Phonon-magnon mechanism and quantized disorder in MnAs

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The quantum material MnAs manifests both a magnetic and structural phase transition at 318 K. The origin of this anomaly has been the focus of both experimental and theoretical work for many years. Earlier theoretical work usually involved using many empirical parameters in a stat-mech approach. More recent applications of density functional theory (DFT) have seen some researchers suggesting soft mode phonons coupled to spin may be a promising theoretical direction. Here I introduce a different phonon-magnon coupling in which soft mode phonons resonantly excite magnons localized to distances between in-plane Mn-Mn atoms. I show that these magnons reflect between Mn-Mn atoms setting up antiferromagnetic standing waves. Using a quantum stat-mech approach, I show that this mechanism predicts the disordered Mn-Mn distances, as well as the anomalous temperature behaviors of the lattice parameters and magnetic fields. I further predict hysteresis and magnetic heating/cooling in agreement with experiment, as well as the anomalous thermal and elastic properties.

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I. INTRODUCTION

The anomalous phase transition at $T_c \approx 318$ K in MnAs has been the subject of intense research, both experimental and theoretical, for decades. In 1962 Bean and Rodbell [1] published a free energy model in which the magnetic phase coincided with the geometric phase as seen by expanding the entropy in a power series of adjustable parameters, with the critical temperature depending explicitly on volume. This model fails to explain both the second-order phase transition at 400 K and the metamagnetic phase transition. In 1983 Kato, Nagai, and Aisaka [2] published a free energy approach where the exchange was coupled to the geometry through a series of *ad hoc* parameters which were determined by experiment. Later, Pytlik and Zieba [3] published a Landau type free energy model which predicted the correct phase diagram with two competing order parameters. They introduced an empirical coupling between a magnetic moment in the hexagonal phase and a lattice deformation which was used by the authors of Ref. [11]. More recently, Stefano and Hill used a DFT approach to model the ground state. They found that the ferromagnetism is due to the splitting of degenerate electronic *d* bands [4]. In addition, they did a tight-binding calculation using the equations found in Slater and Koster [5,6] to check the DFT calculation. They found a strong sp^3 bond, as well as strong *p-d* coupling. Rungger and Sanvito undertook an *ab initio* study which showed that the exchange interaction between Mn atoms depends not only on the volume, but the local distortion [7].

Soft mode phonons as postulated by Landau and Lifshitz are thought to be a key mechanism in material phase transitions [8]. Soft modes originate in crystal systems which have an anharmonic potential [9]. In 1972 the authors of Ref. [8] posited that soft modes could cause spin flips, but did not go into detail about exact nature of the mechanism. Lazewski and co-workers [10,11] showed that soft mode phonons somehow couple to spin flips. They also noted that the relevant physics occurs between nearest neighbor Mn atoms, and that the soft modes have frequencies in the THz range. While this model did predict local disorder, the calculated magnitude for thermal displacements for Mn atoms in the hex phase at 300 K differs substantially from that measured by Petkov *et al.* [12]. Recently Yang *et al.* [13] showed that soft modes with specific momentum act to mediate unconventional superconductivity in a monolayer material. Based on this I assume the soft modes are quantized above and below T_c. It is known that the soft mode frequencies decrease during the phase transition [11,12,14], and that different soft modes are linearly independent, which makes them orthogonal to each other [10,11]. Also, Ref. [14] posits that multiple soft modes take part in a phase transition, with one mode being principle. Later, in 2020 Bocarsly *et al.* [15] proposed a mechanism involving competition between magnetic and chemical bonding. They suggested that the local atomic disorder may be invoked to explain the observed low thermal conductivity [16] and anomalous elastic properties [17]. They also stated that the microscopic mechanism governing magnetostructural coupling in this and other materials remains an open question.

The nature of the coupling between soft modes and spin as suggested in Refs. [10,11] suggests a microscopic mechanism that is cooperative. However, the coexistence of the local disorder and the anomalous elastic and thermal conductive properties as suggested by Ref. [15] also point to a cooperative mechanism. Here I introduce a set of equations that simultaneously couple the absorbed soft modes to the local disorder, magnetic, and elastic properties.

To understand how best to model the mechanism, consider the measurements at $T_c \approx 318.0 \pm 2.0$ K done by Petkov *et al.* [12]. It has been observed that the Mn-As distance

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$d_0 = 2.57$ Å stays approximately constant. As such, the only distances that change number are the in-plane Mn-Mn separations. The initial $d_H = 3.72$ Å in the hexagonal phase becomes $d_{01} = 3.38,\ d_{02} = 3.68,\ d_{03} = 3.98$ in the orthorhombic phase. I do not consider motion of the As atoms in this model. The Mn atoms which define these distances along with the vertical Mn-Mn distance shown in Ref. [12] are connected to the same As atom. As such, this structure forms the smallest structure repeated throughout the crystal. In this work I extend the soft mode hypothesis introduced in Ref. [11] and posit a coherent soft mode–magnon coupling to predict the disorder measured in Ref. [12]. Magnons are known to exist in this material below the transition temperature. In the hex phase, the magnetization between Mn atoms must be associated with ground state ferromagnetic magnons [18] as there is only one Mn-Mn distance. It is well known that the ortho phase is unstable, indicating that any magnons which form during the phase transition are antiferromagnetic excitations. As $T \to T_c$ particular soft modes with wavelengths given in Eq. (1) get absorbed to form anti-ferro-magnetic ($J_{\mathrm{AFM}} > 0$) magnons [19,20]. The excited magnons are quantized in such a manner as to be nondegenerate in accordance with the disorder. The emergence of the disorder in MnAs and the abrupt changes in the lattice parameter and magnetization are manifestations of relationships shown in Eqs. (1) and (2) below which are required in order to ensure that the disorder that occurs during the processes $d_H \to d_{0i}$ is quantized. I first posit the existence of a quantized relationship between absorbed soft mode wavelengths and the disordered Mn-Mn distances,

$$T \geqslant T_c \to \left(\lambda_1 = \frac{d_{01}}{3},\ \lambda_2 = \frac{d_{02}}{2},\ \lambda_3 = d_{03}\right). \tag{1}$$

Note that $k_n = 2\pi/\lambda_n$ holds. From the literature [2] a calculated soft mode frequency is $f = 1.133 \times 10^{12}$ Hz. Since soft modes satisfy an anharmonic potential I assume their wave speed can be different from that of the crystal. In addition I could find no measurement of soft mode velocities in the literature. Setting this frequency equal to f_3, I consider the lowest de Broglie wavelength of a single absorbed soft mode. Using Eq. (1), $\lambda_3 \approx d_{03} \approx 3.98$ Å. We can calculate the wave speed for soft modes in the O phase as $v_0 = 450.9$ m/s. Using v_0 and Eq. (1), I calculate the frequency of the first excited state, $\lambda_1 = 1.12$ Å, $f_1 = 4.0 \times 10^{12}$ Hz, and for the second excited state, $\lambda_2 = 1.84$ Å, $f_2 = 2.45 \times 10^{12}$ Hz. A quantum statistical mechanical approach is used to define a free energy that is the sum of energies used to calculate the disorder. These are the energies of absorbed soft modes, magnons, crystal fields, anharmonic potentials, spin-orbit interactions, exchange interactions, and phonon-magnon interactions between Mn atoms. The essence of cooperation is to assume that a fluctuation of this free energy vanishes as $T \to T_c$. All the interactions are known to exist, and fluctuations of this particular combination only vanish under very specific circumstances. Based on the observed hysteresis it is a commonly held assumption that both phases coexist during the transition. Here Eq. (1) quantizes the fluctuations δF_{di} in the local free energies, lifting any degeneracies. Although the effect measured in MnAs is an abrupt phase transition, the authors of Ref. [12] told me the measurements have an uncertainty ($T_c \pm 2.0$ K). I assume that a "locally preferred structure" [21] in MnAs is a given As atom connected to a set of six Mn atoms whose in-plane distances are in a quantum superposition centered around an in-plane distance $d_{02} = 3.68$ Å. During the phase transition a particular set of these distances "freeze out." As $T \approx T_c$, the fluctuation of the free energy δF_{dH} of the initial in-plane distance $d_H = 3.72$ Å becomes unstable ($\delta F_{dH} \neq 0$) due to thermal fluctuations. To partially stabilize ($\delta F_{dH} \to \delta F_{d_2} \approx 0$) absorbs two soft mode phonons with frequency f_2 to manifest a new in-plane Mn-Mn bond length $d_{02} = 3.68$ Å. Now δF_{d_2} is unstable with respect to thermal fluctuations which are orthogonal to d_2 that are also in plane. δF_{d_2} further stabilizes by absorbing soft mode phonons of frequencies f_1, f_3 ($\delta F_{d_2} \to \delta F_{d_1} \approx 0, \delta F_{d_3} \approx 0$) to form Mn-Mn bond lengths of $d_{01} = 3.38,\ d_{03} = 3.98$ which are approximately orthogonal to d_{02} [12]. During the phase transition the Mn-Mn distance is expanding/contracting as a function of temperature. I assume the change in each Mn-Mn distance (δd_i) brought about by thermal fluctuations satisfies equipartition [22],

$$\delta d_i = \sqrt{k_B T/\kappa_i}. \tag{2}$$

Here κ_n is a parameter which is calculated (to first order) in terms of the first derivative of the anharmonic (deformation) potential between Mn atoms using tight-binding theory [7] in the next section. Equations (1) and (2) can be used to calculate the transition temperature $T_c \approx 318.0$ K, thus showing that $T \to T_c$ is a function of the geometry [12]. As each distance d_n expands/contracts, this quantity determines which soft modes are absorbed. Equation (1) is required for the coherent transfer of energy between soft mode phonons and magnons. This quantization leads directly to the anomalous temperature dependence of the structural and magnetic phase transitions by quantizing the fluctuations in the free energies δF_{di}. This acts to lift any degeneracy in the three "mixed state" Mn-Mn distances. In addition, the condition introduced in Eq. (1) manifests in the quantized fluctuation of certain variables shared by each free energy in such a way as to reduce the number of parameters required to fit the data. These fluctuations δF_{di} will be used to calculate $\delta\phi_i(T)$ defined below. Using the same approach as in the glass [22] I assume each in-plane Mn-Mn distance as can be written as

$$d_i \simeq d_0[\phi_0 + \delta\phi_i(T)], \tag{3}$$

with $\delta d_i = d_0 \delta\phi_i$. Here $\delta\phi_i$ is the order parameter which optimizes the fluctuation δF_i in the free energy that couples two Mn atoms. As such, it is the local order parameter associated with a given soft mode. For $T \geqslant T_c$ there are three order parameters $\delta\phi_i(T),\ \ i = 1, 2, 3$ and there are three independent soft modes $\omega_{sm(i)},\ i = 1, 2, 3$. From Ref. [23], $T \approx T_c \to \omega_{sm(i)} \approx 0$. The expectation value $\langle\delta\phi_i\rangle$ is negative for $d_i < 3.72$, and positive for $d_i > 3.72$. As measured $\langle\delta\phi_i(T)\rangle$ is the angular fluctuation associated with a given in-plane Mn-Mn distance as a function of temperature. Each $\delta\phi_i$ is unique as well as quantized through assuming $\delta F_{di} \approx 0$. The phonon-magnon process is shown below in Fig. 1.

I now consider the formation of the frozen magnon standing waves. Coherent transfer between phonons and magnons has been observed in a single nanomagnet [24]. More recently,

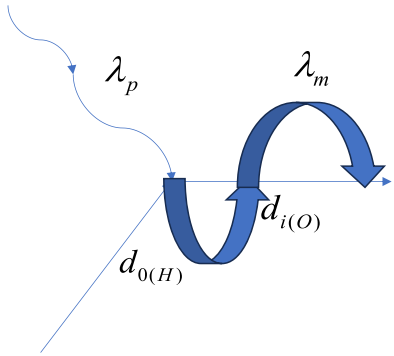

FIG. 1. Here a soft mode λ_P is absorbed by initial Mn-Mn distance $d_{0(H)}$ to simultaneously emit a magnon λ_m and excited Mn-Mn distance $d_{i(O)}$.

spin standing waves have been observed in a van der Waals magnetic material [25], as well as in magnonic crystals [26]. More recently Kishine *et al.* published a theory of standing spin waves in a finite size lattice [27]. It has been observed that the magnetic moments on the Mn atoms go from ferromagnetic (FM) to antiferromagnetic (AFM) during the phase transition. These AFM in turn reflect between the second nearest neighbor in-plane Mn atoms, which are strongly coupled to Mn atoms in the vertical directions through either FM or AFM interactions, depending on the geometric phase. Consider the boundary condition imposed by the type of quantization shown in Eqs. (1) and (2). Since the allowed wavelengths are not multiples of each other periodic boundary conditions do not apply and instead of propagating around the plane the magnons reflect between each Mn-Mn pair, forming standing waves [25–27]. I further show that the oscillations of these standing waves become a constant independent of time, leaving only local magnetization.

II. MODEL

In this section all Mn-Mn distances are in Å. Assume $d_0 = 3.57$, $d_H = 3.72$ respectively. During the phase transition the bond distance in Eq. (3) is either expanding or contracting as a function of temperature. In an earlier paper [19] on Leuco dyes I assumed that the equal partition is satisfied during the phase transition and the thermal expansion/contraction of a single Mn-Mn in-plane distance can be written as $\kappa_n(\pm\delta d_n)^2 \approx k_B T$, $n = 1, 2, 3$, where δd_n is the temperature dependent fluctuation in the bond length which depends on the soft mode absorbed/emitted through the parameter κ,

$$\delta d_n = \sqrt{\frac{k_B T}{\kappa_n}}. \tag{4}$$

In order to use κ to determine the new Mn-Mn distances through Eq. (3) it must be evaluated at T_c. Consider the sum $\sum_i V_{\mathrm{TB}i(n)}$ of Slater-Coster tight-binding (TB) [7] terms defined below for each Mn-Mn distance. This is an anharmonic potential. The quantity κ is calculated from this potential. Now we consider the terms $\delta\sum_i V_{\mathrm{TB}}$. The coupling between $|4s\rangle, |3d\rangle$ orbitals on adjacent Mn atoms is an empirical tight-binding term [8] defined as

$$V_{ss\sigma(i)} = \eta_{ss\sigma}\frac{h^2}{m{d_i}^2},\ \eta_{ss\sigma} = -1.40. \tag{5}$$

Here $i = 1, 2, 3$. The coupling between $|3d\rangle, |4s\rangle$ orbitals on adjacent Mn atoms [8] is defined as

$$V_{sd\sigma(i)} = \eta_{sd\sigma}\frac{h^2 r_d^{3/2}}{m{d_i}^{7/2}},\quad \eta_{sd\sigma} = -3.16. \tag{6}$$

Similarly the couplings between $|3d\rangle$ orbitals on adjacent Mn atoms are [8] defined as

$$V_{ddj(i)} = \eta_{ddj}\frac{h^2 r_d^{3/2}}{m{d_i}^{7/2}},\ j = \sigma, \pi,\ \eta_{dd\sigma} = -16.2,\ \eta_{dd\pi} = 8.75. \tag{7}$$

Here $h^2/m = 7.62$ eV Å^2 and r_d is an empirical parameter which describes

The term $\sum_i \delta V_{\mathrm{TB}}$ is different for each bond in that it involves direction cosines and depends on the direction of the bond. We note that all three bonds in the plane have different directions. We calculate the fluctuation in Eq. (7) as

$$\delta V_{ss\sigma(i)} = \eta_{ss\sigma}\frac{\partial}{\partial d_i}\left(\frac{h^2}{m{d_i}^2}\right)\frac{\partial d_i}{\partial\delta\phi_i}\delta\phi_i = -2\eta_{ss\sigma}\frac{h^2}{m{d_i}^3}d_0\delta\phi_i. \tag{8}$$

We calculate the fluctuation in Eq. (6) as

$$\delta V_{sd\sigma(i)} = -\eta_{sd\sigma}\frac{7}{2}\frac{h^2 r_d^{3/2}}{m{d_i}^{9/2}}d_0\delta\phi_i. \tag{9}$$

Last, we calculate the fluctuations on Eq. (7) as

$$\delta V_{ddj(i)} = -\eta_{ddj}\frac{7}{2}\frac{h^2 r_d^{3/2}}{m{d_i}^{9/2}}d_0\delta\phi_i,\ j = \sigma, \pi. \tag{10}$$

The sum can be written [7] in terms of direction cosines (l, m, n),

$$\delta\sum_i V_{\mathrm{TB}} = \left\{\begin{matrix} f_{ss\sigma i}(l,m,n)\delta V_{ss\sigma i} + f_{sd\sigma i}(l,m,n)\delta V_{sd\sigma i} \\ +f_{dd\sigma i}(l,m,n)\delta V_{ddi}\end{matrix}\right\}. \tag{11}$$

I take a derivative with respect to each order parameter and again assume equal partition. This is reasonable as this is considered a "reversable" phase transition,

$$\lim_{T\to T_c}\delta\sum_n V_{\mathrm{TB}} = \frac{\partial\sum_i V_{\mathrm{TB}i(n)}}{\partial d_n}\frac{\partial d_n}{d_0\partial\phi_n}\delta\phi_n \approx \frac{\partial}{\partial(d_0\delta\phi_n)}\frac{\kappa_n\left({d_0}^2{\delta\phi^2}_n\right)}{2}. \tag{12}$$

I obtain

$$\kappa_n \simeq \lim_{T\to T_c}\left[\frac{\partial\sum_n V_{\mathrm{TB}i(n)}}{\partial d_n}\frac{1}{(d_0\delta\phi_n)}\right],\ n = 1, 2, 3. \tag{13}$$

This calculation is done iteratively using Eq. (14) below by adjusting the direction cosines in Eq. (11). I obtain the direction cosines for the disorder from Ref. [10] to fix these. I obtain ($\kappa_1 = 0.23$, $\kappa_2 = 16.52$, $\kappa_3 = 0.39$) in units

of (eV/Å^2) respectively, thus the magnitude of the disorder depends crucially on the direction cosines, i.e., the geometry. The temperature dependence is implicit and κ_n by itself is not sufficient to determine the complicated behavior of the order parameter. As in Ref. [19] I assume that an expanding/contracting Mn-Mn distance can be written as

$$d_n = (d_H \pm \delta d_n) = \left(d_H \pm \sqrt{\frac{k_B T}{\kappa_n}} \right). \tag{14}$$

The sign depends on the sign of the order parameter $\delta\phi_n$. From Eq. (2) the soft mode wavelengths with the lowest energies satisfy $n\lambda_n = d_{0n}$, $n = 1, 2, 3$, so the propagation constants are

$$k_n = \frac{2\pi}{\lambda_n} = \frac{2\pi n}{d_{0n}}, \quad n = 1, 2, 3. \tag{15}$$

During the hex part of the phase transition ($T \leqslant T_c$), the fluctuation δF_H of the free energy of the in-plane (Å) Mn-Mn distance $d_H = 3.72$ becomes unstable,

$$\lim_{T_{\text{below}} \to T_c} \delta F_H \neq 0. \tag{16}$$

To ensure

$$\lim_{T_{\text{below}} \to T_C} \delta F_H \simeq 0 \tag{17}$$

requires $d_H \to d_1 = 3.68$, $d_2 = 3.38$. This in turn implies that the angular fluctuation $\delta\phi_i(T)$ in Eq. (3) in the last section is negative, and we have

$$d_n = \left(d_H - \sqrt{\frac{k_B T}{\kappa_n}} \right), \quad n = 1, 2. \tag{18}$$

Here I take $k_B = 8.617 \times 10^{-5}$ eV/K. Equation (8) means that d_n contracts as a function of temperature and couples only to full wavelength soft modes. Note that half wavelengths are not allowed, as absorption of these would correspond to ferromagnetic magnons. For the $d_H \to d_3 = 3.98$ transition,

$$d_3 = \left(d_H + \sqrt{\frac{k_B T}{\kappa_3}} \right). \tag{19}$$

I now construct free energies to calculate each $\delta\phi_i(T)$. I assume that each Mn atom has an atomic configuration $|3d^5\rangle|4s^2\rangle$ which couples both to an As atom forming the $d_0 \approx 2.57$ Å bond, and to the nearest neighbor Mn atom forming a weak metallic bond. Each Mn-Mn pair coupling involves several energies. These are the tight-binding (TB) $\sum_i V_{\text{TB}i(n)}$ terms coupling d and s electrons between each atom, the exchange interaction, the spin-orbit interaction, and the crystal-field splitting on each Mn atom. Each pair also interacts with soft mode phonons which I will show give rise to standing wave magnons along d_n. As per suggestions made in the literature [1] I assume that the soft modes propagate between Mn atoms. The phonon-magnon interaction as presented in the literature [21,22] involves second quantization. Before applying second quantization I define the initial free energy of the ith Mn-Mn bond,

$$F_i = \left\{ \sum_j \xi_{\text{CF}(ij)} + \sum_j^2 \mu_i(J_i) + \sum_j V_{\text{TB}(ij)} + \xi_{pm} + J\vec{S}_{ij} \cdot \vec{S}_{ik \neq j} + \sum_i \hbar\omega_{smi} \right\}. \tag{20}$$

Here I assume that $\sum_j \xi_{\text{CF}(ij)}$ is the sum of crystal-field splittings of the electron levels on both Mn atoms which I assume is the original $|3d\rangle$ splitting associated with the hexagonal symmetry. μ_i is the spin-orbit coupling on both atoms; as mentioned, $\sum_i V_{\text{TB}_i}$ are the TB matrix elements coupling the $|3d\rangle|4s\rangle$ between nearest neighbor Mn atoms which include orbital hopping terms, J is the exchange interaction between Mn atoms, and ξ_{pm} is a soft mode phonon-magnon interaction, which I define later. As mentioned, I assume that the soft modes (before they get absorbed to form magnons) are initially quantized [17] and owing to the fact that I assume only soft mode frequencies take part in this free energy (course graining) I include $\sum_{ij} \hbar\omega_{smij}$. Taking a variation of Eq. (20) yields

$$\delta F_i \approx \lim_{T \to T_c} \left\{ \begin{array}{l} \delta\xi_{\text{CF}(i)} + \left(\sum_{ik}^2 \delta\mu_k(j_k) + \sum_{ik}^2 \mu_k(\delta j_k) \right) \\ \quad + \delta \sum_i V_{\text{TB}i} + \delta\xi_{pm} + \delta J(\vec{S}_i \cdot \vec{S}_j) + J\vec{S}_i \cdot \delta\vec{S}_j + \hbar\delta\omega_{smi} \end{array} \right\} \approx 0, \tag{21}$$

where $\delta \sum_k^2 \mu_k(j_k) = [\sum_{ik}^2 \delta\mu_k(j_k) + \sum_{ik}^2 \mu_k(\delta j_k)]$, small $j_k = l \pm s$ is the total angular momentum on the kth atom in the ith bond, and J is the exchange energy. Here I consider the variations in the energy terms in Eq. (21) which allow us to obtain $\delta\phi_i(T)$. First, consider the fluctuation in the crystal-field coupling $\delta\xi_{\text{CF}(i)}$. It is well known that the original crystal-field splitting $\xi_{\text{CF}(i)}$ lifts the degeneracy in the d electrons in each Mn atom based on the geometric symmetry of the crystal [28]. I assume that the fluctuation in this quantity only exists during the phase transition. The magnitude and sign of this fluctuation to first order depends on the geometric symmetry. I define this quantity for the jth bond with respect to Fig. 13 in the discussion section as

$$\delta\xi_{\text{CF}(J)}\ (\text{eV}) = \sum_i^5 (E_{ij(O)} - E_{ij(H)}), \quad i = xy, xz, yz,\ x^2 - y^2,\ 3z^2 - r^2. \tag{22}$$

Here $E_{ij(O)}$ is the level shift $(+/-)$ from $E=0$ for the ith d orbital on a Mn atom in the jth bond in the orthorhombic geometry. Note that for a structural change $\delta\xi_{\mathrm{CF}(J)}$ (eV) $\neq 0$. I calculate that $\delta\xi_{\mathrm{CF}(J)}$ (eV) <0 for all three d_j. Next consider the term $\delta\sum_k^2 \mu_k(j_k)$. In the ensuing discussion I use J_i to symbolize the exchange between two electrons in the ith bond, and j as a good quantum number in the spin-orbit interaction. I take j to be a good quantum number with $j=l\pm s,\ l=2\hbar,\ s=\hbar/s,\ z=25$ for Mn. This term couples $\vec{l}_i\cdot\vec{S}_i$ on the same Mn atom, and so it does not depend on $\delta\phi_i(T)$. I assert that I can use a modified version of Eq. (9.82) found in Ref. [29],

$$\mu_n(d_n,\, j_n) = 2\left\{\left(\frac{e^2 z}{2m_e^2c^2}\frac{1}{d_n^3}\right)\left(\frac{1}{9}\right) \times\left[\frac{j_n(j_n+1)-l_n(l_n+1)-3/4}{l_n(l_n+1)(2l_n+1)}\right]_i\right\},\quad n=1,2,3. \tag{23}$$

Since the $|3d\rangle$ electrons which mediate the exchange are itinerate I assume that the range of the interaction is (d_n). I show in Sec. III that the magnitude of the spin-orbit coupling in Eq. (23) above for each Mn-Mn distance lies within the range (0.017–0.027) (eV), which is the smallest energy of any of the terms I consider. These are in agreement with spin-orbit couplings for other quantum materials discussed in Ref. [30]. Consider the fluctuation in $\mu(d_i)$ with respect to d_i. This is of the order $\delta\mu(d_i)\approx 1/d_i^4$. This is a magnitude smaller, so I assume to first order,

$$\lim_{T\to T_c}\frac{\delta\mu_i}{\delta d_i}\approx 0. \tag{24}$$

This approximation should not affect the behavior of the fluctuation in the free energy as $T\to T_c$. Consider the fluctuation $\sum_{ik}^2\mu_k(\delta j_k)$ during the phase transition. I assume an initial configuration $j_H=l+s,\ l=2\hbar,\ s=\hbar/s,\ z=25$ for Mn in the hex phase. For all three transitions we have

$$\Delta_{so(j)} = \left(\sum_i^2 \mu_n(\delta j_n)\right) = 2[\mu_n(d_n,\, j_n)-\mu_H(d_H,\, j_H)],\ n=1,2,3, \tag{25}$$

where I assume that $j_n=l-s$ to accommodate the spin flip which occurs when hex $\to$ ortho. Next consider fluctuation in the spin part of the exchange, term $J\delta\vec{S}_i\cdot\vec{S}_{j\neq i}$ []. This term is $(-)$ for the hexagonal structure and $(+)$ for the ortho structure. Here I use $a_{\downarrow\downarrow}/a_{\uparrow\downarrow}$ to represent the annihilation of a FM/AFM magnon, and $a^\dagger{}_{\downarrow\downarrow}/a^\dagger{}_{\uparrow\downarrow}$ to represent the creation of the same. I write

$$\frac{J_i}{\hbar^2}\delta\vec{S}_i\cdot\vec{S}_{j\neq i} = (J_{\mathrm{AFM}(i)}a^\dagger_{\sigma(i)}a_{H(i)} - J_{\mathrm{FM}(i)}a^\dagger_{H(i)}a_{\sigma(i)}). \tag{26}$$

Here $a^\dagger_{\sigma(i)}$ creates an AFM magnon at position (i) and $a_{H(i)}$ destroys a FM magnon at position (i). Initially I assume the exchange energies satisfy $|J_{\mathrm{AFM}}|\approx|J_{\mathrm{FM}}|$. Based on an expression for the exchange energy found in Ref. [31] I use Ref. [29] to approximate this as $J_n\approx\frac{e^2}{4d_n}$, with $e^2=14.40$ eV Å [8]. Now convert from atomic variables to magnon variables, $c_k=\frac{1}{\sqrt{2}}\exp(ikd_i)a_{\sigma(i)}$. Consider the fluctuation in the soft mode term, $\hbar\delta\omega_p$. DFT studies [2] have shown that the frequency decreases as the system undergoes the phase transition which I interpret to mean a mode ω_{sm} gets absorbed. As mentioned, the soft mode phonons have multiple k values. Based on Eqs. (1) and (2), I write the component wave functions as

$$\Psi_i = \Phi_i\cos(k_id_i-\omega_it). \tag{27}$$

In terms of soft modes the author of Ref. [30] states

$$\omega_i^2\approx(T-T_c). \tag{28}$$

As mentioned, I assume that a soft mode along each d_i gets absorbed during the transition. The initial (hex) state is a collection of soft mode phonons of energy $\hbar\omega_p$ and momentum $p_n=\hbar k_n$ which get absorbed/emitted in the final/initial state,

$$\lim_{T\to T_c}\hbar\delta\omega_p = \hbar\omega_{pk}\left(b^\dagger_{k_H}b_{k_H}+b^\dagger_{k_n}b_{k_n}\right). \tag{29}$$

Here k_n is a soft mode wave vector in the ortho phase and k_H is the corresponding vector in the hex phase. The magnon states are

$$\lim_{T\to T_c}\hbar\delta\omega_m = \hbar\omega_m(c^\dagger_{k_H\sigma}c_{k_H\sigma}+c^\dagger_{k_n\sigma}c_{k_n\sigma}). \tag{30}$$

Here $k_{H\sigma}$ is a magnon wave vector in the hex phase with J_{FM} (parallel spins) and $k_{n\sigma}$ is the corresponding wave vector in the ortho phase with $J_{\mathrm{AFM}(n)}$ (antiparallel) spins. The next term to consider is the phonon-magnon interaction as most simply described in Kittel [31],

$$\delta\xi_{pm} = \sqrt{2}[(\hbar\omega_m)b_{k_n}c^\dagger_{k_n}e^{-ik_nd_n}-(\hbar\omega_p)b^\dagger_{k_n}c_{k_n}e^{+ik_nd_n}]. \tag{31}$$

Taking the real part and noting that Eqs. (26) and (31) can be combined,

$$\left[\delta\xi_{pm}+\frac{J}{\hbar^2}\delta\vec{S}_i\cdot\vec{S}_{j\neq i}\right] = \sqrt{2}[(J_{\mathrm{FM}}a_{\downarrow\downarrow}+\hbar\omega_kb_k)c^\dagger_{\uparrow\downarrow k}\cos(k_id_i) - (J_{\mathrm{FM}}a^\dagger_{\downarrow\downarrow}+\hbar\omega_kb^\dagger_k)a_{\uparrow\downarrow}\cos(k_id_i)] \tag{32}$$

Equation (31) implies a new AFM magnon amplitude, $J'_{\mathrm{AFM}}\approx(J_{\mathrm{FM}}+\hbar\omega_k)$, or that the energy of the AFM is equal to the energy of the FM plus the energy of the absorbed soft mode phonon. The energy of the magnon-phonon coupling is coherent,

$$J_{\mathrm{AFM}(n)}(d_n) = J'_{\mathrm{AFM}}\cos(k_nd_n),\ n=1,2,3. \tag{33}$$

The energy of the soft mode enters the distance d_n through Eq. (33),

$$\lim_{T\to T_c}J'_{\mathrm{AFM}}\cos(k_nd_n) = (J_{\mathrm{FM}}+\hbar\omega_k). \tag{34}$$

This expression clearly shows the interplay between exchange, soft mode energy, and Mn-Mn spacing. The last term is the variation of exchange with respect to d_n,

$$\delta J\vec{S}_i\cdot\vec{S}_j = \frac{\partial}{\partial d_n}J_{\mathrm{AFM}}\delta\phi_n = -J_n\sin(k_nd_n)k_nd_0. \tag{35}$$

Including time dependence in the exchange,

$$J_{\mathrm{AFM}(n)}(d_n,t) = J'_{\mathrm{AFM}(n)}\cos(\vec{k}_n\cdot\vec{d}_n-\omega_{mn}t),\ n=1,2,3. \tag{36}$$

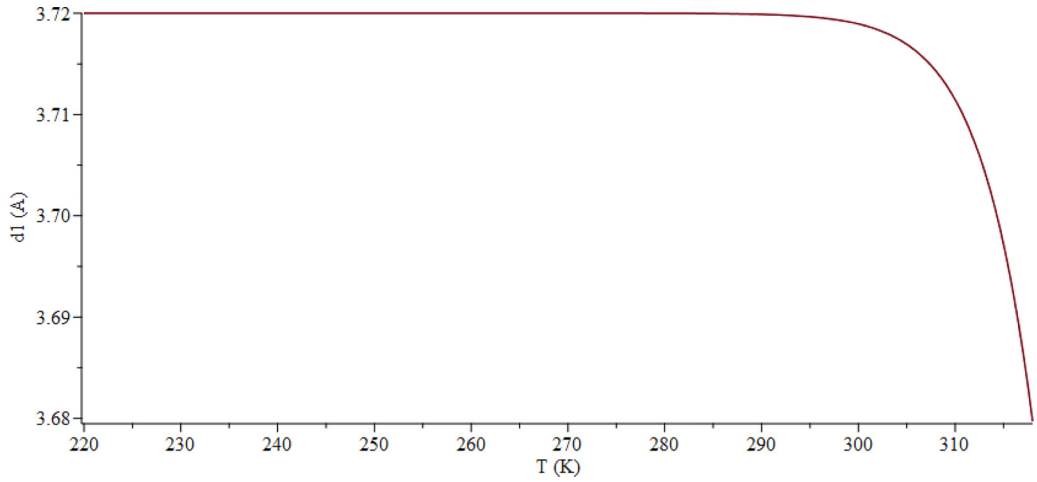

FIG. 2. Disorder calculated using Eq. (55) with $d_1 = (d_H + d_0\langle\delta\phi_1(T)\rangle)$ for $d1 : 3.72 \rightarrow 3.68$ Å. Note here that the onset of disorder begins to occur around 285 K.

The frequency ω_m of the magnon satisfies a dispersion relation similar to one introduced by Kittel [31],

$$\omega_{mn} \approx \frac{J_n \cos(k_n d_n)}{\hbar}. \tag{37}$$

Note that $\Gamma_n \neq \omega_n$. Owing to the quantization condition in Eq. (1), the lowest energy excitations in the O mode are antiferromagnetic magnons. The energy in the above magnon standing wave [25–27] reflected between Mn atoms can be written as

$$\xi_{sw(n)} = 2J_n \cos(k_n d_n) \sin(\Gamma_n t). \tag{38}$$

Before evaluating this, consider the temperature dependence of the phase. Substituting Eqs. (17) and (18) into Eq. (36) for the nth Mn-Mn distance becomes

$$\xi_{sw(n)} = 2J_n \cos\left[\frac{2\pi}{\lambda_n}\left(d_0 \pm \sqrt{\frac{k_B T}{\kappa_n}}\right)\right] \sin(\Gamma_i t). \tag{39}$$

In the limit $T \rightarrow T_c$ we obtain

$$\lim_{T \rightarrow T_c} 2J_n \cos\left[\frac{4\pi}{\lambda_n}\left(d_0 \pm \sqrt{\frac{k_B T}{\kappa_n}}\right)\right] \sin(\Gamma_n t) \approx 2J_n \sin(\Gamma_n t). \tag{40}$$

We can use this expression to find a limit on the relaxation time of the phase transition,

$$\lim_{T \rightarrow T_c} \Gamma_n \approx \frac{2J_n}{\hbar}. \tag{41}$$

The term $\sin(\Gamma_i t)$ oscillates in time with a frequency $\approx 10^{15}$ Hz. To obtain a "frozen" standing wave we must consider the interaction of this magnon with a magnon in an adjacent plane. Given the distance and the fact the that d electrons are itinerant, I assume that exchange manifests the coupling between magnons in the planes above and below $H = \sum_{i \neq j}^{n} J_i' \vec{S}_i \cdot \vec{S}_j$. The equation of motion [29] for a spin

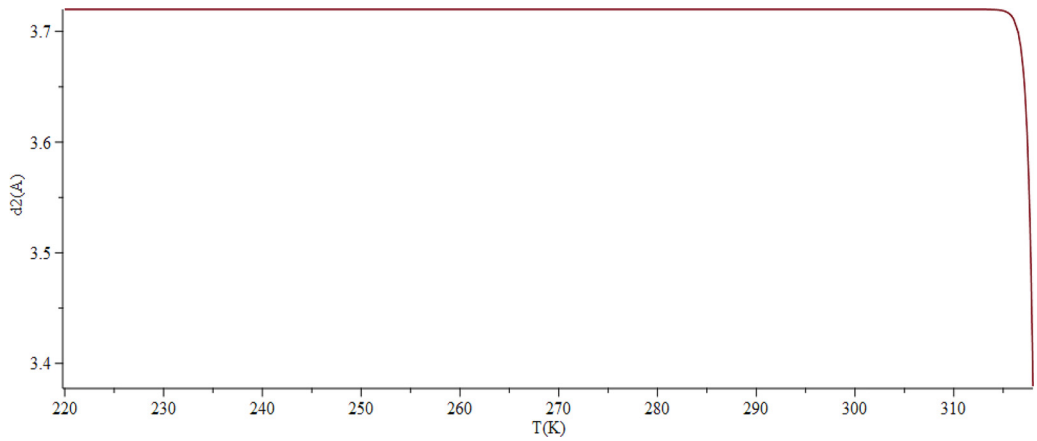

FIG. 3. Disorder calculated using Eq. (55) with $d_2 = (d_H + d_0\langle\delta\phi_2(T)\rangle)$ for $d2 : 3.72 \rightarrow 3.38$ Å. Note here that the onset of disorder begins to occur around 305 K.

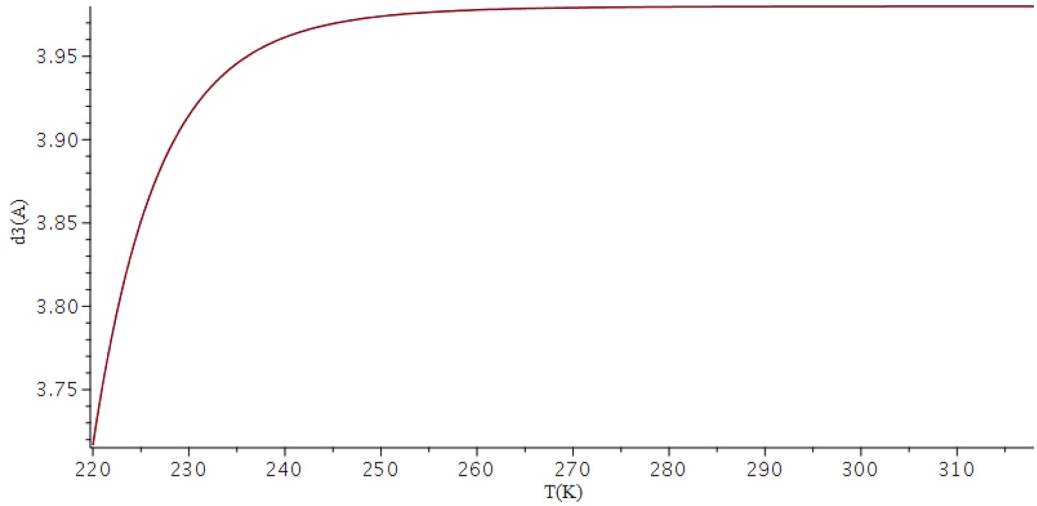

FIG. 4. Disorder calculated using Eq. (55) with $d_3 = (d_H + d_0\langle\delta\phi_3(T)\rangle)$ for $d3 : 3.72 \rightarrow 3.98$ Å. Note here that the onset of disorder begins to occur around 220 K.

S_j in the jth magnon standing wave is

$$i\hbar\frac{dS_i}{dt} = \left(\sum_{i\neq j}^{n} J_i'|S_i|\right)|S_j|\cos\theta_{ij}. \tag{42}$$

This has as a solution

$$S_j = \sum_{i\neq j}^{n} S_i \exp\left(-i\frac{J_i'}{\hbar}\cos\theta_{ij}t\right). \tag{43}$$

Substituting this into Eq. (37) yields

$$\xi_{pm(j)}(J, \Psi_{sm}) = 2J_{0(j)}\sin(\Gamma_i t)\sum_{i\neq j}^{n}\exp\left(-i\frac{J_i'}{\hbar}\cos\theta_{ij}t\right). \tag{44}$$

Defining $\Gamma'_i = \frac{J_i'\cos\theta_{ij}}{\hbar}$ and expanding the exponential yields

$$\xi_{pm(j)}(J, \Psi_{sm}) = 2J_{0(j)}\sin(\Gamma_j t)\sum_{i\neq j}^{n}[\cos(\Gamma_i' t) - i\sin(\Gamma_i' t)]. \tag{45}$$

This becomes

$$\xi_{pm(j)}(J, \Psi_{sm}) = 2J_{0(j)}\sum_{i\neq j}^{n}[\sin(\Gamma_j t)\cos(\Gamma_i' t) - i\sin(\Gamma_j t)\sin(\Gamma_i' t)]. \tag{46}$$

For the limit of long measurement times note that

$$\lim_{t\rightarrow\infty}\sum_{i\neq j}^{n}[\sin(\Gamma_i t)\cos(\Gamma_j' t)] \approx 0.$$

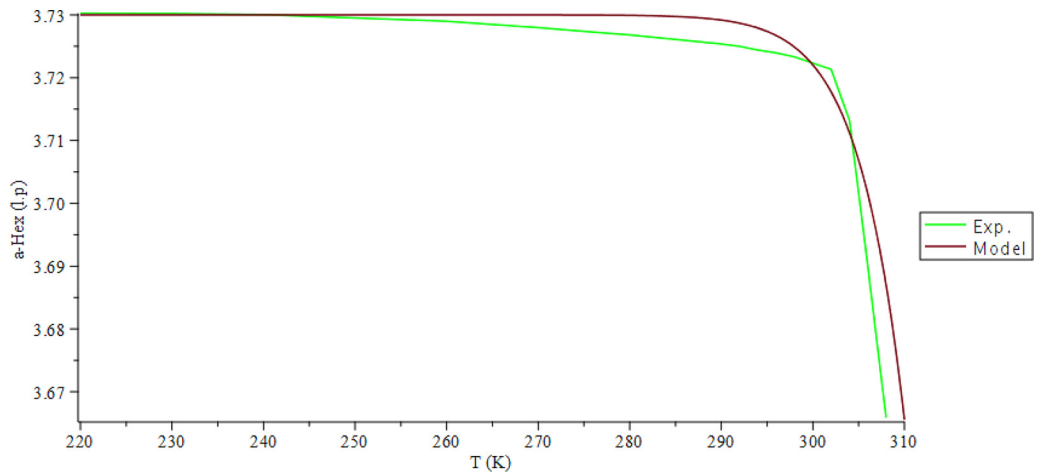

FIG. 5. a-hex lattice parameter. The error in the data is $\Phi = \pm 2.0$ K. The red line is a superposition $[d_1(T) + d_2(T)]/2$ of the plots in Figs. 1 and 2 obtained using Eq. (55). Note the convergence at both temperature extremes.

Thus Eq. (43) reduces to

$$\xi_{pm(i)}(J, \Psi_{sm}) \approx -2iJ_{0(i)} \sum_{i \neq j}^{n} \sin(\Gamma_i t) \sin(\Gamma_j^{'} t). \tag{47}$$

The exchange interaction acts predominantly between d electrons in nearest neighbor in-plane Mn-Mn distances. These terms vanish for long times unless we assume a resonance condition, $\Gamma_i \cos(\vec{k}_i \cdot \vec{d}_i) = \Gamma_j^{'} \cos(\vec{k}_j \cdot \vec{d}_j)$. Owing to the quantization introduced in Eq. (1), two nearest neighbors satisfy this condition. Noting that $\sin^2(\Gamma_i t) = 1/2$, we take the absolute value of Eq. (48) to obtain

$$\left|\xi_{pm(i)}\right| \approx 2J_{0(i)}, \tag{48}$$

which is a frozen AFM standing wave. The quantization condition in Eq. (1) lies at the heart of the temperature behavior ($T \rightarrow T_c$) of the fluctuation in the exchange. The inclusion of H (applied magnetic field) results in shifting T_c either up or down (magnetic cooling). The author of Ref. [10] reminded me that this effect is nonlinear. Here I treat H as coupling directly to the magnon standing wave in each bond. Equation (34) becomes

$$\begin{aligned}&(J_{0(n)} + H)\cos(k_n d_n) \\ &\quad = (J_{0(n)} + H)\cos\left[\frac{2\pi}{\lambda_n}\left(d_0 \pm \sqrt{\frac{k_B T}{\kappa_n}}\right)\right].\end{aligned} \tag{49}$$

All these terms can be combined in Eq. (3) to yield an expression for $\delta\phi$,

$$\lim_{T \rightarrow T_c} \delta\phi_{0i} = \frac{\left\{-\left(\sum_i \delta\Delta_{\mathrm{CF}i} + \hbar\delta\omega_{sm}\right) - \mu \sum_j \vec{l}_j \cdot \delta\vec{S}_j - \frac{J}{\hbar^2}\delta\vec{S}_i \cdot \vec{S}_{j\neq i}\right\}}{\left\{\delta \sum_i V_{\mathrm{TB}i} + \kappa d_0^2 + \left(\frac{\partial}{\partial d_i} J_{\mathrm{AFM}} d_0\right)\vec{S}_i \cdot \vec{S}_{j\neq i}\right\}}, \tag{50}$$

so the order parameter $\delta\phi_i$ is both maximized and quantized at the phase transition temperature. To obtain the expectation value $\langle\delta\phi_i(T)\rangle$ of the order parameter one must first define a partition function in terms of the fluctuations in the energies,

$$Z_i = \left\{\begin{array}{l} \exp\left(-\frac{\delta\xi_{\mathrm{CF}(i)} d^{\dagger}_{\delta\xi} d_{\xi}}{k_B T}\right) + \exp\left(-\frac{\mu|2\mathbb{Z}|\left|\frac{\hbar}{2}\right|\left(\cos\theta_O a^{\dagger}_{\downarrow\uparrow} a_{\downarrow\downarrow} - \cos\theta_H a^{\dagger}_{\uparrow\uparrow} a_{\uparrow\downarrow}\right)}{k_B T}\right) \\ + \exp\left(-\frac{\left[(J_{\mathrm{AFM}}(d_n) \pm H) a^{\dagger}_{\uparrow\downarrow} - \left(J_{\mathrm{FM}} a^{\dagger}_{\downarrow\downarrow} + \hbar\omega_k b^{\dagger}_k\right) a_{\uparrow\downarrow}\right]}{k_{\mathrm{B}} T}\right) \\ + \exp\left(-\frac{\hbar\omega_{sm}\left(b_k - b^{\dagger}_k\right)}{k_{\mathrm{B}} T}\right) + \exp\left(-\frac{(J_{\mathrm{AFM}(n)} \pm H)\sin(k_n d_n) k_n}{k_{\mathrm{B}} T}\right) \end{array}\right\}. \tag{51}$$

We have for the order parameter

$$\langle\delta\phi_i(T)\rangle = \frac{\delta\phi_{0i}\left[\exp\left(-\frac{(J_{\mathrm{AFM}(n)} \pm H)\sin(k_n d_n) k_n}{k_B T}\right) + \exp\left(-\frac{\delta\sum_j V_{\mathrm{TB}(j)}}{k_{\mathrm{B}} T}\right)\right]}{Z_i}, \tag{52}$$

where I have used Eq. (50). The effect on the volume due to application of an external field H is obvious in this expression. The sign of the applied field can be seen to affect $\langle\delta\phi_i(T)\rangle$. We now calculate the differential exchange,

$$\langle J_{\mathrm{AFM}}(T)\rangle = \frac{\langle\delta\phi_i(T)\rangle\left\{(J_{\mathrm{AFM}(n)} \pm H)\sin(k_n d_n) k_n \exp\left(-\frac{(J_{\mathrm{AFM}(n)} \pm H)\sin(k_n d_n) k_n}{k_{\mathrm{B}} T}\right)\right\}}{Z_i}. \tag{53}$$

Note that this calculation involves the expectation value of the order parameter $\langle\delta\phi_i(T)\rangle$, which effectively determines the temperature dependence of the differential exchange.

III. RESULTS

I first consider plots of the calculated changes (disorder) in the in-plane Mn-Mn distances as functions of temperature (see Figs. 2–8). All data are from Ref. [12].

A. Magnetic heating

It has been observed that different applied H fields shift the temperature of the a-hex lattice parameter (see Fig. 9). Here I calculate the shifts in the a-hex parameter due to applied H fields of differing magnitude and compare them to the data.

B. Magnetic cooling

The slope of these calculated magnetization curves satisfies

$$\frac{\Delta T}{\Delta H} = \frac{(312.0 - -308.0)\ \mathrm{K}}{2.0T} = 2.0\ \mathrm{K/T}.$$

This is in agreement with hysteresis data [12] (see Fig. 10).

IV. DISCUSSION

Since the disordered distances d_i are "excitations" of d_H one could assume that some patterns between energy variables in Eqs. (55) and (56) may display quantization. The anharmonic potential $\Delta V_{\mathrm{TB}i}$ is not quantized as exactly as the shift

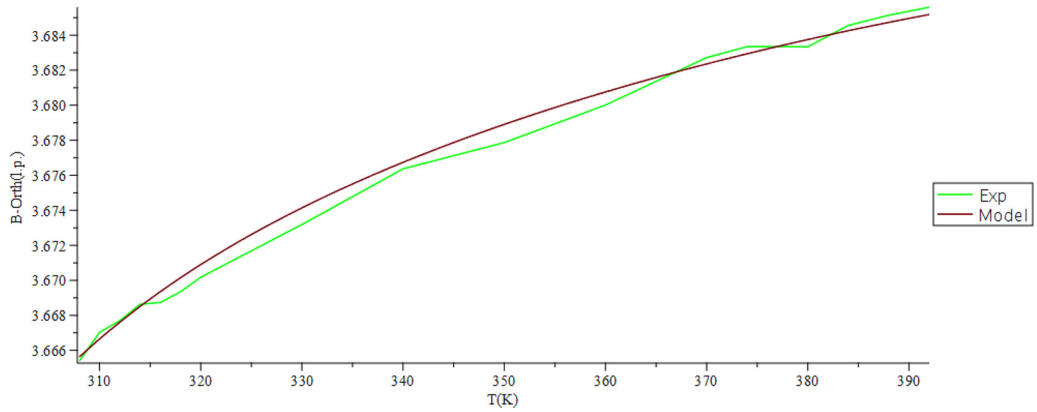

FIG. 6. *B*-ortho lattice parameter. The red line is a superposition of $[d_1(T) + d_2(T)]/2$ as $T : 3.65 \rightarrow 3.68$ K using Eq. (55) as described above. Note the concave nature of the temperature dependence of this process.

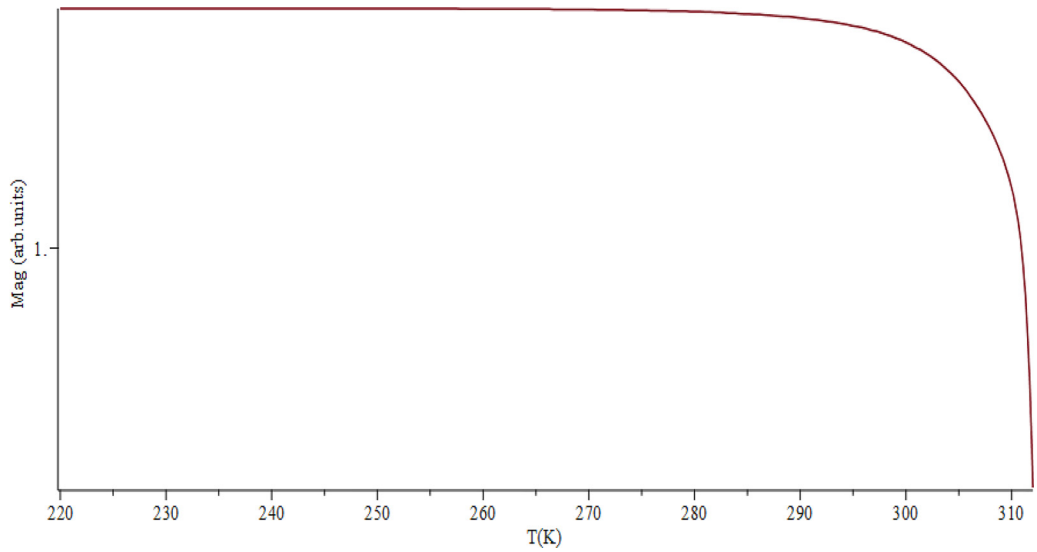

FIG. 7. Superposition of differential magnetization for $d1$ and $d2$ at applied $H = 1.0$ T calculated using Eq. (56). Note that the slope is not as steep as the *a*-hex lattice parameter shown in Fig. 8 and the zero occurs at $T \approx 312.0$ K.

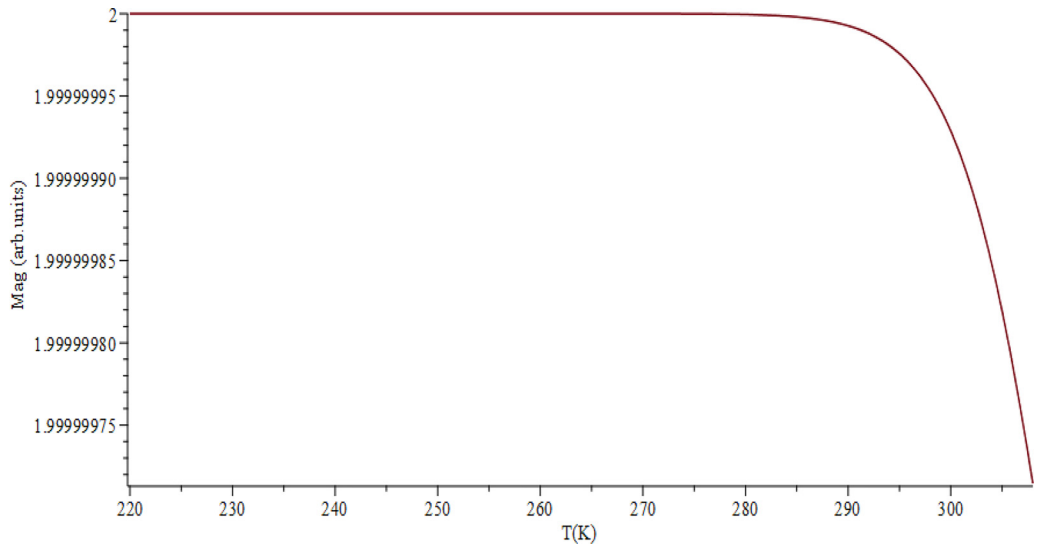

FIG. 8. Superposition of differential magnetization for $d1$ and $d2$ at applied $H = -1.0$ T calculated using Eq. (56). Note that the slope is approximately the same as in Fig. 6, but that the temperature of the zero occurs at $T \approx 308.0$ K. The author of Ref. [12] told me this is a hysteresis effect.

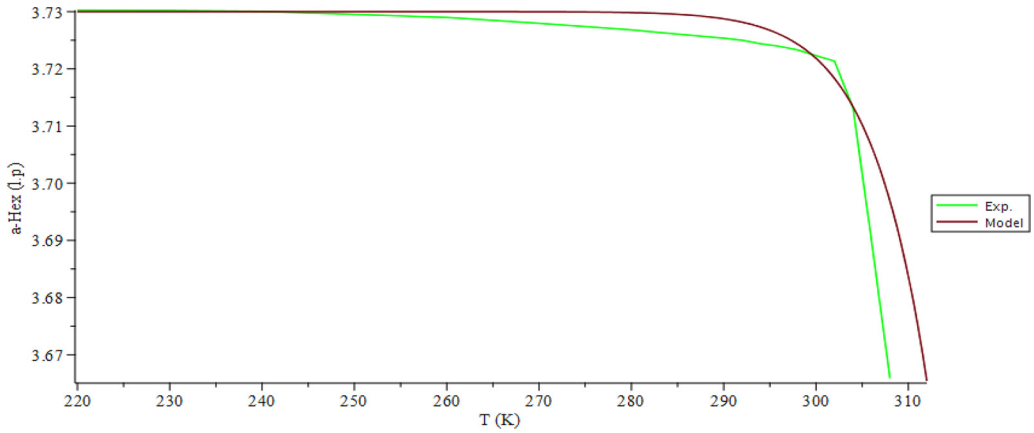

FIG. 9. Calculated a-hex lattice parameter for applied $H = 1.0$ T calculated using Eq. (56) compared to data. Note that the zero occurs at $T \approx 312.0$ K.

in magnetization so this model mixes quantum and empirical energy fluctuations. It can therefore be inferred that the states which give rise to the disorder are mixed states. The mechanism responsible for the disorder begins with the quantization of the wavelengths as shown in Eq. (1). The cooperative nature of the mechanism suggests that some quantity may exist derivable from the fluctuations in the free energy that converges around the transition temperature. Consider a fluctuation of the structural entropy for a given path $dS_i(d_H \rightarrow d_i)$ as defined below:

$$dS_i \approx \lim_{T \rightarrow T_c} \frac{\left\{\Delta hf_i + \Delta\xi_{cf(i)} + \Delta_{so(i)} + \delta\xi_{sw(i)} + \frac{d_0}{\delta\phi_i}\left(\Delta V_{\mathrm{TB}i} + \frac{\Delta J}{\hbar^2}\vec{S}_i \cdot \vec{S}_{j\neq i}\right)\right\}}{T}. \tag{54}$$

dS_i is equivalent to the fluctuation in entropy associated with the path specific to the formation of disorder d_i with $\delta\phi_i(T)$ removed. These are plotted in Fig. 11

The removal of $\delta\phi_i(T)$ from the magnetostructural energy fluctuation in Eq. (54) makes the entropic paths converge around some value of T. Now consider the ratios

$$\left[\left.\frac{dS_1}{dS_2}\right|_{T\approx 310\ \mathrm{K}} \approx \left.\frac{dS_1}{dS_3}\right|_{T\approx 318\ \mathrm{K}} \approx 1\right], \tag{55a}$$

$$\left[\left.\frac{dS_2}{dS_3}\right|_{T\approx 318\ \mathrm{K}} \approx \frac{3}{4}\right]. \tag{55b}$$

I interpret the intersections to mean that processes shown in Eq. (55a) are reversable from these approximate temperatures. Note that only $dS_1/\Delta T$ intersects both slopes. And since dS_1 is the fluctuation in entropy of the highest excited state, it should cross both dS_2 and dS_3. As such, I posit that Eqs. (55a) and (55b) are an emergent property resulting from

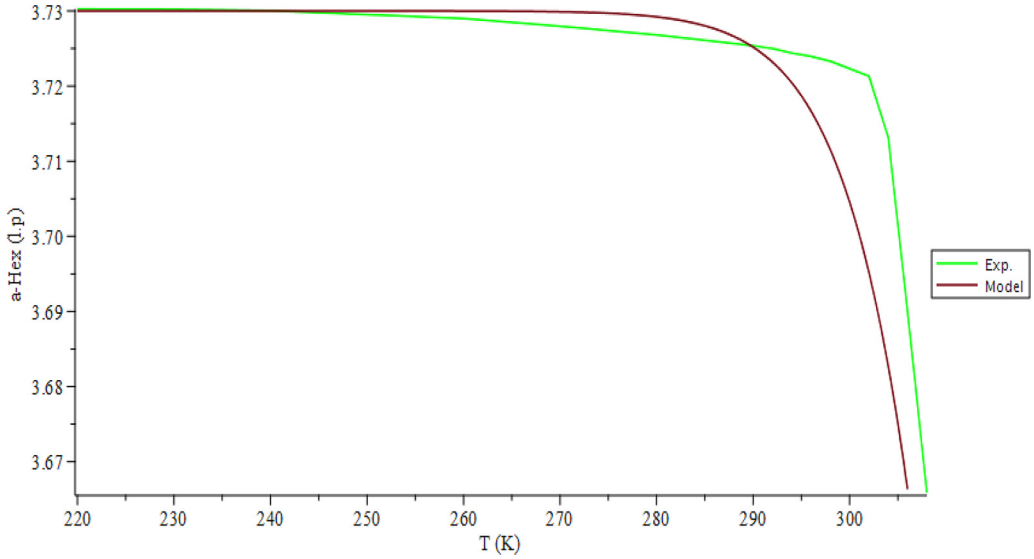

FIG. 10. Calculated a-hex lattice parameter for applied $H = -1.0$ T calculated using Eq. (56). Note that the zero occurs at $T \approx 306.0$ K.

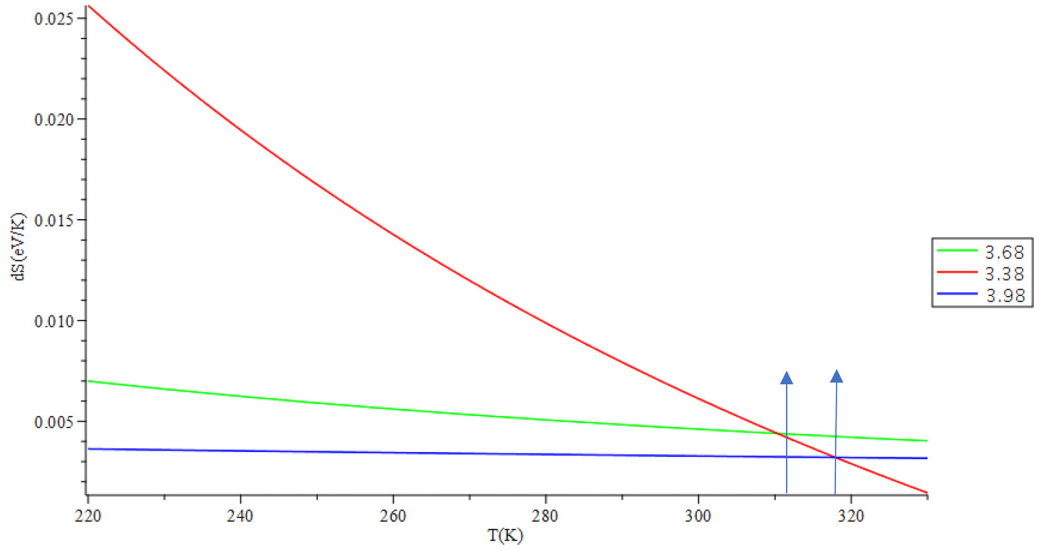

FIG. 11. Fluctuation in structural entropy dS (eV/K) as functions of temperature for each d_i. Here $dS_1 : 3.72 \rightarrow 3.38$, $dS_2 : 3.72 \rightarrow 3.68$, $dS_3 : 3.72 \rightarrow 3.98$.

the quantization defined in Eqs. (1)–(3). In light of all of this the measured value $T_c \approx 318.0$ K can be explained by comparing the probability for each of these processes to occur,

$$P(T)_i \approx \frac{\left\{\exp\left(-\frac{\Delta V_{\mathrm{TB}i}}{k_{\mathrm{B}}T}\right) + \exp\left(-\frac{\frac{\Delta J}{\hbar^2}\vec{S}_i\cdot\vec{S}_{j\neq i}}{k_B T}\right)\right\}}{Z_i}. \tag{56}$$

This is plotted in Fig. 12.

Note these probabilities are not normalized with respect to the same partition function, so they do not sum to 1. Note that the probability for ΔS_3, the lowest excited state, becomes maximal and remains constant around $T \approx 240$ K. The fact they converge at T_c is another indication of reversibility. My calculations show that Δ_{so} (eV) $< \Delta_{cf}$ (eV), which is consistent with Ref. [30]. Now consider the sign of the fluctuations in the crystal field. Fig. 13 depicts a hexagonal to orthorhombic transition.

The energy splitting labeled between the $|d_{xy}\rangle$ levels is defined as $\delta\xi_{xy} = (E_{xy(O)} - E_{xy(H)}) < 0$. Each disordered Mn-Mn d_i has its own level structure. Since this is a "high spin" material, it is difficult to know how the total fluctuation on each d_i is distributed among the levels. However, I obtain $\delta\xi_{\mathrm{CF}(J)}$ (eV) < 0, $j = 1, 2, 3$ indicating structure changes which are consistent with Ref. [28]. Using $J = l - s$, $j = 2\hbar$, $s = \hbar/2$ in Eq. (23) to obtain a spin orbit energy. Usually the spin-orbit energy is a magnitude smaller than crystal-field crystal energy, however in this case we are dealing with the differences in these energies, so the dynamic pathways may be competitive. Consider the vertical distance between Mn atoms in the hex phase, $d_{vH} = 2.85$ Å. Using κ_2 in Eq. (19) I obtain $\lim_{T\rightarrow T_c} d_v = 2.88$ Å in agreement with Ref. [12], showing that the hypothesis applies to Mn atoms out of plane. The authors of Ref. [16] measured an anomalously low thermal conductivity for a sample of MnAs. In Fig. 14 I plot the calculated thermal diffusivity, Fig. 14 shows the

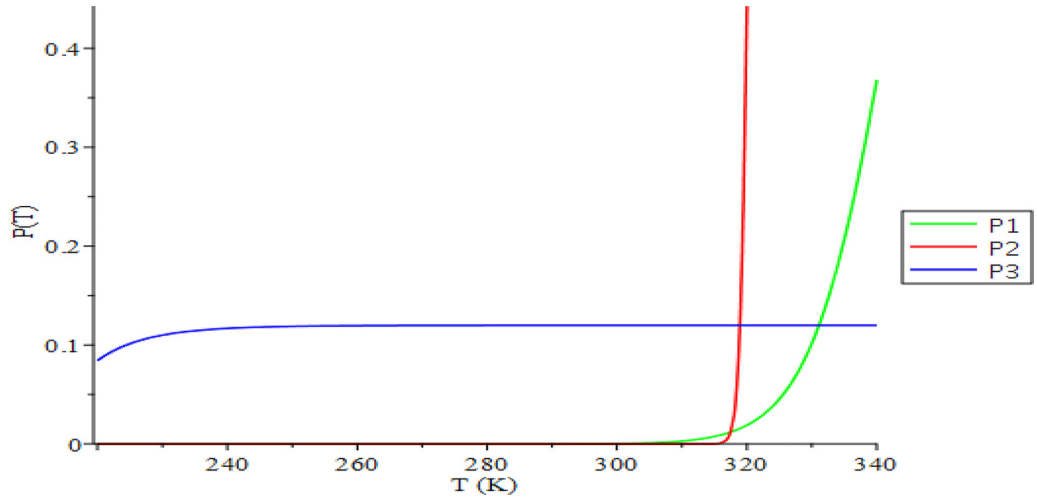

FIG. 12. Superposition of magnetostructural probabilities for these processes to occur. Note that they all converge at $T = 318.0 \pm 2.0$ K.

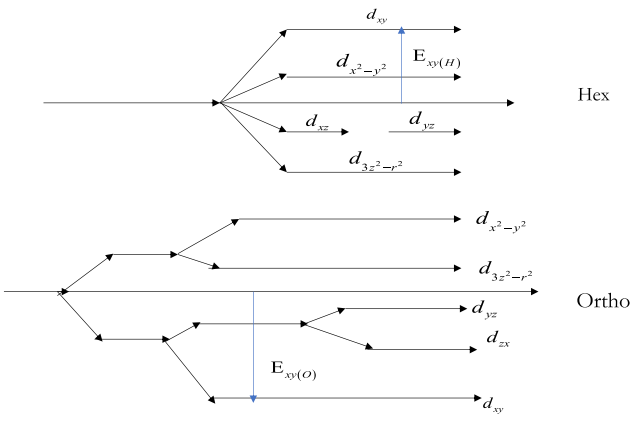

FIG. 13. This shows the hexagonal → orthorhombic change in crystal-field level splittings for MnAs.

anomalous dip at $T \approx 318.0$ K as measured in Ref. [16]. This calculation is a direct consequence of the presence of the disorder as manifested in the free energy. The authors of Ref. [17] noted anomalous elastic properties with elastic constants depending on direction and temperature. Consider the κ_n calculated using Eq.(13). This shows that the "spring constants" all vary in terms of Mn-Mn direction as evaluated at $T \approx 318.0$ K. The value for κ shifts in going from the hex-ortho structures as measured in Ref. [17]. Last, the authors of Ref. [15] observed (computationally) that the $|d_{x^2-y^2}\rangle$ orbital manifests an increase in interaction energy for the disordered states. My calculations bear this out.

V. CONCLUSIONS

Earlier work on this phenomenon used a statistical mechanical approach [1–3] which involved inserting the transition temperature in as a parameter. These models did not predict the measured local disorder [12]. Later approaches [10,11,15] introduced soft mode-spin coupling but did not predict the correct magnitudes of disorder. Disorder is not simple, so the quantum mechanics required to predict it may be complicated. The simplest assumption is that the disorder is quantized in integer multiples of absorbed soft modes. Thus the d_i in the ortho phase can be interpreted as "excitations" of d_H through Eq. (1). I also assumed this approach would have to include cooperative interactions between several quantized entities. I used a quantum statistical approach to show that absorbed soft mode phonons simultaneously excite lattice distortions (disorder) and antiferromagnetic magnons between adjacent Mn atoms bonded to the same As atom. These in turn reflect between adjacent Mn atoms owing to boundary conditions to become standing waves. These standing waves "freeze in" due to interaction with similar waves above and below in the lattice. The disorder changes the lattice parameter thereby causing a shift in the crystal-field splitting on each Mn atom. I showed that shifts in spin-orbit effects are negligible. The phonon-magnon interaction manifests as a term $J\cos(K_n d_n)$. The quantization of this term as introduced in Sec. I manifests both in the hex lattice parameter as well as the C-ortho lattice parameter. The local disorder is used to calculate the transition temperature, anomalous elastic properties [16], thermal diffusivity [17], as well as several phenomena associated with the phase transition observed in Ref. [12]. The initial quantization conditions ultimately manifest as a convergence of entropy fluctuations at $T_c \approx 318.0$ K. I regard this as an emergent property. Future work will include similar investigations of other quantum materials, in particular ones exhibiting the metal-insulator transition along with induced disorder.

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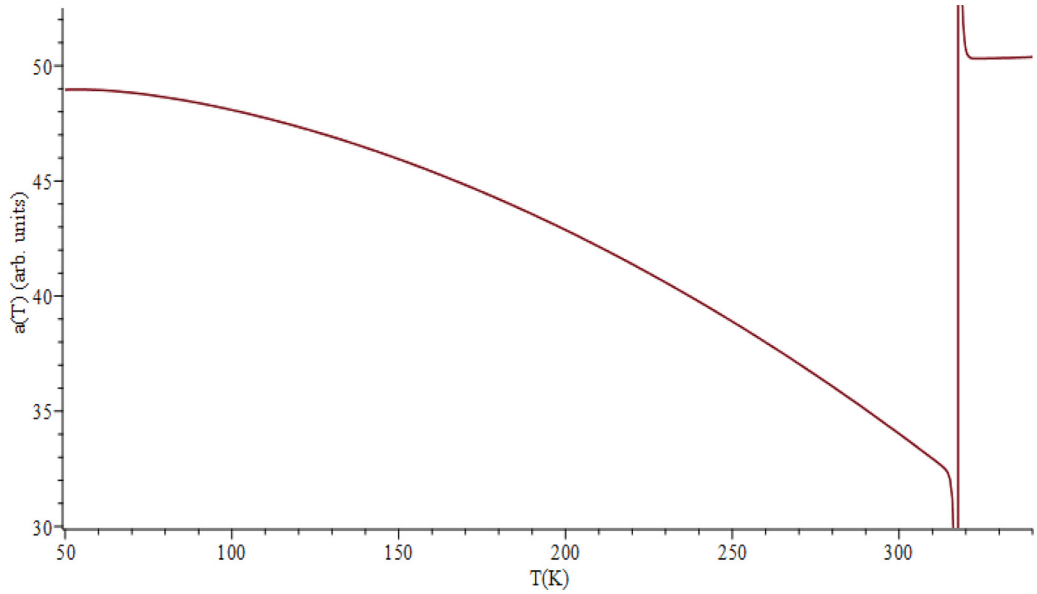

FIG. 14. Plotted calculated thermal diffusivity (arb. units) for MnAs.

T. Cancio for useful discussions. Last I wish to thank the referees for suggesting changes which made the paper more understandable, and the late W. A. Harrison, whose approach I have tried to emulate.

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