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Disorder–order transitions in the perovskite metal–organic frameworks [(CH₃)₂NH₂][M(HCOO)₃] at high pressure[†]

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High-pressure single-crystal X-ray diffraction was performed on dimethylammonium metal formates (DMAMF), [(CH₃)₂NH₂][M(HCOO)₃] where M = Mn²⁺, Fe²⁺, and Cu²⁺, in order to compare the high-pressure phases with the known low-temperature ferroelectric (for DMAMnF) and multiferroic (for DMAFeF) phases. The ambient phases of dimethylammonium metal formates were stable up to 5.53(8), 5.7(3), and 7.3(2) GPa for DMAMnF, DMACuF, and DMAFeF, respectively. At higher pressures, phase transitions occurred that were initiated by the structural distortions of the metal formate framework. The distortions are accompanied by loss of dynamic disorder of dimethylammonium (DMA) in the DMAMnF and DMAFeF compounds, resulting in an antiferroelectric arrangement of the DMA cations. For DMACuF, the Jahn–Teller distortion is reduced upon compression up to ~3.5 GPa; the inability to continue reducing the Cu–O bonding distances beyond this pressure could be responsible for triggering a distortive transition of the copper formate framework at 5.5 GPa. In the case of DMAFeF, the experiment was in addition conducted with a penetrating pressure-transmitting medium (PTM) that resulted in a disorder–order transition of the DMA cation at lower pressures with $p = 4.0(6)$ GPa due to the PTM inclusion.

1 Introduction

The metal formates templated by protonated amines have attracted interest over the years due to the coexistence of electric and magnetic orders,^{1–7} which within certain compositions, can be coupled.^{8–10} In particular, one of the most studied of this family includes the dimethylammonium metal formates.^{6–8,11–17} Their interesting physical properties are observed upon cooling, with a disorder–order transition at 160–270 K that originates from the loss of dynamic disorder of the dimethylammonium cation,^{6,13,16} and an antiferromagnetic ordering for the magnetically active M²⁺ cations below 35–8 K (transition temperatures

vary depending on the M²⁺ cation).¹⁸ Crystal structure analysis suggests that at ambient conditions, the dimethylammonium cation is dynamically disordered over three positions and upon cooling adopts one orientation, creating an electric dipole.¹⁹ The disorder–order transition of the DMA cation is also supported by NMR, electron paramagnetic resonance studies, and Raman and IR data^{15,20–23} although these reveal that the methyl groups of the DMA cation can continue to rotate even within its ordered orientation.^{15,20,22} Neutron total scattering measurements that probe the local structure suggest that the framework distortion is also an important parameter in the ordering of the DMA cation.²⁴

Pyroelectric measurements have been reported for [(CH₃)₂NH₂][M(HCOO)₃], where M = Mn²⁺, Fe²⁺, and Co²⁺, allowing electric polarisations, which are related to the ordering of the dimethylammonium cation, to be determined.^{7,8,25–27} For DMAMnF, single-crystal measurements along the [012] direction gave polarisation values of 1.5–2.4 $\mu\text{C cm}^{-2}$ (using an electric field (E) of 7–8 kV cm^{-1}).^{7,26} Surprisingly, DMAFeF gives a much lower polarisation along the same [012] direction at 0.0018 $\mu\text{C cm}^{-2}$ ($E = 5.4 \text{ kV cm}^{-1}$).⁸ Polarisation electric field loops conducted on polycrystalline pellets of DMAMnF and DMACoF show the ferroelectric hysteresis loops with a polarisation saturation of 0.3 $\mu\text{C cm}^{-2}$ ($E = 3.6 \text{ kV cm}^{-1}$) and 1 $\mu\text{C cm}^{-2}$ ($E = 10 \text{ kV cm}^{-1}$), respectively.^{25,28} These differing

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[†] Electronic Supplementary Information (ESI) available: Twin lattices for DMAMF high-pressure phases, DMA orientations in the HP phase, DMAFeF-II structure within the helium loading, DMAMnF-II structure, variable-pressure lattice parameters, conversion of HP to ambient lattice parameters for DMAMFs, and Fe–O bonding distances. CIFs are provided for DMACuF, DMACuF-II, DMAFeF, DMAMnF for all pressures studied, and for DMAFeF-II at 7.87 GPa. The structures upon compression have been deposited to the CCDC with the numbers 1837735–1837748 (for DMACuF), and 1837754–1837769 (for DMAFeF and DMAMnF). See DOI: 10.1039/b000000x/

polarisation values are much lower than the value calculated from *ab initio* calculations at $7.3 \mu\text{C cm}^{-2}$ for the DMAMnF compound.²⁷ The discrepancy could arise from the formation of domain structures,²⁷ especially as the compound is known to show twinning within the ferroelectric phase.¹⁹ However, the polarisation of the DMAFeF compound is magnitudes lower than for DMAMnF and DMACoF, which could suggest different dynamics involving the ordering of the dimethylammonium cation that results in greater disorder. Indeed, Raman and IR studies on DMAFeF and DMAZnF have shown broader peaks and slower transition dynamics for DMAFeF compared to DMAZnF that could be linked to greater disorder in the Fe analogue.²³ These ordered states are important as they could explain the reason for the coupling between the magnetic and electric orders, only observed for DMAFeF in its magnetic state.⁸

While these phenomena are interesting from a technological point of view, for e.g. memory storage devices, the temperatures needed for the multiferroic behaviour in these materials are below 35 K, and the coupling between the magnetic and electric orders is very weak. In an effort to explore different structural configurations with potentially improved physical properties, we study the dimethylammonium metal formates under pressure. The process of reducing the volume of the material can induce both changes in the electric and magnetic ordering through the loss of dynamic disorder of the dimethylammonium cation due to reduced space, and by shortening of the metal–metal distances, respectively. Previous high-pressure Raman studies on DMAMFs have already shown many transitions up to ~ 10 GPa.^{29,30} In particular, three transitions were identified for DMAMnF and DMAMgF (at 1.6(5), 3.7(5), and 5.9(9) GPa for DMAMnF and at 1.9(3), 3.7(3), and 5.4(3) GPa for DMAMgF),^{29,30} and two transitions for DMAcDF (at 1.6(4) and 3.5(1) GPa);³⁰ note that the average of the pressure points before and after the transition were employed, with the error indicating the pressure step. Many other spectroscopic studies have been carried out on related protonated-amine or ammonium metal formates that show transitions under compression,^{5,31–36} however few studies have investigated the structural distortions using diffraction.^{37,38}

Here we concentrate purely on the structural evolution with pressure, and study the $[(\text{CH}_3)_2\text{NH}_2][\text{M}(\text{HCOO})_3]$ compounds where $\text{M} = \text{Mn}^{2+}$, Fe^{2+} , and Cu^{2+} . In particular we follow the behaviour of the dimethylammonium cation under pressure and any ordering that could take place with its consequence on the metal formate framework. In the case of the DMAcDF compound, the DMA cations are already ordered at ambient conditions, so we use this compound as, firstly, a reference to compare to DMAMnF and DMAFeF, and secondly to investigate the effect of pressure on the Jahn–Teller distortion, for which in related copper formates can give rise to multiferroic properties.³⁹

2 Experimental Section

2.1 Synthesis

The dimethylammonium metal formate single crystals were grown from slow diffusion methods within a Schlenk tube using the synthesis strategy from Ref. 40. First 0.5 M of formic

acid and 0.5 M of dimethylamine (2 M in methanol) are mixed with 5 mL of anhydrous methanol and placed at the bottom of the Schlenk tube. Onto this solution, a 0.1 M solution of anhydrous metal(II) chloride dissolved in anhydrous methanol was carefully pipetted. Small crystals would start to grow after a few hours. After a week, the solution was filtered and the crystallites recovered and kept under inert argon atmosphere (especially important for the DMAFeF crystals that can oxidise in air).

2.2 High-pressure diffraction

High-pressure single-crystal X-ray diffraction on dimethylammonium metal formates was measured at the ID15B beamline of the European Synchrotron Radiation Facility, Grenoble up to 10 GPa using monochromatic X-ray radiation ($\lambda = 0.411189 \text{ \AA}$). Membrane driven LeToullec type diamond anvil cells (DACs) were used, equipped with Boehler-Almax anvils. Stainless steel was used as the gasket material, and neon was loaded as the pressure-transmitting medium. Diffraction patterns were collected with a Mar555 flat panel detector using steps of 0.5° oscillations over a total ω scan range of 64° and 76° about the vertical axis for the DACs with opening angles of $\pm 32^\circ$ and $\pm 38^\circ$, respectively. The pressures were measured using the ruby fluorescence method before and after each diffraction measurement. The average of both pressure values was used and the variance was employed to estimate the errors associated with the pressure measurement, in addition to the ± 0.05 error to account for the error in the ruby fluorescence method in the pressure range below 10 GPa.⁴¹ Lattice parameter determination and integration of the reflection intensities were performed using the *CrysAlisPro* software.⁴²

For these experiments, several crystals were loaded within the same DAC as progressive radiation damage could inhibit the phase transition. Thus a crystal was measured up until the phase transition, and the other crystals were measured once or twice before the transition point. This ensured that some crystals had received less radiation damage than the one used to measure up to the transition point. For DMAcDF, three single crystals were loaded. For DMAFeF, two separate loadings were performed. The first contained two crystals that were measured both up to 8 GPa and could determine the pressure dependence of the ambient phase well, but the diffraction quality of the high-pressure phase was not good enough to solve the structure. A second loading was prepared with three crystals which were measured at ambient and then directly at 5.5 GPa before the phase transition. Subsequent measurements were performed up to 10 GPa on all three crystals. For DMAMnF, two crystals were loaded and both measured at ambient conditions. Subsequently, one was measured up to the transition point and the other within the high-pressure phase.

The use of helium as the pressure medium was also tested for DMAFeF at the beamline P02.2 at DESY, Hamburg up to 6 GPa using monochromatic X-ray radiation ($\lambda = 0.28874 \text{ \AA}$). A BX90 diamond anvil cell was used with rhenium as the gasket. Diffraction patterns were collected with a PerkinElmer area detector using steps of 0.5° oscillations over a total ω scan range of 76° about the vertical axis.

3 Results

4 DMACuF

The ambient structure of dimethylammonium copper formate (DMACuF) is the only compound within the $[(\text{CH}_3)_2\text{NH}_2][\text{M}(\text{HCOO})_3]$ series that does not display dynamic disorder of the dimethylammonium cations. This may arise due to the Jahn–Teller (JT) distortion of the Cu^{2+} , as the hydrogen bonding from the N–H units form with the oxygen of the formate that belongs to the long M–O bond (2.499 Å, compared to the four equatorial M–O bonds at 1.974 Å). The weaker M–O bond that arises from the JT distortion thus allows greater negative charge to reside on the O, allowing for a stronger N–H...O bonding, consequently giving rise to an ordered DMA cation. The ambient structure was refined in the space group $I2/a$ (with the cell parameters $a = 11.4256(2)$ Å, $b = 8.7357(4)$ Å, $c = 8.8578(3)$ Å, $\beta = 96.180(2)^\circ$), preferred over the $C2/c$ standard setting because the β angle is closer to 90° , as was first determined by Ref. 44.

In order to obtain the unique behaviour of the unit cell compression in the ambient monoclinic $I2/a$ phase, the pressure dependence of the principal axes were calculated using PASCAL [Fig-

ure 1].⁴³ The principal axes $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$ are related to the lattice parameters by the following relations: $\mathbf{x}_1 = -0.211\mathbf{a} + 0.977\mathbf{c}$, $\mathbf{x}_2 = -\mathbf{b}$, and $\mathbf{x}_3 = 0.901\mathbf{a} + 0.434\mathbf{c}$. There is some degree of anisotropy in the compressibility (K) of the principal axes, namely that $\mathbf{x}_1$ is more compressible than the other two directions. This could be due to the formation of the N–H...O hydrogen bonding mainly within the ab -plane thus making these axes more resistant to compression compared to the c -direction which lacks hydrogen bonding and is the main component of $\mathbf{x}_1$.

The main structural rearrangements upon compression in DMACuF involve collective octahedral rotations in order to reduce its volume. For visualising the octahedral tilt evolutions, the Cu–Cu–O angles (consisting of formate-connected Cu^{2+}) were calculated and the pressure dependence of the average values are shown in Figure 2(a). Comparison of these angles at the highest pressure point (9.4 GPa) and at ambient indicate that the octahedra rotate up to 6° upon compression. The two long M–O bonds originating from the Jahn–Teller distortion of the Cu^{2+} (Cu–O_{JT}) are greatly affected by pressure and decrease rapidly upon compression but begin to plateau at a value of ~ 2.3 Å at around 3.5 GPa [Figure 2(b)]. Within the plateau formation, at pressures (p) between $5.36 < p \leq 5.96$ GPa, a phase transition oc-

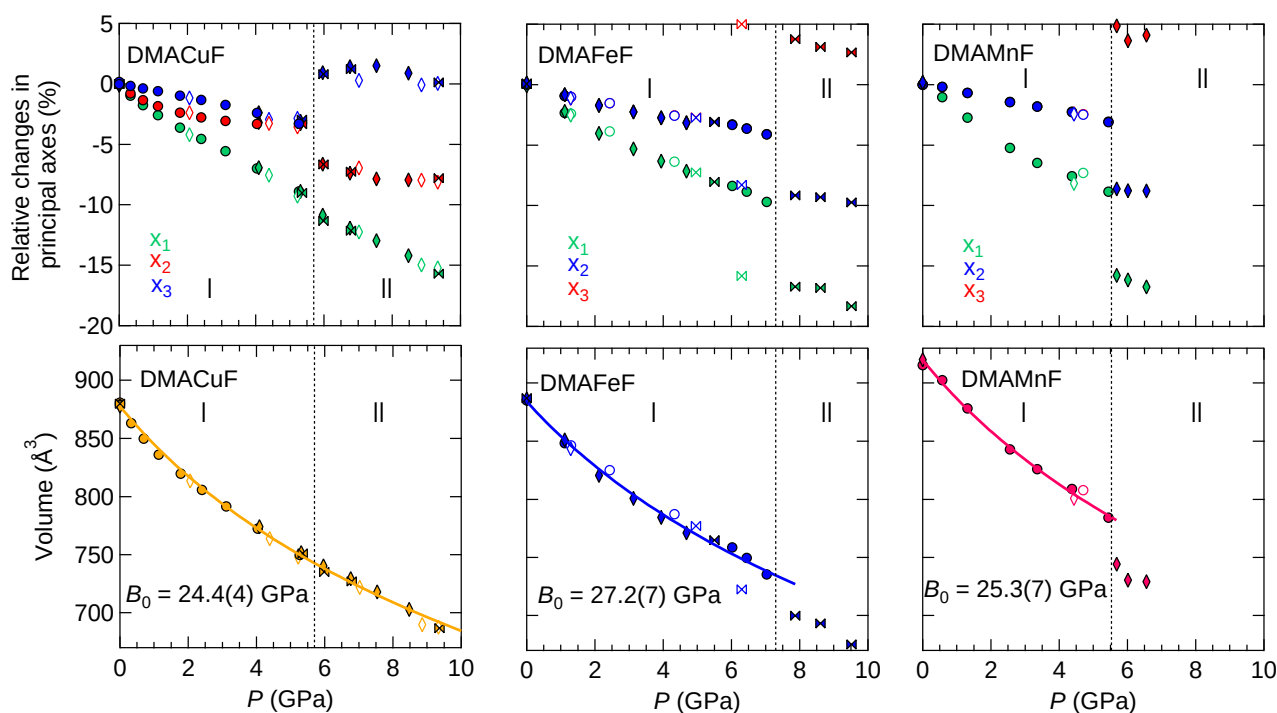


Fig. 1 Relative changes in the principal axes and volumes (within the same monoclinic or triclinic setting, see SI) versus pressure calculated using PASCAL⁴³ for DMACuF (left), DMAFeF (middle), and DAMnF (right). The different symbols represent the different crystals used, and open symbols represent unit cells determined upon decompression. In the case of DMACuF, the unit cell parameters obtained upon decompression are determined from Pawley refinements of wide image scans ($\pm 20^\circ$ continuous oscillation in 2 s). A second-order Birch-Murnaghan equation of state was used to fit the volume dependence with pressure (solid line) for the ambient phases in the case of DMAFeF and DMAMnF, and for both ambient and HP phases for DMACuF. The resulting bulk moduli (B_0) from these fits are given within the graphs of the volume pressure dependence for each compound. The principal axes $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$ are related to the monoclinic/triclinic unit cell setting by $\mathbf{x}_1 = -0.211\mathbf{a} + 0.977\mathbf{c}$, $\mathbf{x}_2 = -\mathbf{b}$, and $\mathbf{x}_3 = 0.901\mathbf{a} + 0.434\mathbf{c}$ for DMACuF, $\mathbf{x}_1 = -0.440\mathbf{a} + 0.898\mathbf{c}$, $\mathbf{x}_2 = 0.713\mathbf{a} + 0.701\mathbf{c}$, and $\mathbf{x}_3 = -1\mathbf{b}$ for DMAFeF, and $\mathbf{x}_1 = -0.438\mathbf{a} + 0.900\mathbf{c}$, $\mathbf{x}_2 = 0.715\mathbf{a} + 0.699\mathbf{c}$, and $\mathbf{x}_3 = -1\mathbf{b}$ for DMAMnF. The colouring of the symbols indicates the maximum axis contribution to the principal axes as follows: blue for the a -axis, red for the b -axis, and green for the c -axis. The dashed line indicates the transition point.

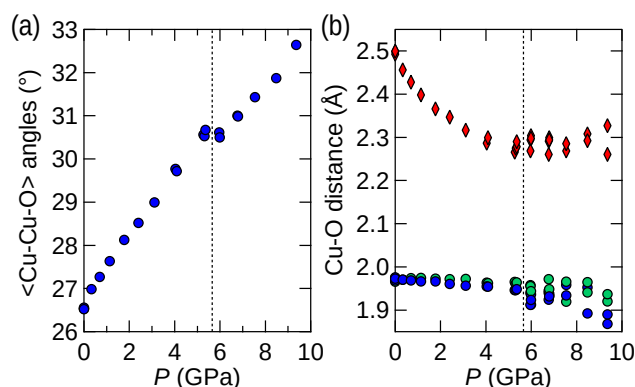


Fig. 2 (a) Average Cu–Cu–O angles that can represent a measure of the tilt angle of the octahedra as a function of pressure. (b) Cu–O bond distances as a function of pressure. The Cu–O_{JT} bond lengths are indicated by red diamond markers and the equatorial Cu–O distances by blue and green circles. The transition point is indicated by the dashed black line.

curs. The close proximity of the transition to the Cu–O_{JT} bond length plateau suggests that the distortion originates from the inability to continue reducing the Cu–O_{JT} bonds for effective volume reduction. Structural transitions have been observed in other Jahn–Teller copper compounds,^{45–47} and interestingly, the transition pressures observed are around 6–8 GPa,^{46,47} similar to the transition pressure of DMACuF.

The high-pressure structure of DMACuF (referred to as DMACuF-II) could be solved and refined in $P\bar{1}$ symmetry [Figure 3]. The transition resulted in the formation of two twin domains, related by 180° rotation about the (0 −0.71 0.71) reciprocal axis [Figure S1]. The unit cell of DMACuF-II is given in Table 1, and its relation to the ambient cell is given by the following matrix

$$\begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}_{P\bar{1}} = \begin{bmatrix} 0.5 & 0 & 0 \\ 0 & 0.5 & 0.5 \\ 0 & -0.5 & 0.5 \end{bmatrix} \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}_{I2/a} \quad (1)$$

The halving of the unit cell along the a -axis in the high-pressure phase gives rise to the occupational disorder of the formate ligands and nitrogen of the dimethylammonium cation in order to keep the topology of the copper formate intact upon the transition, as well as the antiferromagnetic ordering of the dimethylammonium cations [Figure 3]. In order to observe the changes in principal axes of the HP phase in relation to the ambient phase,

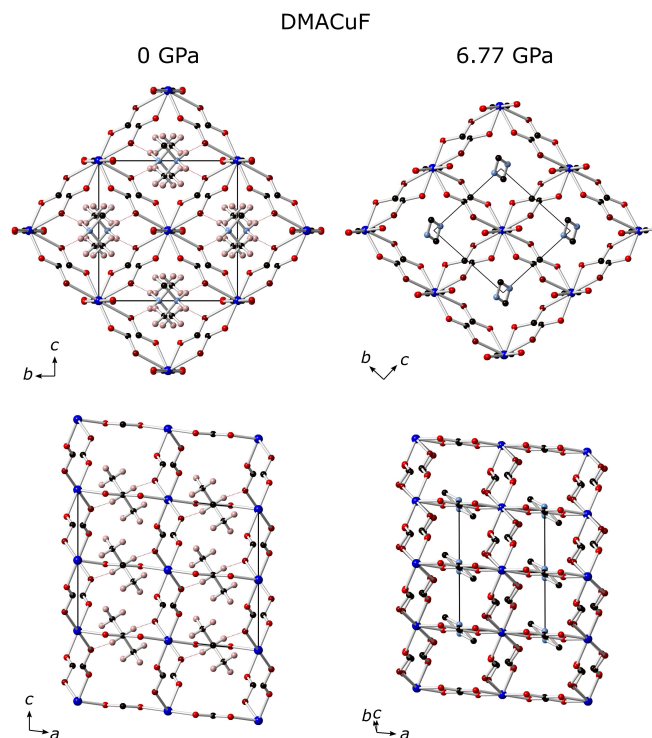


Fig. 3 Crystal structures of DMACuF for both ambient and high-pressure phases (at 0 and 6.77 GPa, respectively). The copper ions are shown as blue, oxygen as red, nitrogen as light blue, carbon as black, and hydrogen as pink. The oxygens with the longer M–O bonding are in darker red. The hydrogen bonding interactions are indicated by the dotted red lines. The unit cell is shown in black.

the unit cell parameters were converted to the equivalent ambient phase unit cell (see SI). Upon the phase transition, there is no detectable discontinuity in the pressure dependence of the volume and a single second-order Birch–Murnaghan equation-of-state can be fitted to the entire pressure range studied [Figure 1]. This behaviour could suggest a second-order phase transition. There is no dramatic structural distortion upon the phase transition, rather a shearing of the square-lattice connectivity as observed down the a -axis, reducing the symmetry to triclinic [Figure 3]. These shearing displacements likely occur due to the inability to continue reduction in volume within the monoclinic symmetry as we observe the principal axis $\mathbf{x}_2$, directly related to the b -axis, that begins to plateau at around 3.5 GPa [Figure 1].

Table 1 Unit cell parameters and space groups (s.g.) of all the DMAMF phases reported in this study. The obverse setting was used for the $R\bar{3}c$ DMAFeF and DMAMnF structures. The asterisks for the M = Fe refers to the compression with helium as the pressure-transmitting medium. A complete list of the unit cell parameters in the whole pressure range are given in SI.

M	s.g.	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)	P (GPa)
Cu	$I2/a$	11.4256(2)	8.7357(4)	8.8578(3)	90	96.180(2)	90	878.97(6)	0
Cu	$P\bar{1}$	5.4601(9)	5.9181(12)	5.784(4)	94.58(4)	90.00(3)	96.582(15)	185.08(13)	5.96(7)
Fe	$R\bar{3}c$	8.2534(2)	8.2534(2)	22.5522(10)	90	90	120	1330.42(9)	0
Fe	$P1$	10.763(11)	8.256(7)	7.985(6)	90.26(6)	91.72(9)	99.47(10)	699.5(11)	7.87(12)
Fe*	$I2/a$	11.685(4)	8.4153(16)	8.2171(17)	90	97.95(3)	90	800.2(3)	4.61(14)
Mn	$R\bar{3}c$	8.33945(16)	8.33945(16)	22.9146(3)	90	90	120	1380.12(4)	0
Mn	$P1$	11.01(3)	8.43(2)	8.130(18)	90.3(2)	92.1(2)	99.3(2)	744(3)	5.69(6)

Within the DMAcF-II HP phase, the framework hinging flexibility is not as dampened by the Cu–formate–Cu bond length decrease as we observe negative linear compressibility (NLC) within the HP phase up to 7.5 GPa ($K_3 = -4.0(8) \text{ TPa}^{-1}$ for p range of 6.0–7.5 GPa). Beyond this pressure, the NLC reverts back to positive linear compressibility (PLC, *i.e.* usual compression). The NLC–PLC switch with pressure has been observed in other flexible framework materials or molecular materials with a hinged-network structure,^{48–51} and originates from the competition between a hinging mechanism and usual bond compression along the hinge lengths.

5 DMAFeF & DMAMnF

DMAFeF and DMAMnF adopt the rhombohedral $R\bar{3}c$ symmetry at ambient conditions with the dynamic disorder of the dimethylammonium cations.^{6,18} Application of pressure should therefore not only affect the metal formate framework, but also the dynamic disorder of the dimethylammonium cations. Compression of the ambient phase gives rise to anisotropic compression for both DMAFeF and DMAMnF [Figure 1], where the c -axis (the principal axis $\mathbf{x}_1$) is twice as compressible as the ab -plane (the

principal axes $\mathbf{x}_2$ and $\mathbf{x}_3$). The compressibilities (K) along each axis are calculated using the equation

$$K_l = -\frac{1}{l} \frac{dl}{dp}, \quad (2)$$

where l is the lattice parameter, and p is the pressure. The linear fits give $K_a = 5.6(2) \text{ TPa}^{-1}$, and $K_c = 18.9(8) \text{ TPa}^{-1}$ for DMAMnF, and $K_a = 7.1(2) \text{ TPa}^{-1}$, and $K_c = 16.3(6) \text{ TPa}^{-1}$ for DMAFeF for the pressure range of 0–5 GPa. This anisotropy arises from the framework angle variations that cause a hinging mechanism, compressing the c -direction and expanding in the ab -plane. However, as the hinging is small ($K_{a\theta} = -5.0 \text{ TPa}^{-1}/K_{c\theta} = +8.4 \text{ TPa}^{-1}$ or $K_{a\theta} = -3.2 \text{ TPa}^{-1}/K_{c\theta} = +5.3 \text{ TPa}^{-1}$ due to hinging alone for DMAMnF and DMAFeF, respectively), the contraction of the M–formate–M links dominate ($K_{M-M} = 10.5 \text{ TPa}^{-1}$ and 10.2 TPa^{-1} for DMAMnF and DMAFeF, respectively). The combination of both structural distortions gives rise to the anisotropy in the compressibilities, although both a - and c -axes exhibit PLC (*e.g.* $K_a = K_{a\theta} + K_{M-M} = 5.5 \text{ TPa}^{-1}$ and $K_c = K_{c\theta} + K_{M-M} = 18.9 \text{ TPa}^{-1}$ for DMAMnF), a phenomenon which has also been observed for the thermal expansion properties of these materials.⁵² The hydrogen

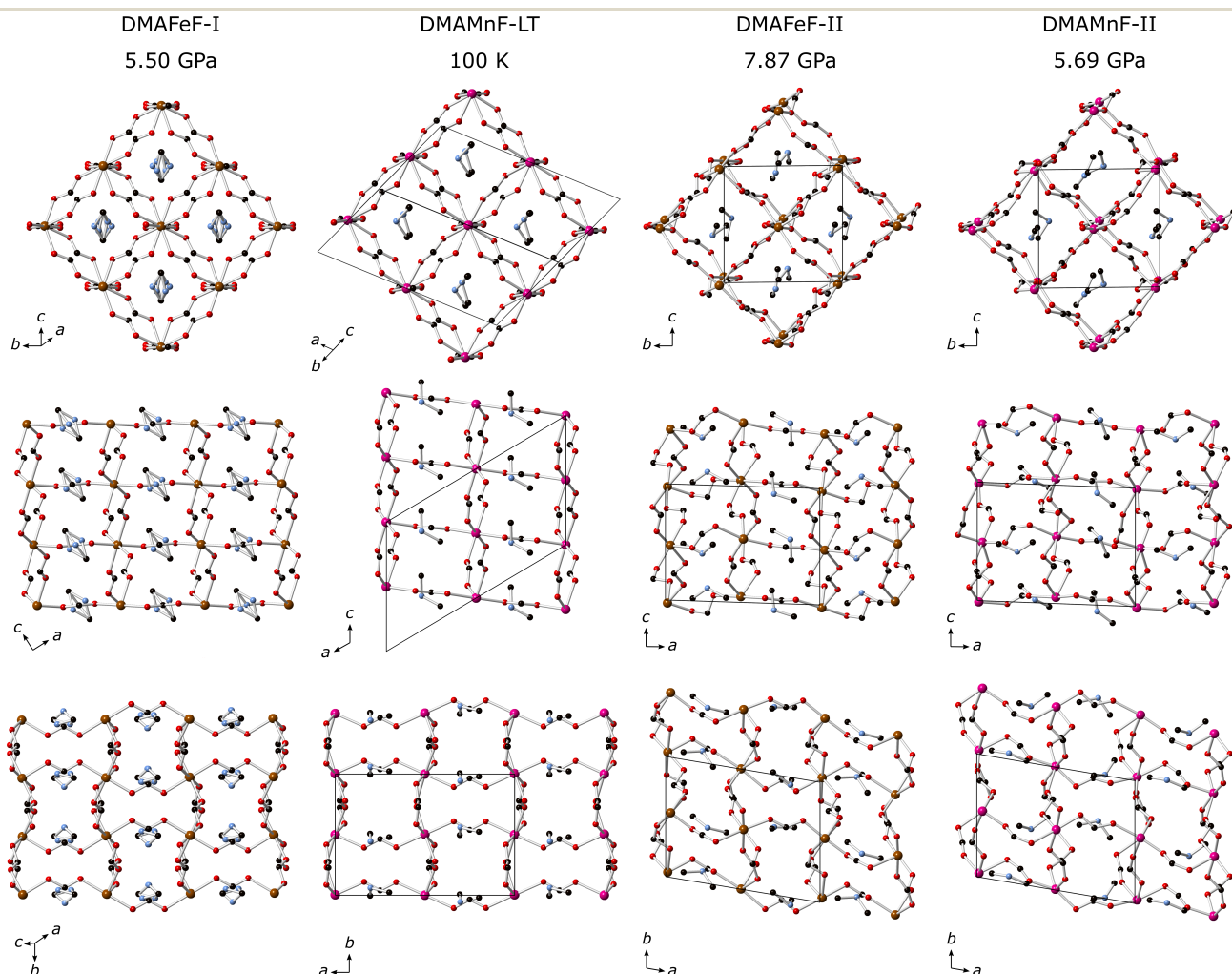


Fig. 4 Crystal structures of DMAMF in the ambient phase (at 5.50 GPa) and low-temperature ferroelectric phase from Ref. 19 in comparison to the high-pressure phases of DMAFeF and DMAMnF.

bonding interactions are within the *ab*-plane and direct the motion of the framework hinging in order to minimise contraction in this plane.

At the pressure $7.10 < p \leq 7.57$ GPa, DMAFeF undergoes a transition from $R\bar{3}c$ symmetry to triclinic $P1$ (DMAFeF-II), resulting in many twin domains [see Table 1 for the HP unit cell]. As the domains were not all equally contributing to the diffraction pattern, the most intense four or three domains were chosen for integration as a twin within *CrysAlisPro*. The three different crystals that were loaded were each measured and from the range of different domains observed from all crystals, six twin domains are thought to be created in each crystal from this transition. Three domains are related by $\pm 120^\circ$ rotations about $(-0.70 \ 0.09 \ 0.71)$ in reciprocal space, and each of these three domains give rise to two further twins from 180° rotation about $(0 \ 1 \ 0)$ [Figure S2].

The relation between the ambient and HP unit cells are given by the following matrix

$$\begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}_{I2/a} = \begin{bmatrix} \frac{4}{3} & \frac{2}{3} & -\frac{1}{3} \\ 0 & 1 & 0 \\ \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{bmatrix}_{R\bar{3}c} \quad (3)$$

This transformation results in the monoclinic $I2/a$ cell of the ambient DMAcF (which is a subgroup of the $R\bar{3}c$ space group), and is directly related to the $P1$ cell upon further distortion of the cell angles and loss of centering, resulting in the triclinic symmetry [Table 1]. The triclinic $P1$ cell of DMAMF-II is a twofold supercell of the primitive rhombohedral lattice. In order to compare the ambient and HP unit cell evolutions, the rhombohedral unit cell was converted into the monoclinic cell using matrix (3) (see SI). The variation in the principal axes of the DMAFeF unit cell (in the monoclinic and triclinic setting) over the entire pressure range are shown in Figure 1.

DMAMnF undergoes a similar high-pressure distortion at a pressure of $5.50 < p \leq 5.56$ GPa. The high-pressure phase exhibited very broad spots that diffracted only up to $1.3 \text{ \AA}$. Consequently, the determination of the twin lattices was challenging, however the following unit cell could be fitted to both the single-crystal data and the extracted powder diffraction profile from the wide image scans $a = 11.01(3) \text{ \AA}$, $b = 8.43(2) \text{ \AA}$, $c = 8.130(18) \text{ \AA}$, $\alpha = 90 = 1.33.3(2)^\circ$, $\beta = 92.1(2)^\circ$, and $\gamma = 99.3(2)^\circ$ (at 5.69 GPa), similar to DMAFeF-II [Table 1]. The equivalent monoclinic cell for DMAMnF was calculated for the rhombohedral phase using matrix 3 (see SI) in order to compare the unit cell evolution through the transition [Figure 1]. The pressure dependence of the volume for both compounds show a discontinuity upon the transition of $\sim \Delta V = 5.1\%$ for DMAMnF and $\sim \Delta V = 3.8\%$ for DMAFeF. This suggests the transition is a first-order type.

A structure solution of the HP phases was initially obtained using shelxt and subsequent Fourier difference maps upon refinement in shelxl were used to complete the structural model.^{53–55} The symmetry used was triclinic $P1$ and the *hkl* data file consisted of several twin domains integrated together from *CrysAlisPro* for both compounds. In the case of DMAMnF, the single-crystal diffraction quality was significantly reduced in the HP phase. Consequently additional restraints were needed for refin-

ing the structure, in particular: the Mn–O, C–O, and N–C bonds, as well as the O–C–O and C–N–C bond angles [Tables S8 and S9]. Both HP phases from DMAFeF and DMAMnF show great similarity [Figure 4], and bear resemblance to the ambient DMAcF structure, only the HP phases exhibit greater distortion. The HP phase consists of ordered dimethylammonium cations and distorted M–formate–M links with 50% exhibiting the syn–anti configurations (where the torsion angle of $M_1\text{--O--C--O}$ is close to 0° while $\text{O--C--O--}M_2$ is near 180°) instead of the purely anti–anti configurations (where both $M_1\text{--O--C--O}$ and $\text{O--C--O--}M_2$ torsion angles are close to 180°) observed in the ambient phase [Figure 4]. The HP phase persists up to the final measured pressures of 10.5 GPa for DMAFeF and 7.5 GPa for DMAMnF. Measurements taken upon decompression show that the transition is reversible although there exists a hysteresis, as observed by the point at 6.3(3) GPa for DMAFeF that is still within the HP phase [Figure 1].

The different crystallographically unique positions of the DMA cation in the unit cell of the DMAFeF-II and DMAMnF-II phases were each collapsed onto one position by translations of ± 0.5 in the *x*, *y*, *z* components, and can be visualised in Figure 5. These orientations reveal two pairs of DMA cations that are within a few tens of degrees in the same plane (yellow/green, and blue/red DMA coloured bonds) and within each pair, the DMA cations are related to each other by $\sim 180^\circ$ rotation. A $\sim 55^\circ$ rotation is observed between the two DMA pairs, where the yellow/green pair is mainly oriented along the *a*-axis, and the blue/red pair mainly along the *c*-axis (or *bc*-plane for DMAMnF-II), similar to the orientation observed in the ambient phase. There is an additional shear in the yellow/green pair as the DMA cations are not observed directly opposite each other, but are slightly displaced along the

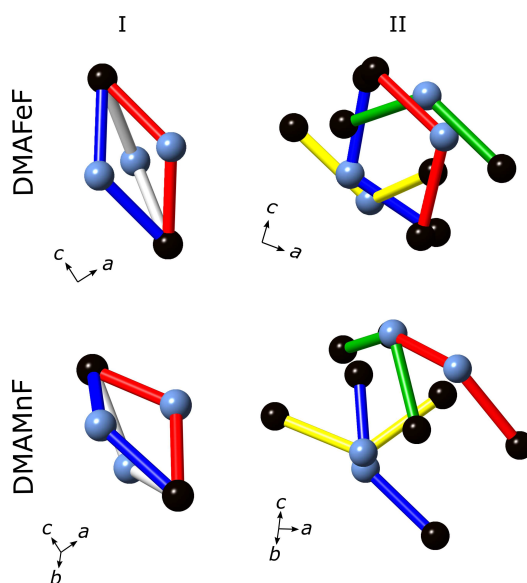


Fig. 5 The DMA cation of DMAFeF and DMAMnF in the ambient and high-pressure phases at 5.50 and 7.87 GPa, and 4.37 and 5.69 GPa, respectively. For the high-pressure phase, all orientations within one unit cell were translated onto one position and the different colours bonds highlight each separate DMA cation.

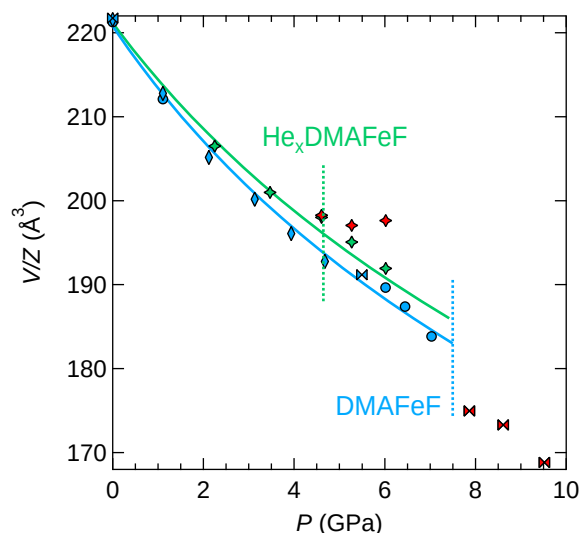


Fig. 6 Pressure dependence of V/Z for DMAFeF compressed with helium and neon as the pressure-transmitting mediums in green and blue, respectively. The different symbols represent different crystals. The dotted lines show the transition points: in green for the DMAFeF with He as PTM, and in blue for DMAFeF with Ne as PTM. The red symbols indicate the HP phases. For the mixture of ambient and HP phases in He_xDMAFeF , Pawley refinements of the powder diffractions extracted from the wide image scans were used to obtain the unit cell parameters.

a -axis for DMAFeF-II. Overall, the orientation of the DMA cations are similar for DMAFeF-II and DMAMnF-II even though the direction giving the most planar configuration of DMA cations was not the same.

While in principle the ordered dimethylammonium cations in the HP phase could display polarity, each DMA cation has a corresponding DMA cation that is related by a $\sim 180^\circ$ rotation, thus cancelling any dipole moment arising from the ordered orientations of the DMA cations. This was double checked by calculating the vectors of the C atom centroid of DMA to N for each of the four independent DMA cations and summed together for DMAFeF-II. The average of the summed vectors from each pressure point suggest that there is little polarity arising from the DMA cations in all three directions for the HP phase [Figure S5].

Compression of DMAFeF was also performed with helium as the pressure-transmitting medium. DMAFeF in He did not compress to the same extent as when loaded with neon, suggesting there was entry of helium into the structure upon increase in pressure. Incorporation of helium into non-porous structures upon compression is a phenomenon that has also been observed in molecular arsenolite,^{56,57} and CaZrF_6 perovskite.⁵⁸ In addition, the phase transition occurred at lower pressures at $3.47 < p \leq 4.61$ GPa compared to the transition in neon which occurs at $7.10 < p \leq 7.57$ GPa [Figure 6]. The ambient phase coexists with the HP phase up until the last measurement at 6 GPa, forming seven domains resulting from the reflections of the ambient phase, and the six twin domains that formed upon the rhombohedral to monoclinic transition [Figures S7–S11]. The coexistence of ambient and HP phases could be due to some radiation dam-

age of the sample, or due to a time dependence for the diffusion of helium into the structure for complete conversion of the ambient to the HP phase. The unit cell of the HP phase is given in Table 1 and was solved with the space group symmetry $I2/a$. The solution of the high-pressure phase bears close resemblance to the ambient structure of DMAcuf, with an ordered DMA cation in an antiferroelectric arrangement [Figure S6 and Tables S3–S4]. The HP phase contains more helium within the structure, due to its larger V/Z value compared to its ambient phase at the same pressure point [Figure 6]. This is due to the loss of dynamic disorder of the dimethylammonium cations, allowing greater space for He atoms to reside in the structure. The incorporation of helium into the structure stabilises the HP phase into monoclinic symmetry, without significant distortions to the iron formate framework, compared to the transformation of DMAFeF to triclinic symmetry when compressed in neon. However, due to the coexistence of ambient and HP phases, and the close proximity of the twin domains in reciprocal space, the structure solution for the HP phase could not be refined below $R = 11.3\%$, and consequently it was not possible to observe the position of the helium atoms within the structure from the diffraction data.

6 Discussion

Upon compressing the DMAMnF and DMAFeF compounds, a structural transition occurs that simultaneously involves (i) the ordering of the DMA cation and (ii) the distortion of the metal formate framework. While these two structural changes occur at the same time and are both responsible for the volume collapse across the transition ($\Delta V = 5.1\%$ and $\Delta V = 3.8\%$ for DMAMnF and DMAFeF, respectively), the difference in the transition pressures (5.53(3) vs. 7.3(2) GPa for DMAMnF and DMAFeF, respectively) suggests that the metal formate distortion is the important trigger for the transition. Previous high-pressure studies on ammonium metal formates also show a trend between metal cation size and the transition pressure, where larger metal cations exhibit lower transition pressures.³⁷ The strength of hydrogen bonding between the DMA cation and the oxygen of the formate could also have an impact on the stability of the framework under pressure, but as the disorder–order transition upon cooling is observed at similar temperatures (180 K and 160 K for DMAMnF and DMAFeF, respectively),⁶ the strength of H-bonding should be quite similar for both compounds. Even if H-bonding had an impact on the transition pressure, the DMAMnF compound should show increased stability to pressure from its stronger H-bonding compared to DMAFeF (inferred from its higher disorder–order transition temperature and greater ionic M–O bonding),^{6,59} while we observe that DMAMnF distorts at lower pressures than DMAFeF.

In the case of DMAFeF compressed in helium, it exhibits the ordering of the DMA cations without distortion of the iron formate through the incorporation of helium atoms in the structure, thus reducing the space for the orientational disorder of the DMA cations. This disorder–order transition of the DMA cations occurs at lower pressure than the iron–formate framework distortion at $p = 4.0(6)$ GPa. Although these mechanisms that include: distortion of the metal formate, strong N–H $\cdots$ O hydrogen bonds due to the JT distortion, and insertion of atoms (e.g He) into the

structure, all lead to ordered DMA cations, none of these allow a ferroelectric ordering of the cation, as is known upon cooling. This could be because the antiferroelectric state allows for the hydrogen bonding interactions to be more evenly distributed about the network of oxygens within the framework, while a ferroelectric ordering forms hydrogen bonds along a specific direction throughout the lattice. The even distribution of H-bonding may give greater structural stability to the framework, which is important under pressure. It is still not clear, however, what parameters favour the ferroelectric arrangement, observed upon cooling, over the antiferroelectric one.

The DMAcuf compound does not show the same stability to pressure as predicted simply by its cation size due to the additional Jahn–Teller distortion that weakens the copper–formate framework. This gives rise to the transition pressure close to that of DMAMnF at 5.7(3) GPa, despite it having the smallest metal cation radii out of Mn^{2+} and Fe^{2+} .⁶⁰ In other studies, the framework flexibility of $[\text{C}(\text{NH}_2)_3][\text{Cu}(\text{HCOO})_3]$ has also been shown to be increased compared to its analogous zinc formate compound due to the presence of the Jahn–Teller distortion.⁶¹ We note that as we observe the reduction in the JT distortion under pressure, multiferroic coupling arising from JT³⁹ would be expected to decrease upon compression or upon chemical substitutions that reduce the volume of the equivalent unit cell.

Low-temperature or high-pressure phases can give some indication of the dynamics present in the ambient phases. The high-pressure phases of DMAFeF and DMAMnF show similar structural distortions, and the orientations of the DMA cations suggest two main sites of disorder related by $\sim 180^\circ$ rotation, instead of the three-fold disorder observed at ambient conditions (DMA cations rotated by 120° to each other). This could arise by a flattening out of the three-fold rotation onto a plane due to more efficient volume reduction. It is interesting to observe a second pair of DMA cations tilted away from the first pair, that could suggest not only a rotational disorder at ambient but also a rocking motion of the DMA cations. However, we note that this tilt could also arise from pressure-induced effects, and may not be necessarily related to the dynamics at ambient conditions. From our data, we cannot extract the subtle differences in hydrogen-bonding of the ordered phases between DMAMnF and DMAFeF that could explain the different low-temperature behaviour, *i.e.* magnetoelectric coupling in the magnetically ordered state for DMAFeF⁸ or paramagnetic state for DMAMnF.⁷

Previous high-pressure calculations and spectroscopy measurements were carried out on DMAFeF and DMAMnF, respectively.^{29,62} However, these reports are not in agreement with our high-pressure diffraction results. In particular, first-principle calculations on DMAFeF under compression up to 6.5 GPa predict the occurrence of a high-spin to low-spin transition on the Fe^{2+} at ~ 4.5 GPa.⁶² Such spin transitions in iron complexes are usually known to give rise to a volume discontinuity,⁶³ however our data do not show any discontinuities in the unit cell parameters nor Fe–O bonding distances [Figure S14] in this pressure range (we note that the small kink observed at 4.8 GPa is due to the neon solidification). The volume discontinuity observed upon the phase transition at 7.3(2) GPa cannot be ascribed to any spin

transition either as it arises from the loss in dynamic disorder of the DMA and the framework distortion (as also observed in DMAMnF). The calculations were performed at 0 K with the low-temperature structure as the model which may present part of the reasons for the discrepancy with the experimental data performed at ambient temperature. In the case of DMAMnF, a high-pressure Raman study suggest the occurrence of three transitions at 1.6(5), 3.7(5), and 5.9(9) GPa,²⁹ while our diffraction study shows a single phase transition at 5.53(8) GPa. Even though the Raman study used a powder sample of DMAMnF with no pressure transmitting medium, the transitions are in agreement with the ones observed in a high-pressure single-crystal Raman study on DMAMgF (at 1.9(3), 3.7(3), and 5.4(3) GPa) with Nujol as the pressure-transmitting medium.³⁰ The two low-pressure transitions observed by Raman but not from our diffraction study are due to vibrational modes from the formate ligand following a weak distortion,³⁰ and no DMA cation modes are affected until the third Raman transition which is accompanied by a large metal formate distortion. It is possible that local distortions occur which are observable from Raman measurements but not from diffraction as the Raman technique is sensitive to local structure, while diffraction probes the long-range order. Thus, the observed Raman discontinuities (at ~ 2 and 4 GPa) could arise from local distortions of the metal formate framework, while the third Raman transition, in agreement with the diffraction result, could correspond to a structural transition. It is also possible that the different pressure-transmitting mediums used between the Raman and diffraction experiments can give rise to the discrepancy, especially as mineral oil can solidify as low as 1.2 GPa.⁶⁴

7 Conclusions

High-pressure diffraction experiments were conducted on DMAMFs for $\text{M} = \text{Cu}^{2+}$, Mn^{2+} , and Fe^{2+} , up to ~ 10 GPa, and a phase transition was observed in all three compounds. The HP phase of DMAcuf, that already consisted of ordered DMA cations at ambient conditions, shows a subtle shearing distortion of the copper formate framework at the pressure point which reflects the ceased reduction in the Cu–O_{JT} bonding distance. The high-pressure phases of DMAFeF and DMAMnF have a similar structure consisting of a distorted metal formate framework and an ordered DMA cation in an antiferroelectric arrangement. Compression of DMAFeF with helium as the PTM gave rise to the disorder–order transition of the DMA cations without large distortion of the iron formate framework. Thus our work shows that application of pressure can induce the disorder–order transition of the DMA cation at ambient temperature not only through a large distortion of the metal formate, but also through the insertion of He atoms. In all the studied structures, an antiferroelectric arrangement of ordered DMA cation was adopted; further investigations would be needed to ascertain the important parameters which favour ferroelectric arrangements of cation ordering.

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