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# Linear antiferromagnetism in $Ba_2CoS_3$†

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**$Ba_2CoS_3$ is the first example of an inorganic solid containing one-dimensional corner-sharing [$Co^{2+}$–anion] chains, which leads to one-dimensional cooperative antiferromagnetism.**

The influence of the discovery of high $T_c$ superconductors[1] on the current inorganic solid state chemistry is enormous and has been analysed by several authors.[2] The chemistry of inorganic solids containing transition metals, which has been for a long time one of the pillars of solid-state chemistry, was partially deprived of its intrinsic variety and restricted almost entirely to the search for cuprates showing superconducting properties.[3] On the other hand, the complexity of the phenomenon of high $T_c$ superconductivity and its close connection to the field of magnetism has given a boost to this field and, in particular, to the area of low-dimensional magnetism. The reason behind this is that one- or two-dimensional magnetic interactions between unpaired spins on $Cu^{2+}$ cations are a common factor among parent materials of high $T_c$ superconductors. The realisation that a deeper understanding of these interactions will help to elucidate the still unknown mechanism behind the phenomenon of superconductivity encouraged the scientific community to investigate materials other than cuprates, partially restoring variety within the chemistry of transition metal compounds. Low-dimensional magnetic interactions are mainly ferromagnetic and antiferromagnetic. These take place among localised unpaired electrons along a chain (one-dimensional structures) or within a plane (two-dimensional structures) and are mediated by the anions bridging the transition metals. The preparation and characterisation of new materials showing low-dimensional magnetism is of paramount importance. The characterisation of one-dimensional materials is particularly welcome, as these systems are rarer than two-dimensional materials.[4]

Traditionally, research on low-dimensional materials is more focused on oxides, mainly because the preparation and characterisation of non-oxide compounds presents more experimental challenges. Nevertheless, progress in synthetic methods has encouraged the preparation of a wider range of non-oxide materials, such as nitrides or sulfides.[5] It is now becoming apparent that non-oxide materials are an important alternative to traditional oxides to study magnetic interactions in solids, considering that anions mediate interactions between transition metals.[6] Importantly, a new direction could arise from in-depth investigations of non-oxide materials, an anion-control based search for novel materials.

It is well known that magnetic properties are closely correlated to structural features. According to the Goodenough–Kanamori–Anderson rules,[7] the [anion–transition metal–anion] angle, $\Phi$, plays an important role in determining the nature and strength of magnetic interactions in transition metal compounds in which the [TM–anion] polyhedra are connected *via* anions and the $\Phi$ angle is mainly determined by the connectivity within the structure of the compound, *i.e.* whether the polyhedra are connected *via* one of their corners ($\Phi \approx 180°$) or one of their edges ($\Phi \approx 90°$).

In this paper, we report the synthesis and characterisation of structural and magnetic properties of the ternary sulfide $Ba_2CoS_3$,[8–10] which constitutes the first example of $Co^{2+}$ compound with corner-linked [$Co^{2+}$–anion] tetrahedra forming one-dimensional chains. $Co^{2+}$ has three unpaired electrons, which pair with the unpaired electrons on neighbouring $Co^{2+}$ *via* $S^{2-}$ bridging anions. The one-dimensional structural arrangement favours one-dimensional antiferromagnetic coupling between unpaired electrons. The synthesis of $Ba_2CoS_3$ was briefly reported by Hong and Steinfink in 1972[11] in a paper concerning phases within the Ba–Fe–S system. However, neither synthetic details, nor structural or magnetic data were included.

Powder X-ray diffraction (PXRD) indicates that $Ba_2CoS_3$ is isostructural with $Ba_2FeS_3$,[11] $Ba_2ZnS_3$,[12] $K_2CuCl_3$, $Cs_2AgCl_3$, $Cs_2AgI_3$, $(NH_4)_2CuBr_3$ and $CuPbBiS_3$.[13] Structural data for $Ba_2ZnS_3$ provided the initial model for Rietveld refinement of the PXRD pattern of $Ba_2CoS_3$. Rietveld refinement was performed using the software package Rietica.[14] A two phase refinement was required to account for the small amounts of BaS which was always present in the reaction product. The profile refinement and a structural representation of $Ba_2CoS_3$ are shown in Fig. 1. The unit cell is orthorhombic and the cell parameters are $a$ = 12.000(1) Å, $b$ = 12.470(1) Å and $c$ = 4.205(2) Å.

$Ba^{2+}$ occupy two distinct crystallographic sites, both coordinated by $S^{2-}$ in a prismatic fashion. One $Ba^{2+}$ is surrounded by six $S^{2-}$ ions at corners of a trigonal prism and an additional $S^{2-}$ is approximately centred above one rectangular face. Seven $S^{2-}$ ions surround the other $Ba^{2+}$ forming a distorted trigonal prism with one face capped.

$Co^{2+}$ is tetrahedrally coordinated by $S^{2-}$ and neighbouring Co–S tetrahedra are connected *via* corners, forming infinite chains. The Co–S tetrahedra are slightly distorted, as the two Co–S bridging bonds are stretched along the chain direction. Those bonds are 2.427(2) Å, which is significantly longer than the two terminal Co–S bonds, 2.330(3) Å and 2.317(3) Å. The bonding angles of S–Co–S deviate from 109.5° by up to several degrees. A similar tetrahedral distortion is also observed in $Ba_2ZnS_3$.

The distance between $Co^{2+}$ cations within each chain (inter-chain) is 4.205(1) Å, whereas the distances between $Co^{2+}$ cations in two neighbouring chains (intra-chain) are 6.153(3) Å and 6.582(3) Å. Neighbouring chains of Co–S tetrahedra are interlayered by Ba-S blocks. This confers one-dimensional character to the Co–S chains.

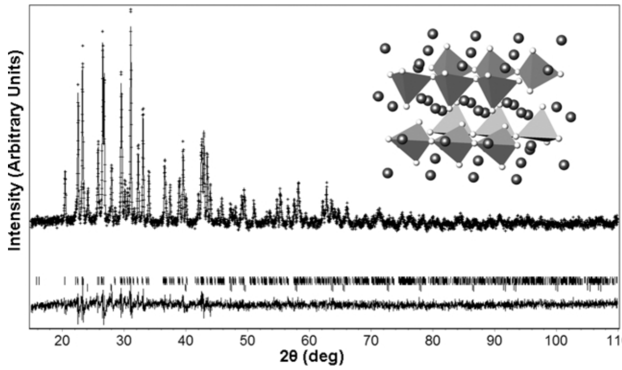

**Fig. 1** Refinement of $Ba_2CoS_3$. Structure of $Ba_2CoS_3$: Black spheres (Ba), grey $CoS_4$ tetrahedra, white spheres (S).

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† Electronic supplementary information (ESI) available: crystallographic data. See http://www.rsc.org/suppdata/cc/b4/b400084f/

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Tetrahedral coordination is often shown by $Co^{2+}$ in solid compounds however; one-dimensional corner connectivity has not been previously encountered in $Co^{2+}$ compounds. $BaCoO_2$ displays tetrahedra sharing corners in a three-dimensional framework,[15] the $A_2CoX_2$ (A = Na, K, Rb, Cs and X = S, Se) family displays edge-sharing linear chains of tetrahedra,[16] $Rb_2Co_3S_4$ displays edge-sharing two-dimensional sheets of tetrahedra,[17] the $A_6CoX_4$ (A = Na, K and X = S, Se) family,[16] $Rb_2CoI_4$[18] and $Li_6CoO_4$[19] display isolated tetrahedra.

The one-dimensional structural character of $Ba_2CoS_3$ is linked to its one-dimensional antiferromagnetic properties.

We measured the magnetic properties of $Ba_2CoS_3$. The magnetic susceptibility ($\chi$) and inverse susceptibility ($1/\chi$) of $Ba_2CoS_3$ as a function of temperature are plotted in Fig. 2. Magnetic constants derived from the experimental data are tabulated in Table 1. The value of the maximum of the susceptibility ($T_{\max}$) was determined by taking the first derivative of the susceptibility *versus* temperature curve. The Weiss constant ($\theta$) and the effective magnetic moment ($\mu_{\text{eff}}$) were determined by a Curie–Weiss fit of the high temperature portion (300–395 K) of the inverse susceptibility curve. The data points at higher $T$ indicate a deviation from Curie–Weiss behaviour and were excluded from the extrapolation of the magnetic constants. It is not clear whether these points are due to the physical upper limits of the instrumentation or electronic effects occurring above room temperature. This phenomenon is currently under investigation.

Nevertheless, the $\chi$ versus $T$ plot (Fig. 2) shows a broad maximum, which is indicative of one-dimensional magnetic ordering. $\theta < 0$ suggests antiferromagnetic coupling between the $Co^{2+}$, and the observed decrease in magnetic susceptibility above $T_{\max}$ implies ordering and interaction between the unpaired spins. There is an upturn in susceptibility at low temperature ($T < 25$ K), which does not lead to any new maxima. The explanation for this upturn in the susceptibility *versus* temperature curve is not straightforward. The absence of a new maximum in the low temperature region may indicate that the spins order ferromagnetically below the upturn temperature though it may also be that the Néel temperature is below 5 K. Alternatively, the low temperature susceptibility behaviour may be a consequence of structural defects or the ubiquitous "Curie tail" commonly observed at low temperature. However, a similar feature was observed in the $Ba_2MnQ_3$ (Q = $S^{2-}$, $Se^{2-}$, $Te^{2-}$) family of compounds with the upturn in susceptibility occurring at lower temperature $T \approx 5$ K.[20] All the members of the $Ba_2MnQ_3$ family display one-dimensional antiferromagnetic interactions between the unpaired spins on the $Mn^{2+}$ cations. Even though $Ba_2CoS_3$ and $Ba_2MnS_3$ are not isostructural they both contain one-dimensional corner-linked linear chains of TM–$S^{2-}$ tetrahedra. The $Ba_2MnS_3$ Weiss constant, which is indicative of the degree of antiferromagnetic coupling, is more negative ($\theta = -317$ K) than the $Ba_2CoS_3$ Weiss constant ($\theta = -143$ K) and this is probably due to the lower number of unpaired electrons for $Co^{2+}$, *i.e.* $S = 5/2$ for $Mn^{2+}$ and $S = 3/2$ for $Co^{2+}$.

Cooperative magnetic interactions depend crucially on the [anion–TM–anion] angle $\Phi$. The majority of research work in this field has concentrated on cooperative interactions between octahedrally coordinated transition metals, either sharing corners ($\Phi = 180°$) or sharing edges ($\Phi = 90°$). A variety of types and strengths of magnetic interactions lies between these two end cases. In $Ba_2CoS_3$ $\Phi = 120.11(8)°$ which makes this compound one of the rare examples of magnetic material with intermediate value for the $\Phi$ angle.

We have reported the preparation and characterisation of structural and magnetic properties for the ternary sulfide $Ba_2CoS_3$. $Ba_2CoS_3$ shows one-dimensional corner connectivity between Co–S tetrahedra, a unique feature among Co compounds. This structural arrangement is responsible for the low-dimensional magnetic interactions displayed by this compound. Low-dimensional solids constitute an important aspect of the wider field of the technologically-orientated research on high temperature superconductivity.

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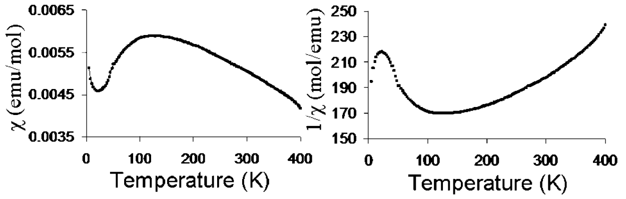

**Fig. 2** Variation of magnetic susceptibility $\chi$ (left) and inverse susceptibility $1/\chi$ (right) with temperature, $T$.

**Table 1** Data obtained from susceptibility plots

| $T_{\text{Max}}$/K | $\theta$/K$^a$ | $\mu_{\text{eff}}{}^a/\mu_B$ | $\chi_{\text{rt}}{}^b$/emu mol$^{-1}$ |
|---|---|---|---|
| 120 | −143 | 3.54 | $5.2 \times 10^{-3}$ |

$^a$ Determined from Curie-Weiss fit of $1/\chi$ vs $T$ plot $^b$ $\chi_{\text{rt}}$ is the room temperature magnetic susceptibility

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8 Polycrystalline samples of $Ba_2CoS_3$ were obtained *via* a solid–vapour reaction between stoichiometric amounts of high purity $BaCO_3$ and CoO and $CS_2$ vapour at 1100 °C for 24h. Carbon disufide is a liquid with a high vapour pressure. If nitrogen gas is bubbled through liquid $CS_2$, the gas acts as a carrier gas allowing a vapour of $CS_2$ to flow through the tubular furnace. Experimentally, the nitrogen cylinder is connected to the Dreschel bottle containing the $CS_2$, with plastic tubing. This is then connected to the furnace tube. The opposite end of the tube is connected to another Dreschel bottle containing paraffin oil—this acts as a post-reaction scrubber, reducing the amount of unreacted $CS_2$ released.
9 Powder X-ray diffraction data were collected on a Siemens D5000 diffractometer (Cu K$\alpha$, 25 °C) over an angular range $10° \leq 2\theta \leq 110°$.
10 Magnetic measurements were conducted in a SQUID Quantum Design magnetometer over the temperature range 5–400K with a magnetic field of 500 Oe. No corrections for diamagnetic contributions or temperature independent paramagnetism were made to the susceptibility data. Corrections were made however, to the mass of sample due to the small amounts of BaS. This was achieved using the quantitative phase analysis feature of the Rietica software, which uses the formalism described by Hill and Howard[21] in determining the weight fraction of each phase within a sample.
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