Magnetic-field-orientation dependence of the metamagnetic transitions in TmAgGe up to 55 T

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Abstract. TmAgGe is an antiferromagnet based on the ZrNiAl structure. At low temperatures the spins are confined to distorted kagome-like planes, wherein the magnetisation is strongly anisotropic. A previous study has shown that a series of stepped magnetic transitions are apparent in low, in-plane magnetic fields and can be explained using a three-fold Ising-like model. Here we present high-magnetic-field magnetisation experiments showing that further stepped transitions are observed when the field is directed out of the kagome planes. Angle-dependent measurements in fields of up to 55 T show that there are at least two distinct and separate energy scales present in this system; the weak exchange interactions and the strong crystalline electric field interactions. Simulations of the magnetisation using a three-dimensional, free-energy minimisation technique allow us to suggest the nature and hierarchy of the forces acting on the Tm3+ moments.

1. Introduction
TmAgGe is a highly anisotropic magnetic material adopting a distorted-kagome lattice similar to the ZnNiAl structure, in which the Tm3+ (4f12, 3H6) moments are confined to the ab-planes at low temperatures (see Figure 1). Geometrical frustration may be expected to arise from antiferromagnetic interactions between spins arranged on a kagome lattice, however no evidence of frustration is observed in this material and the system orders at temperatures below $T_N \approx 4.2$ K, which is similar in magnitude to the Curie-Weiss temperature derived from the susceptibility in the ab-planes [1]. When a magnetic field is applied parallel to the ab-planes a series of step-like transitions are observed in the magnetisation that result in a crystal-field limited saturated paramagnetic state (CL-SPM) at fields above about 2 T. These metamagnetic transitions can be explained by considering interactions between the magnetic moments as well as a strong easy axis anisotropy [2].

The left-hand side of Figure 2 shows the metamagnetic transitions, which appear as peaks in the magnetic susceptibility, at several values of $\phi$, the angle between the magnetic field and the c-axis. We find that these transitions depend only on the component of the magnetic field parallel to the ab-planes. We further find that if a much higher magnetic field is applied another series of abrupt transitions are observed that result in the magnetisation approaching its full saturated
Figure 1. Projection of the distorted kagome structure of TmAgGe in the \(ab\)-plane. Tm: red, Ag: silver, Ge: gold. The shaded areas are the triangles that would be frustrated in the absence of anisotropy. The model used in Section 3 to simulate the magnetisation has the spins labelled 1 - 6 as its repeating structure.

value of 7\(\mu_B\) per Tm\(^{3+}\) ion. These transitions are shown in the right-hand side of Figure 2, and it is found that they depend only on the component of magnetic field perpendicular to the \(ab\)-planes. The complete \((H, \phi)\) phase diagram is shown in Figure 3 where it can be seen that the low- and high-field transitions remain separated at all inclination angles.

In this article we propose the existence of two distinct energy scales in this system. The first of the order of 4 K, which accounts for the observed Néel temperature in the in-plane magnetic susceptibility, and the low-field metamagnetic transitions. It is sensitive only to the component of magnetic field parallel to the \(ab\)-planes and arises from exchange interactions between the Tm ions. The second energy scale is of the order of 100 K and accounts for the departure from paramagnetic behaviour observed in the \(c\)-axis susceptibility at about this temperature [1], and the abrupt features in the magnetic measurements at fields of around 30 T. It is sensitive only to the component of the magnetic field perpendicular to the \(ab\)-planes. We further propose that this energy scale arises from the crystalline electric field (CEF) splitting of the Tm\(^{3+}\) \(J = 6\) multiplet, which at low temperatures leads to the strong easy-axis anisotropy. Similar arguments have been proposed to account for the broad magnetisation features in HoNi\(_2\)B\(_2\)C. [3].

2. Experimental details

The details of the technique used to grow the single crystals of TmAgGe may be found elsewhere [1]. Several oriented single crystals with volumes of the order of 0.7 \(\times\) 0.7 \(\times\) 2 mm\(^3\) were used in the magnetic measurements, which maybe separated into two types: those that make use of a Quantum Design superconducting quantum interference device (SQUID), in which the magnetic moment is measured in quasi-static magnetic fields of up to 9 Tesla and temperatures as low as 2 K; and those performed in pulsed magnetic fields of up to 65 Tesla. The SQUID data are used to calibrate the magnetisation data recorded in the pulsed-field measurements.

The pulsed-field measurements were performed in the National High Magnetic Field Laboratory in Los Alamos, USA. The magnets employed are nitrogen cooled and have rise-times of the order of 10 ms. The magnetisation measurements use compensated micro-coil magnetometers that take advantage of the high \(dB/dt\) environment produced by a pulsed magnet by measuring the voltage induced in the coil by the changing magnetic moment of the sample. In order for this technique to be successful the signal produced by the sample must be carefully separated from the signal produced by the coil alone. This is achieved via a three-stage process. The coil into which the sample is placed is counter-wound in such a way as to be highly compensated to begin with. In addition, the signals from the coil that contains the sample and another, empty coil are subtracted electronically during the measurement. Finally, the sample is mounted so that it can be inserted into and extracted from the coil \textit{in situ}. Two magnetic field pulses are then performed with identical control settings, one with the sample inserted and one with it extracted and the resulting datasets are subtracted from one another, yielding a highly accurate and consistent measurement of the sample’s magnetisation \((M)\). Because the signal is
proportional to $\delta M/\delta B$ the technique is particularly sensitive to abrupt, or step-like transitions. In one of the magnetometers the sample coil may be tilted so that the angle-dependence of the magnetization can be recorded. This was used to obtain the data in Figure 2. The angle of inclination is calibrated by comparing the signal from an empty coil located on the tilting platform, and that from another empty, but static coil. In this case in situ extraction of the sample is not possible and so absolute values of the magnetisation cannot be obtained. All the magnetometers can be placed inside $^3$He cryostats allowing access to temperatures as low as 500 mK.

3. Low-field transitions
The magnetisation of TmAgGe as a function of the magnetic field applied in the $ab$-planes is shown in Figure 4, which is reproduced from Reference [2]. In that reference the authors have shown that the azimuthal angle-dependence of the critical fields and magnetisation values of the observed low-field metamagnetic transitions arise out of competition between exchange interactions, the easy-axis anisotropy and the Zeeman energy [2]. However, the precise details of the interactions between the Tm ions remain unclear. Here we perform classical simulations that make use of a free energy minimisation technique to obtain the repeating magnetic structure and a Hamiltonian that can reproduce the salient features of the experimental magnetisation.
In this way we can, for the first time, find estimates of the strengths of the interactions to which the magnetic moments are subjected. To achieve this we first calculate the free energy of a number of spins acted on by a suitable Hamiltonian, then, using the downhill simplex method of Nelder and Mead [4, 5], find the minimum spin configuration at a given magnetic field. The spins are rearranged, the field increased and the procedure begins again. Careful consideration of the initial conditions enable local minima in the free energy to be avoided.

TmAgGe adopts the ZnNiAl distorted kagome structure shown in Figure 1; here the Tm ions are red, the Ag ions are silver and the Ge ions are gold. Next-nearest-neighbour antiferromagnetic (AF) interactions between the Tm$^{3+}$ ions in the ab-plane would, in the absence of any other interactions, lead to geometrically frustrated triangles of Tm moments, indicated by shaded areas in the figure. The azimuthal-angle dependence of the metamagnetic transitions suggest that each spin is strongly aligned along an easy axis, which passes through the centre of the triangle, resulting in an angular separation of $120^\circ$ [2]. It is this easy-axis anisotropy that alleviates the frustration and allows the material to order at low temperatures.

Now we wish to determine the repeating magnetic structure containing the minimum number of spins that can account for the observed transitions. It is clear that with the magnetic field in the ab-planes each spin can lie parallel or antiparallel to its easy axis and so there are $n^2$ possible configurations, where $n$ is the number of spins included in the model. The degeneracy of these configurations depends on the azimuthal angle of the applied field. In Reference [2] it was shown that the majority of the metamagnetic phases can be accounted for by considering a repeating unit of 6 spins. In the course of the present studies we find that we must include nearest-neighbour ferromagnetic (FM) interactions in the ab-planes as well as the AF interactions and the easy-axis anisotropy in order to successfully simulate the magnetisation. Note that the FM and AF interactions acting on nearest- and next-nearest-neighbours, respectively, are not in competition. Such exchange interactions have already been suggested to be important in CePdAl, which has a similar structure to TmAgGe [6, 7].

Thus the minimum-spin repeating structure is as follows: two triangles of spins are included, labeled 1 - 6 in Figure 1 in which next nearest neighbours 1, 2 & 3 and 4, 5 & 6 interact antiferromagnetically; spin 3 interacts ferromagnetically with its neighbours 4 and 5; and, because every second triangle of spins is considered equivalent, spin 2 has FM interactions
with spins 4 and 6. There are no FM interactions acting on spin 1 in this model; this will be discussed later. The Hamiltonian used in the simulations is given by

\[ H = J_{AF} \sum_{ij} S_i \cdot S_j + J_{FM} \sum_{ij} S_i \cdot S_j + \Delta \sum_i (S_i^\Delta)^2 - g\mu_B \sum_i S_i \cdot B \]  

where the first term on the right is the Heisenberg-type AF interaction; the second term is the FM interaction; \( J_{AF} \) and \( J_{FM} \) are the next-nearest-neighbour AF and nearest-neighbour FM exchange constants and are positive and negative, respectively; the third term is the single ion anisotropy; \( S_i^\Delta \) is the component of the \( i \)th spin along the local easy axis; \( \Delta \) is the anisotropy energy and is negative; finally, the fourth term is the Zeeman energy.

The results of applying this model to simulate the magnetisation of TmAgGe are seen in Figure 5, which shows \( M(B) \) with the field applied along the [110] and [120] directions, and Figure 6 which shows a phase diagram as a function of both the strength of the applied magnetic field and its direction, given by the azimuthal angle, \( \theta \), measured from the [110] crystallographic direction. The colour indicates the magnitude of the magnetisation at that point in the diagram. A spin configuration for each state is also shown. It is seen that the simulations agree well with the experimental data of Ref [2], except for the absence of the \( M_1 \) state in the simulated data. This is to be expected as the configuration that leads to the \( M_1 \) state is known to require a minimum of 18 spins for its definition and so cannot be reproduced by the simple 6-spin model used here [2]. However, all the other features of the experimental data are reproduced.

The azimuthal angle dependences of the critical fields can be obtained by equating the free energies of the metamagnetic states and are as follows:

\[
\begin{align*}
B_c^{AF \to M_2} &\propto J_{AF}/\cos \theta; \\
B_c^{M_2 \to CL-SPM} &\propto (2J_{AF} - J_{FM})/(\cos \theta + \sqrt{3}\sin \theta); \\
B_c^{M_2 \to M_3} &\propto (J_{AF} - J_{FM})/\cos \theta;
\end{align*}
\]
Figure 7. The simulated \((H, \phi)\) low-field phase diagram of TmAgGe, where \(\phi\) is the angle between the magnetic field and the \(c\)-axis, and \(\theta = 20^\circ\) defines the plane of rotation. The magnitude of magnetisation is shown by the colour key. The points are metamagnetic critical fields derived from experimental data and the dotted lines are fits of the data to \(1/|\sin \phi|\).

\[
B_{C}^{M_1 \rightarrow CL-SPM} \propto -J_{FM}/(\cos \theta + \sqrt{3}\sin \theta).
\]

In each case the constant of proportionality is \(J/g_J \mu_B\), where \(J\) is the total angular momentum quantum number and \(g_J\) is the Landé g-factor (\(J = 6\) and \(g_J = 7/6\) for the Tm\(^{3+}\) ion). These functions are shown as lines in Figure 6. Note that in the experimental data the \(M_2 \rightarrow CL-SPM\) transition is obscured by the \(M_1\) state.

From the experimentally determined critical fields it is possible to obtain estimates for the exchange constants and accordingly we find that \(J_{AF} = 0.054\) K and \(J_{FM} = -0.064\) K. The energy ranges of the first two terms in the Hamiltonian of Equation 1 are \(\pm J^2J_{AF}\) and \(\pm J^2J_{FM}\). And so we find, using the above values for \(J_{AF}\) and \(J_{FM}\), that the energy scale at which the exchange interactions are important is \(\sim 4\) K. This is in agreement with the experimental value of \(T_N\).

Although the moments are strongly inclined to lie along the easy axes, the finite value of \(\Delta\) means that they will have a tendency to align parallel to the applied magnetic field, leading to the slight increase of the magnetisation observed in the CL-SPM state as the field rises (see Figure 4). Using this gradient we find that \(\Delta = -4.6\) K. The range of the anisotropy term in Equation 1 is thus \(J^2\Delta \approx 170\) K, explaining why the \(c\)-axis susceptibility departs from a linear temperature dependence just below this temperature. It also explains why, although we have next-nearest-neighbour AF interacting spins on a kagome lattice no evidence for geometrical frustration is observed. Many frustrated planar triangular systems adopt the non-collinear or compromise structure in which the spins lie 120\(^\circ\) apart. The large anisotropy in TmAgGe forces this compromise structure on the system at temperatures far in excess of those at which the AF interactions become important. The compromise structure has a number of different degenerate spin configurations, but in TmAgGe the degeneracy is lifted by the FM nearest-neighbour interactions that lead to the observed ordering at low temperatures and the positive value of the Curie-Weiss temperature derived from the susceptibility in the \(ab\)-planes [1]. These states are then accessible using small in-plane magnetic fields, accounting for the metamagnetic transitions.

Figure 7 shows the phase diagram of TmAgGe as a function of the magnetic field and the inclination angle \(\phi\), simulated using the model described above. Again the colour indicates the magnitude of the magnetisation. It is seen that, in agreement with experiment, the low-field, metamagnetic transitions depend only on the component of the magnetic field in the \(ab\)-planes and hence the critical fields scale as \(1/|\sin \phi|\). The best agreement between the experimentally
observed critical fields shown in Figure 3 and the simulations is found to occur when the plane of rotation is set to be $\theta = 20^\circ$. Experimental data are also plotted in Figure 7 for comparison.

In this section it has been shown that the model and Hamiltonian outlined here successfully describe almost all of the results of the low-field magnetic measurements. However, in order to achieve this success it is necessary to suppress the FM interactions between the spin labelled 1 in Figure 1 and its nearest-neigbours: if these interactions are switched on in the simulations then the angular region over which the $M_3$ state is observed is severely reduced and the $M_2$ state disappears completely, in contradiction to the experimental evidence. The physical interpretation of this is not entirely clear. The most likely explanation is that the 6-spin model we have employed is merely a subset of the actual repeating magnetic structure in the real TmAgGe system, and a larger structure with all the interactions switched on may describe the experimental features as well or better – we already know that at least 18 spins are required to reproduce the $M_1$ state.

4. High-field transitions
The model Hamiltonian of Equation 1 predicts that when subjected to a magnetic field applied parallel to the $c$-axis the low-temperature magnetisation should increase linearly in field with a gradient given by $g_J\mu_B/2\Delta$, reaching its saturated value of $7\mu_B$ per Tm$^{3+}$ ion at approximately 70 Tesla.

Figure 8 shows the experimentally measured susceptibility and magnetisation with $B \parallel c$. It is seen that the magnetisation does indeed increase linearly at low fields (albeit at low temperatures with a shallower gradient than that predicted); however around 30 T the three abrupt transitions mentioned earlier are observed, and the magnetisation approaches its saturated value. These transitions can be seen at temperatures up to at least 70 K, an order of magnitude higher than $T_N$, indicating that they cannot be attributed to antiferromagnetic interactions. Instead they are on an energy scale similar to the anisotropy term Equation 1. The most likely candidate for interactions in this energy scale is CEF splitting of the $J = 6$ multiplet, which gives rise to the easy-axis anisotropy seen at low temperatures. Such splittings would be of the order of $J^2\Delta$ (see the third term in Equation 1). The energy scale of the easy-axis anisotropy is $\sim 170$ K, when the Zeeman energy $= g_J\mu_B JB$ becomes of this order level crossings may be expected, we find
that this occurs when the magnetic field $\sim 36$ T in accordance with the observed transitions.

The Tm ions are located at sites with orthorhombic symmetry $C_{2v}$ (2mm) [8] and so the full CEF term in the Hamiltonian should be [9]

$$CEF = \sum_{n=2,4,6} \sum_{m=0}^{n} B_{n}^{m} O_{m}^{n}$$

where the $B_{n}^{m}$ and $O_{m}^{n}$ are the CEF parameters and Stevens operators, respectively. The operators with $m \neq 0$ contain the angular momentum raising and lowering operators and so if the corresponding CEF parameters are large enough these terms will lead to substantial mixing of the $J_{z}$ energy levels, where $J_{z}$ is the $z$-component of the total angular momentum quantum number.

At high temperatures the gradient of the linear part of the magnetisation with $B_{\parallel} c$ tends towards that predicted by the Hamiltonian of Equation 1, indicating that at these temperatures the $J_{z}$ levels are evenly occupied. At low temperatures the gradient tends to half the predicted value leading to an expected saturated moment of $3.5 \mu_{B}$ per Tm$^{3+}$ ion in the absence of any sudden transitions. This implies that either the ground state, where the moments lie in the $ab$-planes (hence $J_{z} = 0$), has a significant proportion of $J_{z} = 3$ mixed in, or alternatively that it is only separated by small energies from the pure $J_{z} = 3$ state at $T \approx 0.5$ K. Instead of continuing to increase linearly the magnetisation jumps at around 30 T directly to $M \approx 3.5 \mu_{B}$ per Tm$^{3+}$ ion suggesting that the $J_{z} = 3$ energy level crosses the ground state at this field. The values of magnetisation immediately following the other two high-field transitions are suggestive of subsequent crossings by energy levels with significant proportions of $J_{z} = 4$ and $J_{z} = 5$, respectively. Further simulations making use of Equation 2 are required to strengthen these assertions. However the confirmation of this interpretation must await the measurement of the $B_{n}^{m}$ parameters by inelastic neutron scattering.

5. Summary

In summary, we have shown the existence of two distinct energy scales in the anisotropic magnetic system TmAgGe. The first is of the order of 4 K and originates from exchange interactions between the Tm ions. We have used classical simulations to determine a minimum spin repeating magnetic structure together with a Hamiltonian that adequately describes the metamagnetic transitions at these low energies, and have obtained estimates of the exchange constants. The other, larger energy scale is of the order of 100 K and gives rise to the transitions in the magnetisation in perpendicular fields of about 30 T that are reported here for the first time. We suggest that these transitions are due to crossing of CEF-split energy levels.

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[1] Morosan E, Bud’ko S L, Canfield P C, Torikachvili M S and Lacerda A H 2004 J. Magn. Magn. Matter. 277 298
[2] Morosan E, Bud’ko S L and Canfield P C 2005 Phys. Rev. B 71 014445
[3] Abliz M, Kindo K, Kadowaki K, Takeya H 2003 J. Phys. Soc. Japan 72 2599
[4] Nelder J A and Mead R 1965 Computer Journal 7 308
[5] Press W H, Teukolsky S A, Vetterling W T and Flannery B P 1986 Numerical Recipes In Fortran 77 (Cambridge: CUP) p402
[6] Nishiyama M, Oyamada A, Maegawa S, Goto T and Kitazawa H 2003 J Phys: Condens. Matter 15 S2267
[7] Núñez-Regueiro M D, Lacroix C and Canals B 1997 Physica C 282
[8] Baran S, Hofmann M, Leciejewicz J, Penc B, Slaski M and Sztytula A 1998 J. Alloys Comp. 281 92
[9] Walter U 1984 J. Phys. Chem. Solids 45 401