Negative magnetoresistance in Ba_2CoS_3

Thomas Baikie,[a] Vincent Hardy,[b] Antoine Maignan[b] and M Grazia Francesconi*[a]

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A small negative magnetoresistance and metallic-like behaviour has been detected for the first time in a one-dimensional sulfide containing Co^{2+}.

Recently, we reported the characterisation of structural and magnetic properties of Ba_2CoS_3, which constitutes the first example of Co^{2+} sulfide with corner-linked [Co^{2+}-S^{2-}] tetrahedra forming one-dimensional chains.[1] In this paper, we report the characterisation of transport and magneto-transport properties of Ba_2CoS_3. We found that Ba_2CoS_3 shows moderate resistivity, metallic-like features and negative magnetoresistance. This is the first time that such properties are observed within this family of sulfides.

The synthesis of Ba_2CoS_3 was achieved by the reaction of stoichiometric amounts of $BaCO_3$ and CoO (or Co metal powder) under a flow of CS_2 vapour at a temperature of 1100 °C for 24 h. Once the reaction times were complete, the samples were slow cooled to room temperature.

Ba_2CoS_3 is isotypic to Ba_2ZnS_3 and Ba_2FeS_3 but not Ba_2MnS_3 and shows an orthorhombic unit cell with parameters a = 12.000(1) Å, b = 12.470(1) Å and c = 4.205(2) Å.[1] The Ba_2CoS_3 and Ba_2MnS_3 show the same structural feature of chains of vertex sharing MS_4 tetrahedra (M = Co, Mn). Ba_2CoS_3 and Ba_2MnS_3 also show the same one-dimensional antiferromagnetic behaviour.[1] However, there are differences between the structures of Ba_2CoS_3 and Ba_2MnS_3, which mainly result from differing connectivities among the two crystallographically independent barium ions within the structures of the two sulfides (see Fig. 1).[2]

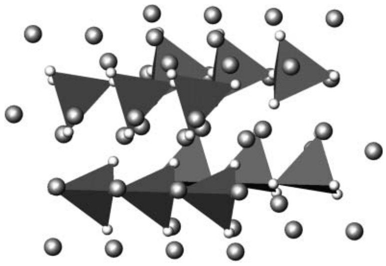

Fig. 1 Structural representation of Ba_2CoS_3: Large dark and small light spheres represent the Ba^{2+} and S^{2-} ions, respectively, and the grey polyhedra represent the CoS_4 tetrahedra.

In previous work carried out by Greaney *et al.*[3] on the Ba_2MnQ_3 (Q = S, Se, Te and mixed anion chalcogenides) family, the authors found that all phases were fairly insulating with a room temperature resistivity of approximately 10^2–10^3 Ω cm. In Ba_2FeS_3, Nakayama *et al.* also reported a very high resistivity at 300 K (~10^4 Ω cm).[4] Interestingly, the present investigation of Ba_2CoS_3 points to a quite different behaviour.

Fig. 2 and 3 display data of resistivity [$\rho(T)$], thermopower [$S(T)$], and magnetic susceptibility [$\chi(T)$], which were recorded on ceramic samples of Ba_2CoS_3.[5]

The Seebeck effect is known to be a powerful technique to give direct insight into the nature of the electronic transport. When working on ceramic samples, one can even argue that it has the advantage to be less sensitive than resistivity to extrinsic features like grain boundaries. In the main panel of Fig. 2, the $S(T)$ curve exhibits a linear regime over a broad temperature range (~50–300 K). Such a feature is known to be a strong indication of

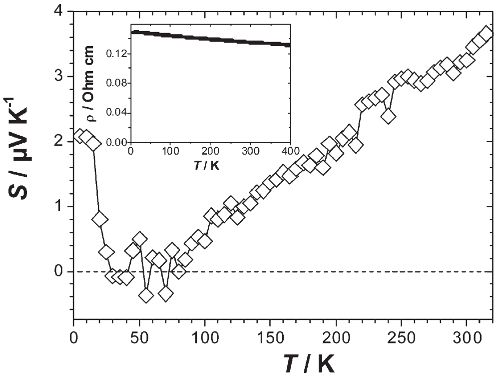

Fig. 2 Temperature dependence of the Seebeck coefficient (main panel) and resistivity (inset). All these data were collected on ceramic samples.

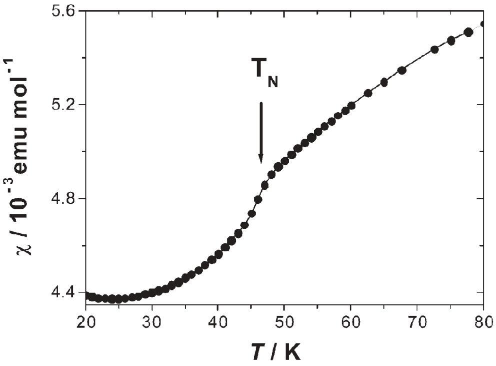

Fig. 3 Temperature dependence of the susceptibility, showing a kink at 46 K.

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[a] *Department of Chemistry, University of Hull, Cottingham Road, Hull, UK HU6 7RX. E-mail: m.g.francesconi@hull.ac.uk; Fax: +44 (0)1482 466410; Tel: +44 (0)1482 465409*
[b] *Laboratoire CRISMAT, UMR CNRS 6508, ISMRA-ENSICAEN, 6 Boulevard du Maréchal Juin, 14050 Caen, Cedex-France. E-mail: vincent.hardy@ensicaen.fr; Fax: +33 (0)231 951600; Tel: +33 (0)231 45263*

a metallic-like conduction mechanism, a situation for which thermopower can be approximated by the expression

$$S = -\frac{\pi^2 k_B^2 T}{3e}\frac{\partial \ln \rho}{\partial \varepsilon} \qquad (1)$$

where ε is the charge carrier energy.[6] In addition, the low values of thermopower (less than 4 μV K^{-1} up to 300 K) lends further support to such a metallic character of the conduction in Ba_2CoS_3.[7]

As shown in the inset of Fig. 2, the room temperature resistivity of Ba_2CoS_3 ($\sim 10^{-1}$ Ω cm) is much lower than those found in Ba_2MnS_3 ($\sim 10^2$–10^3 Ω cm) and Ba_2FeS_3 ($\sim 10^4$ Ω cm). The $\rho(T)$ of Ba_2CoS_3 shows a slight increase in ρ as T is decreased, but this variation is too small to be regarded as an indication of intrinsic semiconducting behaviour. Instead, such an effect is more probably related to the enhanced impact of defects in the case of one-dimensional (1D) conduction. For instance, in the 1D metallic $Sr_2CuO_{3+\delta}$ phase,[8] $\rho(T)$ is found to increase slightly as T is decreased while $S(T)$ exhibits a behaviour typical of a metal (*i.e.*, a combination of features that is similar to that of Fig. 2). The order of magnitude of the resistivity in Ba_2CoS_3 is found to be quite high (10^{-1} Ω cm) for metallic conduction, but it can still be considered within the range of values characteristic of the so-called "bad metals".

The second main feature of the $S(T)$ curve of Fig. 2 is a small but sizeable upturn as T is decreased below about 50 K. It is worth noticing that, around 50 K the values of $S(T)$ are very small and this causes scatter in the data. In compounds showing both metallicity and antiferromagnetic interactions, such an upturn in $S(T)$ was sometimes found to occur at the transition temperature T_N. For instance, a $S(T)$ curve, similar to that of Fig. 2, has been observed for the organic conductor (MDT-TS)$(AuI_2)_{0.441}$, which undergoes an antiferromagnetic transition at $T_N \approx 50$ K.[9] In Ba_2CoS_3, the magnetic susceptibility at high temperature clearly demonstrated the antiferromagnetic nature of the interactions.[1,4] On the other hand, no signature of the Néel temperature has been identified to date. Mössbauer experiments on Ba_2FeS_3, however, clearly established the existence of a three-dimensional (3D) long-range ordering (LRO) at $T = 4.2$ K.[4] By re-investigating precisely the susceptibility of Ba_2CoS_3 at a temperature lower than the temperature of the peak related to short-range ordering ($T < T_{max} = 130$ K), we have detected a kink at 46 K (see Fig. 3) and this is consistent with the signature of a T_N in a spin-chain compound.

Therefore, we suggest that the upturn in the $S(T)$ curve of Ba_2CoS_3 may be related to the onset of the 3D antiferromagnetic LRO.[2]

Fig. 4 displays a series of MR(H) curves, for temperatures between 250 and 10 K. It deserves to be noted that MR reaches significant values at low temperatures. At 10 K for instance, the application of 7 T induces a change in ρ by ~ -1.7 % (value well reproducible among a set of three samples). Such a noticeable negative MR is not so common in one-dimensional sulfides. To the best of our knowledge, the only related result was found in $BaV_{0.8}Ti_{0.2}S_3$, a spin-chain compound which shows a smaller MR effect (~ -0.8 % in 7 T at 80 K).[10]

In order to investigate the origin of this magnetoresistivity, we have recorded curves of magnetization as a function of the magnetic field. In all cases, the M(H) curves were found to exhibit a quasi-linear dependence. Such a behaviour rules out a simple spin polarisation effect as a possible origin of the negative magnetoresistivity. Indeed, as shown Fig. 5, in the case of $T = 10$ K, the MR clearly does not scale with M^2.

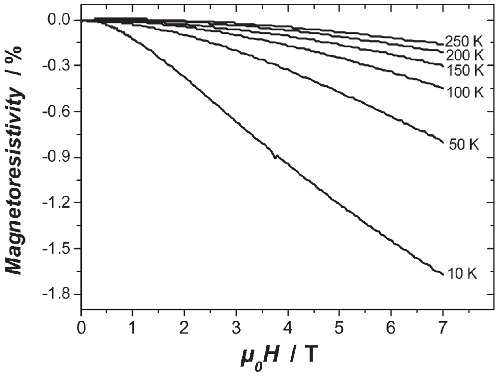

Fig. 4 Field dependence of the magnetoresistivity at different temperatures.

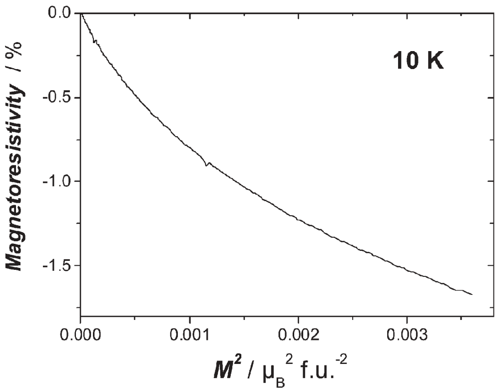

Fig. 5 MR *versus* M^2 at $T = 10$ K, derived from ρ(H) and M(H) data.

In Fig. 4, one observes that the absolute value of MR increases substantially as T is decreased. However, this change is progressive over the whole T range, and we could not detect any clear crossover associated with the onset of the LRO at T_N. It must be recognised that the relationship between magnetism and conductivity in Ba_2CoS_3 is still unclear at the present time. In particular, we emphasize that the origin of the negative MR found in this compound remains an open question, which deserves further investigation.

In conclusion, we have reported that the one-dimensional ternary sulfide Ba_2CoS_3 shows metallic-like features and a small negative magnetoresistance. These findings are important because, despite its small magnitude, negative magnetoresistance has been detected for the first time in a one-dimensional sulfide containing Co^{2+}.

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