Magnetic transitions in the spin $S = \frac{5}{2}$ spin-ladder compound BiMn$_2$PO$_6$ and strong lattice softening in BiMn$_2$PO$_6$ and BiZn$_2$PO$_6$ below 200 K

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The crystallographic, magnetic and thermal properties of polycrystalline BiMn$_2$PO$_6$ and its non-magnetic analogue BiZn$_2$PO$_6$ were investigated by x-ray diffraction, magnetization $M$, magnetic susceptibility $\chi$, heat capacity $C_p$, and $^{31}$P nuclear magnetic resonance (NMR) measurements versus applied magnetic field $H$ and temperature $T$ as well as by density-functional band-theory calculations. Both compounds show a strong monotonic lattice softening on cooling, where the Debye temperature decreases by a factor of two from $\Theta_D \approx 780 K$ at $T = 300 K$ to $\Theta_D \approx 300 K$ at $T = 2 K$. The $\chi(T)$ data for BiMn$_2$PO$_6$ above 150 K follow a Curie-Weiss law with a Curie constant consistent with a $\text{Mn}^{2+}$ spin $S = 5/2$ with $g$-factor $g = 2$ and an antiferromagnetic (AFM) Weiss temperature $\theta_{CW} \approx -78 K$. The $\chi$ data indicate long-range AFM ordering below $T_N \approx 30 K$, confirmed by a sharp $\lambda$-shaped peak in $C_p(T)$ at 28.8 K. The extracted magnetic entropy at 100 K is consistent with spin $S = 5/2$ for the $\text{Mn}^{2+}$ ions. The band-theory calculations indicate that BiMn$_2$PO$_6$ is an AFM spin-ladder compound with dominant interactions $J_1/k_B \approx 6.7 K$ and $J_2/k_B \approx 5.6 K$ along the legs and along the rung of the ladder, respectively. In addition to the long-range AFM ordering at $T_N \approx 30 K$, confirmed by the $\chi$ and NMR measurements, a second magnetic transition at $\approx 10 K$ is observed from the $\chi$ and NMR measurements but is not evident in the $C_p$ data. The $C_p$ data at low $T$ suggest a significant contribution from AFM spin waves moving in three dimensions and the absence of a spin-wave gap. A detailed analysis of the NMR spectra indicates commensurate magnetic order between 10 K and 30 K, while below 10 K additional features appear that may arise from an incommensurate modulation and/or spin canting. The commensurate order is consistent with microscopic simulations that yield a collinear Néel-type AFM spin arrangement both within and between the ladders, despite the presence of multiple weak interactions frustrating this magnetic structure of the Mn spins. Frustration for AFM ordering is manifested in the frustration ratio $f = |\theta_{CW}|/T_N \approx 2.6$, indicating a suppression of $T_N$ compared to the mean-field prediction $f = 1$ in the absence of frustration.

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I. INTRODUCTION

The antiferromagnetic (AFM) two-leg spin ladder is one of the most peculiar low-dimensional lattice topologies. Its properties are quite different from those of a simple spin chain, because the formation of rungs connecting the linear spin chains results in the dimerization and opens the spin gap or increases the size of the gap already existing for an isolated chain, thus protecting the system from a long-range magnetic order (LRO). The family of BiM$_2$PO$_6$ phosphates ($M$ is a transition-metal atom) hosts several interesting spin-ladder materials. Here, two $\text{MO}_5$ square pyramids containing $M$ atoms $\text{M}1$ and $\text{M}2$ in two different crystallographic positions share edges and form rungs of the ladder, as shown for BiMn$_2$PO$_6$ in Fig. [1][2] These rungs connect to each other by corner-sharing of the $\text{MO}_5$ pyramids and build ladders (double chains) running along the $b$ direction. $\text{PO}_4$ tetrahedra connect the ladders and also form additional bridges within individual ladder units. The ensuing atomic arrangement is rather complex and may lead to multiple interactions beyond nearest-neighbor couplings along the leg ($J_1$) and along the rung ($J_3$) of the less studied. They feature weaker quantum fluctuations and, therefore, they are more likely to develop the LRO and conventional physics of classical antiferromagnets.

On the other hand, the larger energy of magnetic interactions in systems with high spin may be comparable to lattice energies and lead to intricate magnetostructural transitions, as in the spin-$\frac{3}{2}$ ladder material BaMn$_2$O$_5$ [3].

Spin ladders with larger magnetic moments are relatively

\[ 5 \text{Sr} \text{Cu}_2\text{O}_3 \] is the only two-leg spin ladder compound where superconductivity has been reported for hole doping at the Sr site under pressure.\[ [\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}] \] is the only two-leg spin ladder compound where superconductivity has been reported for hole doping at the Sr site under pressure.
Indeed, BiCu$_2$PO$_6$, which is the most actively studied member of the BiM$_2$PO$_6$ family, reveals a highly nontrivial microscopic magnetic model\cite{10,12}. It does feature two-leg spin ladders consisting of two Cu chains connected by rung interactions, but the rung interactions are between the structural ladder units, so that rungs of the ladder are formed by the couplings $J_3$ (see Fig. 1), whereas the coupling $J_1$ turns out to be an interladder coupling. Furthermore, the nearest-neighbor couplings $J_1$ are accompanied by next-nearest couplings $J_2$ and $J_2'$ that also run along the ladder (i.e., along $b$) and frustrate $J_1$, thus leading to a very intricate magnetic system\cite{10}. So far, there is no clear consensus on whether BiCu$_2$PO$_6$ should be regarded as quasi-one-dimensional (1D) or quasi-two-dimensional (2D), i.e., whether the couplings $J_3$ (within the structural ladders, but between the spin ladders) are strong enough to build magnetic layers.\cite{13,14,15,16} BiCu$_2$PO$_6$ shows intriguing physical behavior\cite{13}, especially in high magnetic fields, where multiple ordered phases emerge\cite{15,16} and upon doping with nonmagnetic (Zn$^{+2}$) or magnetic (Ni$^{+2}$) impurities\cite{17,18}.

Motivated by this interesting behavior, we studied the Mn$^{+2}$-based analog of BiCu$_2$PO$_6$. While the Cu$^{+2}$ compound features spin-$\frac{1}{2}$ magnetic ions triggering strong quantum fluctuations, BiMn$_2$PO$_6$ (Ref. 19) lies in the opposite limit of spin-$\frac{3}{2}$ ions that should be well described by a classical Heisenberg model. The classical description might have simplified the microscopic analysis and given some clues about the puzzling magnetism of BiCu$_2$PO$_6$. Instead, we find that the replacement of Cu$^{+2}$ with Mn$^{+2}$ leads to a substantial change in the spin lattice, thus rendering BiCu$_2$PO$_6$ and BiMn$_2$PO$_6$ very different even on the level of individual interactions, let alone the ensuing magnetic behavior. In contrast to BiCu$_2$PO$_6$ with the gapped spin-liquid ground state, BiMn$_2$PO$_6$ develops long-range magnetic order below 30 K and shows an additional magnetic transition around 10 K. In the following, we report a comprehensive characterization of this material in terms of its structure, thermodynamic properties, microscopic magnetic model, magnetic ground state, and spin dynamics.

II. METHODS

Polycrystalline samples of BiMn$_2$PO$_6$ and BiZn$_2$PO$_6$ were prepared by solid-state reaction techniques using Bi$_2$O$_3$ (99.999%), MnO (99.99%), ZnO (99.99%), and NH$_4$H$_2$PO$_4$ (99.9%) as starting materials, all from Sigma-Aldrich. The stoichiometric mixtures were heated at 800 °C in flowing Ar and in air with one intermediate grinding each for BiMn$_2$PO$_6$ and BiZn$_2$PO$_6$, respectively.

The resulting samples were single-phase as determined by x-ray diffraction (XRD, PANalytical powder diffractometer and CuK$_\alpha$ radiation, $\lambda_{CuK\alpha} = 1.54182$ Å) at room temperature. Le Bail profile fits to the XRD data were performed using the Jana2006 software\cite{20}.

Magnetic susceptibility $\chi \equiv M/H$ data were measured versus temperature $T$ and applied magnetic field $H$ using a SQUID magnetometer [Quantum Design, Magnetic Properties Measurement System (MPMS)]. Heat capacity $C_p$ data were collected with a Quantum Design Physical Properties Measurement System (PPMS) on pressed pellets using the relaxation technique.

The nuclear magnetic resonance (NMR) measurements were carried out using pulsed NMR techniques on $^{31}$P nuclei with spin $I = \frac{3}{2}$ and gyromagnetic ratio $\gamma I / 2\pi = 17.237$ MHz/Tesla, over the $T$ range $4 \leq T \leq 300$ K. The NMR measurements were done at two radio frequencies of 77.5 MHz and 49.15 MHz. Spectra were obtained either by Fourier transform (FT) of the NMR echo signal or by sweeping the field at fixed frequency. The NMR shift $K(T) = (H_{ref} - H(T))/H(T)$ was determined by measuring the resonance field $H(T)$ of the sample with respect to a standard H$_3$PO$_4$ solution (resonance field $H_{ref}$). The $^{31}$P nuclear spin-lattice relaxation rate $(1/T_1)$ was measured after applying a comb

FIG. 1: (Color online) Crystal structure of BiMn$_2$PO$_6$ and relevant magnetic interactions. Green, brown, and gray polyhedra show Mn1O$_5$, Mn2O$_5$, and PO$_4$, respectively. Bi atoms are not shown. Empty and filled circles denote the Mn1 and Mn2 positions, respectively. Left panel: different projections of the ladder unit. Right panel: overall view of the structure. The antiferromagnetic classical ground state predicted by our electronic structure calculations is shown by arrows. The collinear ordering axis is chosen arbitrarily and may not reflect the actual ordering axis in the crystal. The exchange integrals ($J_{ij}$) in BiMn$_2$PO$_6$ and BiCu$_2$PO$_6$ are listed in Table 1. The crystal structures are visualized using the VESTA software.\cite{21}
TABLE I: Crystallographic data for BiMn2PO6 at room temperature (orthorhombic structure, space group Pnma)\textsuperscript{19}.

Our fitted lattice parameters are \(a = 12.0383(2) \text{Å}, b = 5.3656(1) \text{Å}, \) and \(c = 8.1207(1) \text{Å}\) compared to the reported values \(a = 12.0425(4) \text{Å}, b = 5.3704(1) \text{Å}, \) and \(c = 8.1288(2) \text{Å}\)\textsuperscript{19}.

Our goodness-of-fit is obtained to be \(R_b = 4.9\%\). Listed are the Wyckoff symbols and relative atomic coordinates \(x/a, y/b, \) and \(z/c\) of each atom\textsuperscript{19}.

| Atom | Wyckoff position | \(x/a\) | \(y/b\) | \(z/c\) |
|------|------------------|---------|---------|---------|
| Bi   | 4c               | 0.0950(2) | 1/4     | 0.0120(5) |
| Mn1  | 4c               | 0.1032(6) | 3/4     | 0.6924(6) |
| Mn2  | 4c               | 0.0991(7) | 3/4     | 0.2952(7) |
| P    | 4c               | 0.1970(3) | 1/4     | 0.4744(7) |
| O1   | 8d               | -0.0033(3) | 0.0050(7) | 0.1634(2) |
| O2   | 8d               | 0.1249(2) | 0.4859(4) | 0.4922(5) |
| O3   | 4c               | 0.2895(4) | 1/4     | 0.5983(6) |
| O4   | 4c               | 0.2414(3) | 1/4     | 0.2965(5) |

of saturation pulses.

Individual magnetic couplings in BiMn2PO6 were evaluated from density-functional theory (DFT) band-structure calculations performed in the FPLO code\textsuperscript{21} within the generalized gradient approximation (GGA)\textsuperscript{22} augmented by a mean-field correction for correlation effects in the Mn 3d shell (GGA+\(U\)). We used the on-site Coulomb repulsion parameter \(U_d = 5.5\text{eV}\) and the on-site Hund’s coupling \(J_d = 1\text{eV}\) that yield exchange integrals in quantitative agreement with the experimental data. While no conclusive information on the values of \(U_d\) and \(J_d\) appropriate for Mn\(^{+2}\) is available in the literature, we note that our choice of \(U_d = 5.5\text{eV}\) is compatible with earlier computational studies, where \(U_d = 4 – 6\text{eV}\) has been used.\textsuperscript{23,24} The variation of \(U_d\) in the 4 – 6 eV range leads to marginal changes in the computed exchange integrals. Each exchange integral \(J_{ij}\) was evaluated from total energies of four collinear magnetic configurations, as described in Ref.\textsuperscript{25}.

The magnetic susceptibility and ground state of the DFT-based magnetic model were evaluated by the classical Monte-Carlo spinmc algorithm of the ALPS simulation package\textsuperscript{26}.

Simulations were performed for finite lattices with periodic boundary conditions and up to 4096 sites. Convergence with respect to finite-size effects was carefully checked.

III. RESULTS

A. Crystallography

BiMn2PO6 and its nonmagnetic sibling BiZn2PO6 crystallize in the primitive orthorhombic space group \(Pnma\) (No. 62) containing \(Z = 4\) formula units per unit cell. The crystal structures were solved in Refs.\textsuperscript{19} and \textsuperscript{28} using neutron and x-ray powder diffraction, respectively.

The atomic positions determined by these authors for the respective compounds are given in Tables I and II and the lattice parameters in the respective figure captions. These compounds are isostructural to BiCu2PO6.\textsuperscript{27}

We carried out powder x-ray diffraction measurements of our polycrystalline samples of BiMn2PO6 and BiZn2PO6 and the results are shown in Fig. 2. Le Bail fits of the patterns based on space group \(Pnma\) were done to determine the lattice parameters. Good fits were...
obtained as shown in Fig. 2, and the respective lattice parameters are listed in the captions of Tables I and II. Excellent agreement of our lattice parameters with those previously determined for the two compounds is seen in the respective Table captions.

Details of this crystal structure (Fig. 1) have been discussed in Sec. I. The most notable difference between the Mn$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ compounds lies in the geometry of the MO$_5$ polyhedra. The CuO$_5$ square pyramids feature a 4+1 coordination, with 4 shorter in-plane distances of 1.9–2.0 Å forming a CuO$_4$ plaquette and the fifth apical distance of 2.20–2.35 Å. This 4+1 type of coordination is clearly reminiscent of the Jahn-Teller distortion of Cu$^{2+}$. Neither Mn$^{2+}$ nor Zn$^{2+}$ show this type of distortion. Their MO$_5$ polyhedra are more regular, with all five M–O distances lying in the range of 2.05–2.17 Å for Mn$^{2+}$ (Ref. 19) and 1.97–2.12 Å for the smaller Zn$^{2+}$ cation.

B. Magnetization and Magnetic Susceptibility

The magnetic susceptibility $\chi(T)$ data for BiMn$_2$PO$_6$ measured at $H = 1$ T are presented in Fig. 3a. At high temperatures $T > 150$ K, $\chi(T)$ follows a Curie-Weiss law. With decrease in temperature, a sudden jump at 43 K, a peak at 30 K, and then a change in slope at 10 K were observed in $\chi(T)$ suggesting that there are three possible magnetic transitions at low temperatures as noted by the vertical arrows for $H = 1$ T in Fig. 3(b). No broad maximum associated with dynamic short-range ordering was observed down to low temperatures.

To fit the uniform magnetic susceptibility data at high temperatures, we used the expression

$$\chi = \chi_0 + \frac{C}{T - \theta_{CW}},$$

(1)

where $\chi_0$ is the temperature-independent contribution that accounts for core diamagnetism and Van Vleck (VV) paramagnetism. The second term is the Curie-Weiss (CW) law with Curie constant $C$ and Weiss temperature $\theta_{CW}$. The data above 150 K were fitted with the parameters $\chi_0 = 4(3) \times 10^{-4}$ cm$^3$/mol Mn, $C = 4.4(3)$ cm$^3$/K/mol Mn, and $\theta_{CW} = -78(7)$ K. The error bars were determined by varying the fitted temperature range. This value of $C$ is in good agreement with the value $C = 3.977$ cm$^3$/K/mol Mn for the high-spin state ($S = \frac{5}{2}$) of Mn$^{2+}$ with g-factor $g = 2.00$, as expected for Mn$^{2+}$. Adding the core diamagnetic susceptibility for the individual ions ($\chi_{\text{Bi}^{3+}} = -25 \times 10^{-6}$ cm$^3$/mol, $\chi_{\text{Mn}^{2+}} = -14 \times 10^{-6}$ cm$^3$/mol, $\chi_{\text{Cu}^{2+}} = -1 \times 10^{-6}$ cm$^3$/mol, and $\chi_{\text{O}^{2-}} = -12 \times 10^{-6}$ cm$^3$/mol), the total $\chi_{\text{core}}$ was calculated to be $-12.6 \times 10^{-5}$ cm$^3$/mol. The Van Vleck paramagnetic susceptibility for BiMn$_2$PO$_6$ estimated by subtracting $\chi_{\text{core}}$ from $\chi_0$ is $\chi_{\text{VV}} \approx 4.6 \times 10^{-4}$ cm$^3$/mol Mn. The large negative value of $\theta_{CW}$ shows that the dominant interactions between the Mn spins are AFM. Below 150 K, the $1/\chi$ data in Fig. 3a begin to deviate from the CW fit, which suggests the onset of AFM correlations beyond those described by the Curie-Weiss law.

In order to further confirm the sequence of magnetic transitions at low temperatures, $\chi(T)$ was also measured at different applied fields. As seen in Fig. 3(b), the sudden jump at 43 K observed at $H = 1$ T is completely suppressed at $H = 3$ T. On the other hand, the peak at 30 K and the bump at 10 K are not affected at all by external fields up to 5 T. In a simple antiferromagnet, the magnetic specific heat ($C_{\text{mag}}$) is related to the parallel static susceptibility $\chi$ by Fisher’s relation

$$C_{\text{mag}} \approx A \frac{\partial(\chi(T))}{\partial T},$$

(2)

where the proportionality factor $A$ is expected to be a slowly varying function of $T$ near $T_N$. This relation has
been verified experimentally for some bulk materials.\cite{footnote:1}

For clarity, we have plotted the $T$-derivative of $\chi T$ as a function of $T$ in Fig. 3(c) measured at three different applied fields. Figure 3(c) confirms that the transitions at 30 K and 10 K remain unchanged for $H$ up to 5 T. The feature at 43 K is likely due to the presence of Mn$_3$O$_4$ impurity phase, which orders ferrimagnetically at 42 K.\cite{footnote:2,footnote:3}

While we do not see this impurity in x-ray powder diffraction data (Fig. 2), even a trace amount of Mn$_3$O$_4$ (below 1%) may be sufficient to produce a visible magnetic anomaly around 43 K.

$M(H)$ isotherms were measured at different temperatures, shown in Fig. 4(a), to check for field-induced effects and for the presence of the probable ferrimagnetic Mn$_3$O$_4$ impurity phase in the sample. Above 50 K, $M$ is proportional to $H$ over the whole field range. At 25 K, a non-linearity was observed in the $M(H)$ curve below about 0.3 T suggesting a small ferrimagnetic Mn$_3$O$_4$ impurity contribution in the magnetization. In order to quantitatively estimate the Mn$_3$O$_4$ impurity concentration, we fitted the $M(H)$ isotherm at 25 K in the field range 1 T to 5.5 T by the linear relation $M(H) = M_s + \chi H$, where $M_s$ is the saturation magnetization of the Mn$_3$O$_4$ ferrimagnetic impurity and $\chi$ is the intrinsic magnetic susceptibility of the sample. The obtained value of $M_s \approx 0.00492 \mu_B$/f.u. corresponds to about 0.26 mol\% Mn$_3$O$_4$ impurity ($M_s = 1.87 \mu_B$ f.u. for Mn$_3$O$_4$ at $T = 0$ K).\cite{footnote:4} This small amount is not observable from our x-ray diffraction measurements. At 1.8 K, in the maximum field of 5.5 T, $M \approx 0.26 \mu_B$/Mn is reached, which corresponds to only 5% of the fully polarized magnetization of 5 $\mu_B$/Mn. This agrees with a dominant antiferromagnetic exchange coupling in BiMn$_2$PO$_6$.

To further elucidate the dependence of $M$ on $H$, shown in Fig. 4(b) is a plot of $dM/dH$ versus $H$ at 1.8, 5, 10, and 25 K. A sharp peak is observed at a low field of $\sim 0.1$ T at 25 K that we attribute to the saturation of the Mn$_3$O$_4$ impurity phase that has a Curie temperature of 43 K. At 25 K, the integral of $dM/dH$ versus $H$ from $H = 0$ to 0.5 T is $\sim 39$ G cm$^3$/mol, which is comparable with the value of $M_s$ that we obtained above. We believe that this peak becomes smaller with decreasing $T$ and disappears below 10 K because the thermal energy cannot easily overcome the anisotropy energy of the ferrimagnetic domain walls in Mn$_3$O$_4$ at low fields with decreasing $T$. Therefore the saturation of the ferrimagnetic component of Mn$_3$O$_4$ occurs over a wide field range, resulting in a strong decrease in the height of the low-field peak in $dM/dH$ with decreasing $T$ below 25 K.

In addition to the above extrinsic low-field peak in $dM/dH$ versus $H$ arising from the Mn$_3$O$_4$ impurity phase, we also observe an intrinsic high-field metamagnetic transition at $H \approx 4.5$ T [see Fig. 4(b)]. This transition is not seen at 10 K and therefore likely pertains to the low-$T$ magnetic phase below 10 K only. We refrain here from speculating on the nature of this metamagnetic transition because the magnetic structure below 10 K is not yet known.

C. Heat Capacity

An overview of the $C_p(T)$ data for BiMn$_2$PO$_6$ and the nonmagnetic analogue BiZn$_2$PO$_6$ from 2 to 310 K is shown in Fig. 5(a). A sharp $\lambda$-type anomaly is seen for BiMn$_2$PO$_6$ at $T \approx 29$ K associated with the above long-range AFM order, discussed in more detail below. The Debye model for the lattice heat capacity at constant volume $C_V$ arising from acoustic phonons is given by\cite{footnote:5}

$$
\frac{C_V}{nR} = 9 \left( \frac{T}{\Theta_D} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \, dx,
$$

where $R$ is the molar gas constant, $n$ is the number of atoms per formula unit, and $\Theta_D$ is the Debye temperature. This prediction was recently accurately fitted by

![Figure 4](https://example.com/figure4.png)

**FIG. 4**: (Color online) (a) Magnetization ($M$) as a function of applied field ($H$) measured at different temperatures. (b) Field derivative of magnetization ($dM/dH$) at 1.8 K, 5 K, 10 K, and 25 K as a function of $H$ to highlight the field-induced transition at $\sim 4.5$ T, which appears to be a property of the low-$T$ (< 10 K) magnetic phase. The peak in $dM/dH$ at $\sim 0.2$ T in (b) arises from a Mn$_3$O$_4$ impurity phase (see text).
an analytic Padé approximant which greatly simplifies fitting experimental data by Eq. (3) 35

We fitted the \( C_p(T) \) data for nonmagnetic BiZn\(_2\)PO\(_6\) over the full temperature range by Eq. (3) using the Padé approximant formulation, but the fit was poor. A better fit was obtained to the data just from 200 to 310 K, as shown by the red curve in Fig. 5(a), where the fitted Debye temperature is \( \Theta_D = 637 \) K. The large \( \Theta_D \) is typical of oxides due to the low mass of the O atoms and the strong interatomic bonding involving those atoms. The fit strongly deviates from the data on cooling below \( \sim 200 \) K, which we attribute to anomalous and strong softening of the lattice on cooling. To quantify this softening, the \( \Theta_D \) versus \( T \) was calculated for each data point for the two compounds using the Padé approximant formulation of Eq. (3) and the results are shown in Fig. 5(b), where only the data above 100 K are plotted for BiMn\(_2\)PO\(_6\) because as shown below the magnetic contribution to the heat capacity starts to become significant below this temperature. As seen in Fig. 5(b), \( \Theta_D \) decreases by a factor of about two on cooling from 300 K to 2 K. This is an extremely large change for solids, where the temperature variations below 300 K are typically \( \pm 20\% \) due to differences between the actual phonon densities of states and that assumed in the Debye theory 37

Expanded plots of \( C_p/T^3 \) versus \( T \) for BiMn\(_2\)PO\(_6\) and BiZn\(_2\)PO\(_6\) below 40 K are shown in Fig. 6. The low-\( T \) limit of the Debye theory prediction in Eq. (3) is the so-called Debye \( T^3 \) law, given by 38

\[
\frac{C_V(T \to 0)}{nR} = \frac{12\pi^4}{5} \left( \frac{T}{\Theta_D} \right)^3 \equiv \beta T^3. \tag{4}
\]

For nonmagnetic BiZn\(_2\)PO\(_6\), Fig. 6 gives \( \beta \approx 0.45 \) mJ/mol K\(^3\) at low temperatures. Then using \( n = 10 \) atoms per formula unit, Eq. (4) gives the Debye temperature as \( \Theta_D \approx 350 \) K, consistent with the data for \( T \to 0 \) in the point-by-point plot of \( \Theta_D(T) \) in Fig. 5(b). From Fig. 6, one sees a large enhancement of \( C_p/T^3 \) for BiMn\(_2\)PO\(_6\) above that of BiZn\(_2\)PO\(_6\) at low temperatures. This enhancement presumably originates from the magnetic degrees of freedom (spin waves) in the AFM ordered state below \( T_N \approx 30 \) K, which in turn indicates

\[ \text{FIG. 5: (Color online) (a) Overview of the heat capacity at constant pressure } C_p \text{ versus temperature } T \text{ of BiMn}_2PO_6 (\text{filled blue circles}) \text{ and of the nonmagnetic analogue BiZn}_2PO_6 (\text{filled red squares}) from 2 \text{ to } 310 \text{ K. Also shown is a fit of the Debye heat capacity model in Eq. (3) to the data for nonmagnetic BiZn}_2PO_6 \text{ between } 200 \text{ and } 310 \text{ K, which yields the Debye temperature } \Theta_D = 637 \text{ K. The small dips and bumps in the data for } T \sim 290 \text{ K are believed to be artifacts. (b) Debye temperature } \Theta_D \text{ versus } T \text{ computed using Eq. (3) from the data for the two compounds in (a). Only data above } 100 \text{ K are shown for BiMn}_2PO_6 \text{ because of the additional magnetic contribution below this } T. \text{ The lattices of both compounds show a drastic softening on cooling below } \sim 200 \text{ K.} \]
that any energy gap in the spin-wave spectrum induced by magnetic anisotropy is negligible for $T \gtrsim 3$ K. This topic is discussed in more detail in Sec. [IVC].

The $C_p(T)$ data up to 100 K are shown in Fig. 7(a) for both BiMn$_2$PO$_6$ and BiZn$_2$PO$_6$ where the temperature scale of the latter data was corrected for the difference in formula weights of the two compounds. With decreasing $T$, the magnitude of the negative slope of $C_p(T)$ for BiMn$_2$PO$_6$ increases before a sharp $\lambda$-type anomaly occurs with a peak at the long-range AFM ordering temperature $T_N \approx 29$ K. In order to obtain a quantitative estimate of the magnetic contribution $C_{mag}(T)$ to $C_p(T)$, the mass-corrected $C_p(T)$ of BiZn$_2$PO$_6$ was subtracted from the measured data for BiMn$_2$PO$_6$. The resulting $C_{mag}(T)$ is shown as the red curve in Fig. 7(a). There is no trace of a transition at 43 K, further supporting the extrinsic nature of the feature observed above in $\chi$ at about this $T$.

The Mn ions have oxidation state Mn$^{2+}$ and therefore a $d^5$ electronic configuration. One therefore expects the Mn ions to have high-spin $S = 5/2$ and a high-$T$ molar magnetic entropy of $2R\ln(2S + 1) = 2R\ln(6) = 29.79$ J/mol K, where $R$ is the molar gas constant and a “mol” refers here to a mole of formula units of BiMn$_2$PO$_6$, each of which contains two Mn atoms. To test this hypothesis, we calculated the magnetic entropy $S_{mag}(T)$ from the $C_{mag}(T)/T$ versus $T$ data in Fig. 7(b) (blue symbols) according to

$$S_{mag}(T) = \int_{3.0K}^{T} \frac{C_{mag}(T')}{T'} dT', \tag{5}$$

where 3.0 K is the low-$T$ limit of the data. The derived $S_{mag}(T)$ is shown as the red curve in Fig. 7(b). The value of $S_{mag}$ at 100 K is 31.7 J/mol K, close to the expected value of 29.8 J/mol K. Thus we conclude that the Mn$^{2+}$ cations indeed have spin $S = 5/2$.

An expanded plot of $C_{mag}(T)/T$ versus $T$ for BiMn$_2$PO$_6$ is shown in Fig. 8, together with a fit by the Weiss molecular field theory (MFT) for spin $S = 5/2$ and Néel temperature $T_N = 28.8$ K (red curve) which shows a strong broad peak near 10 K. Therefore the broad hump in the experimental data at $\sim 10$ K is due to the magnetic ordering transition at 28.8 K and not to an additional transition at $\sim 10$ K.

FIG. 7: (Color online) (a) Heat capacity $C_p$ versus temperature $T$ for BiMn$_2$PO$_6$ and the nonmagnetic reference compound BiZn$_2$PO$_6$. The red solid curve is the derived magnetic heat capacity $C_{mag}(T)$. (b) $C_{mag}(T)/T$ and the magnetic entropy $S_{mag}$ as a function of $T$ along the left and right y-axes, respectively. The dashed horizontal line is the value $S_{mag} = 2R\ln 6$ expected per mole of f.u. for Mn$^{2+}$ ($S = \frac{5}{2}$) spins. The downward arrows indicate the two transition points. However, the broad peak in $C_{mag}/T$ at $T \approx 10$ K is not associated with a magnetic transition (see text).

FIG. 8: (Color online) Expanded plot of the magnetic heat capacity $C_{mag}(T)/T$ versus $T$ below 50 K (filled blue circles). The connecting blue line is a guide to the eye. Also shown is the prediction of molecular field theory (MFT) for spin $S = 5/2$ and Néel temperature $T_N = 28.8$ K (red curve) which shows a strong broad peak near 10 K. Therefore the broad hump in the experimental data at $\sim 10$ K is due to the magnetic ordering transition at 28.8 K and not to an additional transition at $\sim 10$ K.
over that $T$ range. Since from Fig. 7(b) the entropy at 100 K of the Mn spins $S = 5/2$ in BiMn$_2$PO$_6$ is completely recovered [$S_{\text{mag}} = 2R\ln(2S + 1)$], the missing area between the MFT curve and the data in Fig. 8 for $T < T_N$ is recovered at $T > T_N$ where the latter entropy gain is due to loss of short-range AFM ordering of the Mn spins with increasing $T$ above $T_N$. There is no clear evidence in Fig. 8 for any magnetic transition at about 10 K that was suggested above from the $M(H,T)$ data. Thus this transition does not cause much change in the $T$ dependence of the magnetic entropy of the system.

The above MFT prediction of $C_{\text{mag}}(T)$ for BiMn$_2$PO$_6$ is exponential at low $T$ because the local exchange field seen by each Mn spin lifts the Zeeman degeneracy which results in energy gaps between the ground and excited Zeeman energy levels of the Mn spin. On the other hand MFT does not take into account spin-wave excitations which would give rise, in the absence of anisotropy effects leading to an anisotropy gap, to a $T^2$ or $T^3$ dependence of $C_{\text{mag}}$ at low $T$ for spin waves confined mainly to a plane (quasi-2D) or spin waves traveling more or less equally in all three directions (3D), respectively. Shown in Fig. 9 are plots of $C_{\text{mag}}/T^2$ (right ordinate) and $C_{\text{mag}}/T^3$ (left ordinate) to examine these two possibilities, respectively. As shown by the dashed-curve power-law extrapolations of the data below 5 K to $T = 0$ which both give nonzero intercepts, either case appears to be consistent with the data, where the intercepts for $T \to 0$ give the potential spin-wave (SW) contributions

$$C_{\text{mag}} = \beta_{\text{SW}} T^3, \quad (3D)$$

$$\beta_{\text{SW}} \approx 5.6 \frac{\text{mJ}}{\text{mol K}^3} \quad (6b)$$

or

$$C_{\text{mag}} = \delta_{\text{SW}} T^2, \quad (2D)$$

$$\delta_{\text{SW}} \approx 1.0 \frac{\text{mJ}}{\text{mol K}^2} \quad (6d)$$

A quantitative evaluation of the spin-wave contribution to the heat capacity is given below in Sec. IV C.

D. Microscopic Magnetic Model

1. Evaluation of magnetic Model

The electronic density of states (DOS) versus energy calculated for BiMn$_2$PO$_6$ is shown in Fig. 10. Although BiMn$_2$PO$_6$ is green-colored and clearly insulating, we find a metallic DOS, because the calculation is done on the simple GGA level without introducing the GGA+U correction for correlation effects, which are responsible for opening the band gap in a Mott insulator. Nevertheless, this simplistic calculation is useful for a direct comparison to the isostructural spin-ladder compound BiCu$_2$PO$_6$ (see Fig. 2 in Ref. [12]). The difference in the electron count is immediately reflected in the position of the Fermi energy that lies in the middle of the 3$d$ band for Mn$^{2+}$ (5 $d$-electrons) and in the top part of the 3$d$ band for Cu$^{2+}$ (9 $d$-electrons). Additionally, the nature of states in the vicinity of the Fermi energy is quite different. In BiCu$_2$PO$_6$, 40% of these states are formed by oxygen, whereas in BiMn$_2$PO$_6$ the hybridization with oxygen is much weaker, so that oxygen contributes only 6% of the states at the Fermi level.

Exchange couplings obtained from the supercell GGA+U method are listed in Table III. We calculated all interactions for Mn–Mn distances up to $7 \text{Å}$ and repeated calculations for different supercells to make sure that longer pathways can be neglected. We find that
TABLE III: Exchange couplings in BiMn$_2$PO$_6$: the Mn–Mn distances (in Å), coordination numbers $z_{ij}$, (number of coupling s per Mn$^{+2}$ ion), exchange integrals $J_{ij}$ (in K), and normalized spin-spin correlations $\langle S_i \cdot S_j \rangle / S^2$. The exchange integrals are calculated within GGA+$U$ using $U_d = 5.5$ eV and $J_d = 1$ eV. The last column lists relevant exchange couplings in BiCu$_2$PO$_6$ according to Ref. 12. For the notation of $J_{ij}$, see Fig. 1. The exchange bonds with $\langle S_i \cdot S_j \rangle / S^2 = +1$ are frustrating for AFM ordering in the proposed structure.

| BiMn$_2$PO$_6$ | BiCu$_2$PO$_6$ |
|----------------|----------------|
| $d_{\text{Mn-Mn}}$ | $z_{ij}$ | $J_{ij}$ | $\langle S_i \cdot S_j \rangle / S^2$ | $J_{ij}$ |
| Mn1–Mn2 | 3.229 | J1 | 5.5 | $-1.0$ | 22 |
| Mn1–Mn2 | 3.627 | J1 | 6.7 | $-1.0$ | 176 |
| Mn1–Mn2 | 4.556 | J1 | 0.35 | $+1.0$ | $< 5$ |
| Mn1–Mn1 | 4.814 | J1 | 0.8 | $+1.0$ | $< 5$ |
| Mn2–Mn2 | 4.898 | J1 | 0.7 | $+1.0$ | $< 5$ |
| Mn1–Mn2 | 4.900 | J1 | 2.2 | $-1.0$ | 154 |
| Mn1–Mn1 | 5.370 | J1 | 0.9 | $+1.0$ | 170 |
| Mn2–Mn2 | 5.370 | J1 | 1.3 | $+1.0$ | 90 |
| Mn1–Mn1 | 6.019 | J1 | 0.6 | $-1.0$ | $< 5$ |
| Mn2–Mn2 | 6.078 | J1 | 0.4 | $-1.0$ | $< 5$ |

BiMn$_2$PO$_6$ follows the conventional spin-ladder scenario. The couplings $J_1$ and $J_3$ along the leg and along the rung of the ladder, respectively, are the two leading interactions in this system (note that we use the notation of Ref. 12, which may be a bit counterintuitive here, but facilitates the comparison to BiCu$_2$PO$_6$). These two couplings follow the short Mn–O–Mn pathways and can be analyzed in terms of Goodenough-Kanamori-Anderson (GKA) rules. Considering the Mn–O–Mn angles of 116.5° for $J_1$ and 96.3° for $J_3$, one may expect a much weaker AFM or even a ferromagnetic (FM) exchange $J_3$, in contrast to the robust AFM exchange $J_1$. On the other hand, the short Mn–Mn distance between the Mn1O5–Mn2O5 pyramids may facilitate the direct Mn–Mn exchange for $J_3$ and provide an additional source of the AFM coupling, thus leading to a nearly ideal spin ladder with $J_1 \approx J_3$.

According to Table III, both BiMn$_2$PO$_6$ and BiCu$_2$PO$_6$ feature solely AFM exchange, but the couplings between the spin-$\frac{5}{2}$ Mn$^{+2}$ ions are much weaker than those between the spin-$\frac{1}{2}$ Cu$^{+2}$, as previously seen in the spin-chain compound BaMn$_2$Si$_2$O$_7$ ($J \approx 12$ K), versus isostuctural BaCu$_2$Si$_2$O$_7$ ($J \approx 280$ K). This difference stems from the reduced hybridization between the Mn 3$d$ and O 2$p$ states that renders superexchange less efficient.

Long-range couplings form triangular loops (Fig. 1) and frustrate the spin lattice of BiMn$_2$PO$_6$. These couplings follow Mn–O–O–Mn pathways and remain relatively weak, below 2.5 K, compared to BiCu$_2$PO$_6$, where the long-range couplings $J_2$, $J_2'$, and $J_3$ are integral to the magnetic model. This difference between the Mn$^{+2}$ and Cu$^{+2}$ compounds should be again traced back to the weaker Mn–O hybridization. Altogether, we find that BiMn$_2$PO$_6$ is quasi-1D with sizable interladder couplings along both $a$ and $c$, whereas BiCu$_2$PO$_6$ is either quasi-1D or quasi-2D and features unexpected long-range couplings along $b$ and $c$ as well as very weak interladder couplings along $a$.

### 2. Molecular field theory

In order to compare calculated exchange couplings with the experiment, we develop Weiss molecular field theory (MFT) for BiMn$_2$PO$_6$. For simplicity, we consider a Heisenberg model with no anisotropy terms except that possibly due to an infinitesimal applied magnetic field $H$. The part $H_i$ of the spin Hamiltonian associated with a particular central spin $S_i$ interacting with its neighbors $S_j$ with respective exchange constants $J_{ij}$ is

$$H_i = \frac{1}{2} \sum_j J_{ij} S_i S_j + g \mu_B S_i \cdot H,$$

where the factor of 1/2 recognizes that the exchange energy is evenly split between two interacting spins, $g$ is the spectroscopic splitting factor ($g$-factor) of a magnetic moment $\mu$, and $\mu_B$ is the Bohr magneton. In the Weiss MFT, one only considers the thermal-average directions of $S_i$ and $S_j$ when calculating their interaction. Furthermore, it is the magnetic moment $\mu$ that interacts with a magnetic field and not the angular momentum $S$ per se. The relationship between these two quantities for an electronic spin and magnetic moment is

$$S = \frac{\mu}{g \mu_B},$$

where the minus sign arises from the negative sign of the electron charge. In the following, the symbol $\mu$ refers to the thermal-average value of a magnetic moment, as is appropriate in MFT. Then the energy $E_i$ of interaction of magnetic moment $\mu_i$, with its neighbors $\mu_j$ is given by Eq. (7) as

$$E_i = \frac{1}{2g^2 \mu_B^2} \mu_i \cdot \left( \sum_j J_{ij} \mu_j \right) - \mu_i \cdot H.$$

In MFT, one replaces the sum of the exchange interactions acting on $\mu_i$ in the first term by an effective magnetic field called the Weiss molecular field $H_{\text{exch}}$, or "exchange field", that is defined by the usual relationship for the rotational potential energy of a magnetic moment in a magnetic field, as in the second term of Eq. (6), as

$$2E_{\text{exch}} = -\mu_i \cdot H_{\text{exch}},$$

where the factor of 2 arises because in MFT all of the exchange energy between $\mu_i$ and $\mu_j$ is attributed to $\mu_j$, as 

$$2E_{\text{exch}} = -\mu_i \cdot H_{\text{exch}}.$$
thus canceling out the factor of 1/2 in Eq. (9). From the first term in Eq. (9) one obtains

\[ H_{\text{exch}} = -\frac{1}{g^2\mu_B^2} \sum_j J_{ij} \hat{\mu}_j. \]  

(11)

Using \( \hat{\mu}_j = \hat{\mu}_j \hat{\mu}_j \) where \( \mu_j = |\hat{\mu}_j| \), the component of \( H_{\text{exch}} \) in the direction of \( \hat{\mu}_i \) is

\[ H_{\text{exch} i} = \hat{\mu}_i \cdot H_{\text{exch}} = -\frac{1}{g^2\mu_B^2} \sum_j J_{ij} \hat{\mu}_i \cdot \hat{\mu}_j = -\frac{1}{g^2\mu_B^2} \sum_j J_{ij} \hat{\mu}_j \cdot \hat{\mu}_j \cdot \cos \phi_{ji}, \]  

(12)

where \( \phi_{ji} \) is the angle between \( \hat{\mu}_j \) and \( \hat{\mu}_i \).

Now we specialize to the treatment of a local-moment magnetic system containing two crystallographically inequivalent sublattices 1 and 2 of identical spins as occurs in BiMn\(_2\)PO\(_6\) with the presence of the Mn1 and Mn2 spins-5/2, respectively. One can separate the sum in Eq. (12) into two sums over spins in the same (s) and different (d) sublattices 1 and 2 of Mn1 and Mn2, yielding

\[ H_{\text{exch 1i}} = -\frac{1}{g^2\mu_B^2} \left( \sum_j^s J_{ij} \mu_{1j} \cos \phi_{ji} + \sum_j^d J_{ij} \mu_{2j} \cos \phi_{ji} \right), \]  

(13a)

\[ H_{\text{exch 2i}} = -\frac{1}{g^2\mu_B^2} \left( \sum_j^d J_{ij} \mu_{1j} \cos \phi_{ji} + \sum_j^s J_{ij} \mu_{2j} \cos \phi_{ji} \right), \]  

(13b)

where \( H_{\text{exch 1i}} \) is the exchange field seen by a Mn spin on the Mn1 sublattice, \( H_{\text{exch 2i}} \) is the exchange field seen by a Mn spin on the Mn2 sublattice and \( \phi_{ji} \) is the angle between the respective magnetic moments. In the paramagnetic state \( \phi_{ji} = 0 \) for all spin pairs, since all moments point in the direction of the applied field, whereas in the AFM-ordered state with \( H = 0 \) one has either \( \phi_{ji} = 0 \) or 180° according to the AFM structure in Table III deduced from our electronic structure calculations for BiMn\(_2\)PO\(_6\).

In MFT, the response of a given magnetic moment to the exchange and applied fields is governed by the Brillouin function \( B_S(y) \) according to

\[ \mu_i = \mu_{\text{sat}} B_S(y_i) \]  

(14a)

where

\[ y_i = \frac{g \mu_B B_i}{k_B T}, \]  

(14b)

\( k_B \) is the Boltzmann constant, the component of the local magnetic induction in the direction of \( \hat{\mu}_i \) is

\[ B_i = H_{\text{exch i}} + H_i, \]  

(14c)

and the saturation moment of each spin is

\[ \mu_{\text{sat}} = g S \mu_B. \]  

(14d)

We write the Brillouin function as

\[ B_S(y) = \frac{1}{2S} \left\{ (2S + 1) \coth \left[ \left(2S + 1\right) \frac{y}{2} \right] - \coth \left( \frac{y}{2} \right) \right\}, \]  

(15a)

for which the Taylor expansion about \( y = 0 \) is

\[ B_S(y) = \frac{(S + 1)y}{3} + O(y^3). \]  

(15b)

a. Paramagnetic State. In the paramagnetic state all induced moments are lined up with the applied magnetic field and one therefore has \( \phi_{ji} = 0 \) for all spin pairs, we assume infinitesimal \( H \) and therefore \( y_i \ll 1 \), and for a spin in either of the two Mn1 or Mn2 sublattices the above equations then yield

\[ \mu_i = \frac{g^2 S(S + 1) \mu_B^2}{3k_B T} (H_{\text{exch i}} + H) \]  

(16)

\[ = \frac{C_1}{T} \left[ -\frac{\mu_i}{g^2 \mu_B^2} \left( \sum_j^s J_{ij} + \sum_j^d J_{ij} \right) + H \right], \]  

where the single-spin Curie constant is

\[ C_1 = \frac{g^2 S(S + 1) \mu_B^2}{3k_B}. \]  

(17)

Solving for \( \mu_i \) gives the Curie-Weiss law

\[ \mu_i = \frac{C_1 H}{T - \theta_{\text{CW}}}, \]  

(18)

where the Weiss temperature is

\[ \theta_{\text{CW}} = -\frac{S(S + 1)}{3k_B} \left( \sum_j^d J_{ij} + \sum_j^s J_{ij} \right). \]  

(19)

This treatment is valid for BiMn\(_2\)PO\(_6\) because Table III gives, for both Mn sublattices in BiMn\(_2\)PO\(_6\), the same values

\[ \sum_j^d J_{ij}/k_B = 21.9 \text{ K}, \quad \sum_j^s J_{ij}/k_B = 5.7(1) \text{ K}. \]  

(20)

Thus for the Mn spins \( S = 5/2 \) in BiMn\(_2\)PO\(_6\), Eq. (19) predicts the Weiss temperature to be

\[ \theta_{\text{CW}}^{\text{calc}} = -80.5 \text{ K}, \]  

(21)

which compares favorably with the observed value of \(-78 \text{ K}.\)

b. Antiferromagnetic State. Within MFT, we obtain the Néel temperature \( T_N \) by setting the magnitudes of the ordered moments of all the Mn spins to be the same, \( \mu_{1j} = \mu_{2j} = \mu_i \), using the values of \( \phi_{ji} \) in Eqs. (13) as given in Table III, canceling out the factor of \( \mu_i \rightarrow 0 \) for \( T \rightarrow T_N \) on both sides of Eq. (14a) using the expansion (15b), and solving for \( T = T_N \), yielding

\[ T_N = -\frac{S(S + 1)}{3k_B} \left( \sum_j^d J_{ij} \cos \phi_{ji} + \sum_j^s J_{ij} \cos \phi_{ji} \right). \]  

(22)
The values of the sums are obtained from the $J_{ij}$ data and the $\cos \phi_{ji}$ values for the calculated AFM structure in Table III. The reason that the $\cos \phi_{ji}$ factor is included even in the second sum over Mn1–Mn1 and Mn2–Mn2 exchange bonds obtained from Table III. Using the data in Table III, Eq. (22) yields

$$\sum_j^d (J_{ij}/k_B) \cos \phi_{ji} = -20.5 \text{ K}, \quad (23a)$$

$$\sum_j^s (J_{ij}/k_B) \cos \phi_{ji} = 1.7(7) \text{ K}, \quad (23b)$$

where the error bar on the second sum reflects the difference between the sums over Mn1–Mn1 and Mn2–Mn2 exchange bonds obtained from Table III. Using the values of the sums in Eqs. (23) gives the prediction of MFT for $T_N$ from Eq. (22) as

$$T_N^{\text{calc}} \approx 55 \text{ K}. \quad (24)$$

This predicted value of $T_N$ is about a factor of two larger than the observed value of $\approx 30 \text{ K}$. Using Eqs. (19) and (22) one obtains the calculated frustration parameter

$$f^{\text{calc}} = \frac{|\theta^{\text{calc}}_\text{CW}|}{T_N^{\text{calc}}} = \frac{\sum_j^d J_{ij} + \sum_j^s J_{ij}}{\sum_j^d J_{ij} \cos \phi_{ji} + \sum_j^s J_{ij} \cos \phi_{ji}}. \quad (25)$$

The above values for $\theta^{\text{calc}}_\text{CW}$ and $T_N^{\text{calc}}$ then yield

$$f^{\text{calc}} = 1.46, \quad (26)$$

which is significantly smaller than the observed value of about 2.6.

### 3. Monte-Carlo simulations

We can also treat the problem numerically by simulating the magnetic susceptibility of our microscopic model with the exchange couplings from Table III. In Fig. 11, we compare the simulated magnetic susceptibility with the experimental data collected at 3 T, where the spurious 43 K feature is fully suppressed. The simulated spin susceptibility curve has been scaled with the spurious 43 K feature is fully suppressed. The simulated Neel temperature ($T_N \approx 27 \text{ K}$) is in good agreement with the experiment, absolute values of the susceptibility below 200 K are slightly underestimated. This discrepancy requires further investigation. It may be related to the pronounced lattice softening that would modify the exchange couplings $J_{ij}$ (our values in Table III are for the room-temperature crystal structure).

Our data give strong evidence for the magnetic frustration in BiMn$_2$PO$_6$. The experimental ratio $f = |\theta^{\text{CW}}_\text{CW}|/T_N = 2.6$ indicates a moderate magnetic frustration. To verify this, we constructed a simplified magnetic model, where the frustration is eliminated by removing the weakest coupling on each triangular loop, so that only $J_1$, $J_3$, $J_4$, $J_{a2}$, and $J'_{a2}$ remain. This way, we obtain a much higher Neel temperature of about 47 K (see the dashed curve in Fig. 11).

Surprisingly, frustration has no visible effect on the classical ground state of BiMn$_2$PO$_6$. We analyze this ground state by calculating normalized spin-spin correlations $(S_i \cdot S_j)/S^2$ at $T = 0.1 \text{ K}$. The normalized spin-spin correlation equals to $+1$ for the parallel spin alignment, $-1$ for the antiparallel spin alignment, and takes intermediate values between $-1$ and $+1$ for noncollinear spin configurations. In our case, all correlations are found to be equal to $\pm 1$, hence a collinear long-range order is expected. The ordering pattern is determined by the strongest couplings on each triangular loop. The antiparallel spin arrangement within the ladder is imposed by $J_1$ and $J_3$, the AFM order along $c$ is driven by $J_4$, and the order along $a$ relies on $J_{a2}, J'_{a2} > J_{a1}$ (see Fig. 1).

### E. $^{31}$P NMR

To further study the nature of the magnetic transitions and to elucidate static as well as dynamic properties of BiMn$_2$PO$_6$, we performed $^{31}$P NMR measurements on BiMn$_2$PO$_6$. An advantage of NMR is that it is not sensitive to impurities. Therefore, one can probe the intrinsic properties of the system. Since all P atoms are crystallographically equivalent (see Table III), for a spin $I = \frac{1}{2}$ nucleus one would expect a single spectral line. Indeed, we observe one narrow spectral line. Figure 12 shows the...
FIG. 12: (Color online) $^{31}$P NMR spectra measured at 77.5 MHz and at different temperatures.

FIG. 13: (Color online) Temperature-dependent $^{31}$P NMR shift $K$ vs. $T$. Inset: $K$ vs. $\chi$ measured at an NMR field of 5 T with temperature as an implicit parameter. The solid red line is the linear fit.

$^{31}$P NMR spectra measured at different temperatures. The line position was found to shift with temperature. Figure 13 presents the $T$-dependence of the NMR shift, $K(T)$. At high-$T$, $K$ varies in a Curie-Weiss manner and shows a change in slope at about 30 K associated with the AFM ordering.

Since the NMR shift is a direct measure of the spin susceptibility $\chi_{\text{spin}}$, one can write $K(T)$ in terms of $\chi_{\text{spin}}(T)$ as

$$K(T) = K_0 + \frac{A_{\text{hf}}}{N_A} \chi_{\text{spin}}(T),$$

where $K_0$ is the $T$-independent chemical shift, $A_{\text{hf}}$ is the hyperfine coupling constant of the $^{31}$P nuclei to the Mn$^{+2}$ spins and $N_A$ is Avogadro’s number. The conventional scheme for calculating $A_{\text{hf}}$ is to obtain it from the slope of a $K$ versus $\chi$ plot with $T$ as an implicit parameter. As seen in the inset of Fig. 13, the $K$ versus $\chi$ plot is a nice straight line at high temperatures ($T = 35 - 250$ K) yielding $K_0 = (0.13 \pm 0.03)\%$ and $A_{\text{hf}} = (7224 \pm 85)$ Oe/$\mu_B$. The temperature-independent shift $K_0$ contains an intrinsic chemical shift together with extrinsic contributions, including the remnant field of the field-sweep magnet that is not known exactly.

The total hyperfine coupling constant at the P site is generally the sum of the transferred hyperfine ($A_{\text{trans}}$) and dipolar ($A_{\text{dip}}$) couplings produced by the Mn$^{+2}$ spins, i.e., $A_{\text{hf}} = z^' A_{\text{trans}} + A_{\text{dip}}$, where $z^'$ is the number of nearest-neighbor Mn$^{+2}$ spins of the P-site. The anisotropic dipolar couplings were calculated for three different orientations using lattice sums. The maximum dipolar field contribution was calculated to be $800$ Oe/$\mu_B$, which is one order of magnitude smaller than the total hyperfine field, suggesting that the dominant contribution to the total hyperfine coupling is due to the transferred hyperfine coupling at the P-site. The total $A_{\text{hf}}$ of the P site with the Mn$^{+2}$ ions is $7224$ Oe/$\mu_B$. As discussed later, each P atom has $z^' = 6$ neighboring Mn$^{+2}$ spins, so the $A_{\text{hf}}$ due to one spin is $A_{\text{hf}}/z^' = 1.2$ kOe/($\mu_B$ Mn) assuming a uniform hyperfine coupling to all $z^'$ Mn spins.

For an $I = \frac{1}{2}$ nucleus, the recovery of the longitudinal magnetization is expected to follow a single-exponential behavior. In BiMn$_2$PO$_6$, the recovery of the nuclear magnetization after a comb of saturation pulses was indeed fitted well by the exponential function,

$$1 - \frac{M(t)}{M_0} = A e^{-t/T_1},$$

where $M(t)$ is the nuclear magnetization at time $t$ after the saturation pulse and $M_0$ is the equilibrium magnetization. The temperature dependence of $1/T_1$ estimated from the above fit is presented in Fig. 14. At high temperatures ($T \gtrsim 70$ K), $1/T_1$ is almost temperature-independent, which is typical in the paramagnetic regime ($T \gg J_{\text{max}}/k_B$), where $J_{\text{max}}$ is the maximum exchange constant in the system. With decrease in $T$, $1/T_1$ decreases slowly for $T < 70$ K and then shows a peak at around 30 K. This decrease in $1/T_1$ with decreasing $T$ above $T_N$ resembles the behavior of the AFM square-lattice compound Pb$_2$VO(P0$_4$)$_2$. The peak at $T_N \simeq 30$ K is associated with the onset of 3D-LRO and is consistent with the thermodynamic measurements. For $T < T_N$, $1/T_1$ decreases rapidly.

The $^{31}$P spectrum measured at 77.5 MHz is broadened abruptly below $T_N$ indicating that the P site is experiencing the static internal field in the ordered state. In order to precisely probe the line shape associated with the magnetic ordering, we remeasured the spectra below 45 K at a
FIG. 14: (Color online) $^{31}$P $1/T_1$ and the corresponding $1/\chi T_1 T$ as a function of $T$ are plotted along the left and right $y$-axes, respectively. The solid blue line corresponds to $1/T_1 \propto T^3$.

FIG. 15: (Color online) Field-sweep $^{31}$P NMR spectra measured at 49.15 MHz in the low-$T$ regime.

lower frequency of 49.15 MHz. No noticeable line broadening was observed around 43 K, again suggesting that the transition at 43 K observed in the above $\chi(T)$ data is extrinsic. As demonstrated in Fig. 15, with decrease in $T$, a systematic line broadening on either side of the narrow central line occurs below 30 K. This line broadening increases and the intensity of the central line decreases with decreasing temperature. At low-$T$ the broad line takes almost a rectangular shape down to 10 K, whereas below 10 K the edges of the line are smeared following the 10 K magnetic transition, which is seen in thermodynamic measurements (Sec. III B). The possible origin of these changes in the line shape is discussed in Sec. IV A.

Even far below 10 K, the central line related to the high-$T$ paramagnetic phase does not disappear from the experimental spectra completely. The coexistence of the high-$T$ phase with the low-$T$ phase has been observed before in BaCuP$_2$O$_7$ (Ref. 43), (Li,Na)VGe$_2$O$_6$ (Ref. 47–49), and (Ca$_4$Al$_2$O$_6$)Fe$_2$(As$_{1-x}$P$_x$)$_2$ (Ref. 50). One could argue that the coexistence of the two phases is due to a spread of the transition temperatures within the polycrystalline sample, but in such a case it would seem quite unlikely to observe the distinct peak in the temperature dependence of $1/T_1$, as seen in Fig. 14. Another possible origin of the narrow central line is the presence of crystal defects or local dislocations in a polycrystalline sample.

A very broad background signal was also observed at 4.2 K extending over a large field range. This signal can be attributed to the $^{209}$Bi nuclei.

IV. DISCUSSION

A. Long-range magnetic order

Our thermodynamic and NMR measurements consistently show two intrinsic magnetic transitions in BiMn$_2$PO$_6$. The first transition at $T_N \approx 30$ K corresponds to the onset of long-range AFM order that manifests itself by the kink of the magnetic susceptibility, the $\lambda$-type anomaly in the specific heat, the maximum in $1/T_1$, and the broadening of the $^{31}$P NMR line. The second transition around 10 K reveals weaker features reminiscent of a spin reorientation transition. In the following, we analyze experimental signatures of these transitions in NMR.

At $T \leq T_N$, the $^{31}$P NMR line broadens abruptly and appears in an almost rectangular shape at low temperatures, similar to that reported for (Li,Na)VGe$_2$O$_6$, CuV$_2$O$_6$, BaCo$_2$V$_2$O$_8$, and BaCuP$_2$O$_7$ in the AFM-ordered state. The broad and rectangular NMR spectra at $T \leq T_N$ represent the powder spectra of a commensurate antiferromagnetically ordered phase in which the P-site feels the internal field of Mn$^{2+}$ spins. If the P-site is located symmetrically between the neighboring up and down spins, their hyperfine fields induced at this site will be equal and opposite. In this case, one finds a symmetric powder spectra or, for a single crystal, two narrow lines of equal intensity will appear on both sides of the zero-shift position, as in Pb$_2$VO(PO$_4$)$_2$ and (Ba,Sr)Fe$_2$As$_2$.

In order to determine the magnitude of internal field $H_i$ at the $^{31}$P NMR site, we calculated the line shape of the NMR spectrum in the AFM ordered state, and fitted
the calculated spectrum to the experiment. In powder samples, the angle between the direction of the external magnetic field \( H \) and that of internal magnetic field \( H_i \) due to the AFM ordered spins is randomly distributed. Therefore, the NMR spectrum denoted by \( f(H) \) has the form:

\[
f(H) \propto \frac{H^2 - H_i^2 + \omega^2/\gamma_N^2}{H_i^2 H^2}, \tag{28}
\]

where \( \omega \) is the NMR angular frequency, which is assumed to be larger than \( \gamma_N H_i \). The spectrum has two cutoff fields, \( \omega/\gamma_N - H_i \) and \( \omega/\gamma_N + H_i \), at which the spectrum has two sharp edges. In powder samples, these sharp edges are normally smoothened because of the inhomogeneous distribution of internal fields. This effect is modeled by the Gaussian distribution function for \( H_i \).

Finally, the spectra were simulated using the convolution of Eq. (28) and the distribution function as

\[
F(H) = \int_0^\infty f(H - H')g(H') \, dH', \tag{29}
\]

where \( g(H') \) is the aforementioned Gaussian distribution function. Since in the AFM-ordered state the center of gravity of the rectangular spectra coincides with the zero-shift position, \( \omega/\gamma_N = 2.845 \) T for \( ^3\text{P} \) nuclei. The parameters used to simulate the spectrum at \( T = 10 \) K are \( H_i = 6.546 \text{ kOe} \) and \( \Delta H_i \approx 0.13 \text{ kOe} \).

To understand the origin of the internal field at the P-site, we analyze the coupling of P to the Mn\(^{\text{III}}\) ions, as shown in Fig. 18, where each P is coupled to six Mn\(^{\text{III}}\) ions from three different ladders (site a from ladder-1, site b from ladder-2, and sites c–f from ladder-3). In BiCu\(_2\)PO\(_6\), the square-planar geometry of Cu\(^{\text{II}}\) leads to the half-filling of a single 3d orbital that, consequently, eliminates the hyperfine couplings to sites a and b.

![Fig. 16](image-url)  
**Fig. 16:** (Color online) \(^3\text{P} \) NMR spectra in the ordered state at \( T < T_N \approx 30 \) K measured at 49.15 MHz. The solid lines represent the calculated spectra at different temperatures using Eq. (28) with a distribution function \( g(H) = \frac{1}{\sqrt{2\pi\Delta H_i^2}} \times \exp \left[ -\frac{1}{2} \left( \frac{H - H_i}{\Delta H_i} \right)^2 \right] \). The vertical dashed line represents the zero-shift central position \( \omega/\gamma_N = 2.845 \) T for \( ^3\text{P} \) nuclei. The parameters used to simulate the spectrum at \( T = 10 \) K are \( H_i = 6.546 \text{ kOe} \) and \( \Delta H_i \approx 0.13 \text{ kOe} \).

![Fig. 17](image-url)  
**Fig. 17:** (Color online) \( T \)-dependence of the internal field \( H_i \) obtained from \(^3\text{P} \) NMR spectra measured at 49.15 MHz at \( T \geq 10 \) K in the ordered state. \( H_i \) is proportional to the Mn\(^{\text{III}}\) sublattice magnetization. The solid line is a fit of the data above 26 K by Eq. (30) with \( H_0 \approx 8760 \) Oe, \( T_N = (30 \pm 1) \) K, and \( \beta = 0.325 \pm 0.02 \).

The \( T \)-dependence of the internal field \( H_i \) at the \(^{31}\text{P} \) site, which is proportional to the Mn sublattice magnetization in the ordered state, was obtained from fitting our \( F(H) \) data with Eq. (29). It is shown in Fig. 17 that \( H_i \) reaches saturation and remains almost constant at higher temperatures, \( H_i(T) \) decreases towards \( T_N \). In order to extract the critical exponent (\( \beta \)) of the order parameter (sublattice magnetization), \( H_i \) versus \( T \) was fitted by the power law

\[
H_i(T) = H_0 \left( 1 - \frac{T}{T_N} \right)^\beta, \tag{30}
\]

where \( H_0 \) is a constant. For an accurate determination of the critical exponent \( \beta \), we used data points close to \( T_N \), i.e., in the critical region. As shown in Fig. 17 by fitting the data points in the temperature range 26 K \( \leq T \leq 30.5 \) K with Eq. (30) we obtained \( H_0 \approx 8760 \) Oe, \( T_N = 30 \pm 1 \) K, and \( \beta = 0.325 \pm 0.02 \). For comparison, we included the data points below 26 K and arrived at the lower value of \( \beta \approx 0.27 \) with \( T_N \approx 30.13 \) K. The critical exponent \( \beta \) reflects the universality class or, equivalently, the dimensionality of the spin Hamiltonian. The expected values of \( \beta \) for different universality classes are listed in Ref. 10. In BiMn\(_2\)PO\(_6\), the fitted value of \( \beta \) in the critical regime is close to the one expected for the 3D Heisenberg model, thus suggesting the 3D nature of the magnetic ordering transition at 30 K.
Fig. 18: (Color online) The arrangement of spin ladders showing the hyperfine couplings of the P site to six neighboring Mn$^{3+2}$ ions $a$–$f$ from three different ladders.

By contrast, Mn$^{3+2}$ features all five 3$d$ orbitals half-filled, so we expect sizable hyperfine couplings to all six Mn$^{3+2}$ ions around phosphorous.

As discussed above, the hyperfine field at the P-site is mainly due to the transferred hyperfine coupling, so one can understand the spin structure in the ordered state by analyzing the $31P$ NMR spectra. The NMR spectra were found to broaden drastically below $T_N$ suggesting that a net field exists at the P-site due to the nearest-neighbor Mn$^{3+2}$ spins. In Fig. 18 we show the spin configuration in the classical AFM ground state, as derived in Sec. IVIB based on the GGA+$U$ results. Spins on sites $a$, $c$, and $e$ point up, whereas those on sites $b$, $d$, and $f$ point down. However, the hyperfine couplings from these spins do not cancel each other, because the orthorhombic symmetry of BiMn$_2$PO$_6$ leads to four different P–Mn distances, namely, $d_{P-Mn} = 3.579\,\text{Å}$, $d_{P-Mn^b} = 3.321\,\text{Å}$, $d_{P-Mn^{c,e}} = 3.407\,\text{Å}$, and $d_{P-Mn^{d,f}} = 3.271\,\text{Å}$. Therefore, a net field at the P-site is observed experimentally.

**B. Spin Dynamics**

In general, $1/T_1(T)$ is expressed in terms of the generalized susceptibility $\chi_M(q,\omega)$ per mole of electronic spins as:

$$\frac{1}{T_1(T)} = \frac{2\gamma_N^2 k_B}{N^2 \Delta} \sum_q |A(q)|^2 \chi''_M(q,\omega),$$

(31)

where the sum is over wave vectors $q$ within the first Brillouin zone, $A(q)$ is the form factor of the hyperfine interactions as a function of $q$, and $\chi''_M(q,\omega)$ is the imaginary part of the dynamic susceptibility at the nuclear Larmor frequency $\omega$. The uniform static molar susceptibility $\chi = \chi'_M(0,0)$ corresponds to the real component $\chi'_M(q,\omega)$ with $q = 0$ and $\omega = 0$. In the paramagnetic regime, $1/(\chi T)$ should remain $T$-independent.

The $1/(\chi T)$ is plotted along the right $y$-axis in Fig. 14. Instead of a $T$-independent behavior, an increase in $1/(\chi T)$ was observed upon cooling indicating that $\sum |A(q)|^2 \chi''_M(q,\omega)$ increases more than $\chi$ does due to the growth of AFM correlations. This increase persists up to the highest measured temperature.

At sufficiently high temperatures, $1/T_1$ is constant in a system with exchange-coupled local moments and can be expressed within the Gaussian approximation of the correlation function of the electronic spin as:

$$\left( \frac{1}{T_1} \right)_{T \to \infty} = \left( \frac{\gamma_N g \mu_B}{3 \omega_{ex}} \sqrt{2\pi z'} \right) S(S+1),$$

(32)

where $\omega_{ex} = (|J_{max}|/k_B) \sqrt{2zS(S+1)/3}$ is the Heisenberg exchange frequency, $z$ is the number of nearest-neighbor spins of each Mn$^{3+2}$ ion, and $z'$ is the number of nearest-neighbor Mn$^{3+2}$ spins for a given P site. The $z'$ coefficient in the numerator is due to the fact that the P site feels fluctuations arising from all nearest-neighbor Mn$^{3+2}$ spins. Using the relevant parameters, $A_{hf} \approx 7224\,\text{Oe/µm}$, $\gamma_N = 1.08 \times 10^5\,\text{rad s}^{-1} T^{-1}$, $z = 3$, $z' = 6$, $g = 2$, $S = \frac{5}{2}$, and the high-temperature (250 K) relaxation rate of $\left( \frac{1}{T_1} \right)_{T \to \infty}$ is $\approx 12\,800\,\text{s}^{-1}$ for the P site, the magnitude of the maximum exchange coupling constant is calculated to be $J_{max}/k_B \approx 4.3\,\text{K}$, which is in reasonable agreement with our computed exchange couplings in Table III.

In the AFM-ordered state, $1/T_1$ is mainly driven by scattering of magnons off nuclear spins, leading to a power law $T$-dependence. For $T \gg \Delta/k_B$, $\Delta$ is the energy gap in the spin-wave spectrum, $1/T_1$ follows either a $T^3$ behavior due to a two-magnon Raman process or a $T^5$ behavior due to a three-magnon process, while for $T \ll \Delta/k_B$, it follows an activated behavior $1/T_1 \propto T^2 \exp(-\Delta/k_B T)$. As seen from Fig. 14, our $31P$ data below $T_N$ follow a $T^3$ behavior rather than a $T^5$ behavior suggesting that the relaxation is mainly governed by the two-magnon Raman process. However a deviation from the power law was observed for $T \lesssim 10\,\text{K}$ which is either due to the opening of a gap $\Delta$ or due to the formation of an incommensurate or canted AFM ordering. The heat capacity data at low $T$ argue against the spin-gap interpretation as discussed next.

**C. Magnetic Heat Capacity of Spin Waves**

Because the extrapolations of the $C_{mag}/T^2$ and $C_{mag}/T^3$ data for BiMn$_2$PO$_6$ in Fig. 9 to $T = 0$ appear to give nonzero intercepts, these intercepts may represent $T^2$ (2D) or $T^3$ (3D) spin wave contributions to the heat capacity, in which case anisotropy effects are negligible in causing energy gaps in the spin-wave spectra. Here we...
discuss these two potential contributions. For 3D spin-wave propagation along the \(x\), \(y\), and \(z\) axes of a simple orthorhombic spin lattice, the heat capacity per mole of spins \(C_{\text{mag}}^{\text{3D}} \equiv \frac{\beta_{\text{SW}}}{R} T^3\),

\[
\frac{C_{\text{mag}}}{R} = \left( \frac{4\pi^2 V_{\text{spin}}}{15\hbar^3 v_x v_y v_z} \right) (k_B T)^3, \quad (3D) \quad (33a)
\]

where \(V_{\text{spin}}\) is the volume per spin and \(v_\alpha (\alpha = x, y, z)\) are the respective spin-wave velocities. For quasi-2D spin waves in the \(xy\) plane, one obtains \(C_{\text{mag}}^{\text{2D}} \equiv \frac{\delta_{\text{SW}}}{R} T^2\),

\[
\frac{C_{\text{mag}}}{R} = \left[ \frac{6\zeta(3) A_{\text{spin}}}{\pi\hbar^2 v_x v_y} \right] (k_B T)^2, \quad (2D) \quad (33b)
\]

where \(A_{\text{spin}}\) is the area per spin and \(\zeta(z)\) is the Riemann zeta function.

Here we consider simple effective models of spin lattices with nearest-neighbor interactions represented by the Heisenberg Hamiltonian \([\text{Eq. (7)}]\). Following Ref. \[38\] we take the spin wave velocities to be given by

\[
h v_\alpha = \sqrt{6} S J_\alpha a_\alpha \quad (3D, \alpha = x, y, z), \quad (34a)
\]

\[
h v_\alpha = 2 S J_\alpha a_\alpha \quad (2D, \alpha = x, y), \quad (34b)
\]

where \(a_\alpha\) are the lattice parameters in the \(x\), \(y\), and \(z\) directions, respectively. Taking the \(x\), \(y\), and \(z\) directions to be in the directions of the orthorhombic \(a\), \(b\), and \(c\) crystal axes, one obtains \(V_{\text{spin}} = abc\) in 3D and \(A_{\text{spin}} = ab\) in 2D. Then substituting Eqs. \((34)\) into \((33)\) gives the magnetic heat capacities per mole of spins as

\[
\frac{C_{\text{mag}}}{R} = \beta_{\text{SW}} T^3 \quad (3D) \quad (35a)
\]

\[
\beta_{\text{SW}} = \frac{4\pi^2 \sqrt{6}}{15(J_z/k_B)(J_y/k_B)(J_z/k_B)}.
\]

and

\[
\frac{C_{\text{mag}}}{R} = \delta_{\text{SW}} T^2 \quad (2D) \quad (35b)
\]

\[
\delta_{\text{SW}} = \frac{12\zeta(3)}{\pi(J_z/k_B)(J_y/k_B)}.
\]

In view of the complicated set of exchange interactions in BiMn$_2$PO$_6$ revealed by the above electronic structure calculations, here we obtain effective values \(J_{3D}\) and \(J_{2D}\) of the exchange constant from the heat capacity data assuming 2D or 3D propagation of spin waves and compare these values to the range of \(J_{ij}\) values obtained theoretically in Table III. Thus we define

\[
J_{3D} \equiv (J_x J_y J_z)^{1/3}, \quad J_{2D} \equiv (J_x J_y)^{1/2},
\]

and the coefficients in Eqs. \((35)\) become

\[
\beta_{\text{SW}} = \frac{4\pi^2 \sqrt{6}}{15(J_{3D}/k_B)^3}, \quad (37a)
\]

\[
\delta_{\text{SW}} = \frac{12\zeta(3)}{\pi(J_{2D}/k_B)^2}. \quad (37b)
\]

Then using the values of \(\beta_{\text{SW}}\) and \(\delta_{\text{SW}}\) from Eqs. \((36)\), Eqs. \((37)\) give

\[
\frac{J_{3D}}{k_B} = 10 \text{ K}, \quad \frac{J_{2D}}{k_B} = 68 \text{ K}. \quad (38)
\]

The first of these values is similar to the largest AFM exchange constants in Table [11] Therefore the exchange coupling sums in Eq. \((38)\) suggest that (i) the connectivity of the exchange interactions is effectively three-dimensional, and (ii) there are no significant anisotropy gaps in the spin-wave spectra with values greater than roughly 1 K.

D. Microscopic Aspects

Our detailed analysis of the NMR data indicates a commensurate long-range AFM-ordered state of BiMn$_2$PO$_6$ between 10 K and 30 K, whereas additional features, such as an incommensurate modulation or spin canting, may appear below 10 K. Multiple magnetic transitions are not uncommon for frustrated magnets, where the propagation vector of the LRO state changes with temperature.\[60,61\] or a partial disorder emerges in a broad temperature range below \(T_N\).\[62\] However, in BiMn$_2$PO$_6$ both scenarios are rather unlikely, because our classical Monte-Carlo simulations that take account of the magnetic frustration yield a simple, collinear and commensurate state with the propagation vector \(k = 0\) and AFM order both within and between the spin ladders. Numerous long-range couplings tend to frustrate this simple AFM order, yet their effect is not cooperative, hence none of the possible noncollinear spin configurations is preferred over the collinear one. On the other hand, the second transition at 10 K leads to a different type of magnetic order that clearly distinguishes BiMn$_2$PO$_6$ from the family of conventional, nonfrustrated antiferromagnets, where only one magnetic transition should be observed.

The origin of this unusual behavior remains unclear and should be elucidated by future neutron-scattering experiments. Heat capacity data rule out any sizable anisotropy gap, hence the effects of magnetic anisotropy in BiMn$_2$PO$_6$ are likely weak. On the other hand, even a weak anisotropy will eventually frustrate the collinear magnetic order, because different Mn$_2$O$_5$ pyramids have different orientations with respect to the crystallographic axes (Fig. [1]), and no unique spin direction that would be favorable for all Mn sites can be found. Yet another important aspect is the strong lattice softening observed in our heat capacity data (Sec. [III C]). As structural changes may affect exchange couplings, a structure determination at low temperatures and a subsequent re-evaluation of exchange couplings in this low-temperature structure are important for understanding the physics of BiMn$_2$PO$_6$.

Finally, BiMn$_2$PO$_6$ is very different from its structural sibling BiCu$_2$PO$_6$, where quantum fluctuations open a spin gap and prevent LRO in zero field.\[10,12\] Moreover,
fissure is integral to the physics of the Cu$^{+2}$ compound. The strong next-nearest-neighbor couplings $J_2$ and $J'_2$ shift the minimum of the triplet band to an incommensurate position\cite{12,13} so that the magnetic order in BiCu$_2$PO$_6$ is inevitably incommensurate, provided that the spin gap is closed to give way to the LRO. Indeed, BiCu$_2$PO$_6$ reveals a plethora of enigmatic phases in high magnetic fields\cite{14,15}, but their nature is likely different from the two zero-field phases of the Mn$^{+2}$ compound.

V. SUMMARY AND OUTLOOK

Both BiMn$_2$PO$_6$ and the nonmagnetic reference compound BiZn$_2$PO$_6$ show very strong lattice softening on cooling below 200 K, where the Debye temperature $\Theta_D$ decreases from $\sim 600$ K at room temperature to $\sim 300$ K at low temperatures. Most solids show much smaller variations in $\Theta_D$ on cooling due to differences between the actual phonon density of states and that assumed in the Debye theory, so the factor of two monotonic decrease in $\Theta_D$ is very unusual. The lattice properties of these compounds certainly deserve additional investigation.

BiMn$_2$PO$_6$ is an AFM spin-ladder compound with a moderate frustration of both intraladder and interladder couplings. It develops long-range magnetic order below $T_N \simeq 30$ K and additionally shows a second magnetic transition around 10 K. Thermodynamic and NMR measurements suggest a commensurate magnetic order between 10 K and 30 K, whereas the magnetic order below 10 K may be more complex and likely involves spin canting or incommensurate modulation. The low-$T$ heat capacity data indicate that any energy gap in the spin-wave spectrum is $\lesssim 1$ K. Microscopically, magnetic frustration leads to a large suppression of $T_N$, but this frustration has no visible effect on the ordering pattern, at least on the classical level of the Heisenberg model with only isotropic exchange couplings that we investigated. These couplings stabilize a simple collinear Néel-type AFM order.

BiMn$_2$PO$_6$ is remarkably different from other spin-ladder materials and deserves further investigation. Neutron scattering experiments are particularly well suited to investigate the nature of the ordered ground state between 10 K and 30 K as well as below 10 K. We expect that the commensurate AFM structure depicted in Fig. \[\text{Fig.}\] will be observed between 10 K and 30 K, whereas a more complex ordering pattern will be seen at lower temperatures. The magnetic frustration is central to many transition-metal oxides of current interest. Delineating the role of this effect is important for building microscopic theory of complex magnetic materials.

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