

SUPPLEMENTARY INFORMATION

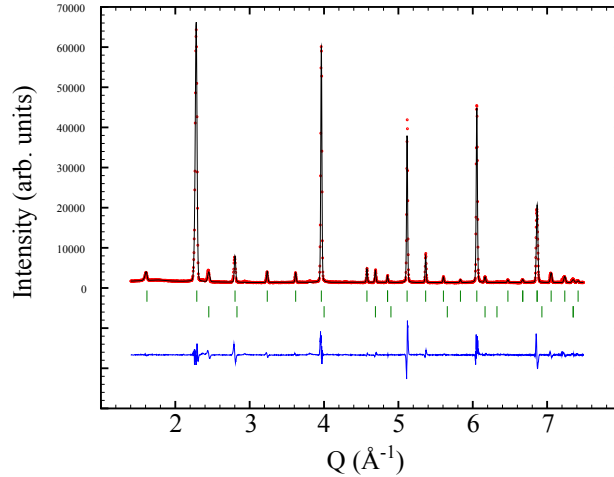


FIG. 1. Rietveld refinement of neutron powder diffraction data collected on the D20 diffractometer, ILL at 285K with neutrons of $\lambda = 1.544 \text{ \AA}$. Red, black and blue lines are the measured, calculated and difference plots, respectively. The upper green tick marks correspond to the Mn_3NiN phase and the lower ones to MnO .

Experimental details

Magnetic measurements were performed using the vibrating sample magnetometer (VSM) option in a Quantum Design Physical Property Measurement System (PPMS-9T). For the high-pressure measurements a CuBe pressure cell was used with Daphne 7373 oil as a transmitting medium and Pb wire as an internal manometer.

Powder neutron diffraction data was collected on the high flux diffractometer D20 at the ILL neutron source with neutrons of wavelength $\lambda = 1.544 \text{ \AA}$. The sample was loaded in a standard vanadium can which was mounted in an orange ILL cryostat. Rietveld refinement of the nuclear and magnetic structure was performed using the FullProf software package.

Heat capacity measurements at atmospheric pressure were performed using a TA Q2000 DSC. High-pressure calorimetry was performed in a MV1-30 high-pressure cell (Unipress, Poland) adapted as a calorimeter by using peltier modules, operating up to 0.6 GPa and from 193 K to 393 K. The sample was mixed with an inert perfluorinated fluid (Galden, Bioblock Scientifics) to remove air and encapsulated within Sn capsules. Two different capsules, using powder and bulk samples respectively, were measured independently. DW-Therm M90.200.02 fluid (Huber Kältemaschinenbau GmbH) was used as a pressure transmitting medium in the pressure circuit.

Entropy calculations

The entropy curve $S - S_{T=210\text{K}}$ at normal pressure appearing in Fig. 1(h) has been calculated simply as the integral of the heat flow, $\frac{dQ}{dT}$, over T, that appears in Fig. 1(g):

$$S(T) - S(T_0) = \int_{T_0}^T \frac{(\frac{dQ}{dT})_{p=0}}{T} dT \quad (1)$$

At high pressures, our device cannot account for the heat flow outside the transition, but it is only able to detect the latent heat. Then we have to make use of the heat flow that does not correspond to the transition (*i.e.* the C_p of each individual phase). Therefore, more precisely, the entropy curves $S - S_{T=210\text{K}}$ at different pressures (those appearing in Fig. 3(c) from which the BCE of Fig. 3(d) and 3(e) have been calculated) are constructed following the method used in Stern-Taulats *et al.*, Appl. Phys. Lett. **107**, 152409 (2015) [1]: Above and below the transition, the entropy is calculated using $\frac{dQ}{dT} = C_p$ in the expression above. In the transition temperature range, we take into

account the contribution of the pressure-dependent heat flow after baseline subtraction (*i.e.* heat flow corresponding to the latent heat of the 1st-order transition, $\frac{dQ}{dT}/T$, shown in Fig. 3(a)), but also we include a contribution of the C_p . This has to be done this way because we do not have a strictly isothermal transition but it takes place in a finite temperature interval, and therefore the heating/cooling of the sample is costly also because of the C_p of each phase. Therefore, in general in the transition range this C_p has contributions from both phases such that each contribution has to be weighted according the corresponding transformed phase fraction. In particular, we take values of the C_p outside the transition extrapolated within the temperature range (*i.e.* avoiding the peak values) of the transition. Of course, this temperature range changes with pressure. Mathematically:

$$S(T, p) - S(T_0, p) = \begin{cases} \int_{T_0}^T \frac{C^{\text{II}}(T')}{T'} dT' & T \leq T_1 \\ S(T_1, p) + \int_{T_1}^T \frac{1}{T'} \left(xC_{\text{p}}^{\text{II}} + (1-x)C_{\text{p}}^{\text{I}} + \left| \frac{dQ(T', p)}{dT} \right| \right) dT' & T_1 < T \leq T_2 \\ S(T_2, p) + \int_{T_2}^T \frac{C^{\text{I}}(T')}{T'} dT' & T_2 < T \end{cases} \quad (2)$$

where the transition at a given pressure occurs between T_1 and T_2 . Here, x is the fraction of the system transformed to phase II and can be extracted from the calorimetric peaks at high pressure (Fig. 3(a)). Notice that the values of C_p that are used within the transition range are those extrapolated from the baseline of the C_p in Fig. 1(g), *i.e.* avoiding the values belonging to the peak, as these are taken into account through $\frac{dQ}{dT}$ obtained from high-pressure calorimetry.

Theoretical Modelling

We designed a simple generic form of G drawing from our previous, detailed ab-initio DFT-DLM theory modelling of the complex magnetic phase diagrams of the heavy rare earth metals [2], transition metal alloys such as FeRh [3] and pertinent to this work Mn₃GaN [4]. This form of G is produced by using the Feynman-Peierls' Inequality [5] and a trial 'spin' Hamiltonian.

$$\mathcal{H}_0(\{\hat{e}_n\}) = - \sum_n \mathbf{h}_n \cdot \hat{e}_n, \quad (3)$$

We solve the statistical mechanics of Eq. (3) [6] by finding the probability

$$P_0(\{\hat{e}_n\}) = \frac{1}{Z_0} \exp[-\beta \mathcal{H}_0(\{\hat{e}_n\})] = \prod_n P_n(\hat{e}_n), \quad (4)$$

where $P_n(\hat{e}_n)$ are the single-site probabilities

$$P_n(\hat{e}_n) = \frac{\exp[\beta \mathbf{h}_n \cdot \hat{e}_n]}{Z_{0,n}}, \quad (5)$$

and Z_0 is the corresponding partition function,

$$\begin{aligned} Z_0 &= \prod_n Z_{0,n} \\ &= \prod_n \int d\hat{e}_n \exp[\beta \mathbf{h}_n \cdot \hat{e}_n] = \prod_n 4\pi \frac{\sinh \beta h_n}{\beta h_n}. \end{aligned} \quad (6)$$

These equations can then be used to carry out the average over $\{\hat{e}_n\}$ of quantities of interest. For example, the thermally averaged orientation at site n is

$$\left\{ \mathbf{m}_n = \int d\hat{e}_n P_n(\hat{e}_n) \hat{e}_n = \left(\frac{-1}{\beta h_n} + \coth \beta h_n \right) \hat{h}_n \right\}, \quad (7)$$

which by definition corresponds to the single-site magnetic order parameter. In addition, the entropy can be calculated as

$$\begin{aligned} S_{\text{mag}} &= \sum_n S_n(\beta h_n) \\ &= -k_B \sum_n \int d\hat{e}_n P_n(\hat{e}_n) \log P_n(\hat{e}_n) \\ &= k_B \sum_n \left[1 + \log \left(4\pi \frac{\sinh \beta h_n}{\beta h_n} \right) - \beta h_n \coth \beta h_n \right]. \end{aligned} \quad (8)$$

Invoking the Peierls-Feynman inequality [5] we obtain an upper-bound G_1 of the exact Gibbs free energy as

$$G_1 = \langle \tilde{\Omega}(\{\hat{e}_n\}) \rangle_0 - TS_{\text{mag}}. \quad (9)$$

where $\langle \cdots \rangle_0$ stands for the average with respect to $\{P_n(\hat{e}_n)\}$. Since the average of the exact Hamiltonian is prescribed by the single-site probabilities, $\langle \tilde{\Omega}(\{\hat{e}_n\}) \rangle_0$ naturally depends on the local order parameters $\{\mathbf{m}_n\}$. Several full DFT-based disordered local moment theory calculations [2–4] have shown that this average is well described by

$$\begin{aligned} \langle \tilde{\Omega}(\{\hat{e}_n\}) \rangle_0 &= - \sum_{n,n'} \mathcal{J}_{nn'}(\mathbf{m}_n \cdot \mathbf{m}_{n'}) \\ &\quad - \sum_{n,n'} \sum_{n'',n'''} \mathcal{K}_{nn'n''n'''}(\mathbf{m}_n \cdot \mathbf{m}_{n'})(\mathbf{m}_{n''} \cdot \mathbf{m}_{n'''}), \end{aligned} \quad (10)$$

where $\mathcal{J}_{nn'}$ and $\mathcal{K}_{nn'n''n'''}$ are constants describing pair-wise and the lowest possible order of multi-site interactions connecting the magnetic order parameters, respectively. Note that Eq. (10) preserves the symmetry $\{\mathbf{m}_n\} \rightarrow -\{\mathbf{m}_n\}$ since these quantities change sign under time reversal. We have found that this expression qualitatively and quantitatively fits our ab-initio DFT-DLM calculations which describe incommensurate magnetism in the heavy rare earth elements [2], the antiferromagnetic-ferromagnetic metamagnetic phase transition in FeRh [3], as well as the first-order paramagnetic-triangular phase transition and the effect of biaxial strain on the magnetic frustration in Mn₃GaN [4]. The key point is that the quartic coefficients $\mathcal{K}_{nn'n''n'''}$ describe multi-site interactions or, equivalently, the effect of magnetic ordering growth on the underlying itinerant electronic structure and how the consequent changes on the spin-polarized electronic structure can affect and qualitatively alter the interactions between the local moments. We use the insights from these calculations to set the generic form of our model Gibbs free energy for Mn₃NiN.

For the Mn₃AN antiperovskites, where there are three Mn atoms inside one unit cell for the triangular phase, the associated magnetic order parameters have equal sizes and form angles of 120 degrees in the (111) lattice plane of the Γ^{4g} and Γ^{5g} structure (or small additional out-of-plane deviations in the Γ^{4g} structure). By naming them as M_1 , M_2 , and M_3 , we can exploit the symmetry and define the following constants

$$\frac{1}{3}A_2(\Delta\omega) = \sum_{nn'} \mathcal{J}_{nn'}(\Delta\omega) \cos(\theta_{nn'}), \quad (11)$$

$$\begin{aligned} \frac{1}{3}A_4(\Delta\omega) &= \\ &\sum_{nn'} \sum_{n''n'''} \mathcal{K}_{nn'n''n'''}(\Delta\omega) \cos(\theta_{nn'}) \cos(\theta_{n''n'''}), \end{aligned} \quad (12)$$

where $\mathcal{J}_{nn'}$ and $\mathcal{K}_{nn'n''n'''}$ are constants describing pair-wise and the lowest possible order of multi-site interactions connecting the magnetic order parameters, respectively, and $\theta_{nn'}$ is the angle between the magnetic order parameters at sites n and n' . Note that they have an explicit dependence on the pressure induced relative volume change $\Delta\omega = \frac{dV}{V}$, where V is the volume. In principal the $\mathcal{J}_{nn'}$ and $\mathcal{K}_{nn'n''n'''}$ constants could be obtained from ab-initio calculations for Mn₃NiN. These calculations are ongoing but we are developing the theory to include the effects of the faster itinerant spin fluctuation effects associated with the Ni sites alongside the slower local moment fluctuations on the Mn sites. In the present work we instead identify their effect in the more compact form of A_2 and A_4 from our experimental data in Mn₃NiN and Mn₃GaN and verify their existence.

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