Exchange interactions in TbMnO$_3$

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Abstract. The most general form of the exchange interaction for Mn atoms in TbMnO$_3$ is derived, including nearest neighbour and next-nearest neighbour interactions. It is found that for each exchange path there are six independent exchange terms, leading to a rather complicated Hamiltonian. Experimentally determined constraints on the Hamiltonian are discussed. Degeneracy lifting in the spin-wave excitation spectrum is also discussed.

1. Introduction
Multiferroics are materials with simultaneous ferroic properties. In most of the multiferroics that have been studied to date, the magnetic ordering and ferroelectricity develop independently at different temperatures leading to a rather weak magnetoelectric coupling. TbMnO$_3$ belongs to an interesting class of multiferroics with a strong magnetoelectric effect. In this class of multiferroics, a magnetic transition into a transverse incommensurate spiral structure breaks the inversion symmetry and induces ferroelectricity [1, 2]. The competing magnetic interactions give rise to a noncollinear magnetic order, an incommensurate modulation and a high degree of degeneracy.

Different theoretical models [3, 4, 5] and symmetry analyses [6, 7] have been proposed to describe the microscopic mechanism in spiral multiferroics with generic features such as polarization flop [8, 9, 10, 11] and magnetic memory effect [12]. It is known that the coexistence and the strong coupling between ferroelectricity and incommensurate magnetism in perovskite manganites are due to Dzyaloshinskii-Moriya interactions, which couple spin interactions and displacements.

The magnetic structure of TbMnO$_3$ has been studied by experiment in four different temperature intervals [13, 14, 15, 16]: i) at room temperature TbMnO$_3$ is paraelectric and paramagnetic; ii) below $T_{N}^{\text{Mn}} = 41$ K Mn moments develop a sinusoidal antiferromagnetic (AF) ordering with the moments along the $b$ axis and an incommensurate wave vector $Q = (0, k_{\text{Mn}}, 0)$ with $k_{\text{Mn}} \approx 0.29$; iii) in the magnetoelectric phase (below 28 K) the Mn moments transform into a cycloidal spiral spin structure with an incommensurate wave vector $k_{\text{Mn}}^{\text{Th}} \approx 0.28$ and a spontaneous polarization appears in the $c$ direction; and finally iv) below $T_{N}^{\text{Tb}} \approx 7$ K, Tb moments display an incommensurate AF ordering. Moreover, neutron scattering experiments have determined the magnetic symmetry [13]. The order parameter of the first magnetic phase transition is described by the irreducible representation $\Gamma_3$ of the little group of $Q$ while at the second transition another order parameter $\Gamma_2$ also appears [1].

In this article we consider a full symmetry treatment of the exchange interaction. A Hamiltonian that includes 24 parameters is derived; however, as we shall show, this parameter
space is greatly constrained by observed phenomenology.

2. Structural details and magnetic operators

The space group of TbMnO$_3$ is Pnma (No. 62, D$_{2h}^{16}$), where the letters nma specify the types of reflections in the a, b and c planes respectively. In particular, the reflections in the a and c planes are glide reflections. However, most published work uses the equivalent space group Pbnm, which places the glide reflection in the a and b planes. In Pbnm the lattice parameters are $a = 5.29314$ Å, $b = 5.8384$ Å and $c = 7.4025$ Å [17]. In the following, we will use the Pbnm orientation exclusively, with the rectangular coordinates $x, y, z$ associated with the directions of the lattice parameters $a, b, c$. The symmetry operations for Pbnm are given in Table 1.

| Operation | Operation in Pbnm | 4b transpositions |
|-----------|-------------------|-------------------|
| (1) E     | 1                 | -                 |
| (2) $C_{2x}$ | $2(\frac{1}{2}, 0, 0) \ x, \frac{1}{2}, 0$ | $(1, 2), (3, 4)$ |
| (3) $C_{2z}$ | $2(0, 0, \frac{1}{2}) \ 0, 0, z$ | $(1, 3), (2, 4)$ |
| (4) $C_{2y}$ | $2(0, \frac{1}{2}, 0) \ \frac{1}{2}, y, \frac{1}{2}$ | $(1, 4), (2, 3)$ |
| (5) I     | 1 0 0,0          | -                 |
| (6) $\sigma_x$ | $b(0, \frac{1}{2}, 0) \ \frac{1}{2}, y, \frac{1}{2}$ | $(1, 2), (3, 4)$ |
| (7) $\sigma_z$ | $m \ x, y, \frac{1}{2}$ | $(1, 3), (2, 4)$ |
| (8) $\sigma_y$ | $n(\frac{1}{2}, 0, \frac{1}{2}) \ \frac{1}{2}, z$ | $(1, 4), (2, 3)$ |

Table 1. Symmetry operations for the space group Pbnm. The first column gives the point group operations, the second column lists the corresponding operations for the space group and the third column shows how the 4b positions of Pbnm are transposed (up to a lattice translation) by each operation.

With four copies of the chemical formula per unit cell, the Mn atoms occupy 4b Wyckoff positions, the Tb atoms occupy 4c positions and the O atoms occupy 4c and 8d positions, as shown in Fig. 1. The coordinates of the Mn positions are $\left(\frac{1}{2}, 0, 0\right), \left(0, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right)$ and $\left(0, \frac{1}{2}, \frac{1}{2}\right)$ for position numbers 1, 2, 3 and 4, respectively. Thus there are twelve magnetic operators per unit cell for the Mn atoms of the form $J_n^a$, where $a = 1, 2, 3, 4$ and $n = x, y, z$.

The Fourier transform is defined over the Brillouin zone,

$$J_i^n(\vec{k}) = \sum_j e^{-i\vec{k}(\vec{j}+\vec{i})} J_j^n$$  \hspace{1cm} (1)

where the sum is over all lattice sites in the crystal and $\vec{i}$ are the coordinates of the ith Wyckoff position within each site. The operators corresponding to the irreducible representations of an arbitrary $k$-vector are

![Figure 1. Or-thorhombic unit cell of TbMnO$_3$.](image1)

![Figure 2. Character table for $C_{2v}$](image2)
\[ \Gamma_k^i (k) = \sum_j e^{-ik \cdot \mathbf{r}_j} \left\{ J_{j,1}^x e^{-ik \cdot \mathbf{r}_{j,1}} + J_{j,2}^x e^{-ik \cdot \mathbf{r}_{j,2}} - J_{j,3}^x e^{-ik \cdot \mathbf{r}_{j,3}} - J_{j,4}^x e^{-ik \cdot \mathbf{r}_{j,4}} \right\} \]
\[ \Gamma_k^2 (k) = \sum_j e^{-ik \cdot \mathbf{r}_j} \left\{ J_{j,1}^y e^{-ik \cdot \mathbf{r}_{j,1}} - J_{j,2}^y e^{-ik \cdot \mathbf{r}_{j,2}} + J_{j,3}^y e^{-ik \cdot \mathbf{r}_{j,3}} + J_{j,4}^y e^{-ik \cdot \mathbf{r}_{j,4}} \right\} \]
\[ \Gamma_k^3 (k) = \sum_j e^{-ik \cdot \mathbf{r}_j} \left\{ J_{j,1}^z e^{-ik \cdot \mathbf{r}_{j,1}} - J_{j,2}^z e^{-ik \cdot \mathbf{r}_{j,2}} + J_{j,3}^z e^{-ik \cdot \mathbf{r}_{j,3}} - J_{j,4}^z e^{-ik \cdot \mathbf{r}_{j,4}} \right\} \]
\[ \Gamma_k^4 (k) = \sum_j e^{-ik \cdot \mathbf{r}_j} \left\{ J_{j,1}^x e^{-ik \cdot \mathbf{r}_{j,1}} + J_{j,2}^y e^{-ik \cdot \mathbf{r}_{j,2}} + J_{j,3}^z e^{-ik \cdot \mathbf{r}_{j,3}} + J_{j,4}^y e^{-ik \cdot \mathbf{r}_{j,4}} \right\} \]
\[ \Gamma_k^y (k) = \sum_j e^{-ik \cdot \mathbf{r}_j} \left\{ J_{j,1}^y e^{-ik \cdot \mathbf{r}_{j,1}} + J_{j,2}^y e^{-ik \cdot \mathbf{r}_{j,2}} - J_{j,3}^y e^{-ik \cdot \mathbf{r}_{j,3}} - J_{j,4}^y e^{-ik \cdot \mathbf{r}_{j,4}} \right\} \]
\[ \Gamma_k^y (k) = \sum_j e^{-ik \cdot \mathbf{r}_j} \left\{ J_{j,1}^z e^{-ik \cdot \mathbf{r}_{j,1}} - J_{j,2}^z e^{-ik \cdot \mathbf{r}_{j,2}} + J_{j,3}^z e^{-ik \cdot \mathbf{r}_{j,3}} - J_{j,4}^z e^{-ik \cdot \mathbf{r}_{j,4}} \right\} \]
\[ \Gamma_k^y (k) = \sum_j e^{-ik \cdot \mathbf{r}_j} \left\{ J_{j,1}^x e^{-ik \cdot \mathbf{r}_{j,1}} + J_{j,2}^y e^{-ik \cdot \mathbf{r}_{j,2}} + J_{j,3}^z e^{-ik \cdot \mathbf{r}_{j,3}} + J_{j,4}^y e^{-ik \cdot \mathbf{r}_{j,4}} \right\} \]

For \( \mathbf{Q} = (0, 0.295, 0) \), the wavevector associated with the magnetic transition at \( T = 42 \) K, the little group is \( C_{2v} \). The labels of the operators shown above correspond to the irreducible representations of \( C_{2v} \).

3. Exchange interaction and single ion anisotropy

There are two nearest neighbour exchange paths. The shortest one is in the \( c \) direction of length \( \sqrt{2} = 3.701 \) Å and pairs Mn atoms in position 1 with atoms in position 3 and atoms in position 2 with atoms in position 4. Each atom has two nearest neighbours in this path. The other nearest neighbour exchange path is within the \( ab \) plane of length \( \frac{1}{2} \sqrt{a^2 + b^2} = 3.940 \) Å and pairs atoms 1 with 2 and 3 with 4. For this path, each atom has four nearest neighbours. A third path, similar to the second path, of length \( \frac{1}{2} \sqrt{a^2 + 3b^2} = 9.149 \) Å, connects next-nearest neighbours in the \( ab \) plane. The third path is the source of frustration that leads to the spiral magnetic phase. There are several other exchange paths that are shorter than the third path; however the third path is possibly enhanced by super exchange interactions through the \( 8d \) O atoms, which are only 0.63 Å away from the midpoint of the path.

Each of the three exchange interactions is usually treated as a single, isotropic term of the form \( \sum_{ij} \mathbf{J}_i \cdot \mathbf{J}_j \). Some analyses have been extended to include anti-symmetric terms of the form \( \sum_{ij} \mathbf{D} \cdot \mathbf{J}_i \times \mathbf{J}_j \), where \( \mathbf{D} \) is a constant vector. However, the point group symmetry allows for a total of six independent exchange terms for each path, three symmetric and three anti-symmetric. These are:

\[ \mathbf{J}_1^x \mathbf{J}_2^x + \mathbf{J}_3^x \mathbf{J}_4^x \]
\[ \mathbf{J}_1^x \mathbf{J}_2^y + \mathbf{J}_3^y \mathbf{J}_4^y \]
\[ \mathbf{J}_1^x \mathbf{J}_2^z + \mathbf{J}_3^z \mathbf{J}_4^z \]
\[ \mathbf{J}_1^y \mathbf{J}_2^x + \mathbf{J}_3^x \mathbf{J}_4^y \]
\[ \mathbf{J}_1^y \mathbf{J}_2^y + \mathbf{J}_3^y \mathbf{J}_4^y \]
\[ \mathbf{J}_1^y \mathbf{J}_2^z + \mathbf{J}_3^z \mathbf{J}_4^y \]

for the first path and

\[ \mathbf{J}_1^x \mathbf{J}_2^x + \mathbf{J}_3^x \mathbf{J}_4^x \]
\[ \mathbf{J}_1^y \mathbf{J}_2^y + \mathbf{J}_3^y \mathbf{J}_4^y \]
\[ \mathbf{J}_1^z \mathbf{J}_2^z + \mathbf{J}_3^z \mathbf{J}_4^z \]
\[ \mathbf{J}_1^x \mathbf{J}_2^y + \mathbf{J}_3^y \mathbf{J}_4^x \]
\[ \mathbf{J}_1^y \mathbf{J}_2^y + \mathbf{J}_3^y \mathbf{J}_4^y \]
\[ \mathbf{J}_1^z \mathbf{J}_2^z + \mathbf{J}_3^z \mathbf{J}_4^z \]

for the second and third paths. In addition, there are six single ion anisotropy terms, which include effects of the local environment on the spin states,
\[ J_1^2 + J_2^2 + J_3^2 + J_4^2 \]
\[ J_1^2 J_1^2 - J_2^2 J_1^2 + J_3^2 J_3^2 - J_4^2 J_4^2 \]
\[ J_1^2 J_1^2 + J_2^2 J_2^2 - J_3^2 J_3^2 - J_4^2 J_4^2 \]
\[ J_1^2 + J_2^2 + J_3^2 + J_4^2 \]

Considering the exchange interaction and single ion anisotropy on the entire lattice, and using the Fourier transform of the magnetic operators, the Hamiltonian is

\[ H = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d^3k \sum_{ij} \left[ J_{1,ij} \cos \frac{k_x}{2} \right. \]
\[ \times (-\Gamma_1^1(k)\Gamma_1^1(-k) + \Gamma_2^2(k)\Gamma_2^2(-k) - \Gamma_3^3(k)\Gamma_3^3(-k) + \Gamma_4^4(k)\Gamma_4^4(-k)) \]
\[ + \left( J_{2,ij} \left[ \cos \left( \frac{k_x}{2} + \frac{k_y}{2} \right) + \cos \left( \frac{k_x}{2} - \frac{k_y}{2} \right) \right] + J_{3,ij} \left[ \cos \left( \frac{k_x}{2} + 3\frac{k_y}{2} \right) + \cos \left( \frac{k_x}{2} - 3\frac{k_y}{2} \right) \right] \right) \]
\[ \times (-\Gamma_1^1(k)\Gamma_1^1(-k) + \Gamma_2^2(k)\Gamma_2^2(-k) - \Gamma_3^3(k)\Gamma_3^3(-k) + \Gamma_4^4(k)\Gamma_4^4(-k)) \]
\[ + D_{ij}(\Gamma_1^1(k)\Gamma_1^1(-k) + \Gamma_2^2(k)\Gamma_2^2(-k) + \Gamma_3^3(k)\Gamma_3^3(-k) + \Gamma_4^4(k)\Gamma_4^4(-k)) ] \]

where \( J_{n,ij} = J_{n,ji} \) represent the six exchange couplings for each of the three paths and \( D_{ij} \) are the single ion anisotropy parameters. The spiral magnet phase is described by the order parameter \( \Gamma_3^3(Q) \). The Hamiltonian must be minimised at this wavevector, which implies that \((-J_{1,yy}/2 + J_{2,yy})\sin k_{yx}/2 + 3J_{3,yy} \sin 3k_{yx}/2 = 0 \). In addition, the sum of the coefficients of each term \( |\Gamma_1^1(k)|^2, |\Gamma_2^2(k)|^2 \) \( \text{and} \ |\Gamma_3^3(k)|^2 \) must be positive, and the coefficients of \( \Gamma_1^1(k)\Gamma_y^y(-k) \) and similar terms are also constrained.

The Hamiltonian (2) also describes excitations in the system, namely spin waves. Generally speaking, the spin wave spectrum will become non-degenerate due to anisotropy in the Hamiltonian, and a mixing of polarisations in each mode can be expected due to anti-symmetric terms in the Hamiltonian.

In conclusion, we have derived a general exchange Hamiltonian which includes nearest neighbour and next nearest neighbour (in the \( b \) direction) interactions, as well as single ion anisotropy terms.

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