First-order transitions at the Néel temperatures of trigonal SrMn$_2$P$_2$ and CaMn$_2$P$_2$

N. S. Sangeetha, Santanu Pahkira, Q.-P. Ding, H.-C. Lee, V. Smetana, A.-V. Mudring, Y. Furukawa, and D. C. Johnston

$^1$Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA
$^2$Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
$^3$Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius väg 16 C, 106 91 Stockholm, Sweden

(Dated: August 20, 2021)

Single crystals of CaMn$_2$P$_2$ and SrMn$_2$P$_2$ were grown using Sn flux and characterized by room-temperature single-crystal x-ray diffraction, electrical resistivity $\rho$, heat capacity $C_p$, and magnetic susceptibility $\chi = M/H$ measurements versus temperature $T$ and magnetization $M$ versus applied magnetic field $H$ isotherm measurements. The x-ray diffraction results show that both SrMn$_2$P$_2$ and CaMn$_2$P$_2$ adopt the trigonal CaAl$_2$Si$_2$-type structure. The $\rho(T)$ measurements demonstrate insulating ground states for both compounds with intrinsic activation energies of 0.124 eV for SrMn$_2$P$_2$ and 0.088 eV for CaMn$_2$P$_2$. The $\chi(T)$ and $C_p(T)$ data reveal a weak first-order antiferromagnetic (AFM) transition at the Néel temperature $T_N = 53(1)$ K for SrMn$_2$P$_2$ and a strong first-order AFM transition at $T_N = 69.8(3)$ K for CaMn$_2$P$_2$. Both compounds show an isotropic and nearly $T$-independent $\chi(T \leq T_N)$. $^{31}$P NMR measurements confirm the strong first-order transition in CaMn$_2$P$_2$ but show critical slowing down near $T_N$ for SrMn$_2$P$_2$ thus evidencing second-order character. The NMR measurements also indicate that the AFM structure of CaMn$_2$P$_2$ is commensurate with the lattice whereas that of SrMn$_2$P$_2$ is incommensurate. These first-order AFM transitions are unique among the class of trigonal (Ca, Sr, Ba)Mn$_2$(P, As, Sb, Bi)$_2$ compounds which otherwise exhibit second-order AFM transitions. This result presents a challenge to understand the systematics of magnetic ordering in this class of materials in which magnetically-frustrated antiferromagnetism is quasi-two-dimensional.

I. INTRODUCTION

The Mn-based 122-type pnictides AMn$_2$P$_n$ (A = Ca, Sr, Ba; $P_n$ = P, As, Sb, Bi) have received attention owing to their close structural relationship to high-$T_c$ iron pnictides. The undoped Mn pnictides are local-moment antiferromagnetic (AFM) insulators like the high-$T_c$ iron pnictides. The Mn-based 122-type pnictides recent density-functional theory (DFT) calculations for the 122 pnictide family have suggested that the trigonal 122 transition-metal pnictides which have the CaAl$_2$Si$_2$ structure might comprise a new family of magnetically-frustrated materials in which to study the potential superconducting mechanism. It had previously been suggested on theoretical grounds that CaMn$_2$Si$_2$ is a fully-frustrated classical magnetic system arising from proximity to a tricritical point.

The electrical resistivity $\rho$ and heat capacity $C_p$ versus temperature $T$ of single-crystal CaMn$_2$P$_2$ were reported in Ref. 10. The compound is an insulator at $T = 0$ and undergoes a first-order transition of some type at 69.5 K.

Raman spectra of CaMn$_2$P$_2$ versus $T$ suggested the formation of a crystallographic superstructure below 69.5 K. However, the authors’ magnetic susceptibility $\chi(T)$ measurements revealed no magnetic transition at that temperature. Previous studies on polycrystalline SrMn$_2$P$_2$ showed that it is an insulator at room temperature with AFM ordering at $T_N = 53(1)$ K. SrMn$_2$P$_2$ transforms from its trigonal CaAl$_2$Si$_2$-type structure at atmospheric pressure $p$ to the tetragonal ThCr$_2$Si$_2$ structure (space group $I4/mmm$) after treatment at $p = 5$ GPa and $T = 900$ °C.

Here we report the detailed properties of trigonal Mn pnictides CaMn$_2$P$_2$ and SrMn$_2$P$_2$ single crystals. We present the results of single-crystal x-ray diffraction, electrical resistivity $\rho$ in the $ab$ plane versus temperature $T$, isothermal magnetization versus applied magnetic field $M(H)$, magnetic susceptibility $\chi(T)$, heat capacity $C_p(H, T)$, and $^{31}$P NMR measurements. We find from $C_p(T)$, $\chi(T)$, and NMR that CaMn$_2$P$_2$ exhibits a strong first-order AFM transition at $T_N = 69.8(3)$ K whereas SrMn$_2$P$_2$ shows a weak first-order transition at $T_N = 53(1)$ K but with critical slowing down on approaching $T_N$ from above as revealed from NMR, a characteristic feature of second-order transitions. Thus the AFM transition in SrMn$_2$P$_2$ has characteristics of both first- and second-order transitions. The $\chi(T)$ data also reveal the presence of strong isotropic AFM spin fluctuations in the paramagnetic (PM) state above $T_N$ up to our maximum measurement temperatures of 900 K and 350 K for SrMn$_2$P$_2$ and CaMn$_2$P$_2$, respectively.
arising from the quasi-two-dimensional nature of the Mn spin layers \[14\] together with possible contributions from magnetic frustration.

Remarkably, our studies of SrMn$_2$P$_2$ and CaMn$_2$P$_2$ reveal the only known members of the isostructural trigonal class of materials with general formula AMn$_2$P$_2$ containing Mn$^{2+}$ spins $S = 5/2$ that exhibit first-order AFM transitions, where $A =$ Ca, Sr, or Ba and the pnictogen $Pn = P$, As, Sb, or Bi. The others show second-order AFM transitions, including CaMn$_2$As$_2$ \[15\], SrMn$_2$As$_2$ \[11\], SrMn$_2$Sb$_2$ \[8\], SrMn$_2$Sb$_2$ \[17\] \[20\], SrMn$_2$Sb$_2$ \[18\], and CaMn$_2$Bi$_2$ \[21\]. The AFM transition in the monoclinic compound Li$_2$MnO$_3$ containing a Mn honeycomb lattice with Mn$^{4+}$ spins $S = 3/2$ is also second order \[22\].

Following the experimental details in Sec. II, the single-crystal structure data for single-crystal SrMn$_2$P$_2$ and CaMn$_2$P$_2$ are given in Sec. III the $\rho(T)$ data in Sec. IV our studies of $M(H)$ and $\chi(T)$ in Sec. V the $C_p(T)$ measurements in Sec. VI the NMR results in Sec. VII Concluding remarks are given in Sec. VIII.

II. EXPERIMENTAL DETAILS

Single crystals of SrMn$_2$P$_2$ and CaMn$_2$P$_2$ were grown in Sn flux. High-purity elements Sr (99.99%) from Sigma Aldrich and Ca (99.98%), Mn (99.95%), P (99.999%), and Sn (99.999%) from Alfa Aesar were taken in the molar ratio (Sr,Ca):Mn:P:Sn = 1.05:2:2:20 and placed in an Sn flux. High-purity elements Sr (99.99%) from Sigma and Sn (99.999%) from Alfa Aesar were taken in the monoclinic compound Li$_2$MnO$_3$ containing a Mn honeycomb lattice with Mn$^{4+}$ spins $S = 3/2$ is also second order \[22\].

Following the experimental details in Sec. II the single-crystal structure data for single-crystal SrMn$_2$P$_2$ and CaMn$_2$P$_2$ are given in Sec. III the $\rho(T)$ data in Sec. IV our studies of $M(H)$ and $\chi(T)$ in Sec. V the $C_p(T)$ measurements in Sec. VI the NMR results in Sec. VII Concluding remarks are given in Sec. VIII.
TABLE I. Refined crystallographic parameters obtained from single XRD of SrMn$_2$P$_2$ and CaMn$_2$P$_2$ crystals. The atomic coordinates in (Sr,Ca)Mn$_2$P$_2$ of the hexagonal unit cell are Sr/Ca: 1a (0, 0, 0); Mn: 2d (1/3, 2/3, $z_{	ext{Mn}}$); and P: 2d (1/3, 2/3, $z_{	ext{P}}$).

| Structure | SrMn$_2$P$_2$ | CaMn$_2$P$_2$ |
|-----------|---------------|---------------|
| Space group | CaAl$_2$Si$_2$-type trigonal | CaAl$_2$Si$_2$-type trigonal |
| Lattice parameters | | |
| $a$ (Å) | 4.656(6) | 4.1013(3) |
| $c$ (Å) | 7.138(1) | 6.8564(6) |
| $c/a$ | 1.7136(5) | 1.6717(3) |
| $V_{\text{cell}}$ (Å$^3$) | 107.27(4) | 99.88(2) |
| Atomic coordinates | | |
| $z_{\text{Mn}}$ | 0.62033(7) | 0.62441(4) |
| $z_{\text{P}}$ | 0.2726(1) | 0.26155(9) |

were used for NMR measurements. $^31$P NMR spectra were obtained either by fast Fourier transform (FFT) of the NMR echo signals under an external magnetic field of ~ 7.01 T or by sweeping the external magnetic field $H$ at a constant resonance frequency of 121 MHz. The $^31$P spin-lattice relaxation rate ($1/T_1$) was measured with a saturation recovery method. $1/T_1$ at each $T$ was determined by fitting the nuclear magnetization $M$ versus time $t$ using the stretched exponential function $1 - M(t)/M(\infty) = e^{(-t/T_1)^\beta}$, where $M(t)$ and $M(\infty)$ are the nuclear magnetization at time $t$ after the saturation and the equilibrium nuclear magnetization at $t \rightarrow \infty$, respectively. All the relaxation data were well fitted with the stretched exponent $\beta = 1$ in the paramagnetic state for both samples. In the AFM state, $\beta \sim 0.6 \pm 0.15$ was used for SrMn$_2$P$_2$. For CaMn$_2$P$_2$ in the AFM state, $\beta = 1$ was used. However, at low temperatures below ~ 20 K, we observed a slight deviation from the function and fitted with two $T_1$ components and took the long component as $T_1$.

III. CRYSTAL STRUCTURE

SEM images of the crystal surfaces indicated single-phase crystals. EDX analyses of the chemical compositions were in agreement with the expected 1:2:2 stoichiometry of the compounds and the amount of Sn incorporated into the crystal structure from the Sn flux is zero to within the experimental error.

Single-crystal XRD measurements on CaMn$_2$P$_2$ and SrMn$_2$P$_2$ confirmed the single-phase nature of the compounds and the CaAl$_2$Si$_2$-type crystal structure of each that is shown in Fig. 2. The crystal data are listed in Table I. The lattice parameters $a$ and $c$ of the trigonal structure (hexagonal unit cell) are in good agreement with previous values [10, 13]. The crystal structure of CaMn$_2$P$_2$ at 293 and 40 K was found to be the same [10]. However, as noted in the Introduction, Raman spectra of CaMn$_2$P$_2$ versus $T$ suggested the formation of a crystallographic superstructure below 69.5 K, which was stated to be consistent with the authors’ single-crystal x-ray diffraction data [10].

IV. ELECTRICAL RESISTIVITY

The $ab$-plane $\rho(T)$ data from 270 to 400 K for SrMn$_2$P$_2$ and from 150 to 300 K for CaMn$_2$P$_2$ are shown in Figs. 3(a) and 3(b), respectively. For both compounds $\rho$ first increases slowly with decreasing $T$ and then increases more rapidly. The data demonstrate that both SrMn$_2$P$_2$ and CaMn$_2$P$_2$ have insulating ground states.
We fitted the respective $\rho(T)$ data over restricted temperature intervals by

$$\log_{10} \rho = A + 2.303 \left( \frac{\Delta}{k_B T} \right),$$

where $A$ is a constant, $k_B$ is Boltzmann’s constant, and $\Delta$ is the activation energy.

Plots of $\log_{10} \rho$ vs $1/T$ are shown in the insets of Figs. 3(a) and 3(b) for SrMn$_2$P$_2$ and CaMn$_2$P$_2$, respectively. For SrMn$_2$P$_2$, the high-$T$ data between $\approx 270$ K and 400 K are nearly linear in $1/T$ and were fitted by Eq. (2), yielding the intrinsic activation energy $\Delta = 0.124(3)$ eV as shown by the solid straight line in the inset of Fig. 3(a), and the extrapolations as dashed lines. The fitted activation energy is of the same order as found previously for isostructural BaMn$_2$Sb$_2$ [17]. However, the value here is much larger than the activation energy found for polycrystalline SrMn$_2$P$_2$ over the temperature range 200–300 K, which was 0.0129(2) eV [11].

For CaMn$_2$P$_2$, the data between 220 K and 300 K and between 197 K and 164 K were respectively nearly linear in $1/T$ and were fitted by Eq (2), yielding the intrinsic activation energy at high $T$ as $\Delta = 0.088(1)$ eV, whereas the extrinsic activation energy at low $T$ is $\Delta = 0.012(1)$ eV. The fits are shown in the inset of Fig. 3(b) as the solid straight lines and the extrapolations by dashed lines. For comparison, the high-$T$ intrinsic activation energy reported recently for single-crystal CaMn$_2$P$_2$ from $ab$-plane $\rho(T)$ data was $\Delta = 0.040$ eV and the extrinsic low-$T$ value was 0.00064 eV [10].
FIG. 4. (a) Temperature dependent zero-field-cooled magnetic susceptibility $\chi(T)$ of SrMn$_2$P$_2$ in a magnetic field $H = 0.1$ T applied in the $ab$ plane ($\chi_{ab}$) and along the $c$ axis ($\chi_c$). (b) The expanded plot of $\chi(T)$ between 1.8 and 100 K to highlight the transition. Inset: Derivative $d[\chi_c(T)/dT$ versus $T$ for $H || c$, yielding $T_N = 53(1)$ K.

FIG. 5. Zero field cooled magnetic susceptibility $\chi_{ab}$ and $\chi_c$ versus $T$ for 1.8 K ≤ $T$ ≤ 900 K measured in $H = 3$ T.

V. MAGNETIC SUSCEPTIBILITY AND MAGNETIZATION VERSUS FIELD ISOTHERMS

A. SrMn$_2$P$_2$

Figure 4(a) shows the zero-field-cooled (ZFC) magnetic susceptibility $\chi(T) \equiv M(T)/H$ of SrMn$_2$P$_2$ in a magnetic field $H = 0.1$ T applied in the $ab$ plane ($\chi_{ab}$) and along the $c$ axis ($\chi_c$). These data exhibit an AFM transition at $T_N = 53(1)$ K, clearly seen from the peak in the expanded plot of $d[\chi(T)/dT$ versus $T$ in Fig. 4(b) according to the Fisher relation [32]. The $\chi(T)$ below $T_N$ is almost isotropic and the magnetic phase transition is sharper in $\chi_c(T)$. According to molecular field theory, the isotropic and nearly $T$-independent $\chi(T \leq T_N)$ suggests that the ordered moments form an AFM $c$-axis helix or $ab$-plane cycloidal structure with an approximately 120° turn angle, irrespective of the value of spin $S$ [33, 34]. As will be shown below, $^{31}$P NMR measurements suggest an incommensurate AFM state. Similar behaviors have been observed in 120°-ordered compounds such as VF$_2$ and VBr$_2$ [35]. The suggested magnetic structure in SrMn$_2$P$_2$ is different from the magnetic structure of the isostructural compound SrMn$_2$As$_2$ that was found to have a collinear AFM structure with the ordered moments aligned in the $ab$ plane, but with three approximately equally populated domains at an angle of 120° from each other [16]; we found similar behavior in SrMn$_2$Sb$_2$ [17]. Neutron-diffraction measurements are needed confirm the magnetic structure in SrMn$_2$P$_2$.

Figure 5 shows $\chi(T)$ of SrMn$_2$P$_2$ from 1.8 K to 900 K measured in $H = 3$ T. Unlike most local-moment antiferromagnets for which $\chi(T)$ decreases above $T_N$ according to the Curie-Weiss law, the $\chi(T)$ above $T_N$ in SrMn$_2$P$_2$ increases with $T$ above $T_N$, exhibits a broad maximum at about 300 K and then slowly decreases. Therefore, the present data suggest that strong dynamic AFM fluctuations occur up to at least 900 K, similar to corresponding data for the isostructural compounds (Sr,Ca)Mn$_2$(As,Sb)$_2$ [15, 17]. Within a local-moment picture, these features at $T > T_N$ are characteristic of a quasi-one or -two-dimensional antiferromagnet. Similar results were obtained for a polycrystalline sample of SrMn$_2$P$_2$ [11, 36].

$M(H)$ isotherms for a single crystal of SrMn$_2$P$_2$ with $H || ab$ and $H || c$ are shown in Figs. 6(a) and 6(b), respectively. The data for $M_{ab}$ and $M_c$ are proportional to $H$ at all temperatures, indicating the absence of significant ferromagnetic or saturable paramagnetic impurities. The nearly isotropic $M(H, T < T_N)$ data for both
field directions are consistent with the nearly isotropic behavior of \(\chi(T)\) in Fig. 4(a).

We obtain an estimate of the exchange interactions between the Mn spins-5/2 in SrMn\(_2\)P\(_2\) as follows. We assume that all spins are identical and crystallographically equivalent as in CaMn\(_2\)P\(_2\) and SrMn\(_2\)P\(_2\). Within a local-moment Heisenberg picture, molecular-field theory predicts a magnetic susceptibility

\[
\chi = \frac{C}{T - \theta_p},
\]

where \(C\) is the Curie constant per mole of spins given by

\[
C = \frac{N_A g^2 S(S + 1)}{3k_B},
\]

\(N_A\) is Avogadro’s number, \(g\) is the spectroscopic splitting factor of a spin, and \(k_B\) is Boltzmann’s constant. The

paramagnetic Weiss temperature \(\theta_p\) is given by

\[
\theta_p = -\frac{S(S + 1)}{3k_B} \sum_j J_{ij},
\]

which contains the sum of the Heisenberg exchange interactions \(J_{ij}\) between a central spin \(i\) and its neighbors \(j\) with which it interacts and an AFM \(J\) is positive. Here, because a formula unit of SrMn\(_2\)P\(_2\) contains two magnetic Mn atoms, and if \(C\) is expressed in cgs units of \(\text{cm}^3\cdot\text{K per mole of formula units, we get}

\[
C_{\text{f.u.}} = \frac{2N_A g^2 S(S + 1)}{3k_B},
\]

Then using \(g = 2\) and \(S = 5/2\) gives

\[
C_{\text{f.u.}} = 8.75 \frac{\text{cm}^3\cdot\text{K}}{\text{mol f.u.}}.
\]

It is clear from Fig. 4(a) that \(\chi_{ab}(T)\) does not attain Curie-Weiss behavior up to 900 K. However, if we calculate a \(T\)-dependent \(\theta_p\) from Eq. 3a given by

\[
\theta_p(T) = T - \frac{C_{\text{f.u.}}}{\chi(T)},
\]

where \(\chi(T) = \chi_{ab}(T)\) is the magnetic susceptibility per mole of formula units as in Fig. 4, we expect \(\theta_p(T)\) to asymptote to its actual value \(\theta_p\) as the dynamic short-range correlations diminish with increasing \(T\).

Figure 7 shows a plot of \(\theta_p\) versus \(T\) obtained from the data in Fig. 5 using Eq. 6. The data appear to asymptote at high temperatures to a value

\[
\theta_p \sim -3500 \text{ K},
\]

where the negative sign indicates AFM interactions. Then using Eqs. 3c and 7 we obtain

\[
\sum_j J_{ij} = -\frac{3k_B \theta_p}{S(S + 1)} \sim 0.10 \text{ eV}.
\]
If it is assumed that a given Mn spin only interacts with its three nearest neighbors in the corrugated honeycomb lattice with exchange interaction $J$, then $J \sim 34$ meV.

### CaMn$_2$P$_2$

The zero-field-cooled (ZFC) magnetic susceptibilities $\chi \equiv M/H$ versus $T$ measured in $H = 0.1$ T and $H = 3$ T applied in the $ab$ plane ($\chi_{ab}$) and along the $c$ axis ($\chi_{c}$) for a single crystal of CaMn$_2$P$_2$ are shown in Figs. 8(a) and 8(b), respectively. At first glance, there is no a clear feature of any magnetic phase transition up to 350 K. However, an expanded plot of $\chi_c(T)$ data in the inset of Fig. 8(b) shows a first-order AFM transition at $T_N = 69.8(3)$ K. Contrary to our findings, Ref. [10] found that CaMn$_2$P$_2$ does not show any long-range magnetic ordering below 400 K. Instead, they found a first-order structural transition at $T^\ast = 69$ K from electrical resistivity and heat-capacity measurements and also found that $T^\ast$ increases with increasing pressure. From the nearly isotropic $\chi_c(T)$ below $T_N$ in Fig. 8(b), we suggest that the AFM structure is, or is similar to, a 120° $c$-axis helix or $ab$-plane cycloid [33, 34].

Like SrMn$_2$P$_2$, CaMn$_2$P$_2$ is a low-dimensional antiferromagnet as seen by the very broad apparent maximum in $\chi(T)$ above $T_N$ in Fig. 8(b). Indeed the Curie-Weiss temperature region of $\chi$ is not reached up to 350 K, indicating that strong AFM correlations survive to significantly higher temperatures than plotted. Previous studies of Mn pnictides suggested that for the $d^8$ electronic configuration of Mn$^{2+}$ ($S = 5/2$) in trigonal Mn pnictides, the nearest-neighbor interactions are very strong and these compounds tended to have AFM correlations or develop long-range AFM order due to the competition among different exchange interactions between the Mn sites [2, 3, 12, 17].

In addition, a small upturn in $\chi_c(T)$ is seen in Fig. 8(a) below about 300 K. This is likely due to FM MnP impur-
rity with Curie temperature \( T_c = 291.5 \) K \[37\] that are present on the crystal surface and/or as an inclusion in the crystal, similar to BaMn\(_2\)As\(_2\) \[2\] and SrMn\(_2\)As\(_2\) \[15\] crystals with MnAs impurities. From a comparison of Figs. 3(a) and 3(b), this FM MnP impurity is most clearly seen in the \( \chi'(T) \) data with \( H = 0.1 \) T. In addition there is a small upturn in \( \chi(T) \) data below \( \approx 40 \) K which is likely due to the contribution of paramagnetic impurities.

Figures 10(a) and 10(b) show \( M(H) \) isotherms for CaMn\(_2\)P\(_2\) with \( H \) in the \( ab \) plane and along the \( c \) axis, respectively. The \( M(H) \) data are almost linear for each temperature indicating that the amount of ferromagnetic seen in Fig. 3(a) is very small. The intrinsic magnetic behavior of \( \chi_{ab} \) data were extracted and for which the \( M_s(H) \) data in Fig. 8(b) were measured with \( H = 3 \) T. Therefore, we obtained the intrinsic \( \chi \) from the isotherm data according to

\[
M(H, T) = M_{\text{sat}}(T) + \chi_{\text{int}}(T)H, \tag{9}
\]

where \( M_{\text{sat}}(T) \) is the saturation magnetization due to the FM impurities. The \( T \to 0 \) value of \( M_{\text{sat}} \) for CaMn\(_2\)P\(_2\) is 2 G cm\(^2\)/mol = 0.00036 \( \mu_B \)/f.u., which corresponds to 0.03 mol\% of MnP impurities using the saturation moment \( \approx 1.33 \) \( \mu_B \)/f.u. \[37\] for MnP. The \( \chi(T) \equiv M(T)/H \) data in Fig. 8(b) were measured with \( H = 3 \) T. Therefore, we obtained the intrinsic \( \chi \) from the isotherm data according to

\[
\chi_{\text{intrinsic}}(T) = \frac{M_{\text{measured}}(T) - M_{\text{sat}}(T)}{3 T}. \tag{10}
\]

The \( \chi_{\text{intrinsic}}(T) \) data are shown by the filled black squares in Fig. 8(b) and the black solid line is a guide to eye. It is seen that the \( \chi_{\text{intrinsic}}(T) \) data for CaMn\(_2\)P\(_2\) follows the behavior of \( \chi_{ab} \), which means that there is no intrinsic anisotropy between the \( ab \)-plane and \( c \)-axis magnetization data, similar to SrMn\(_2\)P\(_2\) as seen in the previous section.

VI. HEAT CAPACITY

Figures 11(a) and 11(b) show zero-field \( C_p(T) \) data for SrMn\(_2\)P\(_2\) and CaMn\(_2\)P\(_2\), respectively. The sharp peaks in \( C_p(T) \) at 53 K in SrMn\(_2\)P\(_2\) and at 69.8 K in CaMn\(_2\)P\(_2\) are at the respective Néel temperatures of the two compounds found from the above \( \chi(T) \) data. The \( C_p(T) \) value obtained at 300 K is smaller than the classical Dulong-Petit limit of 3n\( R \) \( \approx 124 \) J/mol-K for both compounds and similar to that reported in Ref. 10 for CaMn\(_2\)P\(_2\). Figures 6 and 8 demonstrate that strong dynamic short-range AFM correlations persist up to high temperatures, as was previously found for the isostructural compounds CaMn\(_2\)As\(_2\) and SrMn\(_2\)As\(_2\) \[12\]. Thus extraction of the \( T \)-dependent lattice contribution to the heat capacity below 300 K which could then reveal the \( T \) dependence of the magnetic contribution is not possible with the information available.
As seen in Figs. 11(a) and 11(b), in both compounds the experimentally-observed heat-capacity peak at $T_N$ is very sharp, indicating weak and strong first-order transitions in SrMn$_2$P$_2$ and CaMn$_2$P$_2$, respectively. Near $T_N$, the respective data were obtained utilizing the single-pulse slope-analysis method as discussed in Section II. Figures 12(a) and 12(b) compare the conventionally-measured and slope-analyzed $C_p(T)$ data close to the first-order magnetic transition (FOMT) region of SrMn$_2$P$_2$ and CaMn$_2$P$_2$, respectively. The slope-analyzed data show higher peak values than the conventionally-measured data.

For both compounds, the peak values of $C_p(T)$ obtained from the conventional measurement technique are seen from Fig. 12 to be about a factor of two smaller than those from the slope-analyzed data. From the latter data, the height of the $C_p$ peak for SrMn$_2$P$_2$ above background is about 40 J/molK, whereas that for CaMn$_2$P$_2$ is about 1000 J/molK, indicating a much larger latent heat in CaMn$_2$P$_2$. This difference is clearly visible in the temperature-response versus time $T(t)$ plots around the respective FOMT for SrMn$_2$P$_2$ and CaMn$_2$P$_2$ as shown in Figs. 12(c) and 12(d), respectively. For a FOMT, the $T(t)$ curve exhibits a plateau at the transition temperature associated with the latent heat, as clearly observed for CaMn$_2$P$_2$ at $T_N$. Such a plateau is replaced by a region of negative curvature for SrMn$_2$P$_2$ indicating a much smaller latent heat associated with the FOMT for SrMn$_2$P$_2$.

The latent heat $Q$ associated with the FOMT for both compounds was calculated by first subtracting the respective $C_p(T)$ backgrounds using a polynomial fit and then measuring the area under the resultant peak. For SrMn$_2$P$_2$ we obtained $Q \approx 8.7$ J/mol at $T_N \approx 53$ K, whereas for CaMn$_2$P$_2$ we obtained $Q \approx 152$ J/mol at $T_N = 69.5$ K. The difference in the latent heat estimated from the conventionally-measured data and the slope-analyzed data is negligible for SrMn$_2$P$_2$ and is only $\sim 11$ J/mol for CaMn$_2$P$_2$ as shown in the insets of Figs. 12(a) and 12(b), respectively. The heat-capacity peak value in CaMn$_2$P$_2$ obtained from the slope-analyzed measurements is larger than obtained previously [10]. As shown in Figs. 12(e) and 12(f), an applied field $H = 9$ T has negligible influence on $C_p(T \approx T_N)$ for both SrMn$_2$P$_2$ and CaMn$_2$P$_2$, respectively.

VII. NUCLEAR MAGNETIC RESONANCE

A. SrMn$_2$P$_2$

1. $^{31}$P NMR spectrum

Figure 13(a) shows the typical $T$ dependence of $^{31}$P NMR spectra above $T_N$ for $H \parallel ab$ plane (black lines) and $H \parallel c$ axis (red lines). For each magnetic field direction, we observed a single line as expected for the nuclear spin $I = 1/2$ NMR spectrum. However, although the NMR line is relatively sharp at high $T$, the spectra show asymmetric shapes. Since we used a single crystal for our measurements, the asymmetric shape indicates a slight distribution of the hyperfine field at the P sites and/or the presence of more than two P sites. Since only one P site is expected from the crystal structure, the origin of the asymmetric shape of the spectra is not clear at present.

Figure 13(b) shows the $T$ dependence of the NMR shift for $H \parallel c$ axis ($K_c$) and $H \parallel ab$ plane ($K_{ab}$) determined by the peak position for each spectrum. Both $K_c$ and $K_{ab}$ decrease with decreasing $T$ as in the case of the aforementioned magnetic susceptibility. The NMR shift has contributions from the $T$-dependent spin part $K_{\text{spin}}$ and a $T$-independent orbital part $K_0$. $K_{\text{spin}}$ is proportional to the spin susceptibility $\chi_{\text{spin}}$ through the hyperfine coupling constant $A$ giving $K(T) = K_0 + A \chi_{\text{spin}}(T)$, where
N\textsubscript{A} is Avogadro's number. Figure 13(c) plots $K_{ab}$ and $K_c$ against $\chi_{ab}$ and $\chi_c$, respectively, with $T$ as an implicit parameter. Here we use the magnetic susceptibility measured at $H = 3$ T. $K_{ab}$ and $K_c$ vary with the respective $\chi$ as expected, although one can see a slight deviation from the linear relationship for $H \parallel c$. The deviation could be due to the broadening of the spectrum below 100 K for $H \parallel c$.

We estimated the hyperfine coupling constants $A_e = (7.0 \pm 0.1)$ kOe/$\mu_B$ and $A_{ab} = (4.4 \pm 0.1)$ kOe/$\mu_B$ by fitting the data in Fig. 13(c) above 100 K. From the estimated hyperfine coupling constant

$$A_{iso} = \frac{5.23 \pm 0.10}{\mu_B} \text{kOe/}\mu_B \text{ and the axially-anisotropic hyperfine coupling constant } A_{ax} = \frac{(0.9 \pm 0.1)}{\mu_B},$$

from the relations $A_{iso} = (A_e + 2A_{ab})/3$ and $A_{ax} = (A_e - A_{ab})/3$. The $A_{iso}$ originates from the transferred hyperfine interactions between the $^{31}$P nucleus and its neighboring Mn$^{2+}$ ions through the mixing of the Mn 3d and P 2s orbitals and/or polarization of inner-core $s$ electrons via the P 2p orbitals. On the other hand, the $A_{ax}$ part comes from the dipolar interactions from the Mn$^{2+}$ spins at the P site and/or on-site dipolar field from the polarization of P 2p orbitals. It is noted that the hyperfine coupling constant at the P site is dominated by the isotropic part, although there is a $\sim 17\%$ contribution of the axially component with respect to the isotropic part.

When $T$ is lowered close to $T_N \approx 53$ K, as shown in Fig. 13(a) for $H \parallel ab$, a single sharp NMR line (denoted by $P_{HT}$ in the figure) suddenly broadens due to the internal field ($H_{int}$) at the P site produced by the Mn$^{2+}$ ordered moments in the AFM state. The observed spectra become nearly independent of $T$ below 40 K as shown in Fig. 13(b), where the two peak positions denoted by $P_{1}$ ($H_{p1}$) and $P_{2}$ ($H_{p2}$) in Fig. 13(a) are plotted versus $T$.

The internal field $H_{int}$, which is proportional to the Mn$^{2+}$ sublattice magnetization, was determined as half of the separation between $P_{1}$ and $P_{2}$. The temperature dependences of $H_{int}$ are shown in Fig. 13(c) from which we estimated the critical exponent of the order parameter (sublattice magnetization). $H_{int}$ was fitted by the power law $H_{int} = H_{int,0}(1 - T/T_N)^\beta$ with $T_N = 53.0$ K. The solid line in the figure shows the curve with $H_{int,0} = 0.175$ T and $\beta = 0.13$. Here the value of $\beta$ is much smaller than expected for any three-dimensional magnetic material with a second-order phase transition such as $\beta = 0.33-0.367$ for 3D Heisenberg, 0.31–0.345 for 3D XY, and 0.31–0.326 for 3D Ising models \cite{38}, but close to 0.125 for the 2D Ising model \cite{38}. These results suggest a second-order phase transition. In addition, we were able to follow the reduction in $H_{int}$ near $T_N$ and also detected a critical-slowing-down behavior in the $T$ dependence of $1/T_1$ around $T_N$ (shown below). Therefore, the magnetic
phase transition for SrMn$_2$P$_2$ is considered to be characterized as a second-order phase transition. However, the above $C_p(T)$ data suggest a weak first-order transition, so the transition at $T_N$ has characteristics of both orders of the transition. On the other hand, we will show below that CaMn$_2$P$_2$ exhibits a strong first-order phase transition where we observed a clear jump in the order parameter just below the magnetic phase transition temperature and also no observation of critical slowing down in $T_1$ measurements, in contrast to our observations for SrMn$_2$P$_2$.

The broad NMR spectra observed below $T_N$ indicate a distribution of internal fields $H_{\text{int}}$ which is reminiscent of a two-horn structure expected for an incommensurate helical structure, as has been observed in EuCo$_2$P$_2$ [37] and EuCo$_2$As$_2$ [41]. In fact, the observed spectrum is reasonably reproduced by that calculated for an incommensurate helical AFM state shown by the green area assuming an internal field along the $ab$ plane $H_{\text{int},ab} = 2.0$ kOe, although we note that one needs to introduce another P site with a smaller $H_{\text{int},ab} = 0.5$ kOe (shown by the light red area). The red curve is the sum of the two calculated spectra. The origin of the two P sites is not clear at present; however, it seems to be consistent with the observed $^{31}$P NMR asymmetric spectra in the PM state which suggests that there is more than one P site having a different hyperfine coupling constant in the system. It is also noted that we consider only the isotropic hyperfine field for the calculation for simplicity; therefore, the slight deviation between the calculated and observed spectra could be due to the axially anisotropic part of the hyperfine field.

A similar, but much broader, two-horn-like spectrum was observed for $H \parallel c$ in the AFM state as shown in Fig. 13(b). Here we were able to measure the spectrum only at 1.6 K and not at higher $T$ due to poor signal intensity. The observed spectrum was also reasonably reproduced by a calculated spectrum for the incommensurate AFM state where again we assumed two different P sites with different internal fields along the c axis $H_{\text{int},c} = 8.5$ kOe (green area), and $H_{\text{int},c} = 4.5$ kOe (light red area). As for $H \parallel ab$, the observed spectrum was not perfectly reproduced by the calculated spectrum. However, we consider that the analysis captures the essential point, evidencing the incommensurate AFM state in SrMn$_2$P$_2$.

Our NMR results are consistent with previous $\chi(T)$ data for a polycrystalline SrMn$_2$P$_2$ sample and associated powder neutron-diffraction data [36] that suggested the presence of a complex low-dimensional incommensurate AFM structure of high-spin Mn$^{2+}$ below $T_N = 32(2)$ K with significant short-range AFM order well above $T_N$. 

\[ \text{FIG. 13. (a) } ^{31}\text{P-NMR spectra under a magnetic field } H \sim 7.0122 \text{T parallel to the c axis (black) and parallel to the ab plane (red) at various temperatures in SrMn$_2$P$_2$. The vertical dashed line represents the zero-shift position (} K = 0). (b) Temperature dependence of the } ^{31}\text{P-NMR shifts } K_c \text{ and } K_{ab}. \] 

\[ \text{FIG. 14. (a) Field-swept } ^{31}\text{P-NMR spectra at a resonance frequency of } f = 121 \text{ MHz for } H \parallel \text{ab plane at various temperatures in SrMn}_2\text{P}_2 \text{ below } T_N. \text{ The black curves are the observed spectrum. The green and light-red areas are calculated spectra with an incommensurate helical AFM state with different internal fields of } H_{\text{int}} = 2.0 \text{ and 0.5 kOe, respectively. The red curve is the sum of the two calculated spectra. (b) Field-swept } ^{31}\text{P-NMR spectrum at 1.6 K for } H \parallel c. \text{ The black curves are the observed spectra and the other colored areas and line are the same with different internal fields (see text). (c) Temperature dependence of the peak positions for P$1$ and P$2$ defined in (a). (d) Temperature dependence of } H_{\text{int}} = (H_{P1} - H_{P2})/2. \text{ The solid line is the calculated result of } H_{\text{int}} = H_{\text{int},0}(1 - T/T_N)^{\beta} \text{ with } H_{\text{int},0} = 0.175 \text{T}, \beta = 0.13 \text{ and } T_N = 53.0 \text{ K.} \]
is usually explained by a critical slowing down of spin phase transition for the AFM-PM transition in SrMn$_2$O$_{3}$ for $H \parallel$ $ab$ plane. The blue circles and triangles in the AFM state of SrMn$_2$O$_{3}$ for $H \parallel ab$ are the results measured at nearly zero shift and the P2 positions, respectively. For the AFM state of CaMn$_2$O$_{3}$, $1/T_1$ was measured at the P3 position for $H \parallel c$ and at the lowest field peak for $H \parallel ab$. The blue and red straight lines show the power law dependences $1/T_1 \propto T_0^0.5$ and $T^4$, respectively.

2. $^{31}P$ spin-lattice relaxation rate $1/T_1$

Figure 15 shows the temperature dependence of the $^{31}P$ spin-lattice relaxation rate divided by temperature $1/T_1T$ for $H$ parallel to the $c$ axis and the $ab$ plane. For $H \parallel ab$, $1/(T_1T)_{ab}$ was measured at the peak position for the spectra in the PM state and at nearly zero shift position of the spectra in the AFM state, while $1/(T_1T)_{c}$ for $H \parallel c$ was measured only in the PM state due to poor signal intensity in the AFM state.

As seen in the figure, with decreasing temperature, both $1/T_1T$ gradually increase and strongly enhance below ~60 K. For $H \parallel ab$, $1/T_1T$ starts to decrease just below $T_N = 53$ K, exhibiting a clear peak in $1/T_1T$ which is usually explained by a critical slowing down of spin fluctuations expected for a second-order phase transition. Thus our $1/T_1T$ data show the nature of the second-order phase transition for the AFM-PM transition in SrMn$_2$O$_{3}$.

In order to discuss magnetic fluctuation effects in the PM state, it is useful to re-plot the $1/T_1$ data by changing the vertical axis from $1/T_1T$ to $1/T_1T\chi$ as shown in Fig. 16. In general, $1/T_1T$ can be expressed in terms of the imaginary part of the dynamic susceptibility $\chi''(\bar{q},\omega_0)$ per mole of electronic spins as

$$\frac{1}{T_1T} = \frac{2\gamma^2 k_B}{N_A} \sum_{\bar{q}} |A(\bar{q})|^2 \chi''(\bar{q},\omega_0), \quad (13)$$

where the sum is over the wave vectors $\bar{q}$ within the first Brillouin zone, $A(\bar{q})$ is the form factor of the hyperfine interactions and $\chi''(\bar{q},\omega_0)$ is the imaginary part of the dynamic susceptibility at the Larmor frequency $\omega_0$. On the other hand, the uniform $\chi$ corresponds to the real component $\chi'(\bar{q},\omega_0)$ with $q = 0$ and $\omega_0 = 0$. Thus a plot of $1/T_1T\chi$ versus $T$ shows the $T$ dependence of $\sum_{\bar{q}} |A(\bar{q})|^2 \chi''(\bar{q},\omega_0)$ compared to that of the uniform susceptibility $\chi'(0,0)$. Since $1/T_1T$ probes magnetic fluctuations perpendicular to the magnetic field, we calculated $1/(T_{1,\perp}T\chi_0)$ using the relation $1/(T_{1,\perp}T) = 1/(T_{1,\perp}T\chi)$, when examining the character of magnetic fluctuations in the ab plane. Similarly, we estimated $1/(T_{1,\parallel}T\chi)$ for magnetic fluctuations along the $c$ axis from the relation

$$1/(T_{1,\parallel}T) = 2/(T_{1,\parallel}T_{0}) - 1/(T_{1,\parallel}T-c). \quad (14)$$

As shown in Fig. 16, both $1/(T_{1,\perp}T\chi_{0})$ and $1/(T_{1,\parallel}T\chi_{c})$ increase with decreasing $T$. The results imply that $\sum_{\bar{q}} |A(\bar{q})|^2 \chi''(\bar{q},\omega_0)$ increases more than $\chi'(0,0)$, evidencing a growth of spin fluctuations with $q \neq 0$. Thus we conclude that AFM fluctuations exist in the PM state in SrMn$_2$O$_{3}$. It is noted that the AFM fluctuations are more enhanced along the $c$ axis than within the $ab$ plane in SrMn$_2$O$_{3}$. It is also interesting to point out that from the smooth extrapolation of the $T$ dependence of both $1/(T_{1,\perp}T\chi_{0})$ and $1/(T_{1,\parallel}T\chi_{c})$, the AFM fluctuations seem to persist up to temperatures...
much higher than 300 K, consistent with the χ(T) results discussed above.

In the AFM state below $T_N$, $1/T_1T$ for $H \parallel ab$ decreases slowly where $1/T_1T$ shows a $T^{0.5}$ power-law behavior. We also measured $1/T_1T$ in the AFM state at the lower field peak (P2) which shows similar power-law behavior with slightly different values (shown by the blue triangles in Fig. 17). In the AFM state, $1/T_1T$ is mainly driven by scattering of magnons, leading to $T^2$ and $T^4$ power-law $T$ dependencies due to a two- or three-magnon Raman process, respectively [44]. The weak $T$ dependence of $1/T_1T \propto T^{0.5}$ below 40 K cannot be explained by the magnon scattering, and suggests the presence of other magnetic fluctuations in the magnetically-ordered state.

B. CaMn$_2$P$_2$

1. $^{31}$P NMR spectrum

Similar $^{31}$P-NMR measurements were performed on CaMn$_2$P$_2$. Figure 17(a) shows the typical $T$ dependence of NMR spectra for $H \parallel ab$ and $H \parallel c$ in the PM state. As in the case of SrMn$_2$P$_2$, a single NMR line was observed. The $T$ dependencies of the NMR shifts are shown in Fig. 17(b) and Fig. 17(c) shows $K-\chi$ plots for both magnetic field directions. From the slopes in Fig. 17(c), the hyperfine coupling constants were estimated to be $A_c = (7.6 \pm 0.1)$ kOe/$\mu_B$ and $A_{ab} = (4.9 \pm 0.1)$ kOe/$\mu_B$ for $H \parallel c$ and $H \parallel ab$, respectively, leading to the isotropic hyperfine coupling constant $A_{iso} = (5.8 \pm 0.1)$ kOe/$\mu_B$ and the axially-anisotropic hyperfine coupling constant $A_{ax} = (0.9 \pm 0.1)$ kOe/$\mu_B$.

Although the $^{31}$P NMR spectra in the PM state and the values of the hyperfine coupling constants in CaMn$_2$P$_2$ are similar to those observed in SrMn$_2$P$_2$, surprisingly, the $^{31}$P NMR spectra in the AFM state below $T_N$ are quite different from the case of SrMn$_2$P$_2$. As shown in Fig. 18(a) for $H \parallel c$, the single NMR line observed in the PM state suddenly splits into mainly three lines at the higher and lower magnetic field positions with a double-peak structure (denoted by P1, P2, P4, and P5) and around a nearly zero-shift position (P3) in the AFM state. The detailed change in the NMR spectrum around zero-shift position are shown in Fig. 18(c). Note here we measured the spectrum with increasing $T$. No $P_{1T}$ signal from the PM state could be observed and only the signal (P3) from the AFM state was detected at 68 K. Then, $P_{1T}$ starts to appear at 69.8 K and the P3 signal disappears completely at 70.2 K. The coexistence of the two signals from the AFM and PM states can be seen in a quite narrow temperature range from 69.8 K to 70 K, indicating a very small hysteresis.

The distinct splittings of the NMR line below $T_N$ clearly indicate that the AFM state is commensurate, which is in strong contrast to the case of the incommensurate AFM state in SrMn$_2$P$_2$. Similar distinct splittings of NMR lines were also observed for $H \parallel ab$ where a more complicated spectrum with at least 20 peaks were detected [see, Fig. 18(b)]. Although the spectrum is complicated and suggests a complex magnetic structure, it is clear that the commensurate nature holds not only along the c axis but also in the ab plane.

Figure 18(d) shows the $T$ dependence of the peak po-
sitions for $H \parallel c$. Clear jumps in the positions due to a finite internal field below $T_N$ can be seen. These results clearly show that the AFM phase transition in CaMn$_2$P$_2$ is of first order, consistent with the results of the $C_p(T)$ measurements.

2. $^{31}$P spin-lattice relaxation rate $1/T_1$

The clear nature of the first-order phase transition in CaMn$_2$P$_2$ can be also detected in the temperature dependence of $1/T_1T$. As shown in Fig. 15 in the PM state, $1/T_1T$ for $H \parallel c$ and $H \parallel ab$ gently increases with decreasing $T$ with no obvious anisotropy. $1/T_1T$ for both magnetic field directions in CaMn$_2$P$_2$ does not exhibit a clear enhancement close at $T_N$, indicating no critical slowing down of the Mn spins as expected for the first-order phase transition. In addition, $1/T_1T$ shows a discontinuous decrease just below $T_N$, which again confirms the first-order nature of the AFM magnetic phase transition in CaMn$_2$P$_2$.

The increases of $1/T_1T$ in the PM state are due to the growth of AFM fluctuations which persist to much higher temperatures above 300 K as in the case of SrMn$_2$P$_2$. However, as shown in Fig. 16 $1/T_1(T_{\chi ab})$ and $1/(T_1\|T_{\chi c})$ are nearly the same which suggests nearly isotropic AFM fluctuations in the PM state of CaMn$_2$P$_2$, in contrast to the case of SrMn$_2$P$_2$.

In the AFM state, the $1/T_1T$ data shown in Fig. 17 were measured at the P3 position for $H \parallel c$ and at the lowest-field peak for $H \parallel ab$. We also measured $1/T_1T$ at different peak positions for both magnetic field directions and found no obvious difference in the values of $1/T_1T$. $1/T_1T$ for $H \parallel c$ and $H \parallel ab$ show $T^4$ power-law behaviors which are consistent with $T^4$ expected for the three-magnon relaxation process in AFM materials where the deviation from the power-law behavior for $T \lesssim 20$ K could be due to relaxation associated with impurities.

VIII. CONCLUDING REMARKS

Single crystals of SrMn$_2$P$_2$ and CaMn$_2$P$_2$ have been grown using Sn flux and characterized by single-crystal x-ray diffraction, electrical resistivity $\rho$, heat capacity $C_p$, and NMR measurements versus temperature $T$, and anisotropic magnetic susceptibility $\chi$ and magnetization $M$ versus $T$ and applied magnetic field $H$ measurements. Room-temperature single-crystal x-ray diffraction measurements confirm that both SrMn$_2$P$_2$ and CaMn$_2$P$_2$ adopt the trigonal CaAl$_2$Si$_2$-type structure containing corrugated honeycomb quasi-two-dimensional Mn spin lattices as previously reported. The $\rho(T)$ measurements demonstrate insulating ground states for both compounds with intrinsic activation energies of 0.124 eV for SrMn$_2$P$_2$ and 0.088 eV for CaMn$_2$P$_2$. The $\chi(H,T)$ and $C_p(T)$ measurements reveal first-order AFM transitions at $T_N = 53(1)$ K and 69.8(3) K for SrMn$_2$P$_2$ and CaMn$_2$P$_2$, respectively.

Li and coworkers reported a first-order transition at 69.5 K at in CaMn$_2$P$_2$ from $\rho(T)$ and $\rho(T)$ measurements in 2020 [10] and from Raman scattering measurements inferred that it was related to a structural transition such as superstructure formation although its potential concomitant magnetic character was not identified.

First-order AFM transitions in $H = 0$ are rather unusual. A first-order magnetostructural transition was observed at $T_N = 205$ K in the body-centered-tetragonal metallic 122-type Fe-based pnictide SrFe$_2$As$_2$ which exhibits a transition to an orthorhombic structure with commensurate, collinear, itinerant, spin-density-wave order [45, 46]. This is a different class of materials from CaMn$_2$P$_2$ and SrMn$_2$P$_2$ which are electrical insulators. The cubic pyrite-structure insulator MnS$_2$ containing Mn$^{2+}$ cations with high-spin $S = 5/2$ and $(S_2)^2^-$ species was found from neutron-diffraction measurements to exhibit a first-order AFM transition at $T_N = 47.7$ K [47, 50]. Other examples of materials exhibiting first-order AFM transitions include insulating UO$_2$ with $T_N = 30.8$ K [51], and MnO$_2$ [52, 53] with $T_N \approx 120$ K, and Cr and Eu metals. The AFM structure in Cr metal below $T_N = 311$ K is an itinerant spin-density wave [54], whereas it is a $S = 7/2$ local-moment helical AFM state below $T_N \approx 90$ K in Eu metal [55, 57].

In a series of papers, it was found that symmetry considerations and renormalization-group theory could determine whether or not a given material would exhibit a first-order transition at its Néel temperature [58, 61]. The theory correctly predicted the occurrence of first-order transitions in the above materials UO$_2$, MnO, Cr, and Eu at their respective Néel temperatures. It would be interesting to see if the same theory would predict the observed first-order AFM transitions in CaMn$_2$P$_2$ and SrMn$_2$P$_2$. If not, then a structural transition at $T_N$ would evidently be required to explain the observed first-order transitions. For example, a crystal-structure distortion at $T_N$ was stated to result in a first-order AFM transition in GeNCr$_3$ [62].

ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

[1] J. An, A. S. Sefat, D. J. Singh, and M.-H. Du, Electronic structure and magnetism in BaMn$_2$As$_2$ and BaMn$_2$Sb$_2$, Phys. Rev. B 79, 075120 (2009).
[2] Y. Singh, A. Ellern, and D. C. Johnston, Magnetic transport and thermal properties of single crystals of the layered arsenide BaMn$_2$As$_2$, Phys. Rev. B 79, 094519 (2009).

[3] D. C. Johnston, R. J. McQueeney, B. Lake, A. Hohecker, M. E. Zhitomirsky, R. Nath, Y. Furukawa, V. P. Antropov, and Y. Singh, Magnetic exchange interactions in BaMn$_2$As$_2$: A case study of the J$_1$-J$_2$-J$_3$ Heisenberg model, Phys. Rev. B 84, 094445 (2011).

[4] E. Brechtel, G. Cordier, and H. Schäfer, Preparation and Crystal Structure of BaMn$_2$SB$_2$, BaZn$_2$SB$_2$ and BaCd$_2$SB$_2$, Z. Naturforsch. 34b, 921 (1979).

[5] J. Zeng, S. Qin, C. Le, and J. Hu, Magnetism and superconductivity in the layered hexagonal transition metal pnictides, Phys. Rev. B 96, 174506 (2017).

[6] J. B. Fouet, P. Sindzingre, and C. Lhuillier, An investigation of the quantum J$_1$-J$_2$-J$_3$ model on the honeycomb lattice, Eur. Phys. J. B 20, 241 (2001).

[7] I. I. Mazin, CaMn$_2$SB$_2$: a fully frustrated classical magnetic system, [arXiv:1309.3744](https://arxiv.org/abs/1309.3744).

[8] J. W. Simonson, G. J. Smith, K. Post, M. Pezzoli, J. A. B. Morris, D. E. McNally, J. E. Hassinger, C. S. Nelson, G. Kolliar, D. N. Basov, and M. C. Aronson, Magnetic and structural phase diagram of CaMn$_2$SB$_2$, Phys. Rev. B 86, 184430 (2012).

[9] D. E. McNally, J. W. Simonson, J. A. B. Morris, G. J. Smith, J. E. Hassinger, L. DeBeer-Schmitt, A. I. Kolesnikov, I. A. Zaliznak, and M. C. Aronson, CaMn$_2$SB$_2$: Spin waves on a frustrated antiferromagnetic honeycomb lattice, Phys. Rev. B 91, 180407(R) (2015).

[10] Y. J. Li, F. Jin, Z. Y. Mi, J. Guo, W. Wu, Z. H. Yu, D. S. Wu, S. H. Na, C. Mu, X. B. Zhou, Z. Li, K. Liu, L. L. Sun, Q. M. Zhang, T. Xiang, G. Li, and J. L. Luo, First-order transition in trigonal structure CaMn$_2$P$_2$, Euro. Phys. Lett. 132, 46001 (2020).

[11] S. L. Brock, J. E. Greedan, and S. M. Kauzlarich, Resistivity and magnetism of AMn$_2$P$_2$ (A =Sr, Ba): The effect of structure type on physical properties, J. Solid State Chem. 113, 303 (1994).

[12] W. Xie, M. J. Winarski, T. Klimczuk and R. J. Cava, A tetragonal polymorph of SrMn$_2$P$_2$ made under high pressure—theory and experiment in harmony, Dalton Trans., 46, 6835 (2017).

[13] A. Mewis, AB$_2$X$_2$-Compounds with the CaAl$_2$Si$_2$ Structure, V[1] The Crystal Structure of CaMn$_2$P$_2$, CaMn$_2$As$_2$, SrMn$_2$P$_2$, and SrMn$_2$As$_2$, Z. Naturforsch. 33b, 606 (1978).

[14] M. E. Lines, Magnetism in Two Dimensions, J. Appl. Phys. 40, 1352 (1969).

[15] N. S. Sangeetha, A. Pandey, Z. A. Benson and D. C. Johnston, Strong magnetic correlations to 900 K in single crystals of the trigonal antiferromagnetic insulators SrMn$_2$As$_2$ and CaMn$_2$As$_2$, Phys. Rev. B 94, 094417 (2016).

[16] P. Das, N. S. Sangeetha, A. Pandey, Z. A. Benson, T. W. Heitmann, D. C. Johnston, A. I. Goldman, and A. Kreyssig, Collinear antiferromagnetism in trigonal SrMn$_2$As$_2$ revealed by single-crystal neutron diffraction, J. Phys.: Condens. Matter 29, 035802 (2017).

[17] N. S. Sangeetha, V. Smetana, A.-V. Mudring, and D. C. Johnston, Antiferromagnetism in semiconducting SrMn$_2$SB$_2$ and BaMn$_2$SB$_2$ single crystals, Phys. Rev. B 97, 014402 (2018).

[18] S. Bobev, J. Merz, A. Lima, V. Fritsch, J. D. Thompson, J. L. Sarrao, M. Gillessen, and R. Drönswia, Unusual Mn–Mn Spin Coupling in the Polar Intermetallic Compounds CaMn$_2$SB$_2$ and SrMn$_2$SB$_2$, Inorg. Chem. 45, 4047 (2006).

[19] W. Ratchiff II, A. L. Lima Sharma, A. M. Gomes, J. L. Gonzalez, Q. Huang, and J. Singleton, The magnetic ground state of CaMn$_2$SB$_2$, J. Magn. Magn. Mater. 321, 2612 (2009).

[20] C. A. Bridges, V. V. Krishnamurthy, S. Poulton, M. P. Paranthaman, B. C. Sales, C. Myers, and S. Bobev, Magnetic order in CaMn$_2$SB$_2$ studied via powder neutron diffraction, J. Magn. Magn. Mater. 321, 3653 (2009).

[21] Q. D. Gibson, H. Wu, T. Liang, M. N. Ali, N. P. Ong, Q. Huang, and R. J. Cava, Magnetic and electronic properties of CaMn$_2$Bi$_2$: A possible hybridization gap semiconductor, Phys. Rev. B 91, 085128 (2015).

[22] S. Lee, S. Choi, J. Kim, H. Sim, C. Won, S. Lee, S. A. Kim, N. Hur, and J.-G. Park, Antiferromagnetic ordering in Li$_2$MnO$_3$, J. Phys.: Condens. Matter 24, 456004 (2012).

[23] APEX3, Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

[24] SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

[25] L. Krause, R. Herbst-Immer, G. M. Sheldrick, and D. J. Stake, Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination, Appl. Crystallogr. 48, 3 (2015).

[26] G. M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination, Acta Crystallogr. A 71, 3 (2015).

[27] G. M. Sheldrick, Crystal structure refinement with SHELXLX, Acta Crystallogr. C 71, 3 (2015).

[28] V. Hardy, Y. Bréard and C. Martin, Derivation of the heat capacity anomaly at a first-order transition by using a semi-adiabatic relaxation technique, J. Phys.: Condens. Matter 21, 075403 (2009).

[29] H. Suzuki, A. Inaba, C. Meingast, Accurate heat capacity data at phase transitions from relaxation calorimetry, Cryogenics 50, 693 (2010).

[30] F. Guillou, A. K. Pathak, D. Paudyal, Y. Mudryk, F. Wilhelm, A. Rogalev, and V.K. Pecharsky, Non-hysteretic first-order phase transition with large latent heat and giant low-field magnetocaloric effect, Nat. Commun. 9, 2925 (2018).

[31] PMMS Heat Capacity Option User’s Manual, 1085-150, Rev. M7, Quantum Design, December 2017.

[32] M. E. Fisher, Relation between the specific heat and susceptibility of an antiferromagnet, Phil. Mag. 7, 1731 (1962).

[33] D. C. Johnston, Magnetic Susceptibility of Collinear and Noncollinear Heisenberg Antiferromagnets, Phys. Rev. Lett. 109, 077201 (2012).

[34] D. C. Johnston, Unified molecular field theory for collinear and noncollinear Heisenberg antiferromagnets, Phys. Rev. B 91, 064427 (2015).

[35] K. Hirakawa, H. Ikeda, H. Kadowaki, and K. Ubboshi, J. Phys. Soc. Jpn. 52, 2882 (1983).

[36] S. L. Brock, J. E. Greedan, and S. M. Kauzlarich, A Test of the Application of Extended Hückel Calculations to the ThCr$_2$Si$_2$ and CaAl$_2$Si$_2$ Structure Types: the Case of SrMn$_2$P$_2$ and BaMn$_2$P$_2$, J. Solid State Chem. 109, 416 (1994).
