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Chemical bonding and magnetic exchange in two-dimensional \([M(TCNE)(NCMe)_2]X~(M=Fe, Mn; X=FeCl_4, SbF_6)\) magnets: A pressure study

Alex E. Midgley,\(^1\) Christopher Olson,\(^2\) Christopher L. Heth,\(^2\) Anthony N. Caruso,\(^1\) Michael B. Kruger,\(^1\) Gregory J. Halder,\(^3\) John A. Schlueter,\(^4\) and Konstantin Pokhodnya\(^2,\)\(^,\)a)

\(^1\)Department of Physics and Astronomy, University of Missouri-Kansas City, Kansas City, Missouri 64110, USA
\(^2\)Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, North Dakota 58108, USA
\(^3\)X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Ave, Argonne, Illinois 60439, USA
\(^4\)Materials Science Division, Argonne National Laboratory, 9700 South Cass Ave, Argonne, Illinois 60439, USA

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Pressure-dependent X-ray diffraction studies reveal the bulk modulus and compression anisotropy of the 2D magnet [Mn(TCNE)(NCMe)_2]SbF_6. The Raman response of this and the similar [Fe(TCNE)(NCMe)_2]FeCl_4 layered magnet, shows that the evolution of the \(a_g\) \(\nu_{C=N}\) frequency correlates well with the magnetic exchange and \(T_c\) variations of these materials under pressure. There is a significantly more complex correlation between the \(a_g\) \(\nu_{C=N}\) frequency and \(T_c\) despite the fact that some unpaired \(\pi^*\) electron density \((\sim 0.125\ e)\) is localized on each of TCNE nitrile \(N=\mathrm{C}\) group. The shortening of the M–NC bond with pressure \((<0.5\ \text{GPa})\) does not result in a \(T_c\) increase, which suggests a more complex bond length magnetic exchange relationship. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4770057]

I. INTRODUCTION

The relationship between bonding and magnetic exchange in molecule-based solids remains a stimulating problem of contemporary magnetism. The M[TCNE] \((M=3d\text{ metal}; \text{TCNE} = \text{tetracyanoethylene})\) class of molecule-based magnets has been and continues to be extensively studied\(^1\)\(^–\)\(^3\) since \(V[\text{TCNE}]\) \((x \sim 2)\) exhibits one of the highest critical temperatures, \(T_c\), of \(\sim 400\ \text{K}\)\(^4\) and its highly spin-polarized conduction and valance bands make it suitable for magneto-optical\(^5\) and magneto-electronic applications.\(^6\) However, despite great advances in determining and understanding the M[TCNE] spin polarized electronic and magnetic structure,\(^7\)\(^–\)\(^10\) revealing the particular factors mediating a strong super-exchange (i.e., \(\sigma\)-donation or \(\pi\)-backbonding) remains elusive.

Application of hydrostatic pressure changes the molecular orbital overlap engaged in bond formation and may potentially enable identification of its role in the magnetic exchange interaction, thus providing a valuable insight into the mechanism of magnetic ordering in molecule-based magnets. The dependence of the magnetic properties on hydrostatic pressure has been determined for the ferromagnetic charge-transfer salt [Fe\(^{\text{II}}\)(C\(_3\)Me\(_5\))\(_2\)](TCNE)\(^{11}\) and one-dimensional magnetic chains of [Mn\(^{\text{III}}\)TPP][TCNE],\(^12\)\(^,\)\(^13\) as well as for both quasi-two-dimensional [Fe(TCNE)(C\(_4\)CN)\(_8\)]\(^{14}\) and three-dimensional [Mn(TCNE)\(_3\)]\(_2\)[I\(_3\)]\(_0\)\(^{15}\) magnets. In all studied compounds, the \(T_c\) increases with pressure, and this behavior is generally ascribed to the enhancement of the intra-chain/layer M[TCNE] super-exchange interaction. It should be noted that in [Mn\(^{\text{III}}\)TPP][TCNE] the \(T_c\) growth is preceded by its initial rapid decrease with pressure up to \(\sim 2\ \text{kbar}\). This unusual behavior is conventionally attributed to a phase transition in the spin and/or lattice system that presumably weakens the ferromagnetic dipolar interaction between chains. In contrast, the decrease of \(T_c\) with pressure in the two-dimensional Cu\(_2\)(OH)\(_3\)(n-C\(_{\text{m}}\)H\(_{2\text{m}+1}\)CO\(_2\))\(_2\)\(\text{H}_2\text{O}\) molecular magnet was assigned to small variations of the Cu–O–Cu bond angles within the layer.\(^16\)

Recently, it was shown that monitoring the frequencies of \(C=\mathrm{C}\) and \(\text{C}=\mathrm{N}\) bonds by Raman spectroscopy can provide quantitative information about the degree of ligand-to-metal charge transfer in [M(TCNE)(NCMe)\(_2\)]\(_2\)Sb\(_6\) \((M=\text{Fe, Mn, Ni})\) layered magnets.\(^17\) The application of high pressure shortens all TCNE bonds, as well as the metal-to-nitrogen and nitrile group bonds, thus altering total orbital overlap. In addition, it causes the reduction of the interlayer distances affecting the dipole-dipole, inter-layer coupling. Accordingly, by carefully monitoring the Raman response in conjunction with the evolution of the crystal structure under pressure, the effect of all these factors on the super-exchange and, consequently, on the ordering temperature may be revealed. While the Raman spectra evolution of neutral TCNE under hydrostatic pressure is well documented,\(^18\) the information about its anion-radical is rather sparse, and the Raman studies on TCNE compounds are limited to weak charge transfer or low orbital overlap TCNE complexes.\(^19\)

In this report, we present a systematic study of Raman properties of two structurally similar two-dimensional...
TCNE-based magnets of \([\text{Fe(TCNE)(NCMe)}_2\text{FeCl}_4]\) (1) and \([\text{Mn(TCNE)(NCMe)}_2\text{SbF}_6]\) (2) compositions as a function of hydrostatic pressure. Both structures consist of buckled layers of TCNE anions coordinated to four metal ions, with SbF\(_6^-\) or FeCl\(_4^-\) anions occupying the voids between the layers.\(^{17,20}\)

For compound 2, the Raman response was analyzed in conjunction with its unit cell parameter variation under pressure. The Raman response of the isolated TCNE\(^{--}\) anion in paramagnetic tetra-n-butylammonium tetracyanoethenide, \([\text{Bu}_4\text{N}]\text{TCNE}\), hereafter (3), as a function of pressure is also reported to gauge the effect of bond compression in the TCNE\(^{--}\) molecule itself.

II. EXPERIMENT

Samples 1–3 were prepared according to procedures described in Refs. 17 and 20–22. All studies were performed on powder samples that were loaded, transferred, and measured under inert conditions (<1 ppm H\(_2\)O and O\(_2\)).

Polycrystalline powder samples of 1–3 with particle size <10 \(\mu\)m were loaded in a symmetrical diamond-anvil cell (DAC) with silicone oil as the pressure transmitting medium, and a small amount (< 5%) of ruby powder for pressure measurements. Diamond anvils with 350 \(\mu\)m culets were used for compression; spring-steel gaskets with sample chamber diameters of \(\sim 150 \mu\)m contained the sample, ruby, and silicone oil mixture between the diamonds. Raman spectra were collected in a backscattering geometry. The 514.5 nm line of an argon ion laser was used for excitation, with 27 mW incident on the diamond anvil. A Kaiser supernotch plus filter was used to separate Rayleigh scattering from the Raman-scattered light, which was dispersed with a Spectrapro 500i spectrograph and detected with a Spec-10 liquid-nitrogen-cooled CCD detector. Raman spectra were collected with a resolution of 2 cm\(^{-1}\) up to a pressure of 8 GPa.

The pressure-dependent structure of compound 2 was probed using synchrotron-based powder diffraction for the sample within a DAC. In situ X-ray diffraction data (\(\lambda = 0.60666 \text{\AA}\)) were collected at the 1-BM beamline at the Advanced Photon Source, Argonne National Laboratory, in combination with a Perkin-Elmer amorphous silicon area detector. Room temperature diffraction patterns for DAC-loaded sample 2 were recorded at \(\sim 50\) different pressures in the range of 0–2 GPa. Polycrystalline NaCl was included as an internal pressure marker,\(^{23}\) and perfluoro(butyltetrahydrofuran) (Fluorinert, FC-75) was used to mediate hydrostatic compression (hydrostatic limit: 1.2 GPa). The raw images were processed within Fit-2D,\(^{24}\) refining the sample-to-detector distance and tilt of the detector relative to the beam based on the data obtained for a LaB\(_6\) standard. Lattice parameters were determined from Le Bail fits to the diffraction data within GSAS.\(^{25}\)

Pressure-dependent magnetic susceptibility data were collected with a Quantum Design MPMS-7XL SQUID using a piston-based pressure cell (MCell 10, EasyLab Industries, with maximum pressure of 1.2 GPa). Polycrystalline sample 2 was loaded in the cell with Daphne oil pressure transmitting fluid and a tin wire as a pressure standard. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization temperature dependencies at 10 Oe were collected for pressure loadings up to 1.02 GPa. The remanent magnetization was collected at zero field on warming, after cooling the sample to 2 K at 100 Oe.

III. RESULTS AND DISCUSSION

The Raman spectra of isolated TCNE\(^{--}\) anion in \([\text{Bu}_4\text{N}]\text{TCNE}\) at different pressures are shown in Figure 1. The isolated TCNE molecule and its anion radical possess a D\(_{2h}\) symmetry, and 11 out of 12 predicted Raman active modes have been observed and assigned previously.\(^{26,27}\) All five \(a_g\) modes at 2195, 1420, 613, 539, and 135 cm\(^{-1}\) related to C\equivN, C=C stretching, two C=C=N bending and (NC)--(CN) scissoring modes,\(^{26,27}\) as well as less characteristic 249, 557, 2126 cm\(^{-1}\) \(b_2g\), and 440 cm\(^{-1}\) \(b_3g\) modes, can be readily identified up to 5 GPa, albeit blueshifted comparing to the ambient pressure spectrum.\(^{26}\) In the region of \(v_{C=C}\) stretching a less intense band at 1429 cm\(^{-1}\) (at ambient pressure) is observed, which is not expected in the first-order Raman spectrum, and, therefore, could be interpreted as a combination band.\(^{18}\) Another unexpected relatively weak band is observed at 2186 cm\(^{-1}\) in the \(v_{C\equivN}\) region. It could be a manifestation of the Raman inactive \(b_{3g}\) mode due to a slight deviation of the TCNE anion symmetry from D\(_{2h}\) in the solid.

The frequencies of all Raman modes, as well as their full width at half maximum, increase with increasing pressure up to \(\sim 5\) GPa, and this effect is fully reversible. It should be noted that the frequencies of bands at 1429 cm\(^{-1}\) and 2186 cm\(^{-1}\) increase also with pressure, but at a much smaller rate than the adjacent \(a_g\) bands. Consequently, the band at 2186 cm\(^{-1}\) becomes much better resolved, while the band at 1429 cm\(^{-1}\) totally overlaps with the \(v_{C\equivN}\) peak as pressure increases. We focused our study on the two most pressure (and ligand-to-metal charge transfer, \textit{vide infra}) sensitive characteristic stretching modes, i.e., \(v_{C\equivN}\) at 1420 cm\(^{-1}\) and \(v_{CN}\) at 2195 cm\(^{-1}\). Their pressure peak frequency dependencies are shown in Figure 2.

A linear frequency increase with pressure for both \(v_{C\equivN}\) and \(v_{C\equivN}\) modes with practically the same rates of \(\partial\nu/\partial P = 7.53\pm0.24\) and 7.49±0.57 cm\(^{-1}/\)GPa, respectively, was also observed. Above \(\sim 1.8\) GPa both slopes significantly

FIG. 1. Raman spectra of isolated TCNE\(^{--}\) in [Bu\(_4\)N][TCNE] at different pressures.
decrease to 5.0 and 2.5 cm$^{-1}$/GPa, respectively, most probably indicating a phase transformation. It should be noted that the corresponding $\partial \omega / \partial P$ values of 4.89 and 5.67 cm$^{-1}$/GPa for the neutral TCNE (monoclinic phase, up to 2.5 GPa) are substantially lower than those for the [TCNE]$^-$ in accord with the expected softening of C=C and C≡N bonds due to populating of antibonding $\pi^*$ molecular orbital that is localized over the central $sp^2$ carbon atoms ($\sim 1/2$ e) and the terminal nitrogen atoms ($\sim 1/8$ e each). Since both $\nu_{C\equiv N}$ and $\nu_{C=C}$ vibrations are very characteristic, it is conceivable to assume that the pressure induced frequency shift is the result of the corresponding bond length shortening and, therefore, better orbital overlap. To model this process, TCNE$^-$ anion geometry was optimized using unrestricted hybrid density functional theory (DFT) with the Dunning/Huzinaga valence double zeta basis set (UB3LYP/D95V) in the GAUSSIAN 03 software package. The molecular vibration spectra were calculated for the optimized C≡N bond length as well as for nine other geometries, in which the bond length was consecutively decreased by 0.001 Å. As expected, the frequency shift depends linearly on the bond length compression $\Delta L$ resulting in $\partial \omega / \partial L$ value of $\sim 533$ cm$^{-1}$/Å. On the basis of Rietveld analysis, the TCNE C=C bond length at ambient pressure and 2.1 GPa was estimated to be 1.32 ± 0.01 and 1.34 ± 0.05 Å, respectively. Presuming linear pressure dependence, the $\partial L / \partial P$ parameter for C=C bond can be estimated as $\sim 10^{-2}$ Å/GPa. Calculated on the basis of our DFT, the $\partial \omega / \partial P$ value of 5.33 cm$^{-1}$/GPa is reasonably close to the experimentally observed 7.5 cm$^{-1}$/GPa. Consequently, it might be concluded that the experimentally obtained $\partial \omega / \partial P$ for TCNE$^-$ molecule can be used as a measure of the effect of bond compression on the corresponding characteristic optical phonon frequencies in the M-TCNE magnets.

The Raman spectra of (I) at 0.19, 0.49, 0.80, 1.65, 2.36, and 3.69 GPa in the $a_g$ regions are shown in Figure 3. Pressure
The frequency of the CN bond more than in the isolated TCNE$^-$ causing more rapid growth of $\nu_{C\equiv N}$ frequency with pressure.

The preliminary results on magnetic behavior of 1 under pressure up to 1.5 GPa are in accord with our findings on $\nu_{C\equiv C}$ frequency evolution with pressure. It was shown that there are at least three pressure intervals in which the magnetic ordering temperature, $T_c$, changes with pressure in a markedly different way. As pressure is increased up to $\sim 0.4$ GPa, the $T_c$ rises only slightly ($\sim 3$ K/GPa) in agreement with the observation of minor changes in metal-to-ligand charge transfer, thus, implying that insignificant changes in magnetic exchange occur between $3d$ electron of Fe ion and $\pi^*$ ligand electron. In the range $0.4 < P < 0.8$ GPa, $T_c$ increases substantially faster by the rate of $\sim 30$ K/GPa reaching $T_c$ of 106 K. In this range $\partial \nu_{C\equiv P}$ value doubles implying a substantial rise in magnetic exchange. Above 0.8 GPa both $T_c$ and $\partial \nu_{C\equiv P}$ become almost pressure insensitive; it should be noted that the magnetization value decreases with pressure, and above 1.3 GPa it drops several orders of magnitude suggesting a possible phase transition.

The Raman spectra of 2 at 0.22, 0.30, 0.40, 0.58, 0.80, 1.07, 1.79, 2.6, and 3.3 GPa in the $a_g$ regions are shown in Figure 5. Pressure dependences of the $\nu_{C\equiv C}$ and $\nu_{C\equiv N}$ peak frequencies are shown in Figure 7. The $\nu_{C\equiv C}$ frequency initially increases with pressure; however, between 0.2 and 0.4 GPa its value changes within 1 cm$^{-1}$ experimental error (1448.6 $\pm$ 0.5 cm$^{-1}$). A significant $\nu_{C\equiv C}$ frequency shift ($\sim 3$ cm$^{-1}$ with respect to 0.4 GPa value) is observed at 0.58 GPa, which corresponds to $\partial \nu_{C\equiv P}$ of 16.7 cm$^{-1}$/GPa growth rate. Similarly, practically no pressure dependence of magnetic ordering temperature, $T_c$, was also observed in this pressure interval (vide infra).

With the further pressure increase the $\partial \nu_{C\equiv P}$ rate demonstrates a tendency to decrease, and above $\sim 1.8$ GPa the frequency shift is linear with pressure ($\partial \nu_{C\equiv P} \sim 3.5$ cm$^{-1}$/GPa). The frequency of the $\nu_{C\equiv N}$ mode grows almost linearly with pressure up to $\sim 1.0$ GPa. In this pressure range, growth rate is 220% higher ($\partial \nu_{C\equiv P} = 14.6$ cm$^{-1}$/GPa) than similar value for the corresponding ion mode. Above 1 GPa the $\nu_{C\equiv N}$ mode frequency growth rate saturates, and above $\sim 1.8$ GPa
FIG. 5. Raman spectra of [Mn(TCNE)(NCMe)2]SbF6 in the a_g mode regions at different pressures.

the frequency becomes pressure independent suggesting a phase transformation.

Pressure-induced changes in the orthorhombic lattice of [Mn(TCNE)(NCMe)2]SbF6 are shown in Figure 6. The volume of the unit cell varies continuously through the whole pressure range. Using the EOS-FIT v 5.2 program by Angel, a Birch-Murnaghan equation of state (1) was fit to the P-V data to give the bulk modulus \( K_0 \) of 10.4(16) GPa, and \( K' \) of 12(5). This \( K_0 \) value is similar to the \( K_0 \) value of 15 GPa reported for FePM2Cl2 (PM = pyrimidine/C4N2H4), i.e., a molecule-based magnet (\( T_c = 6.7 \) K), in which Fe(II) ions are connected via :N–CH–N: fragments of the conjugated pyrimidine rings forming a three-dimensional network. The slightly lower \( K_0 \) value in 2 reflects the two-dimensional character of the Mn \( \mu_4 \)-TCNE (the ligand bridging four Mn\(^{2+}\) ions) inorganic polymer network.

In the crystal structure of 2 each Mn ion is octahedrally coordinated to a CN group nitrogen of four \( \mu_4 \)-TCNE\(^{-} \) ligands forming a layer and two apical MeCN ligands. Due to the canting of the adjacent MnN\(_6\) octahedron C\(_4\) axis by \( \pm 12^\circ \) with respect to the crystal ac plane, the TCNE anions undulate about this plane remaining roughly parallel to it (see Figure 6, inset B), with a and c crystallographic axes coinciding with two C\(_2\) symmetry axes of TCNE molecule (see Figure 6, inset A) and the b axis being perpendicular to the molecular plane. The TCNE remains relatively rigid up to \( \sim 1 \) GPa, especially along c axis with some compression (\( \sim 1.2\% \)) along a axis that is parallel to C=C bond direction. Interestingly, none of the lattice constants demonstrate abrupt changes, thus suggesting that the structural motif remains relatively intact.

However, it should be noted that the non-monotonic \( \nu_{C=C} \) mode frequency variation with pressure in 2, as well as the high rate of \( \nu_{C=N} \) stretching mode frequency increase with pressure (Figure 7), suggests that some structural changes within Mn \( \mu_4 \)-TCNE layer may take place. At the ambient

FIG. 6. Pressure-induced changes in the [Mn(TCNE)(NCMe)2]SbF6 lattice constants: a (▲); b (■); c (●) and unit cell volume V (♦); dotted line is a fit to Eq. (1). (Inset) Views along b-axis (a) and a-axis (b).
pressure the layer buckling manifests itself by a slight deviation of the TCNE molecule from D_{2h} symmetry, i.e., there is a dihedral angle of \( \sim 170^\circ \) between two symmetrical planes formed by two vinyl and two nitrile carbons (Figure 6, inset A). In addition, the N≡C–C fragments are slightly bent, forming an angle of \( \sim 169^\circ \) between N≡C and C–C bonds.

Since the XRD experiments under pressure have shown practically no lattice shrinkage along c-axis up to 1 GPa, no additional buckling is expected. We speculate that the lattice compression along the a-axis causes shortening of both C=C and N≡C bonds and may subsequently increase the Mn–N≡C and N≡C–C bond angles (both \( 169^\circ \)) toward \( 180^\circ \). Both bond length and/or bond angle changes may facilitate better Mn and N lone pair orbital overlap\(^{35}\) accompanied by a partial withdrawal of anti-bonding charge density from the C≡N bond, thus causing a significant increase of the \( \nu_{\text{C}=\text{C}} \) frequency growth rate with pressure compared to that for the isolated TCNE ion.

It should be noted that a significant intensity redistribution between \( a_g \) and \( b_{2g} \) C–C≡N bending modes (551 and 567 cm\(^{-1}\), respectively, at ambient pressure) was observed upon pressure application. These changes are clearly seen above 0.6–0.8 GPa (Figure 5) indicating some molecular geometric changes that indirectly support the mechanism of intramolecular structural changes proposed above. Interestingly, similar behavior of these bending modes, albeit at a much higher pressure (>4 GPa), is observed in the isolated TCNE\(^{+}\) ion (see Figure 1) implying that this molecule is significantly less robust when coordinated within the buckled \( \mu_4\)-TCNE layers.

The initial increase of the \( \nu_{\text{C}=\text{C}} \) mode frequency with pressure (Figure 7), as well as its rapid growth at \( P > 0.6 \) GPa, may indicate some charge transfer changes (via \( d-\pi^* \) orbital overlap or \( \pi\)-backbonding) and, consequently, better magnetic exchange and \( T_c \) enhancement with pressure. The mechanism of almost total compensation of the \( \nu_{\text{C}=\text{C}} \) mode frequency growth with pressure in the 0.2 < \( P < 0.5 \) GPa range is unclear. We speculate that it may be related to some previously mentioned small structural (bond length and/or bond angle) changes that can create favorable conditions for \( \pi\)-backbonding and partially reverse metal-to-ligand charge transfer. Evidently, more detailed Raman measurements combined with XRD study in this pressure region would be of great importance.

To evaluate the effect of pressure on \( T_c \) in 2 and correlate it with the Raman experiment prediction, the measurement of magnetization vs. temperature at various pressures was performed., since the temperature of a remanent magnetization (\( M_r \)) onset is a very good marker of the system’s magnetic ordering.\(^{36}\) Temperature dependences of the remanent and low field (10 Oe) zero-field-cooled magnetizations (\( M_{ZFC} \)) of 2 in the range of \( 10^{-4}\cdots1.2 \) GPa are shown in Figures 8(a) and 8(b), respectively. Since the \( M_{ZFC} \) and \( M_{FC} \) magnetizations coincide in the transition region, we plotted only \( M_{ZFC} \) curves, and the corresponding \( M_{FC} \) curves are shown in Ref. 28.

Interestingly, the temperature of the \( M_r(T) \) onset (marked by arrow) and the temperature at which a tangent at the maximum slope of \( M_{ZFC}(T) \) curve (dotted line) intercepts the T-axis are very close, and both indicate magnetic ordering (\( T_c \)). The pressure dependence of \( T_c \) is shown in the inset. The \( T_c \) values extracted from the \( M_{ZFC}(T) \) curves collected on a

![Fig. 7. Pressure dependence of \( \nu_{\text{C}=\text{N}} \) (o) and \( \nu_{\text{C}=\text{C}} \) (•) peaks frequencies in \([\text{Mn(TCNE)(NCMe)}_2]\text{SbF}_6\).](image)

![Fig. 8. Temperature dependence of the remanent (a) and zero-field-cooled magnetizations (b) of \([\text{Mn(TCNE)(NCMe)}_2]\text{SbF}_6\) at different pressures. The inset is \( T_c \) vs. pressure for two different samples (see text).](image)
different sample of $\mathbf{2}$ at ambient pressure as well as 0.2, 0.4, 0.48, and 0.54 GPa at 50 Oe$^2$ are also included in the inset plot. A slight shift of $T_c$ at ambient pressure ($\sim$ 1 K) is most probably related to a higher magnetic field used in these $M_{ZFC}(T)$ measurements. However, it is clear that in the 0.22–0.54 GPa range $T_c$ is practically pressure insensitive, which is qualitatively in accord with the behavior of the $\nu_{C=N}$ frequency that remains unchanged. To elucidate the mechanism of this unusual pressure dependence in the region, a more detailed study is needed, including XRD experiments.

To evaluate the $T_c$ response to pressure application in different magnetic materials, the Grüneisen parameter is commonly used, which is derived from the experimental pressure dependencies of compressibility and the ordering temperature, with

$$G_m = -d[\ln(T_c)]/d\omega = K_0 d[\ln(T_c)]/dP,$$

where $\omega$ is a volume strain and $K_0$ is a bulk modulus. Assuming that the volume compression of $\mathbf{2}$ in the vicinity of $T_c$ is linear with pressure up to 1.0 GPa and using $K_0$ value at ambient temperature, we estimate $G_m$ value to be $\sim$0.5 close to an ambient pressure and $\sim$0.4 close to 1 GPa. The $G_m$ parameter values for different magnets are shown in Table I.

The $G_m$ value is about 1 for normal metals; however, its absolute value is significantly higher ($G_m\sim$100) for heavy fermion metals and and rare earth perovskite manganites due to a strong volume dependence of the narrow electronic bands.

### Table I. The $G_m$ parameter values for some magnetic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (K)</th>
<th>$d\ln T_c/dP$ (K/Gpa)</th>
<th>$dT_c/dP$ (GPa$^{-1}$)</th>
<th>$K_0$ (GPa)</th>
<th>$\nu_{C=N}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(TCNE)SbF$_6$</td>
<td>75</td>
<td>3–4</td>
<td>0.04–0.05</td>
<td>10.4</td>
<td>12(4)</td>
</tr>
<tr>
<td>Fe(PM)$_2$Cl$_2$</td>
<td>6.3</td>
<td>3–4</td>
<td>0.48–0.64</td>
<td>15</td>
<td>Not reported</td>
</tr>
<tr>
<td>Ni</td>
<td>631</td>
<td>4</td>
<td>0.00634</td>
<td>181</td>
<td>5.2(0.3)</td>
</tr>
<tr>
<td>Mn(TCNE)SbF$_6$</td>
<td>75</td>
<td>3–4</td>
<td>0.040–0.05</td>
<td>54$^a$</td>
<td>12(4)</td>
</tr>
</tbody>
</table>

$^a$Calculated using the compressibility of $\mu_4$-TCNE$^{2-}$ layer (ac plane).

Another possible scenario of non-monotonic $T_c$ vs. $P$ dependence may involve a small TCNE bond angle variation with pressure disrupting the super-exchange pathway.

It may be concluded, for the first time the XRD experiments under pressure established the bulk modulus and compression anisotropy of the 2D magnet $\mathbf{2}$. By monitoring the Raman response of layered magnets $\mathbf{1}$ and $\mathbf{2}$ it was shown that the evolution of $\nu_{C=N}$ frequency correlates well with the magnetic exchange and $T_c$ variations of these materials under pressure. In contrast, the correlation between the $\nu_{C=N}$ frequency and $T_c$ is much more complex despite the fact that some unpaired $\pi^*$ electron density (0.125 e) is localized on nitrile N=C group. The compression of the M–NC bond with pressure (<0.5 GPa) does not result in a $T_c$ increase suggesting a more complex relationship between bond length and magnetic exchange. The obtained results confirm the effectiveness of pressure experiments in studying the mechanism of magnetic ordering in molecule based magnets. They provide a better understanding of the peculiarity of the super-exchange interaction, which is indispensable for establishing the structure-magnetic property correlations in this class of magnetic materials.

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28 See supplementary material at http://dx.doi.org/10.1063/1.4770057 for Figures S1–S3 and Table S1.