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# The magnetic ground state of $CaMn_2Sb_2$

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ABSTRACT

We have determined the ground state of the layered compound $CaMn_2Sb_2$ which crystalizes in the $CaAl_2Si_2$ structure. We have performed specific heat and neutron powder diffraction measurements at different temperatures. The neutron powder diffraction results reveal that the system orders antiferromagnetically at 88 K which agrees with the specific heat measurements. The ground state magnetic structure is consistent with previous theoretical calculations.



## 1. Introduction

The $AM_2X_2$ ternary intermetallic (A = rare or alkaline earth, M = transitionmetal, X = Si, Ge, P, As, Sb) compounds have revealed interesting magnetic properties due to the interplay between their magnetic sublattices [1]. The most abundant structure of these materials is the $ThCr_2Si_2$-type, and special attention has been paid to those with M = Mn. In these systems, the in-plane Mn–Mn distance determines their magnetic structure [2]. In particular, the manganese silicides and manganese germanides are special cases of the latter compounds and for example, $AMn_2(Si,Ge)_2$-alloys studies have found antiferromagnetic ordering of the Mn ions, which is concordance with the lower in-plane Mn–Mn distance as compared to the critical value necessary for the stabilization of antiferromagnetic ordering [3,4].

However, other $AM_2X_2$ ternary systems, instead, crystallize in the $CaAl_2Si_2$-type structure [5,6], and it has recently been found that some of these compounds have complex magnetic structures. Neutron diffraction and magnetic measurements revealed that the $SrMn_2P_2$ system orders antiferromagnetically and that frustration effects are present [7]. On the other hand, in the $EuMn_2P_2$ system [8], the Eu spins align ferromagnetically in the plane with these planes coupled antiferromagnetically along the *c*-axis at about 16.5 K.

It was suggested that the substitution of P and As ions by larger Sb atoms in the $AMn_2(P,As)_2$ series should modify the Mn–Mn distance and thus change their magnetic properties [9]. Following this idea, $YbMn_2Sb_2$ was shown to be magnetically ordered with a complex magnetic ordering of the Mn ions [9].

Recently, $(Ca,Sr)Mn_2Sb_2$ intermetallic compounds were studied, where the $CaMn_2Sb_2$ compound showed magnetic order, with a possible antiferromagnetic coupling between the magnetic moments of the two Mn-ions sublattices [10]. In this work we show neutron diffraction and thermal measurements performed on single crystals and powders of $CaMn_2Sb_2$, which clarify the magnetism of this compound.

## 2. Experimental

The $CaMn_2Sb_2$ single-crystals were grown using Sn as a flux. High purity starting materials (higher than 99.9%) were sealed in vacuum and heated to 1273 K for 48 h. Thereafter, the temperature was decreased to 773 K (cooled at 10 °C/h) where the molten flux

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was removed by centrifugation. X-ray diffraction performed using a Bruker SMART CCD [11] diffractometer verified that the structure can be described as double corrugate layers of $Mn^2Sb^{2-}$ separated by $Ca^{2+}$ planes. The unit cell parameters at room temperature were 4.5294(6) and 7.456(2) Å for the $a$ and $c$ axis, respectively, and the space-group was confirmed as $P\bar{3}m1$. The structural characterization and also details about the method used to obtain the $CaMn_2Sb_2$ crystals used in this work were reported in Ref. [10].

Specific heat measurements were performed using a Quantum Design PPMS system [11]. For the neutron diffraction measurements, approximately 0.5 g of powder were sealed in a vanadium can. Neutron diffraction measurements were performed to determine the magnetic structure on the BT1 powder diffractometer at the NIST Center for Neutron Research using a GE 311 monochromator at a wavelength of 2.0787 Å. Measurements of the order parameter were performed on the BT9 thermal triple axis in triple axis mode with a PG filter before and after the sample at a wavelength of 2.359 Å. The sequence of horizontal collimation in stream order was $40'-47'-40'-80'$.

## 3. Results and discussion

We started our exploration of this compound with specific heat measurements. In Fig. 1, $C/T$ is plotted as a function of temperature, where $C$ includes contributions from electronic, phonon and magnetic terms. In the figure, it can be noted that there is only one sharp feature, which is a peak at $T\sim 83$ K. This would suggest that the true temperature of the magnetic phase transition in this compound is much lower than previously suspected. To further investigate the nature of this transition, we turn to neutron diffraction measurements.

To determine the magnetic structure of the material at low temperature, we start by determining the propagation vector which describes the magnetic structure. We performed measurements at 300, 175, and 5 K. As there are no additional reflections present at 5 K, the propagation vector is $\mathbf{k} = (0, 0, 0)$. Next, we perform representational analysis [12,17] to determine the symmetry allowed magnetic structures for this propagation vector. These calculations were performed with version 2K of the program SARA*h*-Representational Analysis [13]. The results are summarized in Table 1. From this analysis, it is clear that several distinct structures are possible. The spins can either lie in the $a$–$b$ plane, or along the $c$-axis. Canting is not allowed by symmetry. For these two cases, the spins can either be ferromagnetically or antiferromagnetically coupled.

We used GSAS [14,15] to refine the structure at 5 K. Peaks from a minority phase ($\approx 8\%$) of Sn were excluded from the refinement along with V and Ti peaks from the sample can. We stress that the only impurity found in the sample was Sn from the flux used to grow the sample. Testing all of the possibilities allowed by symmetry, we find that the best agreement to the data is obtained for a model in which the moments lie in the $a$–$b$ plane and are antiferromagnetically coupled. While we specifically tested the model with moments along the $a$-axis, powder diffraction is of course unable to determine the actual direction of the moments in the plane for this space group. We found moments of $2.8(1)\mu_B$ on the Mn site. In Fig. 2, we show the results of our refinement performed at 5 K, well into the ordered phase. The inset shows the calculated intensity from the nuclear structure alone. The crystallographic parameters determined from this fit and the statistics characterizing the goodness of fit are shown in Table 2.

**Table 1**
Basis vectors for the space group $P\bar{3}m1$ with $\mathbf{k} = (0, 0, 0)$.

| IR | BV | Atom | $m_{\parallel a}$ | $m_{\parallel b}$ | $m_{\parallel c}$ | $im_{\parallel a}$ | $im_{\parallel b}$ | $im_{\parallel c}$ |
|---|---|---|---|---|---|---|---|---|
| $\Gamma_2$ | $\psi_1$ | 1 | 0 | 0 | 12 | 0 | 0 | 0 |
| | | 2 | 0 | 0 | −12 | 0 | 0 | 0 |
| $\Gamma_3$ | $\psi_2$ | 1 | 0 | 0 | 12 | 0 | 0 | 0 |
| | | 2 | 0 | 0 | 12 | 0 | 0 | 0 |
| $\Gamma_5$ | $\psi_3$ | 1 | 6 | 0 | 0 | 0 | 0 | 0 |
| | | 2 | 6 | 0 | 0 | 0 | 0 | 0 |
| | $\psi_4$ | 1 | −3.464 | −6.928 | 0 | 0 | 0 | 0 |
| | | 2 | −3.464 | −6.928 | 0 | 0 | 0 | 0 |
| $\Gamma_6$ | $\psi_5$ | 1 | 6 | 0 | 0 | 0 | 0 | 0 |
| | | 2 | −6 | 0 | 0 | 0 | 0 | 0 |
| | $\psi_6$ | 1 | −3.464 | −6.928 | 0 | 0 | 0 | 0 |
| | | 2 | 3.464 | 6.928 | 0 | 0 | 0 | 0 |

The decomposition of the magnetic representation for the Mn site $(\frac{1}{3}, \frac{2}{3}, 0.6154)$ is $\Gamma_{Mag} = 0\Gamma_1^1 + 1\Gamma_2^1 + 1\Gamma_3^1 + 0\Gamma_4^1 + 1\Gamma_5^2 + 1\Gamma_6^2$. The atoms of the nonprimitive basis are defined according to 1: $(\frac{1}{3}, \frac{2}{3}, 6154)$, 2: $(\frac{2}{3}, \frac{1}{3}, 0.3846)$.

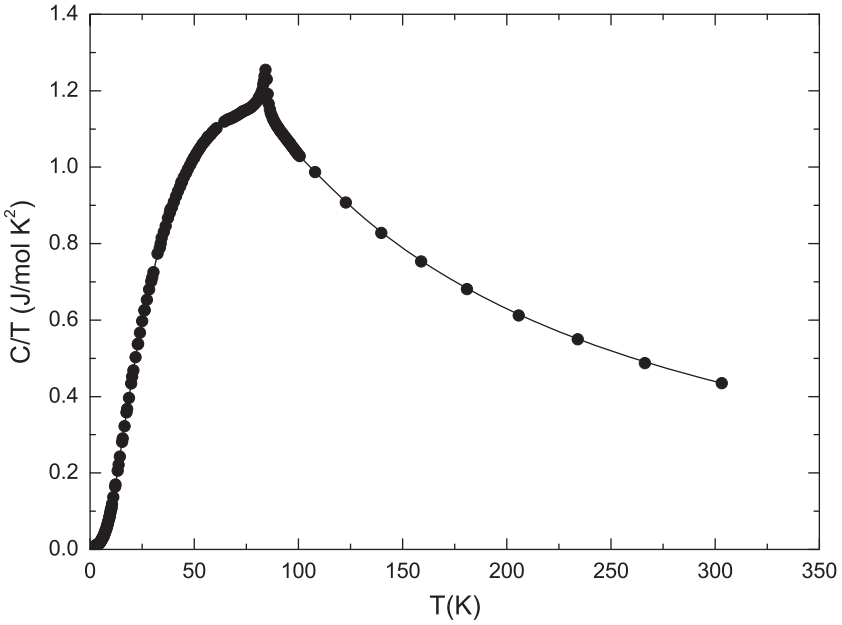


**Fig. 1.** Specific heat measurement performed on a single crystal. Data show a transition to long range order that occurs at $\approx 83$ K.

A cartoon of our structure is shown in Fig. 3. This is broadly consistent with the theoretical model proposed by Bobev et al. [10] in which spins are coupled ferromagnetically within an $a$–$b$ plane and these planes are antiferromagnetically coupled. Even our ordered moment of $\approx 2.8\mu_B$ is in good agreement with their lowest energy model of $3.46\,\mu_B$ when one takes into account that their model is for 0 K and at finite temperatures, spin-waves will reduce the magnitude of the ordered moment. Further checks

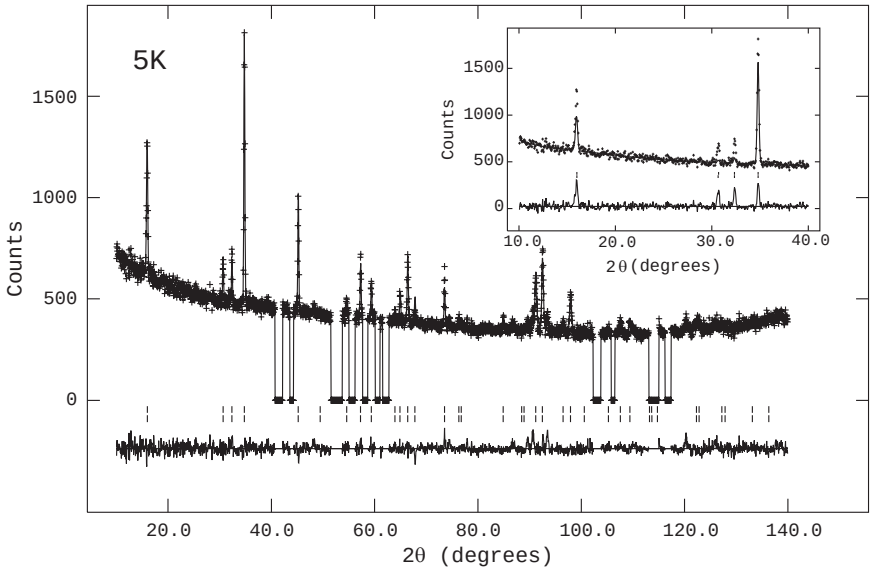


**Fig. 2.** Structural refinement of neutron diffraction data taken at 5 K. Lines represent calculated intensities based on the model described in the text. The inset compares the data to intensities calculated from the nuclear structure alone to emphasize the peaks with magnetic contribution.

**Table 2**
Selected crystallographic data.

| Atom | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|
| Ca | 0 | 0 | 0 | 0.008(4) |
| Mn | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.6154(19) | 0.0022(24) |
| Sb | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.2483(18) | 0.0022(24) |
| Unit cell parameters | $a = 4.5285(4)$ Å | $c = 7.4453(7)$ Å | $V_{cell} = 132.229(20)$ Å$^3$ | |
| Space group | $P\bar{3}m1$ (no. 164) | | | |
| $R_p = 0.0372$ | $R_{wp} = 0.0488$ | $\chi^2 = 1.018$ | $T = 5$ K | |

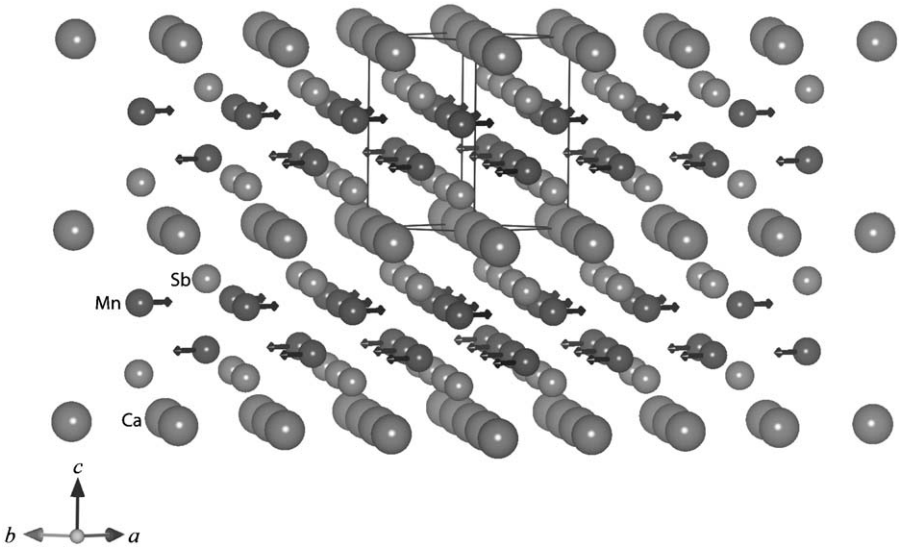


**Fig. 3.** Cartoon of the magnetic and crystallographic structure of $CaMn_2Sb_2$. It should be noted that powder diffraction cannot determine the actual direction of the moments within the $a$–$b$ plane.

against their LDA (GGA) calculations could be done by determining the value of the exchange interaction constant from the difference in the energies determined from their calculations for ferromagnetic and antiferromagnetically coupled Mn moments and comparing that value of $J$ to that determined from spin-wave measurements. However, much larger samples would be needed to perform such measurements. Finally, we note that we believe their calculations were performed without spin–orbit contributions, in which case they would not be sensitive to single ion anisotropy (and would thus be insensitive to the global directions of the moments, that is the energy for a state in which spins lie in the $a$–$b$ plane would be degenerate with one in which the spins were along the $c$-axis). It would be interesting to see if spin orbit interactions were taken into account, if the calculated lowest energy state would be that which we measured with the spins in the $a$–$b$ plane.

Following the determination of the magnetic structure, we measured the order parameter with neutrons. The measurement was performed upon warming by sitting on the (1 0 0) reflection. This reflection was chosen due to a relatively small nuclear contribution in the paramagnetic phase relative to other peaks. The results are shown in Fig. 4. Fits to a mean field order parameter were performed in a range of $10<T<100$ K. This yielded a transition temperature of $T_N = 87.98 \pm 1.22$ K. For the range used, $\chi^2 = 1.82$. The value of the transition temperature is consistent with the specific heat measurements. The poor statistics are due to the extremely small amount of sample available.

While our specific heat results and order parameter measurements are consistent with each other, they contradict the results of Bobev et al. [10]. There are many possible reasons for this. Generally, the first possibility that one considers is sample variation. However, the samples were prepared by the same method by the same group, so this is unlikely to be the cause. Furthermore, in the Bobev [10] paper, the measured transition temperature was close to 250 K, whereas in ours, the temperature is closer to 88 K. This rather large difference in transition temperatures seems difficult to explain from minor variations in sample preparation conditions. A much more likely explanation is to be found by a closer examination of the previously measured susceptibility data.

If we examine the susceptibility measurements in Fig. 4 of the Bobev et al. [10] paper, the AC susceptibility of single crystals has been measured at several different fields. Unfortunately, Ref. [10] does not reveal which axis the susceptibility was measured along, which is rather important for antiferromagnetic systems. Moreover in Ref. [10], there is a claim for a weak transition at 35 K from their measurements. However, as they increase the field, this anomaly vanishes. What is more likely is that they have several small impurity phases present. Neutron diffraction is a volume based technique and will be relatively insensitive to small impurities. However, SQUID measurements are much more sensitive. It is likely is that they have a trace magnetic impurity which orders at around 35 K. In the present work, there is no evidence of additional lines in our neutron diffraction measurement, which makes it unlikely that there is a significant change in magnetic structure. Also, our order parameter measurement shows a relatively smooth transition which does not indicate any anomalies in the magnetic reflection we measured as a function of temperature. If the phase were amorphous, or nanostructured, it would even be difficult to detect with an X-ray diffraction measurement. The disappearance of this "anomaly" with increasing field is likely explained by the presence of a small paramagnetic impurity. A paramagnetic impurity would manifest itself as a "Curie tail", which would grow with increasing field and eventually dominate the signal from their small magnetic impurity.

Now, let us turn to their DC susceptibility measurements on polycrystalline samples (made from crushed single crystals) shown in Fig. 2 of their paper. Here, there is an apparent transition at 250 K. However, we note that the magnitude of this transition is extremely small. Additionally, in their Fig. 3, they show the magnetization measured at 150 and 300 K. Thus, these should be both above and below a magnetic transition. However, the curves are practically identical. Also, with the exception of a low field anomaly, both are linear. Furthermore, the magnitude of the measured moment is 0.15 Bohr magnetons, which is very small for a Mn moment. We also note that there is no evidence of a magnetic transition at 250 K in their AC susceptibility measurements. It is also rather strange that the Curie tail present in the AC susceptibility measurements is not observed at all in the DC susceptibility measurement. However, this could be due to the

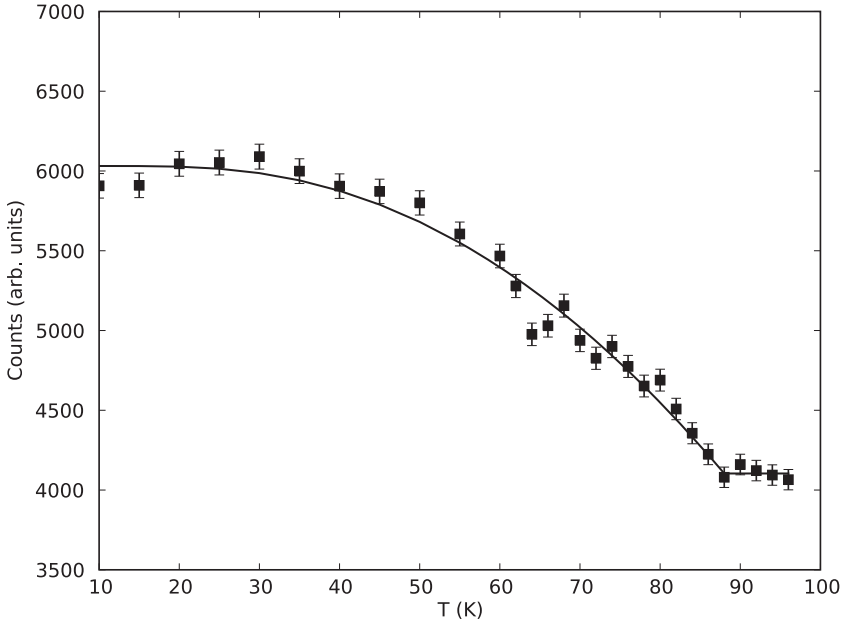


**Fig. 4.** Measurement of the order parameter as described in the text. Lines represent fits to the order parameter [16].

unusually high field used to perform the measurement. We also find no evidence of a phase transition at 250 K in our specific heat measurements. While we did not measure the order parameter to room temperature, we did measure diffraction patterns at 175 K, so if the system were ordered, we should have seen some evidence of magnetic order. The most likely explanation is that the DC susceptibility measurements are sensitive to some magnetic impurity phase to which we are not sensitive to in our neutron diffraction measurements.

In summary, we have determined undoubtfully the magnetic ground state of $CaMn_2Sb_2$. Furthermore, we have determined that the magnetic ordering temperature of 88 K is much lower than that previously reported from magnetization measurements. Our results are in broad agreement with theoretical calculations.

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