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Structural distortions and the insulator to metal transition in $NiCr_{2-x}V_xS_4$

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The insulator to metal transition in $NiCr_{2-x}V_xS_4$ is accompanied by a structural distortion which results in the formation of zigzag chains of cations within the (Cr,V)S_2 layer.

The insulator to metal (ITM) transition[1,2] is of fundamental importance in condensed-matter science and encompasses phenomena as diverse as metallization processes in stars and size-induced transitions in microscopic metal particles.[3] From a chemical perspective, materials which lie close to the metal–insulator divide are of immense interest owing to the unique properties which they frequently exhibit and the opportunities afforded to tailor such properties using chemical control. For example, high temperature superconductivity in the cuprates[4] and the exceptional magnetotransport properties of mixed-manganese oxides[5] are two phenomena which appear to be linked to the proximity of these materials to the metal–insulator boundary.

Our investigations have been directed towards mixed-metal sulfides which lie in this important region of the electronic phase diagram, and have focused on materials which adopt the monoclinic Cr_3S_4 structure. This consists[6] of hexagonally close-packed sulfide layers, between alternate pairs of which, all of the octahedral sites are occupied by cations, giving rise to a unit of stoichiometry CrS_2. Half-occupancy, in an ordered manner, of the remaining octahedral sites between CrS_2 units, leads to a two-dimensional superstructure, with dimensions related to those of the primitive hexagonal unit cell (a_h) by $\surd 3a_h \times a_h$. Progressive substitution of chromium by either divalent vanadium[7] or nickel[8] has been used to effect changes to the physical properties of metallic Cr_3S_4 and the contrasting electronic and magnetic properties of the two resulting non-stoichiometric series, $A_xCr_{3-x}S_4$ (A = V, Ni; $0 \leqslant x \leqslant 1$), may be correlated with differing cation distributions.[8, 9]

This investigation has recently been extended to study the effect of chemical substitution within the MS_2 layers, through preparation of mixed-metal sulfides of general formula $NiCr_{2-x}V_xS_4$ ($0 \leqslant x \leqslant 2$). As the end-member phase $NiCr_2S_4$ is a semiconducting ferrimagnet[10] (T_c = 180 K) whilst NiV_2S_4 appears to be a metallic paramagnet,[11] an ITM transition would be expected in the non-stoichiometric series $NiCr_{2-x}V_xS_4$. The rigid-band model, which successfully accounts for the electronic properties of the stoichiometric end-member phases,[12] predicts all non-stoichiometric materials to be metallic, owing to holes in the t_{2g}-derived band. Here, we report that a critical level of substitution is required before the ITM transition occurs, and that this transition is accompanied by a structural distortion of the MS_2 unit which results in zigzag chains of octahedrally coordinated cations in the fully occupied layer.

All materials were prepared by conventional high temperature techniques. Initial characterisation by analytical electron microscopy, thermogravimetry and powder X-ray diffraction demonstrated that single-phase Cr_3S_4-type materials, with compositions in good agreement with nominal stoichiometries, were produced across the entire series. Transport properties, determined by the four-probe DC technique, clearly indicate semiconducting behaviour in the compositional range $0 \leqslant x \leqslant 0.5$ and metallic behaviour in the range $0.8 \leqslant x \leqslant 2.0$. However, for $NiCr_{1.4}V_{0.6}S_4$, $\rho(T)$ is almost temperature independent down to *ca*. 40 K, below which a slight increase in resistivity is observed leading to ambiguity over the sign of $d\rho/dT$ for materials in the composition range $0.5 < x < 0.8$. This may be the result of the influence of grain boundary resistances arising from the polycrystalline nature of the materials. Nevertheless, it leads to an uncertainty of no more than ±0.15 in the location of the ITM transition. Magnetic susceptibility data suggest that materials with $0 \leqslant x \leqslant 0.6$ exhibit long-range magnetic order. This has been confirmed by low temperature neutron diffraction. Conversely, materials with $0.6 < x \leqslant 2.0$ are paramagnetic, with evidence for spin-glass behaviour at low temperatures. Representative transport and magnetic data for materials in the semiconducting and metallic regions are presented in Fig 1.

Detailed structural studies were carried out by Rietveld analysis using a combination of powder X-ray diffraction and powder neutron diffraction, undertaken at the high-flux reactor, ILL Grenoble. Structural refinements, full details of which will be presented in due course, proceeded smoothly with weighted residuals of 4–7%. In addition to confirming solid-solution behaviour across the whole series, data demonstrate that in the

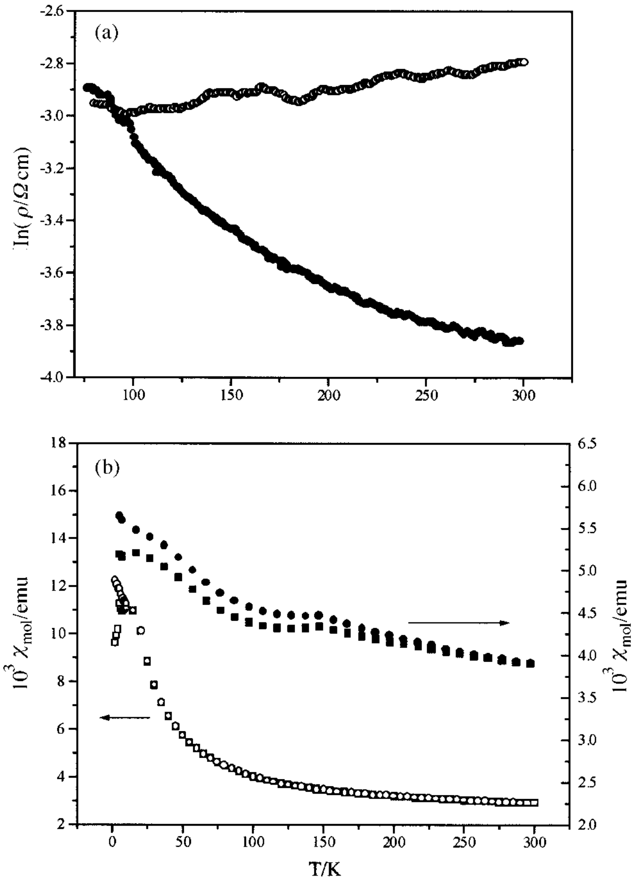
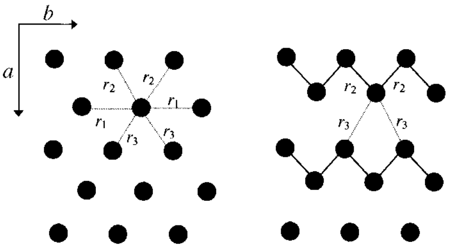


Fig. 1 (a) Resistivity data and (b) magnetic susceptibility data for $NiCrVS_4$ (open points) and $NiCr_{1.6}V_{0.4}S_4$ (solid points). Zero-field-cooled and field-cooled magnetic susceptibilities are denoted by squares and circles respectively.



(a) (b)

Fig. 2 (a) The pseudo hexagonal arrangement of cations in the MS_2 layer in materials with $x \leqslant 0.4$ and (b) the zigzag chains of cations in materials with $x > 0.4$.

non-stoichiometric materials, vanadium substitution occurs exclusively at sites in the fully occupied (MS_2) layer. There was no evidence of ordering of vanadium and chromium cations in the MS_2 layer.

Examination of cation–cation separations reveals that despite the solid-solution behaviour of $NiCr_{2-x}V_xS_4$, vanadium doping induces structural changes in the fully occupied layer, in the region of composition where the change from a magnetically ordered semiconductor to a paramagnetic metal is observed. The geometry of this layer in $NiCr_2S_4$ is shown in Fig. 2(a). Each cation has two neighbours at *ca.* 3.4 Å (r_1) resulting from lattice translation along the *b*-axis, two at a comparatively short distance (r_2) of *ca.* 3.2 Å and two at a slightly greater separation (r_3) of *ca.* 3.6 Å, giving six nearest neighbours in a pseudo-hexagonal arrangement within the layer. Although at low levels of vanadium doping this geometry is little perturbed, above x = 0.4, r_2 begins to decrease and r_3 increase whilst r_1 shows little change across the entire compositional range. Significantly, between x = 0.6 and 0.8, the decrease in r_2 is sufficient to bring it below the critical distance (R_c = 3.09–3.12 Å) proposed by Goodenough[13] for itinerant electron behaviour as a result of direct cation–cation interaction. These changes in cation–cation separations are manifested in an abrupt increase in the ratio r_3/r_2 at compositions with $x > 0.4$ (Fig. 3). This increase corresponds to a change from the pseudo-hexagonal symmetry of the fully occupied layer in $NiCr_2S_4$ to an arrangement in which there are zigzag chains of cations directed parallel to the *b*-axis [Fig. 2(b)]. The separation between cations within the chains (r_2) is considerably shorter than the shortest inter-chain (r_3) distance. These distances are *ca.* 2.9 and *ca.* 3.8 Å respectively, in NiV_2S_4.

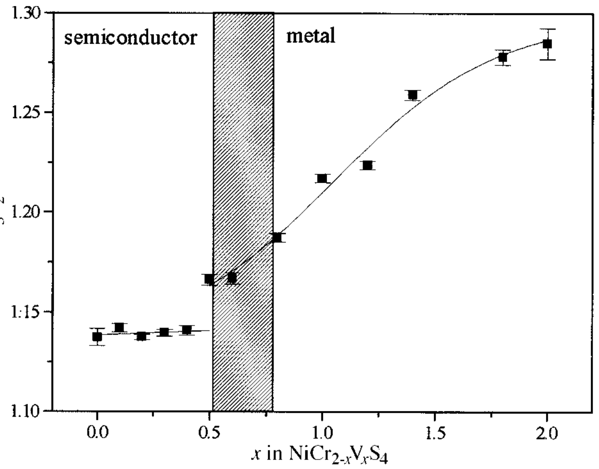


Fig. 3 Correlation between the compositional dependence of the degree of structural distortion within the MS_2 layer and electronic properties. Compositions for which there is ambiguity over the sign of $d\rho/dT$ are indicated by the shaded region.

The data presented here suggest that, contrary to predictions based on changing electron populations, the substitution of Cr^{III} d^3 by V^{III} d^2 is itself insufficient to induce metallization through the introduction of holes into the t_{2g}-derived band. This is a limitation of the approximations of the rigid-band model which ignores the effect of distortions on band structure or changes to band width as substitution proceeds. Using the extended Hückel method, Canadell *et al.*[14] have performed band structure calculations for a series of stoichiometric mixed-metal sulfides containing the MS_2 structural unit. Describing the MS_2 unit in terms of edge-sharing M_2S_6 double octahedral chains, the effect on band structure of distortions which give rise to metal clustering within the MS_2 layer, was investigated. The results demonstrate that when d^2 ions are present in this layer, strong cation–cation interactions within M_2X_6 chains lead to pronounced dispersion of one component of the t_{2g}-derived band and metallic behaviour pertains. The accompanying distortion of the ideal hexagonal array of cations corresponds to a structure in which zigzag clustering of the type depicted in Fig. 2(b) is present. Conversely, calculations reveal that when the t_{2g} manifold is half-filled as in AMo_2S_4, a Peierls distortion within individual M_2S_6 chains gives rise to a diamond clustering within the MS_2 layer and opens a band gap, resulting in semiconducting behaviour. Interestingly, despite the half-filled t_{2g} band, no metal clustering has been observed in materials of the form ACr_2S_4 (A = V, Cr, Ni). This has been attributed to the effects of electron localisation,[14] consistent with the more contracted orbitals of chromium compared to those of molybdenum [R_c(Mo) = 3.97 Å]. With increasing vanadium content in the series, $NiCr_{2-x}V_xS_4$, semiconducting behaviour persists until above some critical composition ($x \approx 0.4$), the MS_2 layer begins to distort resulting in the formation of chains of cations in which the intrachain cation–cation separation becomes lower than the critical distance for direct cation–cation orbital interaction. Of the three components of the t_{2g}-derived band, that in the chain direction, which is predominantly of $d_{x^2-y^2}$ character, shows pronounced dispersion, resulting in metallic behaviour.

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