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The role of spin fluctuations in the anomalous anisotropy of MnBi

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Abstract. MnBi is unusual for having a magnetic anisotropy energy which increases with temperature. Recent theoretical works have studied how the lattice effects the anisotropy. However the role of spin fluctuations has been hitherto overlooked, even though this is the primary mechanism for the temperature dependence of anisotropy in magnetic materials. We have created a model of MnBi including all anisotropy terms which are indicated from experiments and theory. Parameterizing based on experimental measurements we used Callen-Callen theory to calculate the temperature dependence of the magnetic anisotropy due to spin fluctuations. An excellent agreement is found with experiments, across the entire temperature range. Our results indicate the driving force to be the competition between in-plane single ion and out of plane two-ion anisotropies.

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1. Introduction

MnBi has been studied for over 65 years [1] and was initially a candidate material for magneto-optical recording applications [2]. There has been a recent resurgence in interest prompted by the desire to create rare-earth free permanent magnets [3]. MnBi is a candidate material due to its relatively large uniaxial anisotropy at room temperature. Contrary to most magnetic materials, the magnetic anisotropy energy of MnBi increases with temperature, reaching a maximum of 2.2 MJ/m^3 at 450 K, approximately 130% of NdFeB at the same temperature [4] and even 60% of the value of FePt [5]. Recent efforts to understand the origins of this anisotropy and the anomalous temperature dependence have focused on how lattice expansion and phonons effect the magnetic anisotropy [6, 7, 8, 9]. Somewhat surprisingly the effect of the thermal spin fluctuations has not been investigated, despite being the primary cause of the temperature dependence of anisotropy in magnetic materials. Here we construct an empirical model of the microscopic magnetic anisotropy contributions which exist in MnBi. We take care to clarify the difference between the macroscopic, $K_{1,2,3}$, anisotropy coefficients which can be measured experimentally and the microscopic mechanisms which are associated with specific spin correlations and have a well defined temperature dependence described by Callen-Callen theory [10]. Parameterizing the model using existing experimental data from the literature gives a remarkable agreement of the anisotropy energy across the whole temperature range. We also use numerical techniques to confirm the validity of the applicable Callen-Callen scaling laws across the temperature range and when multiple anisotropies are present in the system.

In the so-called low temperature phase (LTP) MnBi has the NiAs structure with alternating planes of Mn and Bi (figure 1). The Mn sites posses a large magnetic moment of 4.02 μ_B and the Bi has almost no net moment at -0.1μ_B. Throughout this work we will therefore ignore spin fluctuations of the Bi spins. The temperature evolution of the anisotropy contains several features. In the ground state the magnetization lies in the a-plane with an total anisotropy energy of -0.25 MJ/m^3 . At 90 K the magnetisation moves abruptly into an easy cone state [11]. Further heating reduces the cone angle gradually and at $T_{SR} = 142$ K the system becomes uniaxial with the magnetization along the c-axis [12]. Most unusually, the magnitude of the uniaxial anisotropy continues to increase with temperature, reaching a maximum of 2.2 MJ/m^3 at 450 K beyond which it slowly decreases. There is no Curie point, the magnetic phase transition from ferromagnetism to paramagnetism, because at 628 K a peritectic decomposition to $Mn_{1.08}Bi$ and liquid Bi occurs, giving the so-called 'high temperature phase' [13].

Recent theories point to lattice effects being the underlying cause of the unusual behaviour of the magnetic anisotropy. Possibilities considered include the effect of anisotropic thermal expansion [6] and magnetoelastic and magnetostrictive coupling [7]. First principles calculations have shown a spin reorientation can occur due to changes in magneto-crystalline anisotropy with changing lattice constants, but at a temperature much higher than found experimentally and without the subsequent large increase in anisotropy [7, 8]. The inclusion of the on-site Coulomb term into such calculations can give a better agreement with experiments [9]. However, all of these works explicitly state they do not include thermal spin fluctuations. This is something which must therefore be investigated as the inclusion of spin fluctuations would not only renormalise the athermal ab initio results significantly, but could play

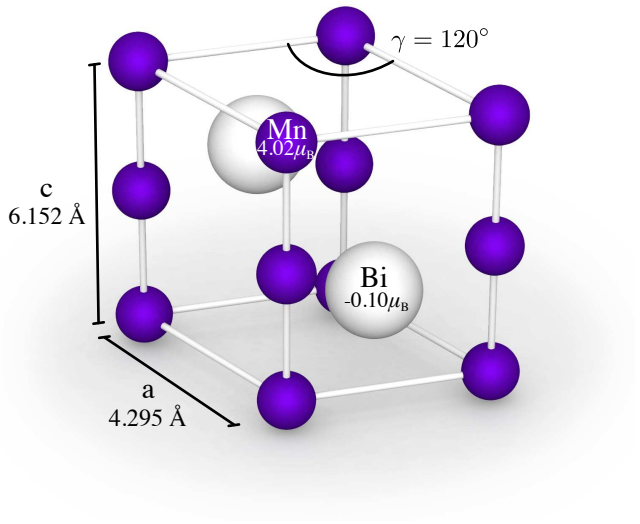

Figure 1. Structure of MnBi which has alternating planes of Mn and Bi.

an important role in the temperature dependence.

2. Theoretical background: Callen-Callen theory

In the Heisenberg, local spin picture of magnetism, temperature causes fluctuations of the atomic scale magnetic moments. The fluctuations give rise to, for example, the temperature dependence of magnetization as the atomic moments become thermally distributed about the field direction, reducing the net projection of the magnetization. The thermal energy also causes the total magnetization to precess in a stochastic manner about the energy minimum. Hence, at non zero temperatures the system explores a finite area of the free energy surface. Thermodynamic quantities are therefore an average over the thermal distribution. This is the process by which spin fluctuations lead to an apparent temperature dependance of the magnetic anisotropy. This is separate from extrinsic considerations such as expansion of the lattice altering the electronic structure of the material. The sampling of the free energy surface from spin fluctuations is described by the theory of Callen and Callen [10] which defines the temperature dependence of the anisotropy in terms of the reduced magnetization $m = M(T)/M(0)$. Most well known is that the anisotropy scales in power laws of the magnetization, although this is derived in the low temperature limit. In principle the scaling can be calculated for arbitrary temperatures, however the derivation assumes no spin-wave interactions which become increasingly important at elevated temperatures. Therefore we later use numerical calculations to check the scaling behaviours across the complete temperature range.

An important distinction must be made between the macroscopic anisotropy energy which is often measured and the the microscopic origin of magnetic anisotropies. The macroscopic uniaxial anisotropy energy is often expressed as

$$E(\theta) = K_1 \sin^2\theta + K_2 \sin^4\theta + K_3 \sin^6\theta, \tag{1}$$

where θ is the azimuthal angle, or sometimes given by the total effective anisotropy

$K_{\text{eff}} = K_1 + K_2 + K_3$. The temperature dependence of the 'K' coefficients has no general form which can be derived because many different anisotropies in the system are mixed together, such as different orders of magneto-crystalline anisotropy, dipole interactions, magneto-elastic effects and so on [14]. Callen-Callen theory on the other hand derives the temperature dependence of these individual terms which can be expressed in polynomials of the spin components. In the low temperature limit the temperature dependence of an anisotropy that is an lth order polynomial in the spin components is

$$\kappa_l(T) = \kappa_l(0)[m(T)]^{l(l+1)/2}. \tag{2}$$

for example, the first order single-ion uniaxial anisotropy is described by the second order Legendre polynomial $\kappa_2(3S_{z,i}^2 - 1)/2$ and therefore scales proportionally to m^3.

Identifying the multiple contributions to anisotropy from experimental data is not straight forward. Anisotropies of different origins are indistinguishable when they have the same angular dependence - except if they have a difference in their characteristic temperature dependence. This is the key to interpreting the anomalous behaviour of MnBi. By identifying the different origins of magnetic anisotropy in MnBi and using the characteristic temperature dependence of each term from Callen-Callen theory, we can build a phenomenological model of the contribution of spin fluctuations to the temperature dependence of the anisotropy. We do not try to identify how different electronic effects contribute to the anisotropy constants, assuming that changes in the electronic structure with temperature are less significant than the role of spin fluctuations. For example it is known that there is a strong Mn-d – Bi-p hybridization, however this could be responsible for single ion and two ion anisotropies, but we cannot identify this definitively and leave this to ab initio works [9].

3. Phenomenological model of MnBi

Uniaxial anisotropy constants K_1, K_2 and K_3 have been measured in experiments [15], and so we include single ion anisotropy contributions to third order. The higher order terms are quite small and are likely to be from magnetocrystalline anisotropy. The K_1 term presumably also contains some magnetocrystalline anisotropy, but probably also a large magneto-elastic contribution due to the extraordinarily large magnetostriction of MnBi [16] . The single-ion contributions are expressed by Legendre polynomials in S_z

$$\mathcal{H}_1 = \sum_i \frac{\kappa_2}{2}\left(3S_{z,i}^2 - 1\right) \tag{3}$$

$$+\frac{\kappa_4}{8}\left(35S_{z,i}^4 - 30S_{z,i}^2 + 3\right) \tag{4}$$

$$+\frac{\kappa_6}{16}\left(231S_{z,i}^6 - 315S_{z,i}^4 + 105S_{z,i}^2 - 5\right). \tag{5}$$

Now it becomes clear that the K's contain contributions of κ's of multiple orders, for example, K_1 is the coefficient for terms in S_z^2 which are present in the second, fourth and sixth order polynomials, κ_2, κ_4 and κ_6 [15]. These three terms have the magnetization dependence

$$\frac{\kappa_2(T)}{\kappa_2(0)} = m^3 \quad \frac{\kappa_4(T)}{\kappa_4(0)} = m^{10} \quad \frac{\kappa_6(T)}{\kappa_6(0)} = m^{21}. \tag{6}$$

The layered structure of MnBi has broken cubic symmetry which leads to a dipole-dipole contribution to the anisotropy. This is described by the Hamiltonian term

$$\mathcal{H}_{\text{dipole}} = -\frac{\mu_{s,i}\mu_{s,j}\mu_0}{4\pi}\sum_{i\neq j}\frac{3(\mathbf{S}_i\cdot\mathbf{r}_{ij})(\mathbf{S}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5} - \frac{\mathbf{S}_i\cdot\mathbf{S}_j}{r_{ij}^3} \tag{7}$$

where μ_s is the magnetic moment, $\mu_0 = 4\pi\times10^{-7}$ N/A^2 is the permeability of free space and $\mathbf{r}_{ij}$ is the vector between spins i and j. This is a property of the bulk lattice and is different from the demagnetizing fields which depend on the shape of the sample. We calculated the value numerically for a bulk system using an Ewald summation, finding a uniaxial $K_1^{dip} = 0.16$ MJ/m^3 at $T = 0$ K. Dipole anisotropy drives the spin reorientation transition in Mn_2Sb [17]. However, in MnBi this contribution is an order of magnitude smaller than the peak of the anisotropy energy and is thus too small to be the dominant mechanism. In principle the temperature dependence of this term depends on the fluctuations of pairs of spins. However these can be factored out as independent in the low temperature regime and is expected to scale with m^2 [10]. We check the scaling across the whole temperature range numerically using constrained Monte Carlo [18] in Fig. 4(b). We the m^2 scaling is valid at any temperature. We will refer to the dipole anisotropic energy as $\delta_z^{(2)}$.

The final anisotropy energy contribution we include is a two-ion anisotropy of the form,

$$\mathcal{H}_2 = -\sum_{ij} d_z^{(2)} S_{z,i} S_{z,j}. \tag{8}$$

The motivation for this term is two fold. The presence of the Bi between the Mn layers is likely to give rise to a significant two-ion exchange between the Mn layers as with other material such as FePt. Magneto-elastic coupling also gives rise to two-ion terms. In a hexagonal system the symmetry allows a uniaxial term proportional to $\sqrt{3/2}(S_{z,i}S_{z,j} - \frac{1}{3}\mathbf{S}_i\cdot\mathbf{S}_j)$ [19]. Within Callen-Callen theory the magnetoelastic anisotropies give rise to the same scaling behaviour as a magnetocrystalline terms and therefore we cannot make a distinction between them within this phenomenological model. The two-ion term is also indistinguishable from the dipole term as it has both the same angular dependence and m^2 temperature dependence.

The final equations for the macroscopic K coefficients are

$$K_1(m) = -\frac{3}{2}(\kappa_2 m^3 + \Delta_2 m^2) - 5\kappa_4 m^{10} - \frac{21}{2}\kappa_6 m^{21} \tag{9}$$

$$K_2(m) = \frac{35}{8}\kappa_4 m^{10} + \frac{189}{8}\kappa_6 m^{21} \tag{10}$$

$$K_3(m) = -\frac{231}{16}\kappa_6 m^{21} \tag{11}$$

where $\Delta_2 = \delta_z^{(2)} + d_z^{(2)}$. $\Delta_2, \kappa_{2,4,6}$ are defined at zero temperature and only these four parameters are required.

Disregarding effects from the sample shape or impurities within the bulk, we have included all magnetic anisotropy contributions which have experimental or theoretical evidence for existence. We now parameterize the model using the torque measurements of Stutius et al. [15] for $K_{1,2,3}$ (figure 2). Using only the lowest temperature ($T = 4$ K) data points, we begin with the highest order term K_3 this uniquely defines the single-ion κ_6 term giving a value of $\kappa_6 = 0.0169$ MJ/m^3 . In a similar way K_2 is a combination of only κ_6 and κ_4 and hence we deduce $\kappa_4 = -0.0062$ MJ/m^3 . More problematic is the

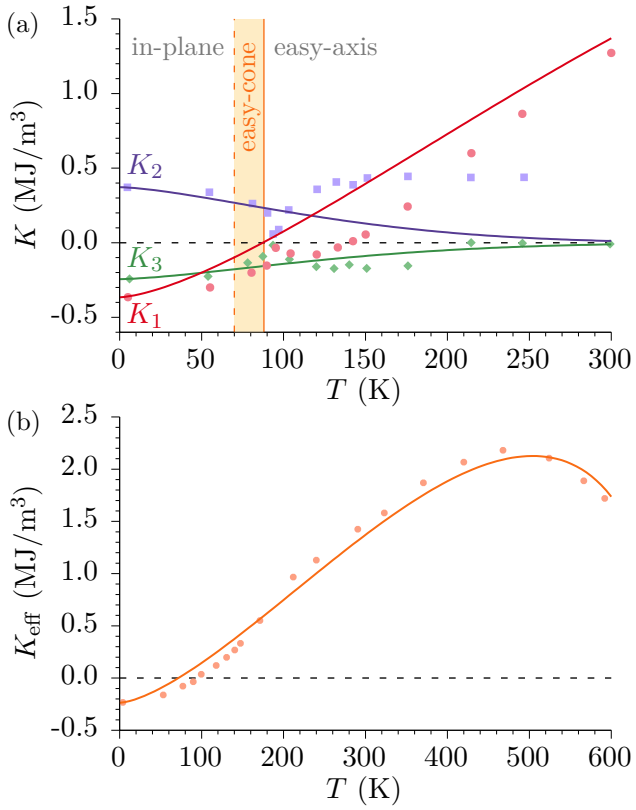

Figure 2. (a) Solid lines - temperature dependence of $K_{1,2,3}$ coefficients from the Callen-Callen model compared to experimental torque measurements [15]. The easy magnetization direction is labelled as found in Fig. 3. (b) Solid line - Total effective anisotropy $K_{\rm eff} = K_1 + K_2 + K_3$ from the Callen-Callen model compared to experimental measurements [15].

K_1 term as it is the sum of $\kappa_{2,4,6}$, dipole and two-ion terms. However, at the peak in $K_{\rm eff}$ at 450 K, κ_4 and κ_6 are very small and the peak value is defined by the sum of Δ_2 and κ_2. The different temperature scaling $\kappa_2 \propto m^3$ and $\Delta_2 \propto m^2$ must therefore be the reason for both the change in sign of K_1 and the peak. The two-ion term must give rise to the uniaxial anisotropy as it has the weaker temperature dependence. This implies the single-ion κ_2 is negative, giving an in-plane anisotropy which is initially slightly larger than than the two-ion term. Our analysis gives the values of $\kappa_2 = 10$ MJ/m^3 - an in-plane anisotropy and $\delta_z^{(2)} + d_z^{(2)} = 14.854$ MJ/m^3 . These values are quite large for anisotropy energies but of the same order of magnitude as predicted by ab initio calculations when the spin-orbit interaction of the Bi is included [9]. There is also a qualitative agreement with ab initio calculations which find a large in-plane magnetocrystalline anisotropy at $T = 0$ K [9, 20].

For the temperature dependence of magnetization we use the data of Guo *et al.* [21] (red circles in figure 4a) fitted by the general equation for magnetization of Kuz'min [22] (red line in figure 4a). Using the equations 9-11 we calculate the temperature dependence of $K_{1,2,3}$ due to spin fluctuations according to Callen-Callen theory. The results in figure 2a show an excellent agreement the experimental data [15].

The sign change and large increase in K_1 is caused by the rapid diminution of the κ_6 energy and the competition between two-ion and single-ion contributions which have opposite sign. The only significant deviation is in the behaviour of K_2 after the reorientation transition. However in this region the experiments were unable to saturate the magnetization and the ability to differential K_1 and K_2 in their analysis is limited. The cusp around T_{SR} is also not reproduced and it is not clear if this is due to the relatively flat energy landscape or the lattice distortion which has been measured [6].

In figure 2b the total anisotropy energy $K_{\mathrm{eff}} = K_1 + K_2 + K_3$ of our model is compared with the experimental measurements [15]. Again a good agreement is found. The model is parameterized from experiments as $T \approx 0$ and 450 K so we expect to reproduce these values. However, that the rest of the curve is in agreement with experiment implies the power laws of the underlying anisotropies are correctly identified. The down turn of K_{eff} above 450 K is dominated by the m^2 term and serves as strong justification for its inclusion.

The existence of a spin reorientation transition is not explicitly guaranteed to occur within our model and no information concerning the reorientation was used to inform our parameterization. Nevertheless, the competition between the in-plane and uniaxial anisotropies and the difference in temperature dependence does lead to the spin reorientation transition. This is caused by the change in sign of K_1 due to the different temperature dependence of κ_2 and Δ_2. Also, the small κ_4 and κ_6 contributions also play an important role, producing additional minima in the free energy landscape (see figure 3) which causes the easy-cone state. At the start of the spin reorientation transition ($T = 65$ K) the first order uniaxial terms combined into K_1 almost completely cancel each other. This leaves a triple minima energy landscape formed by the higher order κ_4 and κ_6 terms. With increasing temperature the two-ion contribution begins to overcome the single-ion in-plane term and the global minimum at $\theta = 90°$ (in-plane) rises in energy causing the two satellite minima at $\theta = 30°$ and $\theta = 150°$ to suddenly become the global energy minima. This causes the magnetization to abruptly reorient from an easy-plane to easy-cone configuration as shown in figure 3b and just as observed in experiments [11]. In a small temperature regime the angle of the easy-cone configuration decreases with increasing temperature until at $T = 88$K the K_1 term changes sign and the system becomes uniaxial. The entirety of this process is qualitatively identical to that which was found experimentally [11, 23, 15], although the transition temperatures in this model are slightly lower. A different subset of the experimental literature finds that the ground state is not completely in-plane and the spin-reorientation proceeds as a gradual canting from in-plane to easy-axis [12, 24, 25]. Within our model we find that small differences in the values of $\kappa_{4,6}$ can change the reorientation behaviour so it is likely that small differences in sample preparation or composition could give different characteristic behaviour, without a significant change in T_{SR} which is strongly determined by the values of κ_2 and Δ_2.

The lattice expansion of MnBi with temperature is anisotropic, with the c/a ratio increasing at higher temperatures. It has been suggested that a sudden jump in the lattice expansion [26] close to T_{SR} maybe be the cause of the reorientation. In principle the lattice expansion can have several effects on the magnetic system. These may have a bearing on the spin fluctations in the Callen-Callen picture because of the modification of the interactions in the Hamiltonian. Firstly, the dipole-dipole anisotropy will increase slightly as the c/a ratio increases. However, given the already small energy contribution from this term, it cannot be regarded as a significant effect.

The lattice expansion is also known to modify the magnetocrystalline anisotropy, which has been studied previously through ab initio techniques, although without regard to the spin fluctuations. Most works have found that the changes in MCA are insufficient to describe the large peak of K_{eff} at high temperatures [7, 8] or cannot describe the change in sign [27]. In more recent first principles work [9], although $K_{\text{eff}}(T)$ was found in good agreement to experiments, the energy landscapes found do not agree with the experimental measurements of K_1, K_2, and K_3. However, if the in-plane κ_2 anisotropy used within the Callen-Callen model reduced, in real terms, as the lattice expanded, then the absolute values of κ_2 and $d_z^{(2)}$ would not need to be so large to reproduce the peak. The last term which would be impacted is the exchange interactions. The effect of lattice expansion on the zero temperature isotropic exchange is small in most magnetic materials with 'good' local moments. The isotropic part of course has no bearing on the anisotropy also. However the two-ion contribution may well be modified, especially because it is the c-axis which is being elongated. That we cannot easily discriminate the κ_2 and $d_z^{(2)}$ except for their temperature dependence has the potential to hide some of the effects of the lattice expansions. Having said that, the good agreement between of K_{eff} with the Callen-Callen scaling for the interim region between T_{SR} and the peak of K_{eff} suggests that the temperature dependence of the Hamiltonian due the lattice expansion is less significant than the effect of the spin fluctuations.

4. Numerical validation of Callen-Callen theory

The Callen-Callen scaling we have used throughout this work is based on the low temperature limit. While the theory also allows one to calculate the general temperature dependence this still assumes spin wave interactions are negligible. We instead have calculated the scaling numerically using the constrained Monte-Carlo method [18]. This allows us to also confirm that there is no anomalous behaviour caused by the presence of multiple anisotropy terms or the spin reorientation.

Williams et al. [28] have determined the Heisenberg exchange constants of MnBi using inelastic neutron scattering. They found a long ranged exchange interaction where the nearest neighbours along the c-axis have a coupling with the antiferromagnetic sign, although the total exchange gives a ferromagnetic ground state. It is not *a priori* clear if these details could also have an effect on the temperature dependence of the anisotropy. We have constructed an atomic scale simulation based on the Heisenberg Hamiltonian which we augment with the anisotropy interactions defined in the preceding sections

$$\mathcal{H} = -\frac{1}{2}\sum_{\langle ij\rangle} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{dipole}} \tag{12}$$

where $\langle ij\rangle$ indicates a limited sum over the interactions upto sixth nearest neighbours as given in Ref. [28]. The very small Bi moments are ignored. The macroscopic torque is then calculated with the magnetization constrained to an azimuthal constraint angle (θ). Note that no applied field is used to enforce the constraint, it is maintained by the Monte Carlo sampling method. The anisotropy coefficients at a given temperature can then be found by fitting

$$\frac{\partial E}{\partial \theta} = \mathcal{T}(\theta) = \sin 2\theta \left(K_1 + 2K_2 \sin^2\theta + 3K_3 \sin^4\theta\right). \tag{13}$$

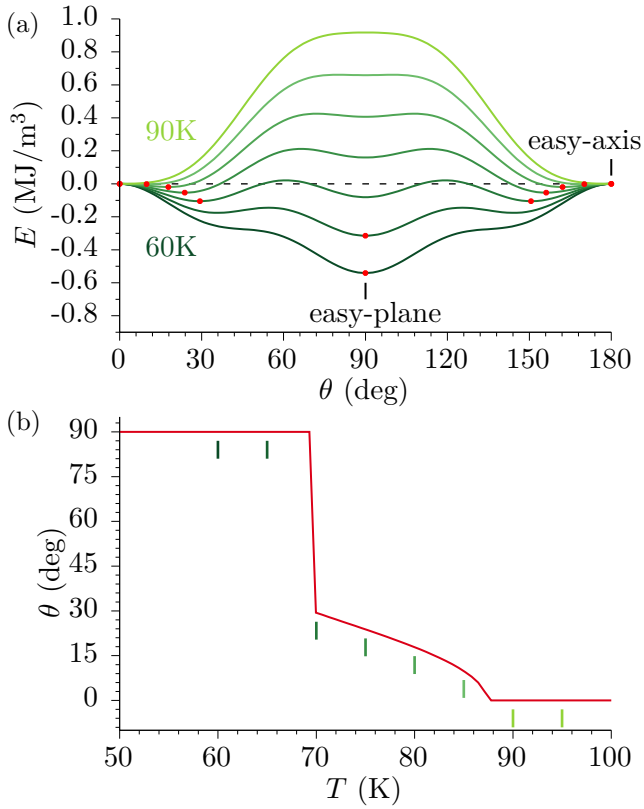

Figure 3. (a) Free energy surface through the reorientation transition for temperatures 60K to 90K at 5K intervals. The red points mark the global energy minimum of the free energy surface at each temperature. (b) The azimuthal angle of the free energy minimum as a function of temperature. The green coloured lines denote the temperatures of the curves in (a).

In figure 4a we present the temperature dependent magnetization calculated using the exchange constants from the neutron scattering. The results agree well with the experimental results [21]. The transition to the high temperature phase means a true Curie temperature cannot be measured in experiments, but extrapolation based on Kuz'min's equation for magnetization gives a value of 707 K compared to 750 K in the calculation. As the neutron measurements where made at 5 K this suggests that lattice expansion has a negligible effect at least on the exchange constants.

The magnetization scaling of the different Hamiltonian terms is given in Fig. 4b and the solid lines are the power laws from the low temperature limit of Callen-Callen theory. The numerical results show the low temperature approximation is good across the entire temperature range for the dipole and two-ion terms. The κ_4 and κ_6 terms show some deviation at higher temperatures, but only once the the value has already decreased by 2 orders of magnitude. Therefore the use of the Callen-Callen scaling relationships within the empirical model is justified.

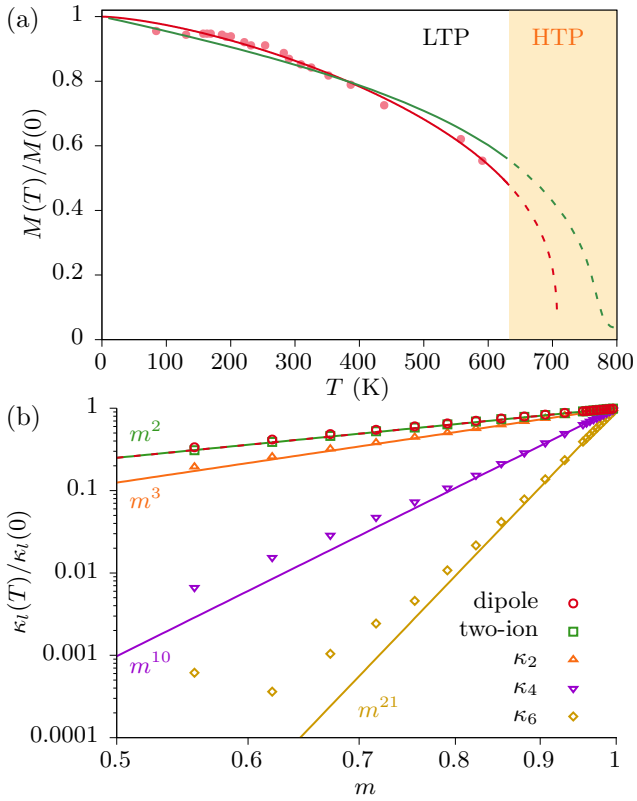

Figure 4. (a) Temperature dependence of MnBi magnetization. Red points are experimental data from Ref. [21] and the solid red line is a fit of the empirical equation of Kuz'min [22], $T_C = 707$ K. The green line is calculated using classical Monte-Carlo simulations where the exchange has been calculated ab initio, $T_C = 750$ K. (b) Magnetization scaling of the anisotropy terms calculated with constrained Monte Carlo (points). Lines show the low temperature scaling from Callen-Callen theory.

5. Conclusion

We have formed an empirical spin Hamiltonian of MnBi including anisotropy terms which have been identified in experiments. Using numerical simulations we have verified that the Callen-Callen theory can be applied in terms of simple power laws on the magnetization. From the model it is clear that spin fluctuations must be considered in understanding the temperature dependence of the anisotropy in MnBi. In this work, changes in the anisotropy due to lattice expansion has not been considered, but it is clear that ab initio results which represent zero temperature properties, must also include the effect of spin fluctuations to successfully understand the temperature dependent behaviour. Based on our results we suggest that it is the competition between a single ion in-plane and two-ion uniaxial anisotropies which causes the anomalous behaviour in MnBi. Further work should be done to understand the contributions of magneto-elastic coupling and the Bi spin orbit coupling to these two terms.

Acknowledgments

Oleg Mryasov passed away at the end of 2015, I enjoyed the short time we spent working together and the inspiration he gave me. This work was supported by C-SPIN, one of the six centres of STARnet, a SRC programme sponsored by MARCO and DARPA. J.B. acknowledges support from the Graduate Program in Spintronics, Tohoku University.

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