JOURNAL OF
Materials
CHEMISTRY
Communication

Structural, magnetic and electronic properties of $Fe_{0.5}Cu_{0.5}Cr_2S_4$

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Received 18th November 1998, Accepted 14th December 1998

The crystallographic and magnetic structures of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ have been examined in order to generate a possible mechanism to explain the CMR behaviour of such spinels. Neutron powder diffraction has revealed that the tetrahedrally coordinated Fe^{3+} and Cu^{+} ions are fully ordered, with the magnetic moments of Fe^{3+} ($\mu_{300} = -1.97(5)\ \mu_B$) aligned antiparallel to those of the octahedrally coordinated Cr^{3+} ($\mu_{300} = 1.49(3)\ \mu_B$). The results suggest a new CMR mechanism, which involves exchange on *three* cation centres ('triple exchange') and requires antiferromagnetic coupling of magnetic spins, in contrast to the manganite perovskites for which double-exchange provides a ferromagnetic state.

High magnetic fields can induce dramatic changes in conductivity in certain materials. This phenomenon, colossal magnetoresistance (CMR), has many potential applications, especially for magnetic recording devices, but our understanding remains incomplete. For example, the 'double-exchange' mechanism[1] proposed for the widely studied manganite perovskites cannot be applicable to the first non-oxidic CMR materials,[2] the thiospinels $FeCr_2S_4$ and $Fe_{0.5}Cu_{0.5}Cr_2S_4$, since they are chemically, structurally and electronically so different from the manganites. Significantly, and in contrast to the well characterised p-type manganites, the two sulfide phases also differ electronically, $FeCr_2S_4$ being p-type whilst $Fe_{0.5}Cu_{0.5}Cr_2S_4$ is n-type. To generate a possible CMR mechanism for these materials, we have examined the crystallographic and magnetic structures of the more complex phase, $Fe_{0.5}Cu_{0.5}Cr_2S_4$, and found the Fe^{3+} and Cu^{+} ions to be ordered, with the magnetic moments of Fe^{3+} and Cr^{3+} aligned antiparallel. The results have allowed us to propose a new mechanism for the observed CMR behaviour. It involves exchange on *three* cation centres ('triple exchange'), requires antiferromagnetic coupling of magnetic spins, and points to other chemical compositions for which similar characteristics might be expected.

Thiospinels, AB_2S_4, have a structure comprising a cubic close packed arrangement of S^{2-} ions with an eighth of the tetrahedral holes and half the octahedral holes occupied by the cations (normally A and B, respectively). Thiospinels can contain a wide variety of cations and display great diversity in magnetic properties, including antiferromagnetism (*e.g.* $Li_{0.5}Ga_{0.5}Cr_2S_4$, $T_N = 14$ K),[3] ferromagnetism (*e.g.* $HgCr_2S_4$, $T_c = 36$ K),[4] ferrimagnetism (*e.g.* $CoCr_2S_4$)[5,6] and helimagnetism (*e.g.* $In_{0.5}Ag_{0.5}Cr_2S_4$).[7] $FeCr_2S_4$ and $Fe_{0.5}Cu_{0.5}Cr_2S_4$ are ferrimagnetic semiconductors,[2] and are the Fe^{2+} and Fe^{3+} end members of the solid solution $Fe_{1-x}Cu_xCr_2S_4$ ($0 \leq x \leq 0.5$). Comprehensive electronic transport and magnetisation measurements have confirmed that the Cu is monovalent, and the conductivity involves electronic exchange between Fe^{2+} and Fe^{3+}.[8] Small deviations from stoichiometry may be responsible for the p- and n-type semiconducting properties of $FeCr_2S_4$ and $Fe_{0.5}Cu_{0.5}Cr_2S_4$, respectively.[2] The possible existence of order involving the tetrahedral Fe^{3+} and Cu^{+} ions in $Fe_{0.5}Cu_{0.5}Cr_2S_4$ is clearly relevant to possible conduction mechanisms based on electrons hopping between Fe centres. Indeed, such cationic order has been found in similar thiospinels containing monovalent and trivalent cations and has been inferred in $Fe_{0.5}Cu_{0.5}Cr_2S_4$ by low resolution neutron diffraction[9] and Mössbauer spectroscopy.[8] Here we report a simultaneous crystallographic and magnetic structure refinement of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ based on ambient temperature neutron powder diffraction data.

$Fe_{0.5}Cu_{0.5}Cr_2S_4$ was synthesised from an intimate, stoichiometric mixture of high purity metal powders and S: Fe (99.99%), Cu (99.999%), Cr (99.5%) and S (99.998%). The mixture was pressed into 7 mm pellets and fired in a sealed evacuated quartz tube at 850 °C for 12 hours. After grinding, the process was repeated to give a single phase sample according to X-ray powder diffraction (Siemens D5000, Cu-Kα_1, transmission mode). Ambient temperature neutron powder diffraction data were collected on the POLARIS diffractometer (ISIS, Rutherford Appleton Laboratory) and Rietveld structure refinement (GSAS suite of programs[10]) utilised both the 35° (A) and 145° (C) banks. Hartree–Fock free ion magnetic form factors were adopted for Fe^{3+} and Cr^{3+}.[11]

Magnetisation data (pendulum magnetometer,[12] 0.2 T, Fig. 1(a)) were consistent with a ferrimagnetic transition temperature of 345(5) K, in good agreement with previously published values (340 K[2] and 349(5) K[13]). Preliminary resistivity and magnetoresistance measurements (6 T) at ambient temperature are also in accord with previous data.[2] Vibrating sample magnetometer measurements (Oxford Instrument 12 Tesla VSM) indicated a saturated moment of 1.73 μ_B (at 2 T) (Fig. 1(b)).

Although the X-ray scattering factors of Fe and Cu are very similar, the neutron scattering lengths are sufficiently different (0.954×10^{-12} cm and 0.772×10^{-12} cm, respectively) to allow the investigation of ordering effects. The neutron diffraction pattern clearly shows weak reflections which are symmetry forbidden in the normal spinel space group, $Fd\bar{3}m$, *e.g.* the (200) reflection at approximately 5 Å (Fig. 2(a)). The additional peaks indicate symmetry reduction to $F\bar{4}3m$ and are consistent with long range order on the Fe/Cu sublattice. Structure refinement (Table 1, Fig. 2) confirmed this order, and indicated ferrimagnetic ordering of the Fe^{3+} and Cr^{3+} moments. The ordering splits the sulfur site into two positions: Fe^{3+} coordinates only to S1 whilst Cu^{+} is bonded to S2. Fig. 3 highlights some important aspects of the structure, which contains chains of edge-linked CrS_6 octahedra joined *via* corners to FeS_4 and CuS_4 tetrahedra in a regular fashion. The Fe–S(1) bond distance (Table 1) is less than Cu–S(2), in accordance with the Fe^{3+} and Cu^{+} ionic radii (0.63 Å and 0.74 Å, respectively[14]); the bond angles reveal no significant distortion from the ideal structure. Removal of the constraints to Fe and Cu occupancies indicated a fully ordered structure, within experimental uncertainty.

The magnetic structure contributes significantly to the A bank neutron diffraction profile (Fig. 2(a)), and the peak at 5.75 Å is predominantly magnetic in origin. The refinement unequivocally indicates that the Fe^{3+} and Cr^{3+} moments ($-1.97(5)\ \mu_B$ and $1.49(3)\ \mu_B$, respectively at 300 K) are coupled antiferromag-

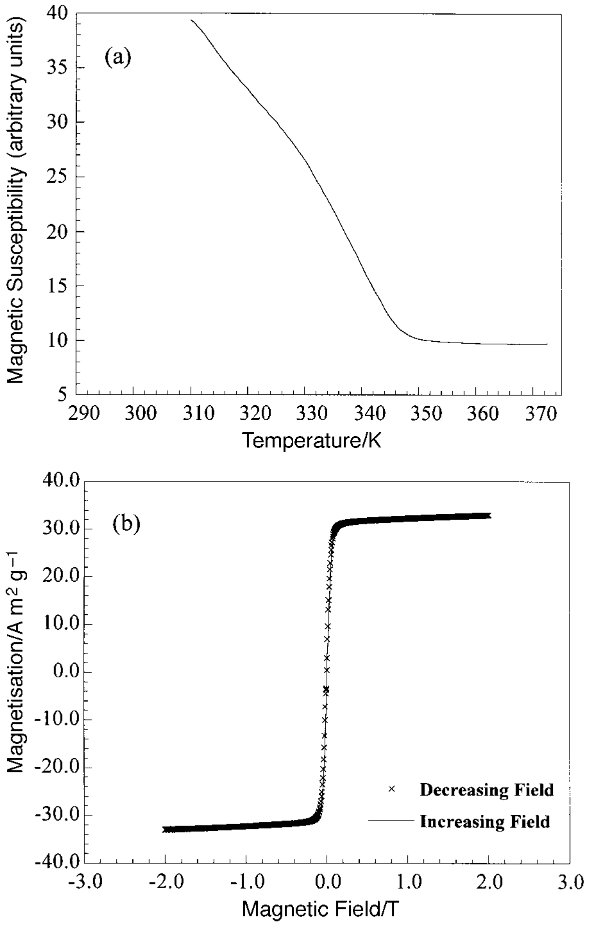

Fig. 1 (a) Magnetic susceptibility *versus* temperature for $Fe_{0.5}Cu_{0.5}Cr_2S_4$. (b) Magnetisation *versus* field (300 K) for $Fe_{0.5}Cu_{0.5}Cr_2S_4$.

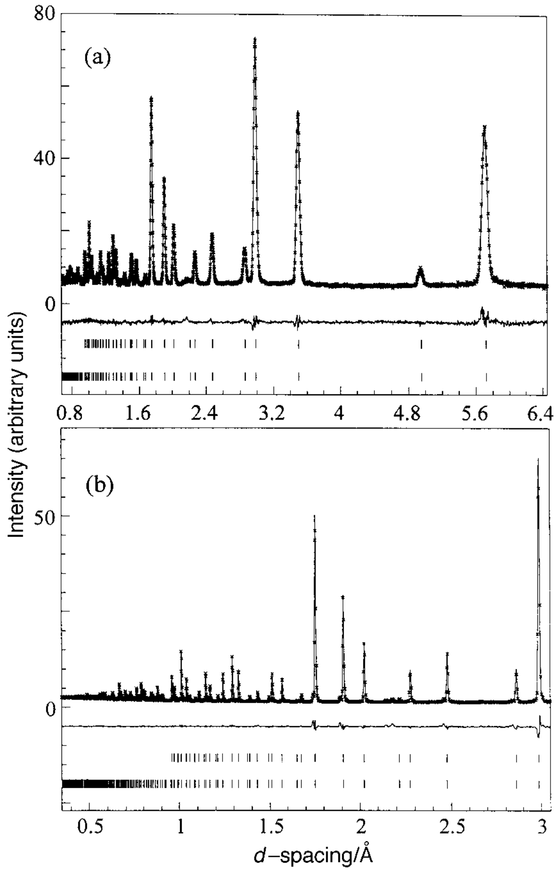

Fig. 2 Ambient temperature neutron powder diffraction profiles for $Fe_{0.5}Cu_{0.5}Cr_2S_4$: (a) 35° bank (A), (b) 145° bank (C). Observed (crosses), calculated and difference profiles are shown together with magnetic (upper tick marks) and nuclear (lower tick marks) reflections. Magnetic contributions were insignificant for $d < 1$ Å.

netically to give an overall magnetic moment of 1.99(8) μ_B per formula unit of $Fe_{0.5}Cu_{0.5}Cr_2S_4$. The reduction in the moments below the free ion values of 5 μ_B and 3 μ_B, respectively, is attributable to thermal effects (the data were collected only 50 K below T_c) and covalence. A more detailed magnetic analysis will be reported subsequently, but it should be noted that at 10 K the Fe^{3+} and Cr^{3+} moments were found to be 3.1(1) μ_B and 2.9(1) μ_B. Thermal effects at this temperature are negligible, and the Cr^{3+} moment is close to the free ion value. The reduced Fe^{3+} moment is now due primarily to covalence, as reported for Fe^{3+} in similar environments (*e.g.* in $KFeS_2$ the moment is 1.9(3)[15]). It should be noted that the direction of the moments cannot be determined from powder data, and the Fe^{3+} and Cr^{3+} moments will be less accurate than implied, since free ion magnetic form factors were adopted even though the bonding, especially for the tetrahedral Fe^{3+}, will have substantial covalent

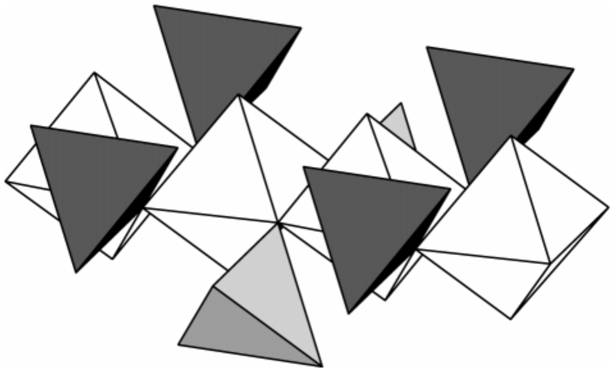

Fig. 3 Structural element of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ showing a chain of CrS_6 octahedra linked to FeS_4 (dark) and CuS_4 (gray) tetrahedra.

Table 1 Refined structural data for $Fe_{0.5}Cu_{0.5}Cr_2S_4$[a]

Atom	Position	x	y	z	$100U/\text{Å}^2$	μ/μ_B
Fe	4a	0	0	0	0.67(2)	−1.97(5)
Cu	4d	0.75	0.75	0.75	1.11(3)	
Cr	16e	0.3749(3)	0.3749(3)	0.3749(3)	0.65(1)	1.49(3)
S1	16e	0.1317(1)	0.1317(1)	0.1317(1)	0.70(4)	
S2	16e	0.6148(1)	0.6148(1)	0.6148(1)	0.61(5)	

[a] $F\bar{4}3m$; $a = 9.9071(1)$ Å. A Bank: $R_{wp} = 3.54\%$, $R_{exp} = 1.68\%$; C Bank: $R_{wp} = 2.63\%$, $R_{exp} = 1.25\%$. Bond distances (Å): Fe–S1 2.261(3)[×4], Cu–S2 2.320(3) [×4], Cr–S1 2.411(3) [×3], Cr–S2 2.382(3) [×3]. Bond angles (°): Cr–S1–Cr 93.1(2) [×3], Cr–S2–Cr 94.8(1) [×3], Fe–S1–Cr 123.21(8).

character. The overall moment therefore agrees satisfactorily with that determined by VSM measurements.

The Zener 'double-exchange' mechanism[1] was originally proposed many years ago to explain the electrical and magnetic properties of manganese perovskites, and now readily rationalises the electrical resistivity changes induced by high magnetic fields. Near T_c, the parallel alignment of the Mn 3d electron spins is facilitated in a magnetic field and leads to a reduced resistance as the mobility of the conduction electrons is no longer impeded by spin disorder. However, there has been no detailed proposal for the mechanism occurring in the thiospinels, and here we propose a new mechanism, which is consistent with the characterisation data now available.

Whereas the magnetic and electrical properties of manganese perovskites are determined by superexchange and double exchange involving 180° Mn–O–Mn σ bonds, a more complex bonding situation exists in thiospinels, and for materials containing octahedral Cr^{3+} ions two exchange interactions normally dominate.[16] Ferromagnetic superexchange occurs on the Cr sublattice *via* 90 °Cr–S–Cr σ/π bonding which links a half-filled $t_{2g}(\pi)$ on one Cr with an empty $e_g(\sigma)$ level on the other. Materials such as $CdCr_2S_4$ are therefore ferromagnetic.[4] In thiospinels with magnetic tetrahedral ions, such as $Fe_{1-x}Cu_xCr_2S_4$, additional coupling links the tetrahedral and octahedral cations. In this case, the Fe–S–Cr angle of 123° gives related σ/π interactions, now providing antiferromagnetic exchange between the half-filled $t_{2g}(\pi)$ Cr orbitals and the half-filled σ Fe orbitals, which are now t_2 owing to the tetrahedral symmetry. We propose that these interactions are fundamental to the cooperative electrical and magnetic transitions in $Fe_{1-x}Cu_xCr_2S_4$.

The electrical behaviour of $Fe_{1-x}Cu_xCr_2S_4$ over the range $0 \leq x \leq 1$ has been reported by Lotgering *et al.*[8] For $0 \leq x \leq 0.5$, the conductivity is dictated by the gradual depopulation of a narrow Fe^{2+} valence band as x increases, providing p-type behaviour for x up to ≈ 0.33 and n-type behaviour for higher values. In accordance with this, the CMR phases $FeCr_2S_4$ and $Fe_{0.5}Cu_{0.5}Cr_2S_4$ were p-type and n-type respectively.[2] Given that the electronic properties are determined by Fe^{2+}–Fe^{3+} exchange, it is important to notice that whereas the Fe magnetic moments are aligned parallel, as in the Mn perovskites, no simple Fe–S–Fe bonding occurs in this structure (Fig. 3), not even in $FeCr_2S_4$, where cation order on the tetrahedral sites is not a factor and all the tetrahedra in Fig. 3 are FeS_4. A simple double exchange mechanism can therefore be dismissed, and electron transfer must occur *via* Fe–S–S–Fe or Fe–S–Cr–S–Fe pathways. We prefer the latter, which invokes only conventional cation–anion covalent interactions. The Cr–S–Fe angle of 123.2° allows the S 3p orbitals simultaneously to form σ-bonds with the octahedral Cr e_g orbitals and π-bonds with the tetrahedral Fe e orbitals, as shown schematically in Fig. 4(a). These interactions are expected to provide facile exchange of the minority spin e electron on Fe^{2+} into the Cr e_g level (to form Cr^{2+}), provided the Cr^{3+} and Fe^{2+} ions are coupled *antiferromagnetically*. A similar process results in transfer from Cr^{2+} to Fe^{3+} to give the required overall Fe^{2+}–Fe^{3+} exchange which is now favoured by exchange interactions on *three* cations with antiferromagnetic order, as shown in Fig. 4(b). This '*triple exchange*' process will produce synergic stabilisation of both the ferrimagnetic spin arrangement and itinerancy of the minority electron; it thereby provides a common rationalisation of the CMR behaviour observed in both p-type $FeCr_2S_4$ and n-type $Fe_{0.5}Cu_{0.5}Cr_2S_4$. It should be noted that the electron transport does not play a major role in the magnetic exchange interactions, and T_c will be largely determined by the conventional superexchange interactions: ferromagnetic Cr^{3+}–Cr^{3+} and antiferromagnetic Fe^{3+}–Cr^{3+}. Nevertheless, it is interesting that for the ferrimagnets ACr_2S_4 (A = Mn, Fe, Co), the T_c for A = Mn (95 K) is lower than that for A = Fe (195 K) and A = Co (240 K),[16] and the suggested mechanism will operate only for A = Fe and Co, where there are respectively one and two minority d electrons on the A cation.

The discovery of CMR behaviour in thiospinel materials has demonstrated a new family of materials capable of displaying this fascinating property. Here several structural features of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ are reported, and a plausible mechanism for the behaviour proposed. The triple exchange mechanism suggests that other ferrimagnetic phases with appropriate electronic configurations may also show large magnetoresistance phenomena, and further investigation of such materials is urgently required.

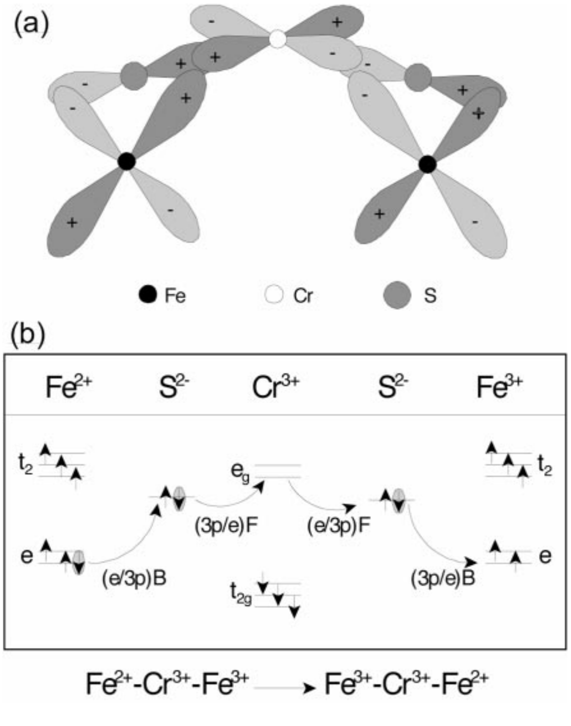

Fig. 4 (a) Schematic representation of the Fe–S(π) and Cr–S(σ) bonding involving a common S 3p orbital with the Fe e and Cr e_g orbitals. The Fe–S–Cr angle is 123.2°. (b) Electron transfer from Fe^{2+} to Fe^{3+} *via* Cr^{3+} with stabilising exchange on all three cations. The mobile electron is circled.

We thank EPSRC for financial support and M. Slaski (VSM), R. Mottram (pendulum balance) and S. Hull (neutron diffraction) for experimental assistance. We also thank R. L. Johnston for useful discussions.

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Communication 8/09032G