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Magnetic and transport properties, and electronic structure of the layered chalcogenide AgCrSe_2

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Abstract

We report a detailed study of the magnetic and transport properties of polycrystalline AgCrSe_2 , a layered magnetic chalcogenide that orders antiferromagnetically without frustration at 55 K. The magnetic ordering corresponds to *in-plane* ferromagnetic interactions with antiferromagnetic coupling between the planes. Transport studies suggest a semiconductor that is at the I–M transition boundary in terms of its resistivity, with variable-range hopping behavior at intermediate temperatures and Efros–Shklovskii hopping at low temperatures. At high temperatures (>340 K) the temperature coefficient of resistance turns positive as a result, we believe, of disorder in the silver sub-lattice. First principles density functional calculations of the electronic structure suggest a magnetic insulator ground state, and means to tune the system to ferromagnetic half-metal. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Compounds of the general formula A–M–X where A is a d^{10} metal ion such as Cu^+ , Ag^+ , or Cd^{2+} ; M is magnetic metal ion such as Cr^{III} ; and X is a chalcogenide ion (S^{2-} or Se^{2-}) are the focus of renewed interest because they can display colossal magnetoresistance (CMR) effects as demonstrated in derivatives of CuCr_2S_4 [1]. They could also be magnetic semiconductors with possible applications in spintronics [2] as exemplified by CdCr_2S_4 [3], which has an interesting electronic structure [4].

Based on an examination of electronic structures of a number of different systems displaying the phenomenon of giant/colossal negative magnetoresistance (GMR/CMR) some of us [5] have pointed out that certain key features seem to be shared by the systems including the nature of spin polarization, and of the states that give rise to conductivity. These features include the presence of two

bands, the one a localized band providing the spin polarization and the other a broader conduction band that is importantly, quite distinct in nature (and sometimes, even origin) from the former. Based on this understanding, we have been interested in searching for GMR/CMR systems that combine a first row transition element such as Cr^{III} —to provide the spin polarization—with a broader s band metal such as Ag. Oxides usually suffer problems associated with poor covalency and hence narrow bands. Chalcogenides such as sulphide and selenides are of more natural choice. In our search, we have come across the interesting layered compound AgCrSe_2 , first prepared by Hahn and de Lorent [6] whose properties we inspect in some detail. The system is not ferromagnetic and therefore shows only rather weak coupling (if any) between magnetism and transport. Our studies however permit us to suggest ways in which it could be doped to give a conducting ferromagnet that would perhaps show GMR.

Previous investigation on AgCrSe_2 has shown that it undergoes a continuous, order to disorder structural phase transition with $T_C = 475$ K [7]. The transition is attributed

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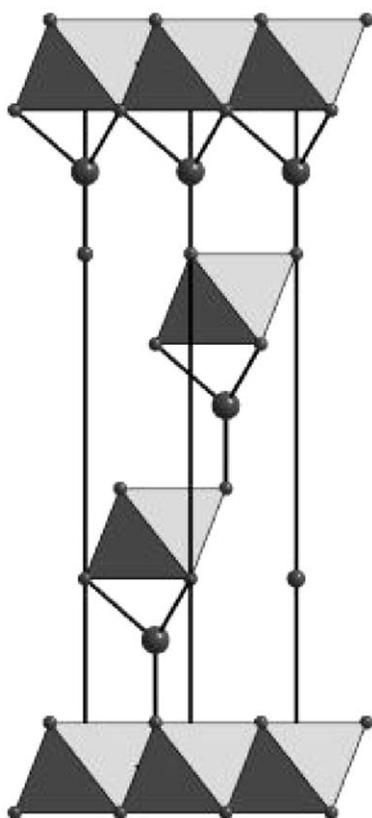


Fig. 1. Crystal structure of $R3m$ AgCrSe_2 showing the Ag atoms as dark grey spheres. The slabs of edge-shared CrSe_6 octahedra extend infinitely in 2D resulting in the structure being layered.

to the disordering of the Ag atoms above T_C , when the space group changes from $R3m$ to $R\bar{3}m$. Studies on magnetic properties of this compound have revealed that it is antiferromagnetic below 50 K with an asymptotic Curie temperature of 72 K [8]. Cr^{III} is ferromagnetic in the layers while the layers themselves couple antiferromagnetically. The coupling constants (using Weiss field model) in the plane and in-between the planes have been reported to be +6 and -1 K, respectively. The ionic conductivity of the compound has been studied by Boukamp and Wiegers [9].

In this communication, we present careful SQUID magnetization and resistivity studies as a function of temperature. We examine these in the light of first-principles electronic structure calculations which have not so far been performed on compounds of this structure type.

2. Experimental

Polycrystalline AgCrSe_2 samples were synthesized in two steps. Elemental Ag, Cr, and Se powders were ground to a homogeneous mixture, pelletized and sealed in a vitreous silica tube under a vacuum of 5×10^{-6} Torr. The tube was

placed in a furnace that was heated to 1073 K at a rate of 10 K/min where it was held for 24 h. The furnace was then switched off. Powder X-ray diffraction patterns show the formation of a pure phase, but the pellets were found crumbled. The powders were therefore reground, pelletized and heat-treated once more in the same fashion.

Powder XRD patterns for Rietveld Refinement were recorded on a 2-axis diffractometer based on a Micro-controlle goniometer and a Rigaku rotating anode X-ray source. Cu $K\beta$ radiation was used in order to span a larger Ewald sphere. The data were treated with the $x\text{ND}$ Rietveld program [10]. Magnetization studies were carried out on a small pellet of the sample using a Quantum Design MPMS SQUID magnetometer. Four-probe electrical transport studies were carried out using Keithley power sources and meters, with electrical contacts being established with silver paint.

3. Computational methods

The crystal structure obtained from Rietveld refinement was used to perform a first-principles electronic structure calculation using the linear muffin tin orbital (LMTO) method within the Atomic Sphere Approximation. The Stuttgart TB-LMTO-ASA program was used for the purpose [11]. Spin polarized calculations were performed within the local spin density approximation (LSDA) using the von Barth–Hedin exchange correlation functional. A detailed description of the LMTO-ASA method, including its applications can be found elsewhere [12]. In these calculations, the partitioning of space into atom-centered and empty spheres is done through an automatic procedure which ensures that the overlap between atomic spheres does not exceed 16%. For the empty spheres, the bases used were 1s orbitals with 2p orbitals being handled through the downfolding technique. The basis sets for the atomic spheres included s, p, and d for Ag (f downfolded); s, p, and d for Cr and s and p (d downfolded) for Se. Scalar-relativistic Kohn Sham equations were solved taking all relativistic effects into account except for the spin–orbit coupling. Three kinds of calculations were performed; without spin-polarization, with ferromagnetic spin polarization, and with a structure wherein the spins were ferromagnetically coupled within the layer, and the layers themselves were antiferromagnetically coupled.

4. Results and discussion

The layered crystal structure of $3r\text{-AgCrSe}_2$ is shown in Fig. 1. The structure can be described as comprising edge-shared CrSe_6 octahedra forming sheets that are separated by tetrahedral Ag ions. Because the AgSe_4 tetrahedra are directed, the room temperature structure is polar (S.G.

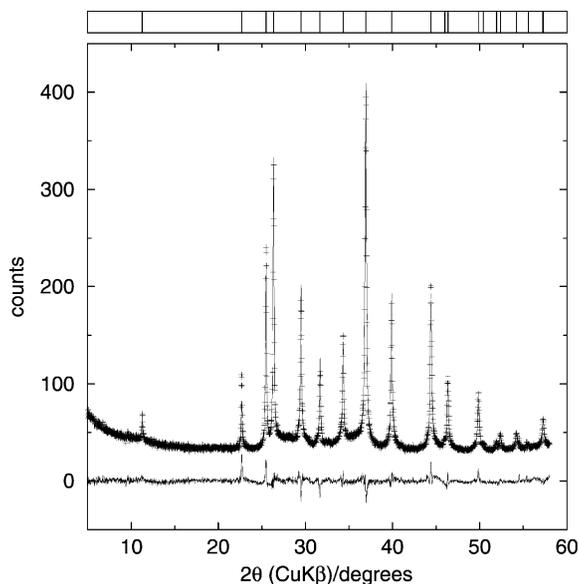


Fig. 2. Powder X-ray diffraction pattern (points) and Rietveld fit (solid line) of AgCrSe_2 . The Rietveld fit made use of the $R3m$ crystal structure. The vertical lines at the top of the figure are the expected peak positions for this structure.

$R3m$). A plot of the Rietveld refined powder X-ray diffraction profile is shown in Fig. 2. The sample is seen to be single phase. The fit is not completely satisfactory as a result of the compound being layered and also due to problems associated with the large *in-plane* motion of Ag^+ [7]. It was not possible to obtain the fit shown in Fig. 2 without allowing the silver atoms to take on large thermal displacement parameters in the plane. Results of the structure refinement are summarized in Table 1 and compared well with the previous report [7].

The temperature dependence of the magnetic susceptibility χ of AgCrSe_2 was recorded on heating in a field of 1.5 T after cooling under zero field. The plot of $1/\chi$ vs. T shown as points in Fig. 3(a) suggests Curie–Weiss behavior (the solid line is the fit) between about 316 and 400 K. From the Curie–Weiss slope, we obtain $\mu_{\text{eff}} = 3.56$ which is slightly quenched from the spin-only value of 3.87 expected for Cr^{III} . The intercept of $1/\chi$ with the T axis is at a positive

Table 1

Results of room temperature Rietveld refinement of the powder X-ray diffraction pattern of AgCrSe_2

Atom	x	y	z (this work)	z [7]
Ag	0	0	0.1507(5)	0.1520
Cr	0	0	0	0
Se ₁	0	0	0.2685(5)	0.2692
Se ₂	0	0	0.7289(5)	0.7328

Space group: $R3m$ (No. 160), $a = 3.6834(6)$ Å, $c = 21.231(3)$ Å (this work), $a = 3.6798$ Å, $c = 21.225$ Å (Ref. [7]), $R_{\text{Bragg}} = 5.23\%$.

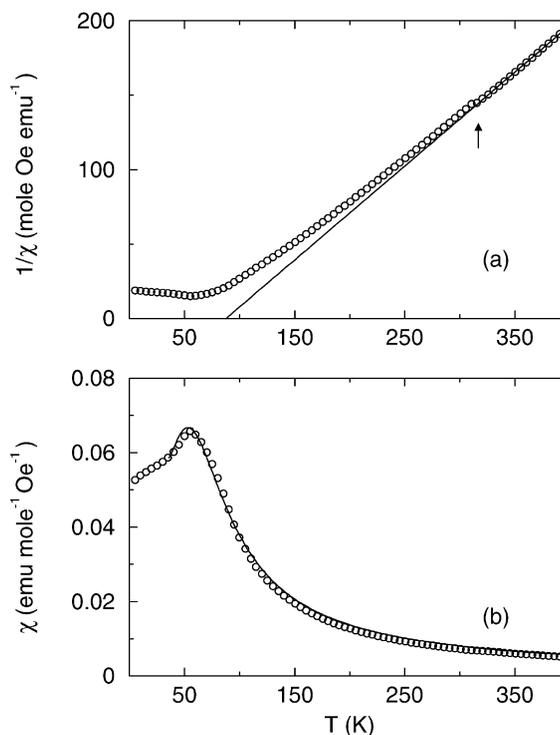


Fig. 3. (a) Inverse magnetic susceptibility of AgCrSe_2 as a function of temperature. The arrow marks an incident at 316 K, (b) magnetic susceptibility as a function of temperature (points). The solid line is a fit using the HTSE as explained in the text.

temperature of 88 K. At 316 K, there is an incident that is clearly observed, below which the susceptibility jumps slightly. The origin of this will be examined presently.

Fig. 3(b) shows the corresponding χ vs. T plot as points. The system is seen to undergo a transition to a bulk antiferromagnet with a peak in χ vs. T at 55 K. The gentle slope (rather than a cusp) arises from the low-dimensional nature of the system. We find that the temperature dependence of the susceptibility is well described using a model that involves ferromagnetic coupling within the 2D triangular lattice of Cr^{III} as described by the high-temperature series expansion (HTSE) of the Heisenberg X–Y ferromagnet [13], in conjunction with a mean-field antiferromagnetic *inter-layer* coupling. This scheme has been successfully applied to other layered magnetic systems [14,15].

The HTSE expression for the layer susceptibility is given by:

$$\chi_{\text{layer}} = \frac{Ng^2\beta^2S(S+1)}{3k_{\text{B}}T} \left[1 + \sum_{i=1}^5 (-1)^i b_i (|J_1|/k_{\text{B}}T)^i \right] \quad (1)$$

where J_1 is the nearest-neighbor coupling within the plane of the Cr^{III} atoms. We have used five b_i terms in the expansion. Schemes to calculate the values of b_i for different lattice topologies and for different electron counts are

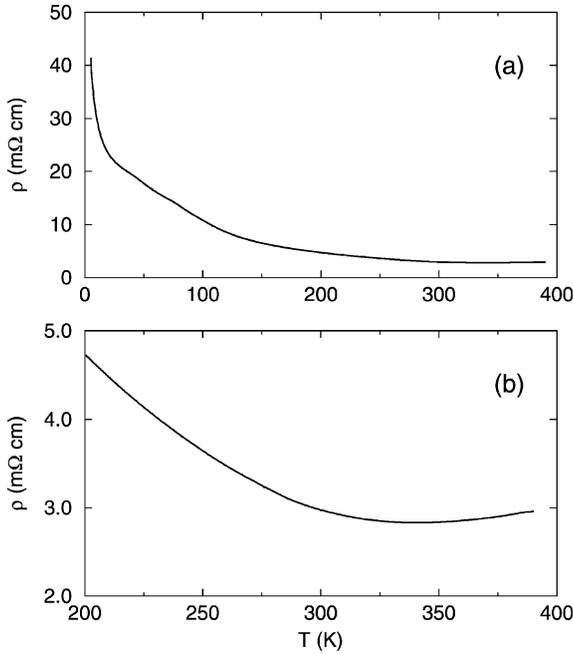


Fig. 4. (a) Resistivity vs. temperature of a sintered pellet of AgCrSe_2 , (b) an expanded view of the high temperature region where the temperature coefficient of resistance changes sign.

provided by Rushbrooke and Wood [13]. J_1 is the coupling within the layer. In conjunction with the mean-field inter-layer coupling we have:

$$\chi_{\text{total}} = \frac{\chi_{\text{layer}}}{1 - (2J_2\chi_{\text{layer}})/(Ng^2\beta^2)} \quad (2)$$

where J_2 refers to the coupling between layers. J_1 and J_2 are fitted against the experimental data using Eq. (2). This gives us the solid line fit in Fig. 3(b) for the parameters with $J_1/k_B = 6.5$ K and $J_2/k_B = -10$ K.

Fig. 4(a) is a plot of temperature-dependence of the electrical resistivity of a sintered pellet of AgCrSe_2 . At low temperatures, the samples display a sharp increase in the resistivity suggesting an insulating ground state. There is a change in the slope of the ρ - T plot in the vicinity of the antiferromagnetic transition near 60 K but we do not have reliable evidence for coupling of charge and spin in our magnetotransport studies (not displayed). At higher temperatures, there is actually an upturn in the ρ - T plot. Usually, this would be interpreted as an insulator-metal transition. This upturn takes place at about 340 K as better seen in Fig. 4(b), where the data have been plotted on an expanded temperature scale. We believe this insulator-metal transition have its origin from changes in the electronic structure rather than from increased mobility of the Ag^+ ions above the structural transition that is expected at 475 K. In any case, the latter would result in activated transport and not a positive temperature coefficient of resistance (TCR). The incident in the magnetic suscepti-

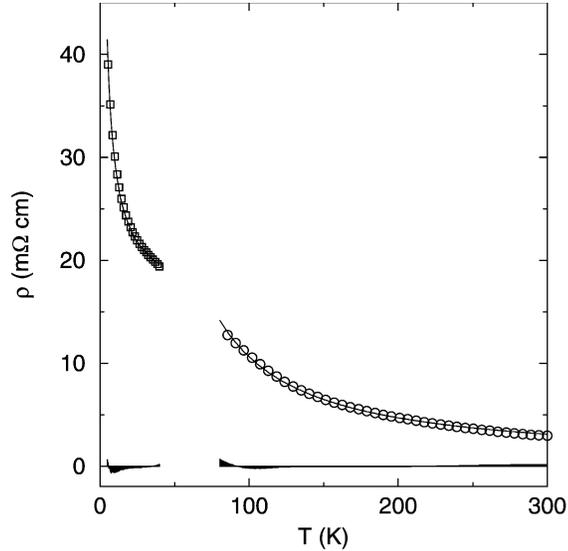


Fig. 5. Fit to the ρ - T curve using VRH at higher temperatures and Coulomb correlation at lower temperature, as explained in the text.

bility at 316 K also attests to some small change in the electronic structure in this range of temperature.

In Fig. 5, we display an attempt to fit the ρ - T data in two separate semiconducting regimes. We use the formula for variable range hopping (VRH) in the higher temperature part (86–300 K) according to the Mott formula [16,17]:

$$\rho = \rho_0 \exp(T_0/T)^{1/4}$$

At lower temperatures (5–40 K) we find a better fit to the so-called Coulomb correlation formula of Efros and Shklovskii (ES) [18]:

$$\rho = \rho'_0 \exp(T'_0/T)^{1/2}$$

The results of these fits are shown as solid lines in Fig. 5 and the residuals from the fit are displayed. In the ES region of the fit, the value of T'_0 is found to be about 8 K. The small value of T'_0 suggests, in agreement with the small resistivity values, that the system is nearly metallic. It is seen that deviations between experiment and fit are small. The change from Mott VRH behavior to the Coulomb-correlation hopping is known from other semiconductor systems [19].

In contrast to the experimental fit to the magnetic susceptibility, the results of electronic structure calculations suggested the following order of increasing stability: paramagnet < layer-antiferromagnet < ferromagnet. The differences in total energy (referenced to the paramagnetic compound) are -1.76 and -1.59 eV. The extra stability of 0.17 eV of the ferromagnetic structure over the antiferromagnetic structure might arise from our use of the room temperature crystal structure for what is in effect, a zero temperature calculation.

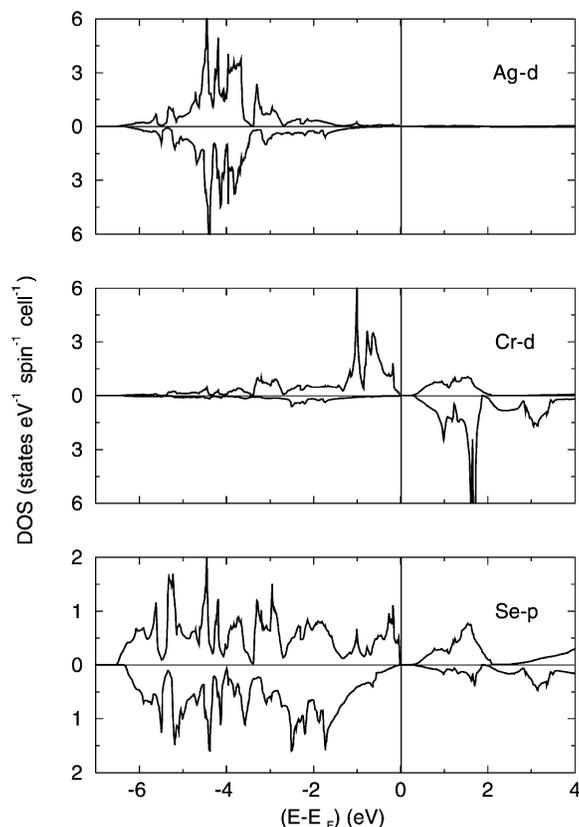


Fig. 6. Projected densities of state from LMTO calculations on AgCrSe_2 . The upper halves of each panel display spin-up states and the lower halves spin-down states.

The projected densities of states for ferromagnetic AgCrSe_2 are shown in the different panels of Fig. 6. In each panel, the top half shows majority (up) spin states and the lower panel, minority (down) spin states. As expected for monovalent, $d^{10} \text{Ag}^I$, the d states are full, not polarized by the Cr^{III} spins, and at least 1 eV below the Fermi energy. The Cr d states are strongly spin polarized, and display a gap because of a 0.5 eV separation between $t_{2g}^3(\uparrow)$ states, and empty $e_g^0(\uparrow)$ and $t_{2g}^0(\downarrow)$ states which are nearly degenerate. AgCrSe_2 , at least computationally, belongs to the rather unusual class of compounds that are ferromagnetic insulators. Se p states shown in the bottom panel are slightly spin-polarized suggesting rather strong Cr-d–Se-p covalency. The calculated band gap of 0.28 eV suggests a system that is more insulating than what is observed in the electrical transport measurements. This discrepancy can be reconciled by considering that: (i) the sample might be non-stoichiometric at a level that is not observed at the level of the X-ray Rietveld analysis and (ii) the intrinsic silver-atom disorder that cannot be accounted for in the calculations might affect the electronic structure.

5. Conclusions

The title compound is at the border between an insulator and a metal, and is closely related to the interesting class of ferromagnetic insulators. The magnetism is characterized by in-plane ferromagnetism, with the planes themselves coupling antiferromagnetically. Electronic structure calculations indicate that the compound is a band insulator. However, calculations are essentially at ‘zero K’ and it is possible that the large displacements of the silver atom affect the electronic structure so that the metal–insulator transition arises from the breakdown of boundary conditions in a manner akin to what happens to Si at the melting point. The electronic structure is interesting in that the compound, if it could be made metallic (substituting Ag by Pd or through the introduction of Ag vacancies), would be a half-metal with only spin-up states at the Fermi energy. The metallicity might result in the coupling between planes becoming *ferromagnetic* through an RKKY mechanism. According to previous studies [5], one might then obtain a compound displaying negative magnetoresistance.

Acknowledgments

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