Magnetic Structure of CaMn$_2$P$_2$

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We report neutron-diffraction results on single-crystal CaMn$_2$P$_2$ containing corrugated Mn honeycomb layers and determine its ground-state magnetic structure. The diffraction patterns consist of prominent $(1/6, 1/6, L)$ r.l.u. ($L$ = integer) reflections, whose temperature dependence is consistent with a first-order antiferromagnetic transition at the Néel temperature $T_N = 70$ K. Our analysis of the diffraction patterns reveals an in-plane $6 \times 6$ magnetic unit cell with highly-ordered spins that in the principal directions rotate by 60-degree steps between nearest neighbors on each sublattice that forms the honeycomb structure. This cycloidal-like magnetic structure belongs to $P\overline{A}c$ magnetic spacegroup.

I. INTRODUCTION

Coupled-spin systems on the honeycomb lattice have gained tremendous interest with the introduction of Kitaev’s model Hamiltonian on this lattice that predicts a spin-liquid state for $S = 1/2$ spins [1, 2]. Experimental results on the honeycomb lattice [3] have also motivated a plethora of theoretical work on the two-dimensional (2D) Heisenberg $J_1 - J_2 - J_3$ model on this lattice [4–10]. It has been found that for $J_3 = 0$, the classical $J_1 - J_2$ Heisenberg model on the 2D honeycomb lattice exhibits a Néel-order ground state for $J_2 < J_1 / 6$ and various degenerate spiral-like states for $J_2 > J_1 / 6$ [5]. The realization of the honeycomb model has been suggested for a wide variety of trigonal $AMn_2Pn_2$ ($A = Sr, Ca; M = Cr, Mn, Fe, Co, Ni; Pn = P, As, Sb, Bi$) compounds with $P\overline{3}m1$ space-group. These compounds contain the transition-metal element in a corrugated honeycomb structure [Fig. 1(b)] formed by two adjacent trigonal layers (sublattices) that are stacked as A/B-type [Fig. 1(a)]. It is interesting to note that the transition-metal bilayer magnetic moments have no intervening binding atoms, as shown in Fig. 1(a), so that the major magnetic coupling between neighbors is likely a direct $M-M$ coupling, and couplings among further neighbors are likely due to $M-Pn-M$ superexchange. Recently, it has been concluded that the superexchange within an Mn-$Pn$-Mn moiety becomes stronger as the atomic number of $Pn$ gets smaller, i.e., stronger for P and weaker for Bi, for similar bond configurations [11].

FIG. 1. (a) Chemical structure of $AMn_2Pn_2$ ($A = Sr, Ca; Pn = P, As, Sb, Bi$) compounds showing the Mn trigonal bilayer without intervening elements. (b) The two trigonal Mn sublattices onto the $ab$-plane are projected, shown with red and green shades. The A and B layers are stacked with two atoms per unit cell (dotted rhombus shows the basal unit cell). The Mn bilayer forms a corrugated honeycomb lattice, where the nearest-neighbor interactions ($J_1$) and the next-nearest-neighbor interactions ($J_2$) are indicated. The magnetic structure shown is typical for the $AMn_2Pn_2$ compounds with $Pn = As, Sb, Bi$; for which $J_1 \gg J_2$, and $J_1$ is antiferromagnetic and $J_2$ is ferromagnetic.

Here, we report neutron-diffraction results on single-crystal CaMn$_2$P$_2$, and determine its ground-state magnetic structure. This compound belongs to the large family of Mn-based trigonal pnictides discussed above that exhibit varying magnetic properties with common char-

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II. EXPERIMENTAL DETAILS AND METHODS

Single crystals of CaMn$_2$P$_2$ were grown in Sn flux, as described previously [12], and the crystal used in this study is from the same growth batch.

Single-crystal neutron-diffraction experiments were performed in a zero applied magnetic field using the TRIAX triple-axis spectrometer at the University of Missouri Research Reactor (MURR). An incident neutron beam of energy 14.7 meV was directed at the sample using pyrolytic graphite (PG) monochromator. A PG analyzer was used to reduce the background. Neutron wavelength harmonics were removed from the beam using PG filters placed before the monochromator and in between the sample and analyzer. Beam divergence was limited using collimators before the monochromator; between the monochromator and sample; sample and analyzer; and analyzer and detector of 60° − 60° − 40° − 40°, respectively. A 40 mg CaMn$_2$P$_2$ crystal was mounted on the cold tip of an Advanced Research Systems closed-cycle refrigerator with a base temperature of approximately 5 K. The crystal was mounted in the (H,0, L) and (H, H, L) scattering planes. The lattice parameters at base temperature are $a = 4.096(1)$ and $c = 6.848(2)$ Å. We also note that our sample consists of at least two crystals that are disoriented with respect to each other, as indicated in Fig. 2. Our diffraction patterns below also show Bragg reflections from the polycrystalline Al sample holder.

III. RESULTS AND DISCUSSION

Diffraction scans along the (H, H, 1) direction at $T = 6$ and 100 K in Fig. 2(a) show the emergence of a prominent peak at $H = 1/6$ r.l.u. (reciprocal lattice units) at low temperatures. As shown Fig. 2(b), the difference between these scans at 6 and 100 K displays magnetic Bragg peaks at $(\eta, \eta, 1)$ and $(1-\eta, 1-\eta, 1)$, where $\eta = 1/6$. Figure 3(a) shows the difference between scans at 6 and 100
FIG. 3. Difference between scans at low and high temperature, as indicated, along (a) ($-1/6, -1/6, L$) showing peaks at integer values of $L$ between $-3$ and $3$ (except for $L = 0$); (b) $(1/6, 1/6, L)$ showing peaks at the integer values of $L$ between $1$ and $3$ (scans with negative $L$ were not accessible due to the experimental setup); (c) $(H, 0, 0)$ showing a weak peak at the nuclear $(1, 0, 0)$ and possibly another at $(2, 0, 0)$. More details on the temperature dependence of the $(1, 0, L)$ peaks are provided in the Supplementary Material [SM] [20]. Signals from the Al sample holder are marked on the figures. As indicated, a minute inclusion of ferromagnetic MnP crystals gives rise to weak peaks.

K along $(-\eta, -\eta, L)$, indicating magnetic Bragg peaks at $L = -3, -2, -1, 1, 2,$ and $3$. Figure 3(b) shows similar observations of magnetic Bragg peaks at $L = 1, 2,$ and $3$ in the direction of $(\eta, \eta, L)$. Scans along $(H, H, 0)$ do not show any newly-emerging peaks at low temperatures (not shown). Figure 3(c) shows the difference of scans along $(H, 0, 0)$ at 6 and 100 K with a weak peak at the nuclear $(1, 0, 0)$ reflection and possibly another very weak one at $(2, 0, 0)$. The other signals that have a negative intensity originate from the Al sample holder. Also, magnetic peaks from a small amount of MnP in the crystal are present in the scan. As noted below, the temperature dependence of $(1, 0, 0)$ does not exhibit a transition at $T_N$. The temperature dependence of the integrated intensity of the $(1,0,1)$ reflections in Fig. 4 shows a very sharp transition at $T = 70(1)$ K that coincides with a previous report that indicates a strong first-order magnetic phase transition at this temperature [12]. The fact that the peak intensities of the $(\pm \eta, \pm \eta, L$) reflections fall off for larger $L$, as expected from the magnetic form factor of Mn$^{2+}$, is further evidence that these newly observed Bragg peaks are magnetic in origin. Below, we propose a magnetic structure that is consistent with all the experimental observations assuming the magnetic propagation vector $\bm{\tau} = (\eta, \eta, 0)$ r.l.u., with $\eta = 1/6$.

To start with, the $(\eta, \eta, 0)$ propagation vector indicates that the magnetic structure consists of a $6 \times 6$ nuclear basal unit cell. Figure 5(a) is a compilation of the magnetic reflections observed in the $(H, H, L)$ plane, where the sizes of the peaks roughly reflect observed intensities. The model structure is constructed by creating a $6 \times 6$ in-plane nuclear unit cell that spans the corrugated honeycomb structure, i.e., the bilayer magnetic structure stacked along the c-axis [Fig. 5(b)]. The red sites correspond to one trigonal magnetic sublattice and the green sites to the other magnetic sublattice. The magnetic model is constructed by assigning an arbitrary moment.
direction at an origin, for instance, at the lower-left corner, and then successively rotating the spin on the nearest neighbors on the same sublattice clockwise by 60°.

The other sublattice is constructed similarly with antiparallel spins with respect to the first sublattice. Note that along the (1,0,0) and (0,1,0) directions, the magnetic structure of each sublattice is a cycloid with a 60° turn angle. Thus, for each sublattice, the overall structure is a cycloid with propagation vector (η,η,0), with η = 1/6.

To model the magnetic intensity, I, we use the following equation:

\[ I = C|f(Q)|^2 \sum_{j=1}^{k} e^{iQ \cdot \mathbf{r}_j} \times (\mathbf{\hat{m}}_j \times \mathbf{\hat{Q}})^2, \]

where C is a normalization factor, Q is the scattering vector, r_j and \( \mathbf{\hat{m}}_j \) are the position of Mn moment and the unit vector of the magnetic moment, respectively. f(Q) is the magnetic form factor of Mn²⁺. Using Eq. (1), the calculated magnetic intensities are shown in Fig. 5(c), in good agreement with the experimental results shown in (a). Inspection of the model structure in (b) shows a global trend where along the long diagonal of a hexagon, all the spins are collinear, and the nearest neighbors are antiparallel.

Our intensity calculation [Eq. (1)] allows us to estimate the average ordered magnetic moment, \( \langle gS \rangle \), in the model structure shown in Fig. 6, where g is the spectroscopic-splitting factor and S is the spin quantum number. By comparing nuclear-peak intensities and their structure factors to the observed magnetic-peak intensities, we estimate \( \langle gS \rangle = 4.2(5) \) μB, typical for Mn²⁺ moments.

To estimate the ratio of \( J_2/J_1 \), we examine various magnetic structures, as shown in Fig. 6 for (a) Néel (\( J_1 >> J_2 \)), (b) Cycloidal, and (c) Trigonal (\( J_1 << J_2 \)) structures. The ground state energy of these structures is calculated by assuming Heisenberg interactions acting between the nearest-neighbor and next-nearest-neighbor...
in-plane sites using the following formula:

\[ E = J_1 \sum_{NN} S_i \cdot S_j + J_2 \sum_{NNN} S_i \cdot S_j \]  

(2)

Consistent with our neutron-diffraction data, the interlayer coupling is ferromagnetic; this term is ignored in Eq. (2). Using Eq. (2) and assuming classical spins \( S = 1 \), we find the ground state energies of each structure to be:

- Magnetic layer coupling is ferromagnetic; this term is ignored in Eq. (2).
- \( E_{\text{Néel}} = -3J_1 + 6J_2 \)
- \( E_{\text{cycloidal}} = -2J_1 + J_2 \)
- \( E_{\text{Trigonal}} = -3J_2 \)

The energy of the cycloidal structure is compared with energies of the other two extreme structures to determine the range of \( J_2/J_1 \) that give rise to the cycloidal structure. By setting up the two inequalities: (1) \( E_{\text{Cycloidal}} - E_{\text{Néel}} < 0 \) and (2) \( E_{\text{Cycloidal}} - E_{\text{Trigonal}} < 0 \), we find the ratio of \( J_2/J_1 \) needed for the cycloidal structure is \( \frac{1}{3} < J_2/J_1 < \frac{1}{2} \). This calculation is not definitive and does not include the strong influence of magnetic fluctuations. Mean-filed calculations show that \( J_2/J_1 = 1.73 \) based on high-temperature measurements of the Curie-Weiss temperature \( \langle 6 \rangle \) of the isostructural SrMn \(_2\)P \(_2\) (see more details in SM).

We emphasize that Fig. 5(b) with magnetic spacegroup \( P_{\lambda c} \) [21] is not unique with our neutron-diffraction observation shown in Fig. 5(a). In fact, systematically searching through the Symmetry-Based Computational Tools for Magnetic Crystallography [21] we find two more magnetic structures, shown in Fig. 7, that are consistent with the diffraction measurements. In both structures, we start with an origin at the lower-left corner, where the spins on the red site and green site are oriented along the \( b \)- and \( a \)-directions respectively. The magnetic structure in Fig. 7(a) has a magnetic space-group \( P_{\varphi} \) [21] and is constructed by rotating the nearest neighbors in the red sublattice counterclockwise and green sublattice clockwise by 60 degrees successively. The other magnetic structure in Fig. 7(b) has a magnetic space-group of \( P_{\varphi} \) [21] and is constructed similarly by rotating the nearest neighbors in the red sublattice clockwise and green sublattice counterclockwise by 60 degrees successively. The energy associated with these two structures, according to Eq. (2), is \( -J_1 + J_2 \). Comparing with the energy associated with the structure mentioned in Fig. 5(b) and assuming the \( J_1 \) interaction to be AFM, the structures described in Fig. 7 are energetically less favorable than the one in Fig. 5(b). Therefore, we propose that the magnetic structure with magnetic space-group \( P_{\phi c} \) shown in Fig. 5(b) is more favorable than the \( P_{\varphi} \) and \( P_{\rho \alpha} \) space-groups shown in Fig. 7. In the SM, we provide more temperature-dependent diffraction results from the crystal that are not correlated with the first-order phase transition at \( T_N = 70 \) K.

IV. CONCLUSIONS

Using neutron-diffraction measurements, we find that below \( T_N = 70 \) K, CaMn \(_2\)P \(_2\) undergoes a first-order antiferromagnetic transition with a magnetic unit cell that is a \( 6 \times 6 \) in-plane chemical unit cell. The average ordered magnetic moment \( \langle gS \rangle = 4.2(5) \) \( \mu_B \). The integrated intensity of the major (1/6,1/6,1) magnetic peak vs. temperature shows an abrupt decrease in intensity at \( T_N \) that is a characteristic of a first-order phase transition. Our estimate of \( \frac{1}{6} < J_2/J_1 < \frac{1}{2} \) suggesting this system is very close to a spiral magnetic structure [5]. In general, although this and other isostructural pnictide systems possess corrugated-honeycomb structures, our results show that the corrugation may not affect the magnetic structure of these systems.
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