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Evidence for a non-double-exchange mechanism in $FeCr_2S_4$

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That there is no valence variation of Fe and Cr ions in stoichiometric spinel $FeCr_2S_4$ is directly proved by the experiments of powder x-ray diffraction, transmission electron microscopy, Mössbauer spectrum, x-ray photoelectron spectroscopy, and electron-spin resonance. These results construct strong evidence of the non-double-exchange mechanism in $FeCr_2S_4$ material with the colossal magnetoresistance effect.

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Since the discovery of colossal magnetoresistance (CMR) phenomenon in $La_{1-x}Ca_xMnO_3$ epitaxial thin films,[1,2] the CMR effect has been widely observed in the polycrystals,[3,4] the single crystals[5–7] and the epitaxial thin films[1,2,8,9] of $La_{1-x}M_xMnO_3$ ($M=$Ca, Sr, or Ba). This conductive behavior is described by the double-exchange (DE) model,[10] which suggests that the conductivity is decided by the hopping of the electrons between hetrovalent Mn^{3+}/Mn^{4+} pairs.[11] Very recently, the CMR effect in $FeCr_2S_4$ (Ref. 12) and $Tl_2Mn_2O_7$ (Refs. 13, 14) has been reported, and it is suggested that the conducting mechanism in these materials may not be caused by the DE of the carriers because there is not valence variation in the stoichiometric spinel $FeCr_2S_4$ or Mn^{3+}/Mn^{4+} mixture in $Tl_2Mn_2O_7$. But no experimental evidence for $FeCr_2S_4$ were provided to support this conclusion in the original paper.[12] Theoretically, the Fe atom can be substituted by the Cr atom in spinel $FeCr_2S_4$ and this substitution will cause the valence variation. Therefore, the DE model may also be effective in stoichiometric spinel $FeCr_2S_4$. The purpose of this paper is to find experimental evidence in which there is the non-double-exchange mechanism in $FeCr_2S_4$. Our experimental results indicate indeed that there is not site exchanging between Fe atoms and Cr atoms, and there is not the Fe mixed valence.

The polycrystalline $FeCr_2S_4$ samples are prepared by the standard solid-state synthesis method.[12] High-purity powders of iron (99.9%), chromium (99.9%) and sulphur (99.9%) are mixed uniformly in a 6 g batche according to the stoichiometric ratio 1:2:4 (by atoms) and sealed into an evacuated quartz tube. The tube is slowly heated from 450 to 850 °C with a step of 50 °C over a period of one week. The initially sintered samples are ground and pressed into round or square-shaped pellets (10 mm diameter, 4 mm thick or $20\times5\times4\ \mathrm{mm}^3$). The pellets are resealed in an evacuated quartz tube and heated up to 950 °C and then remain at the temperature for three days.

The structure of the samples is detected by powder x-ray diffraction (XRD) as shown in Fig. 1, which exhibits the pure phase of spinel $FeCr_2S_4$. The crystal structure at room temperature is determined by Rietveld method.[15] It is found that the crystal belongs to a normal structure of the cubic system. The space group is $Fd3m$. The lattice parameter is $a=0.99941(7)$ nm. Fe, Cr, and S atoms occupy the sites $8a$ (1/8,1/8,1/8), $16d$ (1/2,1/2,1/2), and $32e$ [0.2592(1), 0.2592(1), 0.2592(1)], respectively. The final R_b factor is 0.0416. These data reveal that there is not replacement between Fe and Cr atoms in $FeCr_2S_4$. In order to examine whether there is the structural phase transition in $FeCr_2S_4$, the patterns of XRD from 77 to 300 K at an interval of 5 K are examined. All the peaks and relative intensity have no change. Figures 1(a) and 1(b) only give the XRD patterns at 300 and 160 K, respectively. The reason for choosing these two patterns is that $FeCr_2S_4$ is in a ferrimagnetic phase at 160 K and in a paramagnetic phase at 300 K.

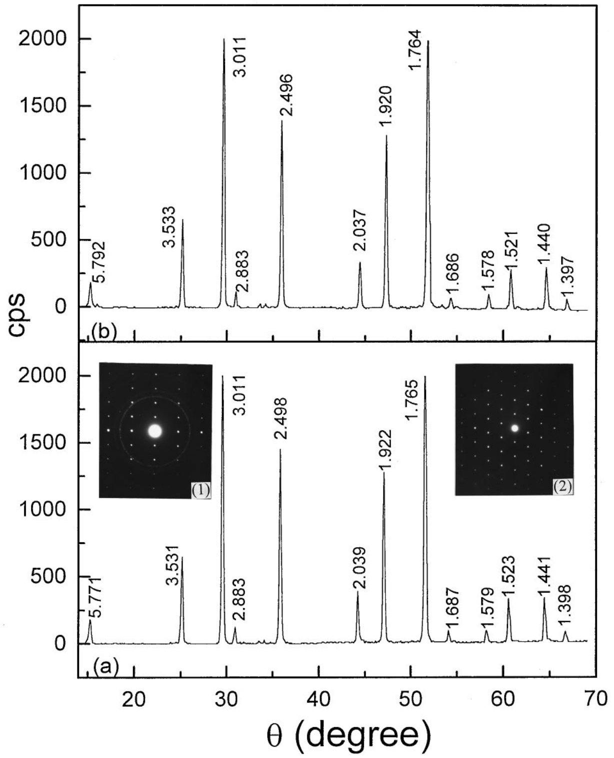

FIG. 1. XRD patterns of the $FeCr_2S_4$ sample at room and low temperatures (a) 300 K; (b) 160 K; Inset (1) and (2) of Fig. 1 show the selected area electron diffraction (SAED) patterns of (211) and (110) for $FeCr_2S_4$, respectively.

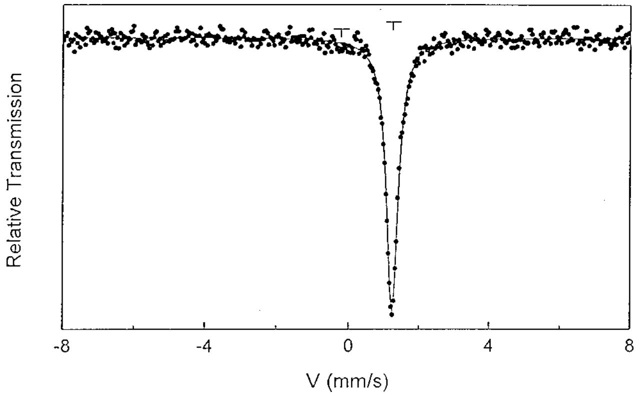

FIG. 2. Mössbauer spectra of $FeCr_2S_4$ at room temperature.

The patterns of selected area electron diffraction (SAED) in $FeCr_2S_4$ display the reflecting planes of (211) and (110). This is in accordance with the data of XRD analysis. When the sample is tilted from [211] [the inset (1) of Fig. 1] to [110] [the inset (2) of Fig. 1], SAED patterns show that there are not any additional spots. These results confirm again that the structure of the compound $FeCr_2S_4$ is a normal spinel one.

If Fe atoms substitute Cr atoms, it must lead to a valence change of Fe and Cr ion. Therefore, the bonding valence of Fe and Cr ions in $FeCr_2S_4$ are studied by the following three experiments:

(1) Figure 2 represents the room-temperature experimental Mössbauer spectrum for $FeCr_2S_4$ as well as its fitting curves. Clearly, only one absorbing peak appears here, with an isomer shift (IS) and a quadruple splitting (QS) being ~1.2 mm/s and 0, respectively. From data analysis, it is concluded that the iron presented in this sample is mainly in Fe^{2+} valence state (99.5%) and a portion of the Fe^{3+} valence state is below 0.5%. This indicates that over 99.5% iron occupy the tetrahedral sites in the form of Fe^{2+}, and the very small quantity of the Fe^{3+} ions (<0.5%) in the lattice could not give rise to the variation of the transport properties.

(2) The x-ray photoemission spectroscopy (XPS) spectra of Fe $2p_{3/2}$ and Cr $2p_{3/2}$ core levels are shown in Figs. 3(a) and 3(b). The sharp peaks of Fe $2p_{3/2}$ and Cr $2p_{3/2}$ core levels are located at the position of 707 and 574 eV, respectively. These results indicate that Fe appears in the form of Fe^{2+} and Cr in the form of Cr^{3+} in $FeCr_2S_4$.

(3) The electron-spin resonance (ESR) pattern is recorded at a Bruker model ER-200D-SRC electron-spin resonance with microwave frequency 9.35 GHz. ESR spectrum at room temperature is shown in the inset of Fig. 3(a). According to the method of Bleaney and Ingram,[16] the Lande g factor is calculated to be $g=1.99$, which is very close to the g factor of Fe^{2+} and Cr^{3+}.[17] This also indicates that there are no Fe^{3+} and Cr^{2+} ions in this system.

Combining the experimental results presented above, it is known that the bonding valence of Fe and Cr ions does not change in $FeCr_2S_4$, thus the conducting mechanism in $FeCr_2S_4$ is not the double exchange.

Then what causes the CMR effect and what is the conducting mechanism in $FeCr_2S_4$? Figure 4 shows the temperature dependence of the resistivity (ρ) at three different values of applied field (0, 3 T, 5 T), which is in agreement with the result reported by Ramirez.[12] At zero field, a maximum value of the resistivity (ρ) is observed at $T=170\,\mathrm{K}$. At $T>170\,\mathrm{K}$, $dR/dT<0$. At temperatures between 140 and 170 K, $dR/dT>0$. As seen in the inset (b) of Fig. 4, the zero-field curve of the $\ln \rho$ vs $1000/T$ is linear at $T>170\,\mathrm{K}$ and $T<140\,\mathrm{K}$. These results indicate that the sample exhibits the semiconducting behavior in those two regions. The inset (a) of Fig. 4 shows the zero-field curve of χ-T. The Curie tem-

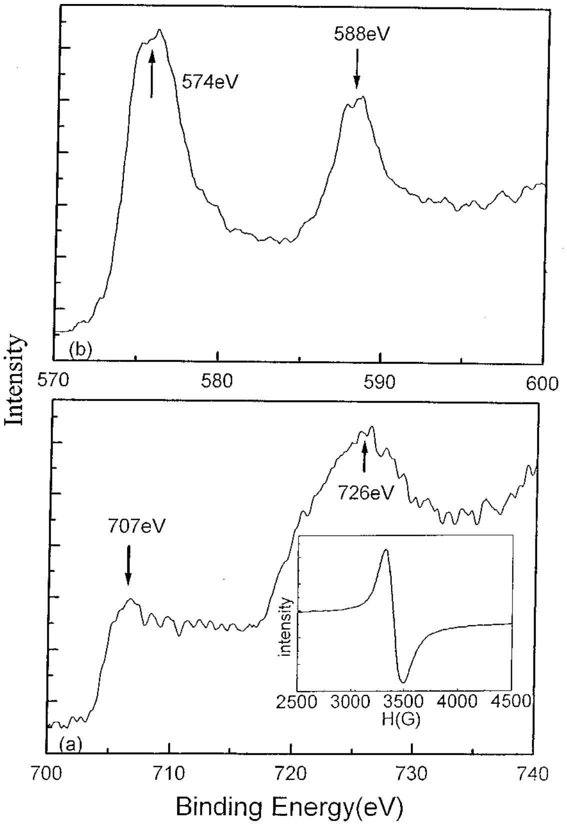

FIG. 3. (a) XPS spectrum of Fe $2p$ core level; (b) XPS spectrum of Cr $2p$ core level; inset (a) shows ESR spectrum for $FeCr_2S_4$ at room temperature.

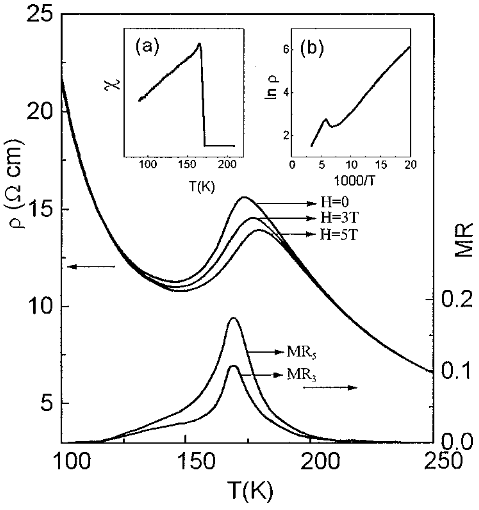

FIG. 4. Resistivity (ρ) and magnetoresistance $[\mathrm{MR}_H=(\rho(0)-\rho(H))/\rho(0)]$, versus temperature for $FeCr_2S_4$; inset (a) shows the zero-field curve of the χ-T; inset (b) shows the zero-field curve of the $\ln \rho$ vs $1000/T$.

perature is $T_C = 170\,\mathrm{K}$. The magnetoresistance $[\mathrm{MR}_H = (\rho(0) - \rho(H))/\rho(0)]$, for $H = 3$ and 5 T, versus temperature are also shown in Fig. 4. The value of MR_5 is comparable to that of the manganite perovskites. When $T < 170\,\mathrm{K}$, the semiconductor-metal transition is attributed to the paramagnetic-ferrimagnetic transition. But it does not change typical *p*-type semiconducting behavior. The CMR effect in $FeCr_2S_4$ is caused by the paramagnetic-ferrimagnetic transition.

In addition, it has been reported that there is a structural phase transition in manganite perovskites $La_{1-x}Ca_xMnO_3$ when it is cooled down. But patterns of XRD from 77 to 300 K at an interval of 5 K for $FeCr_2S_4$ do not change. So such a structural phase transition is not observed in spinel $FeCr_2S_4$ (Fig. 1). This confirms that the conducting mechanism of $FeCr_2S_4$ differs from that of $La_{1-x}Ca_xMnO_3$ completely. So we tend to agree with the mechanism put forward by Haacke *et al.*,[18,19] i.e., the conductivity of $FeCr_2S_4$ originate from the hole conduction in the Fe^{2+} narrow band.

In conclusion, it is found that there is not a mixed valence of Fe^{2+} and Fe^{3+} or Cr^{3+} and Cr^{2+} in $FeCr_2S_4$. The evidence of the non-double-exchange mechanism is experimentally obtained directly. The $FeCr_2S_4$ is a *p*-type semiconductor material with the CMR effect.

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