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Magnetism in $BaCoS_2$

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Abstract

$BaCoS_2$ is a layered Mott-Hubbard insulator that orders antiferromagnetically near 300 K. We report magnetic susceptibility measurements on polycrystalline $BaCoS_2$ from 77 K to 800 K, and in- and out-of-plane measurements on single crystals from 2 K to 350 K. We also report a powder neutron refinement of the magnetic structure of $BaCoS_2$. The neutron measurements indicate that the moments lie in the plane, and that the magnetic unit cell is the same as the (orthorhombic) chemical cell. The ordered moment obtained from the neutron refinement is close to 3 μ_B, indicating that the Co ions are in the high-spin ($S = 3/2$) configuration. The effective moment inferred from the high temperature susceptibility, $p = 5.26\ \mu_B$, is also consistent with high-spin Co^{+2}.

Introduction

Although the existence of $BaCoS_2$ was reported in 1970 by Grey and Steinfink [1], it is only since the 1993 discovery of an unusual insulator-metal transition in Ni-doped $BaCoS_2$ by Martinson, Schweitzer, and Baenziger [2] that interest has developed in the undoped material.

Comparatively little is known about $BaCoS_2$. The structure consists of Co-S sheets sandwiched between rock-salt Ba-S layers [3,4, 5] (see Fig. 1); the approximately 3.5 Å in-plane Co-Co distance compared to the nearly 9 Å out-of-plane distance leads one to expect two-dimensional physical and electronic properties in this material. In-plane resistivity measurements on single crystals [6] indicate that $BaCoS_2$ is semiconducting, with a room temperature resistivity of 0.2 Ω cm and a gap inferred from an Arrhenius law of $2\Delta \cong 0.23$ eV. Magnetic susceptibility measurements on polycrystals [3] indicate that $BaCoS_2$ orders antiferromagnetically near room temperature, and it has been argued [2,3,7] that the Co^{+2} ions are in the low-spin $S = 1/2$ state. The layered structure and the possibility that the magnetic moments are effectively spin-1/2 has fueled speculation [2,3,7] that $BaCoS_2$ is a good analogue to the high-T_C parent compound La_2CuO_4.

Here we present polycrystal susceptibility measurements on $BaCoS_2$ from 77 K to 800 K, in- and out-of-plane susceptibility measurements on single crystals from 2 K to 350 K, and a powder neutron diffraction refinement of the magnetic structure. The effective moment inferred from the high temperature susceptibility is more consistent with $S = 3/2$ ions than with $S = 1/2$ ions. The single crystal susceptibility is very anisotropic, and clearly indicates that the moments order in the Co-S planes. The refinement of the magnetic structure confirms that the moments do lie in the planes with an ordered moment close to 3 μ_B, which is again consistent with $S = 3/2$ Co ions.

Experimental Details

Polycrystalline $BaCoS_2$ was prepared by reacting a pressed pellet of BaS (99.4%), Co powder (99.998%), and S (99.999%) in a carbonized and evacuated silica tube at 925 °C. The total reaction time was ten days, and the sample was reground and repressed twice during that time. At the end of the reaction the silica tube was quenched in a vessel containing liquid nitrogen to avoid formation of Ba_2CoS_3 [3]. Single crystals of $BaCoS_2$ were prepared by mixing stoichiometric proportions of BaS (99.4%) and CoS (99.5%) and placing the mixture in a 5 ml Al_2O_3 crucible. The crucible was sealed in an evacuated silica tube, heated to 1150 °C, and cooled at 2 °C/hr to 950 °C, at which point the tube was removed from the furnace and quenched in a bucket of water. The crystals grow as shiny platelets, typically 3 x 3 x 0.1 mm^3, which can be mechanically removed from the melt. The samples were characterized using powder x-ray diffraction, and good agreement was obtained with an x-ray powder pattern calculated from the structural parameters given by Snyder, Gelabert, and DiSalvo [3]. A few weak impurity lines were observed in the polycrystalline pattern that were not observed in the single crystal pattern. These lines are not characteristic of Ba_2CoS_3 or any other Co-containing phase, but are most likely due to oxide or hydroxide contamination of the commercial BaS as discussed in Ref. 3.

The magnetic susceptibility of a 190 mg $BaCoS_2$ powder sample was measured using a homemade Faraday balance magnetometer equipped with Lewis coils and a cryostat/furnace supplied by George Associates. The Faraday system was calibrated using a NIST MnF_2 standard. The measurements were performed with an applied field of 7 kOe. Magnetization curves were obtained at several temperatures, and the susceptibility was found to be independent of field up to 7 kOe for the temperature range studied. Single crystal magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer and an applied field of 1 kOe. Five single crystal plates (8.1 mg) were stacked together, and the field was applied perpendicular and parallel to the plates. X-ray diffraction was used to confirm that the c-axis lies along the short dimension of the plates.

Neutron-diffraction data were collected using the HB4 high-resolution powder diffractometer at the High-Flux Isotope Reactor at ORNL. This instrument has a Ge (115) monochromator which selects an incident neutron wavelength of 1.5 Å. The neutron wavelength was determined more precisely to be 1.4993(2) Å on the basis of unit cell refinements for the silicon standard reference material 640b. Soller slit collimators of 12' and 20' are positioned before and after the monochromator crystal, respectively. An array of 32 equally spaced (2.7°) ^{3}He detectors, each with a 6' Gd-coated mylar foil collimator, can be step-scanned over a range of up to 40° for scattering angles between 11° and 135°. The sample was placed in a vanadium can for data collection at 20 K, 200 K, and 350 K over the 2-theta range of 11° to 135° in steps of 0.05°. Input for the Rietveld refinement program was prepared by interpolating a constant step-size data set from the raw data, because the spacing between the detectors is not exactly the same. The data were also corrected for the variation in detector efficiencies, which were determined using a vanadium standard.

Rietveld refinements were performed using the program FULLPROF [8]. The refinements were performed using an orthorhombic unit cell with starting values for the lattice parameters, atom fractional coordinates, and atomic displacement parameters taken from Ref. 3.

Results and Discussion

In Fig. 2 we plot the magnetic susceptibility of polycrystalline $BaCoS_2$. As discussed in Ref. 2, the broad asymmetric maximum near the Néel temperature is common in layered antiferromagnets. The inset to Fig. 2 shows a plot of χ^{-1} vs. T. The solid line represents a Curie-Weiss fit to the high temperature portion of the data. The fit yields an effective moment p = 5.26 μ_B, and a paramagnetic Curie temperature θ_P = -1343 K. For a spin-only moment, p = g $[S(S+1)]^{1/2}$. Assuming g = 2 we have p = 1.73 for S = 1/2 and p = 3.87 for S = 3/2. Effective moments for Co^{+2} complexes are typically 4.3 to 5.2 μ_B for high-spin and 1.8 to 2.0 μ_B for low-spin [9], indicating that in $BaCoS_2$ the Co^{+2} ions are almost certainly in the high-spin S = 3/2 configuration.

The magnetic susceptibility obtained on single crystals of $BaCoS_2$ appears in Fig. 3. The most striking aspect of the data is that with the magnetic field applied perpendicular to the Co-S planes there is little indication that the moments have ordered. This observation is consistent with the moments ordering in the plane. Also, above the Néel temperature the out-of-plane susceptibility does not obey a Curie-Weiss law. A possible explanation for this behavior is that a crystal field level is thermally accessible, making the moment temperature dependent. One effect of the non-Curie-Weiss behavior of the out-of plane susceptibility is that it tends to drive up the value of the moment inferred from the polycrystalline data. In fact, a Curie-Weiss analysis of the in-plane data above the Néel temperature yields an effective moment p = 3.39 μ_B and θ_P = -266 K. Because of the small fitting range these numbers should not be taken very seriously, but they certainly suggest that for fields applied parallel to the Co-S layers the moments are effectively spin-3/2.

At 350 K the neutron powder diffraction pattern showed no evidence of any magnetic contribution. The crystal structure was refined using FULLPROF [8]. Although single crystal [5] and powder [4] x-ray refinements indicate the true symmetry to be monoclinic with the unique angle equal to 90.4°, because the axes subtending this angle are nearly equal in length we adopted the higher symmetry *C*-centered orthorhombic cell [3] in our refinements. The refined structural parameters are consistent with published values [3] with the Ba, Co, S1, and S2 atoms located at the 4*g*, 4*g*, 4*g*, and 4*b* positions of the space group *Cmma*, a = 6.4840(7) Å, b = 6.34404(7) Å, c = 8.936(1) Å, z(Ba) = 0.1969(6), *z*(Co) = 0.593(1) and *z*(S1) = 0.8463(8) (where the *z* values are the fractional atomic coordinate).

After cooling to 200 K, several superlattice reflections were apparent and these persisted to the lowest measurement temperature of 20 K. The new reflections indexed with respect to the orthorhombic cell correspond to an antiferromagnetic structure with a propagation vector $\tau = (101)$. A schematic view of the magnetic structure of $BaCoS_2$ appears in Fig. 4. This structure has the Co moments antiferromagnetically aligned and coplanar within the Co_2S_2 layers; adjacent layers along the layer stacking direction are identical. This magnetic structure model was refined using FULLPROF on the 20 K data, allowing the moment direction to rotate within and out of the Co_2S_2 layers. The refined moment per Co atom was found to be 2.63 μ_B, with projections of 2.56 ± 0.05 μ_B and 0.6 ± 0.1 μ_B along **a** and **b**, respectively. Both the in-plane arrangement of the moments and the magnitude of the ordered moment are consistent with the magnetic susceptibility data.

The magnetic structure model reported here confirms the in-plane arrangement of the moments recently reported by Kodama *et al.* in Ref. 10. The authors of Ref. 10 were not, however, able to assign a unique direction to the moments within the Co-S layers, nor was their calculated moment of 2.9 μ_B obtained by least-squares methods.

The results presented above imply that the magnetic interactions in $BaCoS_2$ are strongly two-dimensional. Given that the crystal field levels in Co^{+2} are often highly anisotropic [11], it is likely that the magnetism in $BaCoS_2$ is best described by a 2D Ising model. In support of this conjecture, it should be noted that the magnetic susceptibility of $BaCoS_2$ strongly resembles calculated Ising model susceptibilities [12].

Finally, the results presented here make it considerably more problematic that $BaCoS_2$ be considered as an analogue to the high-T_C parent compound La_2CuO_4, despite their clear structural similarities. $BaCoS_2$ remains interesting, however, as an eminently dopable Mott-Hubbard system, close to electronic and structural instabilities.

Acknowledgments

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Figure Captions

Fig. 1. Structure of $BaCoS_2$, drawn to emphasize the Co-S layers. The spheres represent Ba ions, and the square pyramids represent CoS_5 polyhedra. As discussed in Ref. 3, the Co ions are displaced alternately 0.83 Å above and below the layer plane.

Fig. 2. Magnetic susceptibility of polycrystalline $BaCoS_2$. The inset shows the inverse susceptibility, and the straight line represents a Curie-Weiss fit to the high temperature portion of the data.

Fig. 3. Magnetic susceptibility of single-crystal $BaCoS_2$ with field applied parallel and perpendicular to the Co-S layers. The dashed line represents a calculated polycrystalline average, which is in good agreement with the data presented in Fig. 2.

Fig. 4. Schematic of the refined magnetic structure of $BaCoS_2$ obtained at 20 K. The lattice parameters **a** and **b** refer to the orthorhombic unit cell described in Ref. 3 and used as starting parameters for these refinements. The circles represent Co ions, and the numbers next to the circles are the fractional coordinates in the z direction. At 20K the refined structural parameters are $a = 6.4363(6)$ Å, $b = 6.3902(6)$ Å, $c = 8.8986(8)$ Å, $z(\mathrm{Ba}) = 0.1981(5)$, $z(\mathrm{Co}) = 0.5919(9)$ and $z(\mathrm{S1}) = 0.8472(7)$.

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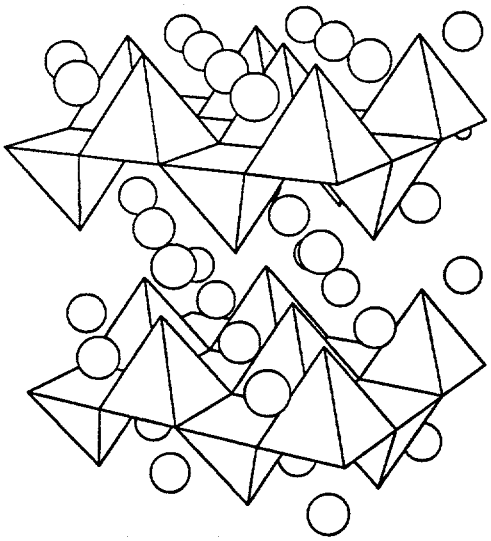

Fig. 1., Mandrus, Journal of Applied Physics

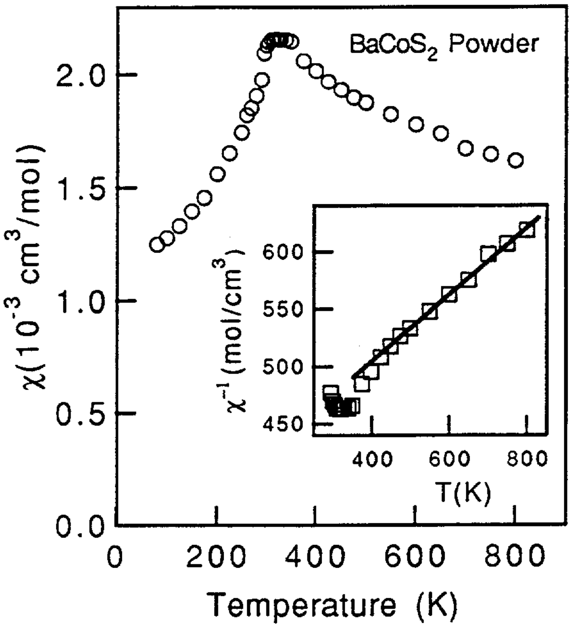

Fig. 2., Mandrus, Journal of Applied Physics

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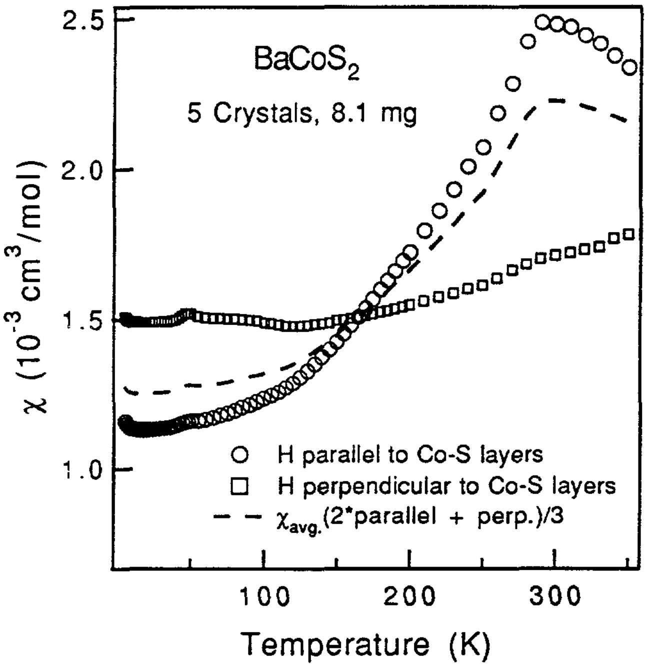

Fig. 3, Mandrus, Journal of Applied Physics

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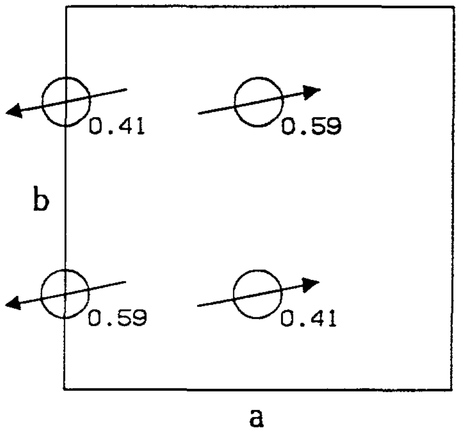

Fig. 4., Mandrus, Journal of Applied Physics