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Quantum Critical Transition Amplifies Magnetoelastic Coupling in Mn[N(CN)]2

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We report the discovery of a magnetic quantum critical transition in Mn[N(CN)]2 that drives the system from a canted antiferromagnetic state to the fully polarized state with amplified magnetoelastic coupling as an intrinsic part of the process. The local lattice distortions, revealed through systematic phonon frequency shifts, suggest a combined MnN octahedra distortion + counter-rotation mechanism that reduces antiferromagnetic interactions and acts to accommodate the field-induced state. These findings deepen our understanding of magnetoelastic coupling near a magnetic quantum critical point and away from the static limit.

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Quantum phase transitions and associated quantum-critical points present a rich and challenging research area that is of current fundamental interest [1]. In contrast to classical phase transitions governed by thermal fluctuations, quantum phase transitions are driven by an external parameter such as magnetic field, pressure, or composition [1]. One case where field works as a quantum tuning parameter is in the suppression of antiferromagnetic order by applied magnetic field where the resulting quantum critical point separates the antiferromagnetic state from the fully polarized paramagnetic state [2–4]. This and other more complicated magnetically-driven transitions [5–7] are of foundational importance to the field of quantum magnetism, yet due to energy scale considerations, real physical systems can be challenging to identify. Molecule-based materials offer a way forward. Their low quantum energy scales are well-suited for investigating magnetically-driven transitions, and their chemical flexibility and softness offer opportunities to tune properties and couple functionality [3, 4, 8]. Mn[N(CN)]2 attracted our attention in this regard [9, 10]. What distinguishes this work from previous efforts to investigate magnetoelastic coupling [4] is the three-dimensionality of this system, the lack of hydrogen-bonding, and easy access to the long range ordered state.

In this Letter, we report the discovery of a magnetic quantum critical transition in Mn[N(CN)]2, the complete magnetic field-temperature phase diagram, and enhanced magnetoelastic coupling through the field-driven transition that we analyze in terms of local lattice distortions. The latter reveals a combined MnN octahedra distortion + counter-rotation mechanism that reduces antiferromagnetic interactions and stabilizes the fully polarized state. Similar local lattice distortions and exchange pathways underpin the remarkable properties of photomagnetic cyanides, ferroelectrics, and correlated oxides [11, 12]. These findings advance the fundamental understanding of quantum phase transitions, provide insight into higher energy scale materials [13], and are relevant to more complicated processes in which magnetic field acts as a tuning parameter including multiferroicity [14], multiple magnetization plateaus [5, 6], and skyrmion lattice development [7].

Powdered Mn[N(CN)]2 was prepared as described in Ref. [9], and isothermal magnetization was measured using a 6 T short-pulse magnet located at the NHMFL [3]. Variable temperature and field spectroscopies were performed in our own lab and at the NHMFL (30-3500 cm−1, 4.2-300 K, 0-35 T, 0.3-1 cm−1 resolution). Density functional calculations were used to expose various properties including lattice vibrations and spin densities. Details are available in Supporting Information.

Figure 1(a) displays the isothermal magnetization of Mn[N(CN)]2 below the antiferromagnetic transition temperature TN = 15.85 K as a function of magnetic field up to 51 T. The 0.5 K data show a linear increase with field above the 0.48 T spin flop transition [10] and a sharp, elbow-like transition to saturation at BH = 30.4±0.1 T after which the fully polarized state is achieved. The 4 K data have a similar profile and a 29.8±0.2 T critical field. This behavior is a signature of a magnetic quantum phase transition [2, 3]. That it occurs at experimentally realizable fields makes it especially attractive. The magnetization in Mn[N(CN)]2 is different than the concavity in lower dimensional sys-
We use mean field theory to relate the critical field \( B_c \) to the exchange interaction as \( g \mu_B B_c = |n(2JS)| \), where \( S = 5/2 \) for Mn\(^{2+} \), \( n = 8 \) is the number of nearest neighbors, \( g = 2.0 \), and \( \mu_B \) is the Bohr magneton.

We find \( J/k_B \leq -1.0 \) K, which compares well with the estimate of \( J/k_B = -0.78 \) K from specific heat measurements [10, 15]. Bringing the extracted critical fields together with previously published work [10] allows us to construct the \( B - T \) phase diagram (Fig. 1(b)). Interestingly, a single value of \( J \) cannot simultaneously account for both magnetic energy scales in this system (\( T_N = 15.85 \) K and \( B_c = 30.4 \) T). Possible origins of this discrepancy include beyond mean field corrections [16] or a field-dependent exchange interaction [5]. Spin density calculations reveal an out-of-phase pattern in the low field antiferromagnetic state and a uniform density in the high field state (Fig. 1), with the majority of spin density on the Mn sites in each case.

Figure 2(a) displays the far infrared absorption spectrum of Mn\([N(CN)]_2\) at 4.2 K. A factor group analysis (space group \( Pmmm \)) predicts 25 infrared active modes \( \Gamma = 7B_{1u} + 9B_{2u} + 9B_{3u} \) [17]. Based on our first principles lattice dynamics calculations and a literature comparison [18], we assign the peaks at 79 and 108 cm\(^{-1} \) to lattice modes with dominant Mn displacement, phonons at 162/167 and 194 cm\(^{-1} \) to N-Mn-N bending, features between 220 and 300 cm\(^{-1} \) to Mn-N stretching modes + ligand bands, and peaks at around 500 cm\(^{-1} \) to NCN in- and out-of-plane bending. A complete assignment is available in the Supporting Information. The magneto-infrared response of Mn\([N(CN)]_2\) reveals remarkable sensitivity to the quantum critical transition.

To emphasize spectral changes through \( B_c \), we calculate the full field absorption difference spectrum, \( \Delta \alpha = \alpha(B = 35 \) T\) - \( \alpha(0 \) T\) (Fig. 2(b)). This difference simultaneously highlights striking change and rigid behavior. The exact course of each mode depends on the precise nature of its displacement pattern. Moreover, the field-dependent features either soften or harden systematically with field, a trend that again correlates with the detailed mode motion. In fact, at heart, \( \Delta \alpha \) changes reflect frequency shifts as evidenced by the symmetric derivative-like structures in the absorption difference spectrum. As an example, Fig. 2(c) displays a close-up view of the absorption difference spectrum for the low frequency Mn displacement modes. The magnitude of \( \Delta \alpha \) increases continuously due to mode softening (inset Fig. 2(c)) until it saturates near 30 T. That the majority of vibrational bands are sensitive to applied field is indicative of local structure deformations on approach to the magnetic transition.

To quantify changes in the vibrational properties of Mn\([N(CN)]_2\) with magnetic field, we integrate the absolute value of the absorption difference as \( \int_\omega \alpha(B) - \alpha(0 \) T\) d\( \omega \) and plot these quantities along with the magnetization (Fig. 2(d)). The field-induced spectral changes grow with increasing field and saturate near 30 T where the transition from canted antiferromagnetic to fully polarized state is complete. In general, magnetoelastic phenomena originate from the magnetic state dependence of the elastic properties, which can vary with magnetization intensity and orientation [19]. For instance, in magnetic alloys, the relationship between volume magnetostriction and magnetization goes as \( \Delta V \sim (M(B))^2 \) [20]. Lattice constants in complex oxides like BaCo\(_2\)V\(_2\)O\(_8\) also display similar dependence [21]. Our work is different in that we employ local probe (rather than bulk) techniques to uncover the microscopic aspects of the local lattice distortion [22]. Comparison of the data in Fig. 2(d) shows that Mn\([N(CN)]_2\) is an example of a molecule-based magnet where the field-induced frequency shifts go as \( (M(B))^2 \), an indication of dominant exchange effects [21, 23, 24]. The strong correlation between phonon behavior and the square of the magnetization suggests that lattice flexibility plays an important role in establishing the fully polarized high field state. Sim-
Our spectroscopic measurements reveal that although many infrared-active phonons are sensitive to applied field and display a similar dependence on \( B \), some changes are more important than others. We use relative absorption difference, \( \Delta \alpha/\alpha \), to quantify the relevance of each mode and the local lattice distortion that it represents. The features at 108, 79, and 272 cm\(^{-1}\) display the largest changes (\( \approx 29, 12, \) and 7\% in a 35 T field, respectively). The two leading modes involve Mn displacements in a shearing-like pattern along \( b \) (108 cm\(^{-1}\)) and \( a \) (79 cm\(^{-1}\)) axes, respectively. The next tier contribution (a Mn-N\(_{eq}\) vibration with a 7\% change at 272 cm\(^{-1}\)) also mainly involves Mn motion but along the \( c \) axis. All three modes soften with increasing field. Figure 2(e, f, g) displays schematic views of these displacement patterns along with an example of pure ligand mode motion at 497 cm\(^{-1}\) which has a 5\% change in a 35 T field.

A natural framework for understanding the magnetoelastic effect in Mn[N(CN)]\(_2\)\(_2\) involves local lattice deformations that modify spin exchange interactions in order to compensate for the increased magnetic energy in the fully polarized state. Analysis of the absorption difference spectra shows that phonons involving mainly Mn centers generally soften with field, and the ligand bands on the contrary, tend to harden on approach to the transition (Table S1, Supporting Information). This behavior points to a more relaxed MnN\(_6\) octahedra (i.e less strained bond lengths and equally distributed local an-
gles) and slightly compressed N-C-N linkages in the high field state. Based on the size of $|\Delta \alpha|/\alpha$ through the 30.4 T magnetic quantum critical transition, the distortion primarily affects the 108 cm$^{-1}$ Mn shearing mode along $b$ (with a 29% change). A similar displacement pattern along $a$ (as represented by the 79 cm$^{-1}$ mode and its 12% change) is a large secondary effect. The predominance of low frequency features in this analysis is indicative of either a real space Mn displacement along $b$ and $a$ or a more complicated distortion of the MnN$_6$ cage. The magneto-infrared spectra provide no evidence for high field symmetry breaking (Fig. 2(c)), a finding that rules out simple transition metal displacement and also the possibility of a high field ferroelectric state [12].

In other words, our data indicates that if Mn displacement is present, it is rather small. We therefore conclude that the primary local lattice distortions through the 30.4 T magnetic quantum phase transition involve deformations of the Mn environment, specifically distortions to the MnN$_6$ octahedral cage.

Examination of the high field data shows that several ligand bands are sensitive to the 30.4 T quantum critical transition as well. Although these changes are not large in terms of $|\Delta \alpha|/\alpha$ (Table S1, Supporting Information), they provide additional information about structural flexibility in Mn[N(CN)$_2$]. One mechanical candidate advanced by our first principles calculations and supported by variable temperature structure work [10] is MnN$_6$ counter-rotation about the c-axis (Fig. S2(b)). Analysis of the spectral changes suggests that this is a reasonable model that brings the various MnN$_6$ and ligand bends together - with the caveat that the MnN$_6$ octahedra are flexible during counter-rotation due to the three-dimensional network. Importantly, the lowest frequency Raman-active mode has a displacement pattern that mirrors the predicted octahedral counter-rotation, providing a natural distortion pathway for the system [26]. Comparison of the relaxed structures in the antiferromagnetic and ferromagnetic states suggests that the rotation will be less than 1°.

The magnetic ground state in metal dicyanamides is well-known to arise from a delicate balance between competing antiferromagnetic and ferromagnetic superexchange interactions [9], with exchange strength depending upon magnetic orbital overlap in the metal-ligand-metal linkage, which in turn varies with bond angles and distances [27]. In general, the total spin exchange $J$ can be expressed as a sum of $J_{\text{FM}}$ and $J_{\text{AFM}}$, where $J_{\text{FM}}$ is the ferromagnetic contribution, and $J_{\text{AFM}}$ is the antiferromagnetic term [28]. Here, $J_{\text{AFM}} \sim \frac{t}{U_{\text{eff}}}$, where $t$ is the overlap integral and $U_{\text{eff}}$ is the effective on-site Coulomb repulsion [28]. As the field-driven magnetic quantum phase transition forces the system to adopt a fully polarized spin alignment, the energy can be reduced by lattice distortions that effectively decrease $t$. This reduces $J_{\text{AFM}}$, and consequently, the overall $J$. Within this picture, MnN$_6$ counter-rotation occurs to lower the total energy of the paramagnetic state forced upon the system by the external magnetic field. Using the prior result [10] that the octahedral tilt is 25.2° at 4.6 K and $B = 0$ T [29, 30], driving the system into the high field state yields (for instance) poorer $t_{2g}(\text{metal})-\pi_g(\text{ligand})$ overlap and a slight increase in the tilting angle. Thus one might speculate that the MnN$_6$ octahedra counter-rotate to reduce $J_{\text{AFM}}$ in the high field state. Perhaps the simplest experimental verification of MnN$_6$ tilting can be found in the field-induced hardening of the NCN bending modes, although our calculations show that $J_{\text{FM}} - J_{\text{AFM}}$ is rather small. Of course an important angular effect that influences the magnetic properties of Mn[N(CN)$_2$]$_2$ is distortion of the MnN$_6$ octahedra as discussed above. Softening of the 272 cm$^{-1}$ Mn-N$_{eq}$ stretching mode provides support for this process since an increase in the N$_{eq}$-Mn-N$_{eq}$ angle is consistent with relaxed c-directed Mn motion in the equatorial plane. The resulting decrease in the supplementary angle blue shifts the 224 cm$^{-1}$ $\nu$(Mn-N$_{eq}$) $ab$-plane displacement mode (Supporting Information). Thus, the field-induced local structure changes around the transition metal center and to the ligand exchange pathway reinforce the magnetic aspects of the transition.

Motivated by the discovery of the magnetoeelastic coupling through the 30.4 T quantum critical transition, we sought to expose local lattice distortions through the 15.85 K paramagnetic $\rightarrow$ antiferromagnetic transition [10]. Our measurements reveal, however, only gradual frequency shifts over the temperature range of investi-
gation with no anomalies at $T_N$ (Fig. 3). This indicates that the development of long range antiferromagnetic order in Mn[N(CN)$_2$)$_2$ takes place with no significant phonon anomalies (and no substantial lattice involvement). More broadly, it demonstrates that while spin-lattice interaction is inherently rather small in this material, the presence of a collective magnetic transition that switches the system between two different magnetic states with simultaneous, compulsory adjustment of the superexchange interactions can strongly amplify the effect [31]. This finding is reinforced by our high field data on the isostructural paramagnet Cu[N(CN)$_2$)$_2$ and suggests that collective transitions can be used to control the interplay between charge, structure, and magnetism.

To summarize, we report the discovery of a magnetic quantum critical transition in Mn[N(CN)$_2$)$_2$ and the magnetostructural coupling associated with it. In addition to revealing how and why the magnetic quantum critical transition amplifies spin-lattice interactions, our work establishes the need to carefully examine magnetostriction effects in magnetic materials that share flexible exchange pathways. These findings also illustrate how external stimuli like magnetic field and temperature in combination with low energy scale molecule-based materials can be used to uncover microscopic aspects of quantum phase transitions that are elusive in high energy scale systems like the oxides [13].

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The strongest near-neighbor magnetic-exchange interaction proceeds through the Mn-N≡C-N-Mn linkage. Here, we employ a single $J$ spin Hamiltonian of the form:

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B B \sum_i S_i^z.$$ 

Definition of $J$ used in Ref. [10] differs by a factor of 2 from $J$ in this paper.


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[26] A direct check of the low frequency Raman mode is impossible at this time due to probe limitations at the NHMFL.


[30] The tilt angle is defined as the the angle between the equatorial plane of the MnN₆ octahedron and the ac plane [10].

[31] Magnetic field induces twice the change in spin-spin correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ compared with temperature [19, 23].