. Fleming, J. M. Philips, *Appl. Phys. Lett.* 64 (1994) 3045.
- [3] C.Zener, *Phys. Rev.* 82 (1251) 403.
- [4] P. G. de Gennes, *Phys. Rev.* 118 (1960) 141.
- [5] A. J. Millis, P. M. Littlewood, B. I. Shraiman, *Phys. Rev.* 118 (1960) 5144.
- [6] G. M. Zhao, M. B. Hunt, H. Keller, *Phys. Rev. Lett.* 78 (1997) 15397
- [7] A. P. Ramirez, R. J. Cava, J. Krajewski, *Nature* 386 (1997) 156
- [8] F. K. Lotgering, R. P. van Staple, G. H. A. M. van der Stehen, J. S. van Wieringen, *J. Phys. Chem. Sol.* 30 (1969) 799
- [9] F. K. Lotgering, R. P. van Staple, *Solid State Commun.* 5 (1967) 143
- [10] V. Fritsch, J. Deisenhofer, A. Loidl, *Phys. Rev. B* 67 (2003) 144419
- [11] M.Lenglet, J. Durr, *Chem. Phys. Lett.* 145 (1988) 139
- [12] K. Ando, *Sol. State Comm.* 36 (1980) 165
- [13] K. S. Kim, *J. Electron Spectr.* 3 (1974) 217
- [14] F. K. Lotgering, R. P. van Staple, *J. Phys. Chem. Slids* 30 (1969) 799
- [15] L. R. Walker, G. K. Wertherim and V. Jaccarino, *Phys. Rev. Lett.* 6 (1961) 98
- [16] J. Danon, "Applications of the Moessbauer effect in Chemistry and Solid-State Physics", *Int. Atom. Ener. Agency (Vienna, 1966)* 89
- [17] H. M. Palmer, C. Greaves, *J. Mater. Chem.* 9 (1999) 637
- [18] Z. R. Yang, S. Tan, and Y. H. Zhang, *Phys. Rev. B* 62 (2000) 13872
- [19] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, *Physica B* 155 (1989) 362
- [20] Mark Rubinstein, D. J. Gillespie, John E. Snyder, and Terry M. Tritt, *Phys. Rev. B* 56 (1997) 5412