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Spin wave dispersion and magnons from short range order in tapiolite ($FeTa_2O_6$); a quasi-two-dimensional antiferromagnet

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Abstract

We describe neutron inelastic scattering measurements of spin waves in the quasi-two-dimensional antiferromagnet $FeTa_2O_6$. The intrinsic spin wave dispersion for a single domain is deduced from linear spin wave theory and used to determine the intra-plane exchange coefficients. Almost dispersion-free excitations are observed along the $\mathbf{c}^*$ direction perpendicular to the magnetic planes. This justifies the neglect of inter-plane coupling, which merely stabilizes the ordered configuration below T_N. Spin wave theory yields values for the nearest neighbour and next nearest neighbour exchange constants on perpendicular diagonals of $J = -0.040(9)$ meV, $J'/J = 0.20(0)$, $J''/J = 0.23(9)$, and the anisotropy parameter $D = 0.31(8)$ meV. The large value of D shows an Ising-like spin configuration to be consistent with the experimental data. Measurements of the temperature dependence of the scattering show that magnetic excitations persist to at least 20 K (over two times T_N) due to the extensive 2D short range order. This is a highly unusual result, and has consequences for the understanding of two-dimensional spin systems.

1. Introduction

Tapiolite ($FeTa_2O_6$) is a naturally occurring mineral possessing planes of Fe^{2+} ions, which are widely spaced and weakly interacting. It is a good example of a 2D magnet, and shows a number of remarkable properties, including dimensional crossover (from 2D to 3D at 7.8 K) that can be seen with great clarity using neutron scattering [1]. It has a relatively complicated (and as yet not completely understood) spin structure, very high energy optical phonons, and

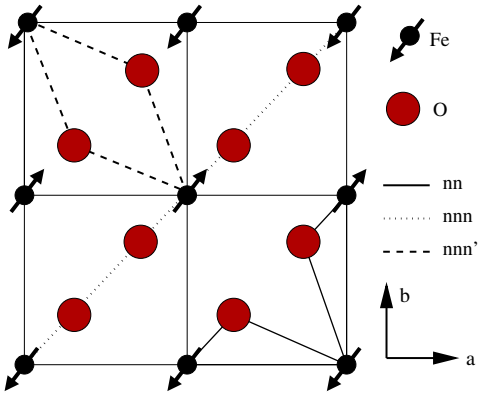

Figure 1. The {001} basal plane of four unit cells of $FeTa_2O_6$, illustrating intra-plane nearest neighbour (nn) and next nearest neighbour (nnn) exchange pathways. Arrows indicate the directions of the magnetic moments. The main interaction between nearest neighbours is between two moments of parallel spin and two of anti-parallel spin, indicating that the spin wave dispersion has an unusual structure. The nearest neighbour pathway has exchange constant J, [110] has $J' = \alpha J$, and $[\bar{1}10]$ has $J'' = \beta J$. The quantization axis z' lies along the indicated spin direction on the $x = y$ line.

(This figure is in colour only in the electronic version)

a static Jahn–Teller distortion showing potential for a significant electron–phonon interaction. Other notable 2D magnets with similar properties include the superconducting cuprates.

In a previous study we investigated the bulk magnetic properties of synthetic single crystals of $FeTa_2O_6$ and discovered that the crystals exhibited strong 2D magnetism associated with extensive short range order (SRO) within the magnetic Fe^{2+} layers [1]. In the current study we determine the magnitudes of the intra-plane exchange coefficients of $FeTa_2O_6$ using neutron inelastic scattering measurements of the spin wave dispersion of $FeTa_2O_6$ at 3 K.

Tapiolite crystallizes into a trirutile system with space group symmetry $P4_2/mnm$ [1]. Cation ordering of interpenetrating edge and corner-sharing Ta–O and Fe–O octahedra leads to layers of magnetic Fe^{2+} ions. The octahedra are locally distorted due to a static Jahn–Teller effect, and possess apical oxygen atoms oriented along [110] and $[\bar{1}10]$ directions in alternate planes. The interaction between next neighbouring planes along the **c** axis, J_c, takes place via three intervening O anions and two Ta cations. As a result, J_c is expected to be significantly smaller than the in-plane interactions.

Intra-layer exchange pathways in $FeTa_2O_6$ are complicated by an asymmetric arrangement of bridging oxygen atoms with differing bond angles and path lengths. The nearest neighbour (nn) and multiple next nearest neighbour (nnn) exchange pathways, superposed upon the accepted magnetic structure of four unit cells of $FeTa_2O_6$, are shown in figure 1. Inspection of the ordered magnetic structure indicates that nnn exchange interactions are important. However, it is difficult to distinguish *a priori* whether it is the linear nnn superexchange along the [110] Fe–O–O–Fe direction or the 160° $[\bar{1}10]$ Fe–O–Fe interaction that is the most dominant.

In a previous analysis of $FeTa_2O_6$ susceptibility data [2], Muraoka *et al* [3] describe the 2D magnetic planes using a Hamiltonian based upon the two-dimensional Heisenberg model with $S = 2$ spins placed on a square lattice:

$$H = -2J \sum_{\langle i,j \rangle}^{\mathrm{nn}} \mathbf{S_i} \cdot \mathbf{S_j} - 2\alpha J \sum_{\langle i,j \rangle}^{\mathrm{nnn}} \mathbf{S_i} \cdot \mathbf{S_j} - D \sum_i |\mathbf{S}_i|^2_{x=y}. \tag{1}$$

The first two terms represent nn and nnn Heisenberg intra-plane exchange interactions; see figure 1. The nn and nnn exchange interactions are denoted as J and J', and their ratio is defined as $\alpha = J'/J$. The two separate pathways along the [110] and [$\bar{1}$10] directions have not been distinguished. The third term represents the $x = y$ axis single-ion anisotropy causing spins to align with that axis, with the subscript denoting the magnitude of the spin projected onto the $x = y$ axis. For $FeTa_2O_6$ the quantization axis is directed along the [110] Fe^{2+}–O^{2-} bond, along which the moments are thought to align. From their analysis Muraoka *et al* obtain the following results: $-0.41 \leqslant J/k_B \leqslant -0.39$ K, $0.6 \leqslant \alpha \leqslant 0.9$, and $6.7 \leqslant D/k_B \leqslant 7.1$ K.

The magnetic structure of $FeTa_2O_6$ has previously been investigated using Mössbauer spectroscopy [2, 4, 5], and powder neutron diffraction measurements [2, 6]. These studies suggest that the spins in $FeTa_2O_6$ are constrained to the a–b plane, with each layer consisting of a collinear arrangement of moments. Opposite spins are oriented along $\pm$[110] directions, figure 1, and the layers either stack antiferromagnetically in the **c** direction, or are rotated by 90° between planes.

This paper is set out as follows. In section 2, we introduce the linear spin wave theory and derive dispersions for a number of minimal models. In section 3, we describe the experimental method used to measure the magnetic excitation spectrum. In section 4, results from constant **q** scans are presented, and the exchange coefficients are determined by fitting the expressions from section 2. Finally the results are summarized in section 5.

2. Spin wave theory

The linear spin wave theory of an antiferromagnet was introduced by Anderson [7] and is well suited to the analysis of systems with large spins. To describe the ground state of $FeTa_2O_6$ two intra-plane exchange interactions need to be included: (1) the antiferromagnetic exchange between nn sites; and (2) an antiferromagnetic exchange interaction along the diagonal of the unit cell to *one* set of nnn atoms. The difference in exchange along the two diagonals is represented by an additional term in the Hamiltonian,

$$H' = -2\beta J \sum_{\langle i,j \rangle}^{nnn'} \mathbf{S_i} \cdot \mathbf{S_j}, \tag{2}$$

i.e. interactions in the [110] direction relate to α and those in the [$\bar{1}$10] direction relate to β.

Small inter-planar interactions act to stabilize the spin wave solution for $T > 0$ (and lead to bulk 3D order below 7.8 K) but are otherwise expected to have a negligible effect within the accuracy of this experiment. A spin of $S = 2$ has been determined previously [1], so it is expected that linear spin wave theory will be quite accurate. Higher order interacting terms, which go as $1/4S$, are only expected to contribute to a renormalization of the interaction parameters J, α, β, and D, while leaving the structure of the unperturbed theory intact.

Three models are proposed.

(1) The first includes only nearest neighbour interactions, and an anisotropy term which aligns spins with the x–y axis (equation (1) with $\alpha = 0$).
(2) The second adds next nearest neighbour coupling and is equivalent to the model from [3] (equation (1) with the α term).
(3) The third includes all possible exchange paths consistent with the crystal symmetry (sum of equations (1) and (2)).

Treatment of the Hamiltonian proceeds in the usual way, with the transformation of equations (1) and (2) using the Holstein–Primakov substitution to introduce creation (and

annihilation) operators, $a^\dagger$ (a) and $b^\dagger$ (b), for bosonic spin excitations on sublattices A and B (spin waves):

$$S_{A-} = S_{x'} - \mathrm{i}S_{y'} = (2S)^{1/2} a_l^\dagger \left(1 - \frac{a_l^\dagger a_l}{2S}\right)^{1/2} \approx (2S)^{1/2} a_l^\dagger \left(1 - \frac{a_l^\dagger a_l}{4S}\right) \tag{3}$$

$$S_{A+} = S_{x'} + \mathrm{i}S_{y'} \approx (2S)^{1/2} \left(1 - \frac{a_l^\dagger a_l}{4S}\right) a_l \tag{4}$$

$$S_{Az'} = S - a_l^\dagger a_l \tag{5}$$

$$S_{B+} \approx (2S)^{1/2} b_j^\dagger \left(1 - \frac{b_j^\dagger b_j}{4S}\right) \tag{6}$$

$$S_{B-} \approx (2S)^{1/2} \left(1 - \frac{b_j^\dagger b_j}{4S}\right) b_j \tag{7}$$

$$S_{Bz'} = b_j^\dagger b_j - S \tag{8}$$

where the primed coordinates represent a rotated basis where the quantization axis is aligned with the z' direction which lies along the line $x = y$.

Linearization of the problem to a soluble form is carried out by neglecting terms in $1/4S$ (i.e. interactions of magnons with each other are neglected) and diagonalizing the Hamiltonian using the Bogoliubov transformation. Some care has to be taken, since the spins in the proposed model are ferromagnetic along the x axis and antiferromagnetic in the y direction, and since the quantization axis in this case is in the xy direction (i.e. parallel to the spins). In practice, one rotates the problem so that there is a z' axis along the real space xy direction to carry out the calculation correctly. Otherwise, the standard definitions of the Holstein–Primakov transformation would have the wrong quantization axis for the model. The resulting expressions are then rotated back into the natural coordinate system for neutron scattering. From the calculation, dispersion relations of the following form are found:

$$\omega_{\mathbf{q}}^{(1)} = 2S\left((D - J\cos(2\pi(k_x + k_y)))^2 - (J\cos(2\pi(k_y - k_x)))^2\right)^{1/2} \tag{9}$$

$$\omega_{\mathbf{q}}^{(2)} = 2S((D - J\cos(2\pi(k_x + k_y)) - J'(\cos(2\pi k_x) + \cos(2\pi k_y) - 4))^2 - (J\cos(2\pi(k_y - k_x)))^2)^{1/2} \tag{10}$$

$$\omega_{\mathbf{q}}^{(3)} = 2S((D - J\cos(2\pi(k_x + k_y)) - J'\cos(2\pi k_x) - J''\cos(2\pi k_y) - 2J' - 2J'')^2 - (J\cos(2\pi(k_y - k_x)))^2)^{1/2} \tag{11}$$

where $J' = \alpha J$ and $J'' = \beta J$. It should be noted that for small $D \lesssim J$, J', the spectrum is not defined at all frequencies. This is expected from the nature of the model and the approximate nature of the spin wave analysis. In carrying out the analysis, we have chosen the quantization axis to lie along the $x = y$ direction. This is the correct axis for large D, where the spins are constrained to lie along the $x = y$ direction, whereas for small D, the quantization axis may be rotated. Thus if there is insufficient anisotropy the above analysis is invalid. We will demonstrate later that the anisotropy term is an order of magnitude larger than the exchange coupling, so the analysis is applicable in this case.

It should be noted that the proposed spin structure has spins in neighbouring layers which are rotated by 90° with respect to one another. Also there is a possibility of two spin domains rotated by 90°. Therefore (as we will show later) the measurements appear to show two modes, whereas each of equations (9)–(11) (relating to each of the three models), which are calculated from the point of view of one domain, predict only one mode. The effect of the domains is

the excitation of spin waves with momentum **q** and **Q** + **q**[Note 7]. Both modes are taken into account during the fitting of the spin wave theory.

3. Experimental method

Natural crystals of tapiolite tend to contain impurities such as Mn^{2+} and Nb^{2+}, and also exhibit a substantial reduction in cation ordering. Hence, for this experiment, synthetic single crystals of $FeTa_2O_6$ were grown using the floating zone method under a controlled atmosphere of Ar, CO, and CO_2. Full details of the crystal growth are described elsewhere [1, 8].

The spin wave dispersion of single-crystal $FeTa_2O_6$ was investigated using the DrüChaL triple-axis spectrometer located at the SINQ neutron source, Paul Scherrer Institut, Switzerland. The sample consisted of a cylindrical single crystal of $FeTa_2O_6$, 0.5 cm in diameter and 2 cm long, with approximately 0.5° mosaic spread. Small portions of the same crystal used in other experiments have indicated our samples to be of good quality and to possess all of the expected magnetic properties [1]. To measure the dispersion of $FeTa_2O_6$ along the **a** and **c** directions the sample was aligned with the (h 0 l) scattering plane horizontal. The crystal was then sealed inside a helium filled can, and cooled to 3 K. Measurements were performed in constant Q mode using a fixed final energy of $E_f = 5.57$ meV, selected using a pyrolytic graphite filter, monochromator, and analyser. The crystal was then remounted in the (h k 0) horizontal plane, and additional measurements were taken.

4. Results and analysis

The temperature dependence of the inelastic scattering in $FeTa_2O_6$ was measured at the zone boundary position **Q** = (0.75 0.75 0) (with the crystal oriented so that the (**a*** **b*** 0) scattering plane was horizontal). Results for various temperatures (3, 8, 10, and 12 K) are shown in figure 2, with the fit obtained from two Gaussians with a linear background. The spin waves remained well defined at temperatures substantially above T_N (which is the temperature at which 3D ordering between the planes is obtained, while short range order in the plane persists to much higher temperatures [1]). This suggests that even above T_N there are large correlated regions in the crystal, through which magnetic excitations can propagate. Between 3 K and T_N the inelastic spin wave spectra remain virtually unchanged. Above $T_N = 7.8$ K, the magnetic excitations begin to become obscured by a large background due to diffuse scattering, which was not present in the 3 K data. At 20 K, which is over two and a half times T_N, magnetic excitations finally disappear within the sensitivity of this experiment.

In scans along [0 0 **q**] obtained close to the (0.5 0 1.5) reciprocal lattice position two modes were consistently observed, separated from one another at the zone centre by approximately 0.73 meV; see figure 3. The energies of the two modes in this direction remained constant at around 1.79 ± 0.05 and 2.52 ± 0.05 meV. As discussed before, two modes are expected, due to the presence of either two domains with perpendicular spins or spins rotated by 90° between alternate layers. The nearly complete absence of dispersion in the direction perpendicular to the magnetic planes is typical of 2D materials and indicates that the inter-plane exchange is much smaller than the intra-plane exchange, providing partial justification for our model.

The dispersion measured along the [1 0 0] direction is shown in figure 4. The dispersion was also measured in the [1 1 0] direction. The results of these measurements are presented in figure 5. To obtain these data the crystal was remounted with the **a** and **b** axes in the scattering

[7] The use of **Q** should not be confused with the full scattering vector.

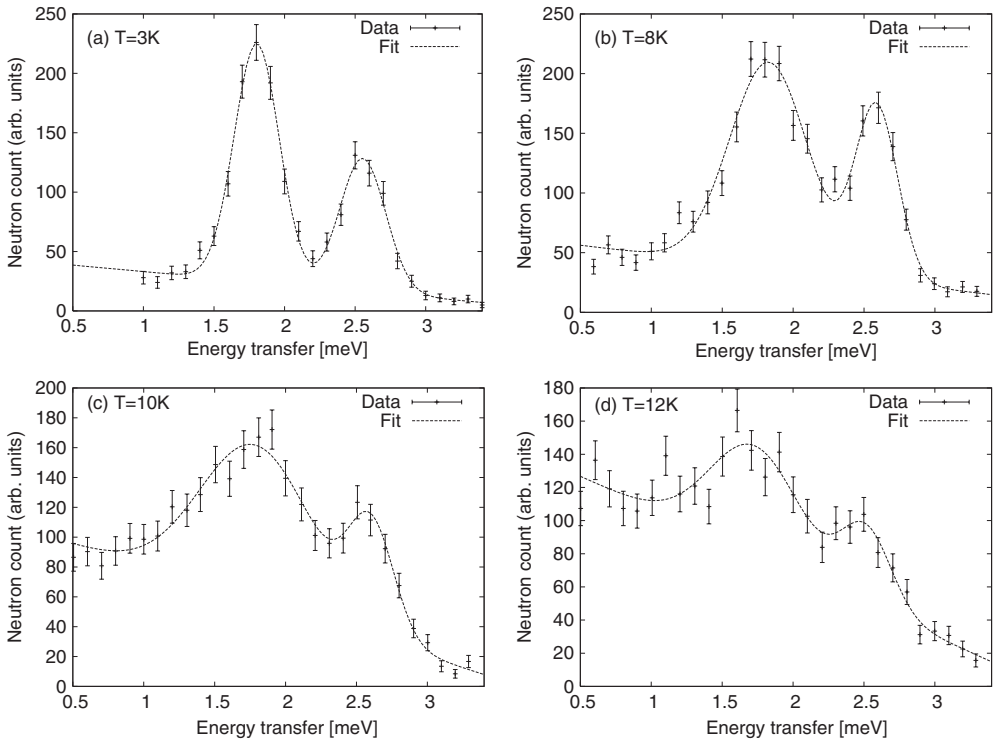

Figure 2. Temperature dependence of constant energy scans at $\mathbf{q} = (0.75, 0.75, 0)$. Data were fitted using two Gaussians with a linear background to take into account diffuse scattering. (a) $T = 3$ K, (b) $T = 8$ K, (c) $T = 10$ K, (d) $T = 12$ K. The presence of magnetic excitations above the Néel temperature ($T_N = 7.8$ K) is remarkable.

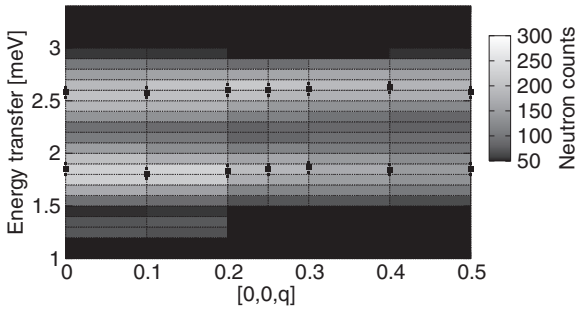

Figure 3. Raw dispersion data measured for a single crystal of $FeTa_2O_6$ along the [0 0 1] direction at 3 K. Markers show the energies of the spin waves, determined by fitting Gaussian peaks. The dispersion is practically flat, confirming the validity of neglecting the inter-plane exchange coefficients in our model.

plane. The measurement therefore corresponds to a path from (0.5 0.5 0) to (1 1 0) along an equivalent portion of the zone wall in both orientations of the Brillouin zone.

The entire 3 K data set in the **ab** plane was fitted to the linear spin wave theory shown in equations (9)–(11). The resulting spin wave dispersion resulting from the fitting of model 3 (equation (11)) for a single domain of $FeTa_2O_6$ is shown in figure 6. From the data, values for

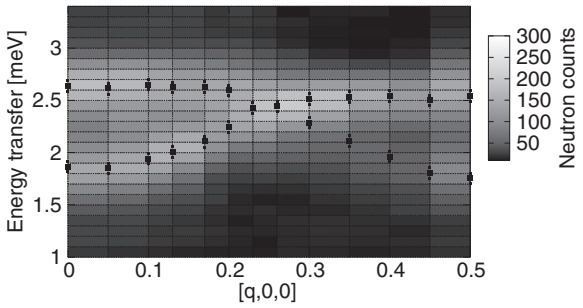

Figure 4. Dispersion data measured for a single crystal of $FeTa_2O_6$ along the [1 0 0] direction at 3 K. Markers show the peak centres estimated using a two-Gaussian least-squares fitting procedure. Beneath the markers lies an image plot constructed from the original data points. Where the peaks are close together in energy space, the fitting was performed with the widths of the Gaussians constrained to be equal. Two modes are seen because of the two perpendicular spin domains in the material.

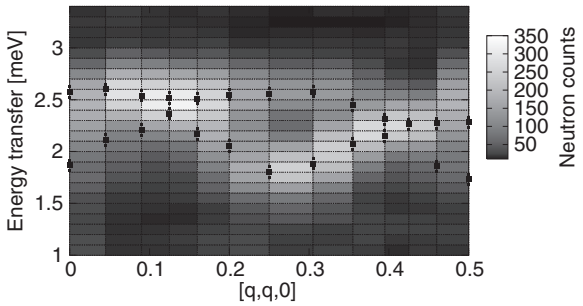

Figure 5. Dispersion curves measured along the [1 1 0] direction from (0.5 0.5 0) to (1 1 0). The markers indicate the positions of the centres of Gaussian fits to the data. At the positions where the excitations were overlapping the fitting was conducted using two Gaussian functions of fixed width. Superimposed is an image plot showing the raw data from the scans. Again, two modes are clearly visible.

the exchange and anisotropy parameters are obtained (see table 1). Of particular interest are the values corresponding to the results in [3], which are in broad agreement with our own.

Finally we plot the dispersion corresponding to model 3 over the whole q_x–q_y plane in figure 7. This shape of the dispersion arises due to the nature of the antiferromagnetism (spin stripes in the x direction), the anisotropy in the model, and the direction of the spins in the ground state.

5. Summary and discussion

Spin wave dispersion curves for a single crystal of $FeTa_2O_6$ were measured at 3 K. We find that the dispersion of $FeTa_2O_6$ is virtually flat along the direction perpendicular to the magnetic planes. This is a common signature of 2D magnetism and is in agreement with our classification of $FeTa_2O_6$ as a quasi-2D antiferromagnet [1]. To disentangle the intrinsic excitation spectra of $FeTa_2O_6$ from modes arising from multiple magnetic domains, modelling of the theoretical dispersion using linear spin wave theory was required. The values for the exchange coefficients and anisotropy parameter of $FeTa_2O_6$ determined from our data are in good agreement with previous estimates obtained from the powder susceptibility by Muraoka

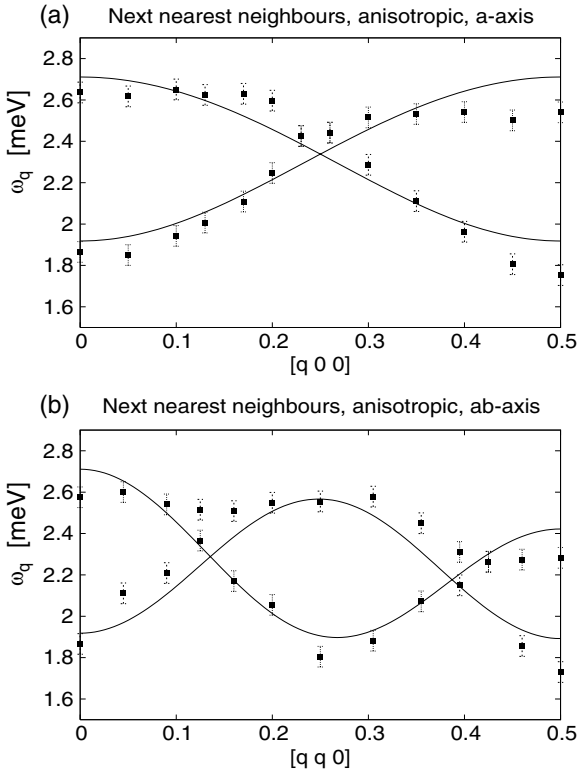

Figure 6. The line shows the fits produced by linear spin wave theory with anisotropic next nearest neighbour interactions. Panel (a): the dispersion along the **a** direction; panel (b): the dispersion along the **a**–**b** direction. The fit is generally good, and the χ^2 of ∼4 indicates that most of the available information has been described.

Table 1. Exchange coefficients for a single crystal of $FeTa_2O_6$ at 3 K, estimated from fitting the observed data using linear spin wave theory. The nearest neighbour model remains the same regardless of the antiferromagnetic vector. Antiferromagnetic vectors have been tried in the **a** and **b** directions for the next nearest neighbour models. A **Q** in the **a** direction is favoured by the lowest χ^2 value. There is little to tell between the two next nearest neighbour models. For comparison, the results for the coefficients determined by Muraoka are also shown (top).

Model	**Q**	J (meV)	J'/J	J''/J	D (meV)	χ^2
Muraoka	**b**/2	−0.035(3)	0.78	n/a	0.29(3)	240
Muraoka	**a**/2	−0.035(3)	0.78	n/a	0.29(3)	61.0
nn	**a**/2, **b**/2	−0.044(9)	n/a	n/a	0.28(8)	6.133
+nnn	**b**/2	−0.044(8)	0.14(9)	n/a	0.31(4)	4.61
$+J''$	**b**/2	−0.044(8)	0.21(6)	0.10(3)	0.31(6)	4.40
+nnn	**a**/2	−0.040(5)	0.22(4)	n/a	0.31(9)	4.10
$+J''$	**a**/2	−0.040(9)	0.20(0)	0.23(9)	0.31(8)	4.09

et al [3]. As the inter-plane exchange is much less than the intra-plane exchange we confirm that the magnetic interactions in $FeTa_2O_6$ are primarily 2D. Remarkably in this quasi-2D material, the simple linearized spin wave theory gave very good agreement with the experimental data. This is attributed to the large value of the spin ($S = 2$) for $FeTa_2O_6$. The large anisotropy

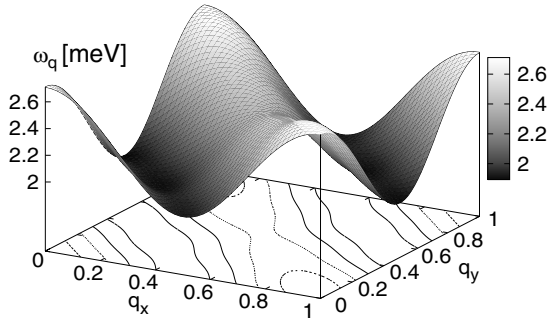

Figure 7. The surface shows the extrapolation of the fit produced by linear spin wave theory to the full q_x, q_y plane. This dispersion arises due to the nature of the antiferromagnetism, the anisotropy in the model, and the direction of the quantization axis.

term indicates that a simple Ising-like model could be employed to describe the magnetic excitations. Also, the magnetic excitations are very stable with regard to temperature, with the dispersion not only remaining unchanged up to the Néel temperature, but also persisting *above* the antiferromagnetic transition temperature. This is highly unusual, since it indicates that spin waves can be created by short range order. To the best of our knowledge, the observation of SRO magnons at significantly higher temperatures than the Néel temperature is unprecedented. It is particularly interesting that such magnons are observed in this material, since above the transition temperature, spins in the *c* direction are essentially uncorrelated and the material effectively acts as a pure 2D system. Typically, spin waves are not thought to be permitted in pure 2D, because of the Mermin–Wagner theorem. It is of clear experimental and theoretical interest to study the existence of SRO magnons in more depth.

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