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Published in:
Nature Materials

DOI:
10.1038/nmat3358

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Solitonic lattice and Yukawa forces in the rare-earth orthoferrite TbFeO$_3$

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The random fluctuations of spins give rise to many interesting physical phenomena, such as the ‘order-from-disorder’ arising in frustrated magnets and unconventional Cooper pairing in magnetic superconductors. Here we show that the exchange of spin waves between extended topological defects, such as domain walls, can result in novel magnetic states. We report the discovery of an unusual incommensurate phase in the orthoferrite TbFeO$_3$ using neutron diffraction under an applied magnetic field. The magnetic modulation has a very long period of 340 Å at 3 K and exhibits an anomalously large number of higher-order harmonics. These domain walls are formed by Ising-like Tb spins. They interact by exchanging magnons propagating through the Fe magnetic sublattice. The resulting force between the domain walls has a rather long range that determines the period of the incommensurate state and is analogous to the pion-mediated Yukawa interaction between protons and neutrons in nuclei.

Materials with magnetic transition metal and rare-earth ions show a variety of spectacular effects originating from the coupling between the two spin subsystems. The transition metal spins interact stronger and order at higher temperatures than the spins of rare-earth ions, but they are also much less anisotropic. That is why their orientation can be controlled by the rare-earth magnetism. Such re-orientation transitions observed in many rare-earth ferrites, chromites and manganites have profound effects on their magnetic, optical and elastic properties$^{1-3}$.

Recently it was realized that interactions between transition metal and rare-earth ions also play an important role in multiferroic and magnetoelectric materials$^{4-7}$. Thus the coupling between the Mn spins forming a spiral state in the multiferroic TbMnO$_3$ and the Ising-like Tb spins leads to a significant enhancement of the electric polarization induced by the spiral$^8$. In GdFeO$_3$ orthoferrite the polarization only appears when the independent magnetic orders of Fe and Gd sublattices are present simultaneously$^9$, whilst in DyFeO$_3$ the interplay between the spins of Fe and Dy ions gives rise to one of the strongest linear magnetoelectric responses observed in single-phase materials$^{10}$.

TbFeO$_3$ is an orthorhombic perovskite (space group $Pbnm$) where Fe spins order antiferromagnetically in what is called G-type order$^{11}$ along the $a$ axis and ferromagnetically (F-type) along the $c$ axis, as shown in Fig. 1c. This type of commensurate spin order, denoted as $G_fF_z$, has an onset at approximately $T_N(\text{Fe}) = 650$ K. On cooling in zero field TbFeO$_3$ undergoes two transitions driven by Tb$\leftrightarrow$Tb and Tb$\leftrightarrow$Fe interactions$^{12,13}$. The ordering of Tb spins at $T_N(\text{Tb})\sim 8.5$ K occurs simultaneously with a rotation of Fe spins in the $ac$ plane, so that below 8.5 K ferromagnetic components of both Fe and Tb spins align along the $a$ axis, whereas their antiferromagnetic components are orthogonal to each other. The magnetic configuration of this intermediate-temperature (IT) phase is $F_xG_y$ for Fe, and $F'_xG'_y$ for Tb (Fig. 1b). However, below $\sim 3$ K there is an further spin re-orientation transition to a low-temperature (LT) phase which flips the Fe spins back to their higher temperature $G_zF_x$ order, while the Tb spins order antiferromagnetically in the $A'_zG'_x$ state (Fig. 1a).

Using single-crystal neutron diffraction we have probed the $A,G$ and F-type orders in TbFeO$_3$ by tracking the intensity of the corresponding magnetic Bragg reflections in zero field and in an applied field along the $c$ axis (see Methods for experimental details). In zero magnetic field our results are consistent with the previously observed sequence of the re-orientation and inverse re-orientation transitions$^{12}$. Above $\sim 8.5$ K we find only G-type reflections, although the development of ferromagnetic order is evident from the enhanced intensities of lattice Bragg reflections. Below 8.5 K we find G- and C-type reflections, whereas below 3 K only A- and G-type reflections can be discerned.

In an applied magnetic field (H$\parallel c$) we find a far more complex behaviour. Here we performed a series of field-cooled measurements, while monitoring accessible A- and G-type reflections. In Fig. 2a we show, in the form of a colour plot, the temperature dependence of scans along $k$ around the A-type (001) reflection. At high temperatures this reflection is absent, as there is no order of an A-type component for either the Fe or Tb magnetic sublattice, as indicated in Fig. 1. However, on cooling, a series of reflections appears below 3.8 K that seem to merge into a single peak below $\sim 2.8$ K. Examination of the wave vector of these reflections, which could be $A'_zG'_x$ or $A'_zG'_y$ in $Pbnm$, demonstrates that the correct wave vector is $A'_zG'_x$.

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reflections easily establishes that they are odd harmonics up to 11th order. The wave vector of the first harmonic is \( \mathbf{Q} = (0, \epsilon, 1) \), with \( \epsilon \sim 0.015 \) r.l.u. (Fig. 2b). The incommensurate periodicity of this phase, which we shall refer to as IC, is approximately 67 units cells or \( \sim 340 \) Å. The full width at half maximum of these reflections is relatively sharp, giving a coherence length of \( \sim 700 \) Å or approximately two full cycles of this unusual order. The transition into the IC phase from below is of first order, exhibiting a \( \sim 0.2 \) K hysteresis measured by tracking the intensity of the (001) reflection, whereas the transition between the IC and the IT phase does not exhibit any hysteresis, as shown by similarly tracking the intensity of the first harmonic reflection (Supplementary Fig. S1).

The physical significance of these observations is that the Tb spin order in a H||c field develops a square-wave modulation—a periodic array of widely separated domain walls in Tb magnetic order. We ascribe the observed scattering to be dominated by Tb spins; first because of its substantially greater intensity compared to the higher temperature Fe order found around, for example G-type reflections, and also because in zero field A-type reflections are associated only with Tb spin order. In the modulated A-state, Tb spins form ferromagnetic stripes in the \( ab \) planes with the width \( 170 \) Å along the \( b \) axis. The \( a \) component of the magnetization alternates from stripe to stripe, whereas the stacking of spins along the \( c \) axis is antiferromagnetic. Investigation of an Fe G-type reflection under the same condition suggests that Fe spins are weakly perturbed by this unusual Tb order (see Supplementary Information).

On cooling below 2.8 K, Fig. 2a would seem to indicate that the Tb modulation abruptly disappears and the Tb subsystem returns to the zero-field state with the uniform \( A'_yG'_y \) order. However, closer inspection of the diffraction data indicates that the (001) reflection on cooling does not yield a simple Gaussian peak shape but rather a Lorentzian, as confirmed by fits to the data. Below, we argue that the Lorentzian peak shape below 2.8 K (Fig. 2c) is indicative of a domain wall disordered phase, which we refer to as LT’.

We have performed measurements similar to those shown in Fig 2a at various fields as well as two zero-field-cooled measurements at 3.0 and 3.3 K where the field was subsequently applied isothermally to map out the various transitions that occur in this lower temperature regime in TbFeO\(_3\). Furthermore, we have conducted capacitance and loss measurements between 0.3 and 10 K in a magnetic field (H\( ||c \)) between 0 and 1.9 T. The transitions that are evident in the neutron data are correlated with anomalies in both the capacitance and loss data (see Supplementary Information), allowing us to construct the phase diagram shown in Fig. 3. Interestingly, the capacitance and loss data imply that if the sample is cooled in zero field below \( \sim 3 \) K and then field is applied, the transition into the LT’ phase is not reversible and this state can then be stabilized in zero field (Supplementary Fig. S5).

Next we discuss the nature of interactions stabilizing such an unusual periodic domain wall array and holding the domain walls at large distances from each other. Well below \( T_{N}(\text{Fe}) ~ 650 \) K the magnitude of the ordered antiferromagnetic moment of the Fe subsystem is independent of temperature, whereas its direction in the \( ac \) plane described by the angle \( \theta \) can vary significantly owing to the low magnetic anisotropy of the Fe\(^{3+} \) ions. In our notations \( \xi_1 = \cos \theta \) is the order parameter of the \( G_x \) state, while \( \xi_2 = \sin \theta \) describes the \( G_z \) ordering. The free energy density of the Fe subsystem is

\[
 f_{Fe} = \frac{c}{2} \left( \frac{d\theta}{dy} \right)^2 + \frac{K}{2} \sin^2 \theta - h \cos \theta
\]

where the first term describes the exchange between Fe spins along the \( b \) axis, the second term is the magnetic anisotropy, which for
K > 0 favours the $G_a$ order, and the last term is the Zeeman interaction with the magnetic field $H_z$ in the $G_a F_y$ state.

The free energy of Tb spins is expanded in powers of the order parameters $\eta$, describing the zero-phase LT state with antiparallel Tb spins in neighbouring $ab$ layers (Fig. 1a), and $\eta$, describing the IT state with parallel Tb spins in neighbouring layers (Fig. 1b):

$$f_{\text{Tb}} = \frac{c_1}{2} \left( \frac{d\eta}{dy} \right)^2 + \frac{c_2}{2} \left( \frac{d\eta}{dx} \right)^2 + \frac{d_1}{2} \eta^2 + \frac{d_2}{2} \eta^2 + \ldots$$

For $\Delta = a_2 - a_1 > 0$ the Tb subsystem would order in the state with $\eta_1 \neq 0$ below some temperature $T_a$, at which $a_1 = 0$. However, the interaction between the Tb and Fe spins favours the IT state with $\eta_1 \neq 0$ and $\theta = \pm \pi/2$, in which both subsystems have a ferromagnetic moment along the $a$ axis. Because $\eta_1$ and $\xi_z = \sin \theta$ transform in the same way (see Supplementary Information), this interaction is a linear coupling,

$$f_{\text{Fe-Tb}} = -\lambda \xi_z \eta_2$$

For $\lambda^2 > \Delta K$ the ‘unnatural’ IT state, with parallel Tb spins in neighbouring layers and Fe spins rotated by 90° away from the easy axis, intervenes between the states with the ‘natural’ orders of Fe and Tb spins. In this way one obtains the zero-field phase diagram of TbFeO$_3$ (refs 12,14).

The symmetry of TbFeO$_3$ also allows for two Lifshitz invariants linear in order parameter gradients,

$$f_i = g_i \left( \eta_1 \partial_y \xi_z - \xi_z \partial_y \eta_1 \right) + g_j \left( \eta_1 \partial_x \eta_2 - \eta_2 \partial_x \eta_1 \right)$$

which favour the experimentally observed periodic spin modulation along the $b$ axis. The first and the second invariants originate, respectively, from the Tb–Fe and Tb–Tb interactions. Similar terms inducing modulations along the $a$ and $c$ axes are forbidden by symmetry. Minimizing the total free energy—the sum of equations (1) through to (4)—we obtain the phase diagram shown in Fig. 4a, which includes a narrow incommensurate phase region, which we identify with the IC phase revealed in our neutron data.

It is important to stress the difference between the IC state in TbFeO$_3$ and the long-period spin spirals in non-centrosymmetric
magnets, also described using Lifshitz invariants\textsuperscript{15}. First, the crystal lattice of TbFeO\textsubscript{3} is centrosymmetric (inversion symmetry is only broken in the LT phase by the Tb spin ordering). Equation (4) is the interaction between two distinct magnetic phases: the LT Tb state (odd under inversion) and the IT phase (even under inversion). It is only effective close to the boundary where these two phases have equal free energies, which is why the IC state is observed in a very narrow region of the phase diagram.

Second, spirals in non-centrosymmetric magnets result from the relatively weak spin–orbit coupling\textsuperscript{15,16}. On the other hand, the coupling equation (4) may originate from a stronger Heisenberg exchange: in the Supplementary Information we give symmetry arguments showing that the exchange interactions between the Tb and Fe spin orders varying along the $b$ axis do not cancel. Furthermore, the coupling between two Tb order parameters (the second term in equation (4)) resulting from interactions between rare-earth spins separated by relatively long distances, is expected to be much weaker than interactions between the Tb and Fe spins described by the first term (in our calculations $g_2 = 0$).

Third and most important, the observation of the large number of Fourier harmonics in the IC state of TbFeO\textsubscript{3} shows that this state is qualitatively different from a magnetic spiral with slowly varying spin vectors. To account for the difference between the isotropic Fe spins and the Ising-like Tb spins\textsuperscript{13,17}, we assumed that $c_1, c_2 \ll c$ and allowed for 40 harmonics in the periodic modulation of order parameters when we minimized the free energy. The resulting incommensurate state is shown in Fig. 4b. Whereas the angle $\theta$ describing the Fe spins undergoes small amplitude fan-like oscillations around zero, corresponding to the oscillations of the weak ferromagnetic moment of Fe ions around the applied magnetic field $H_{\parallel}^z$, the low-temperature Tb order parameter $\eta_1$ exhibits sudden jumps.

To understand the nature of the force that holds these atomically sharp domain walls at distances of $\sim 170 \text{ Å}$ from each other, we (briefly) discuss an interesting field-theoretical interpretation of the coupled system of rare-earth and transition metal spins. Consider a single domain wall located at $y = 0$, where the Ising-like LT order parameter $\eta_1$ shows a discontinuous jump from $-|\eta_1|$ to $+|\eta_1|$ or vice versa (Fig. 5a). Such a kink can be assigned the topological charge $Q = (\eta_1(\infty) - \eta_1(-\infty))/2|\eta_1| = \pm 1$. The free energy per unit area of the domain wall is the ‘bare’ energy $F_{DW}^{(0)}$ resulting from interactions between Tb spins plus

$$F_0 = -2g|\theta(0)|Q + \frac{1}{2} \int d\theta \left[ c \left( \frac{d\theta}{dy} \right)^2 + (K + h)\theta^2 \right]$$

(5)

where the first term is the Lifshitz invariant equation (4) ($g = 2|\eta_1|$ and $g_2 = 0$), describing the interaction between the Tb and Fe spins, while the second term is the free energy of Fe spins for $|\theta| \ll 1$. Equation (5) can be interpreted as an energy of a charged plane with the surface charge density $gQ$ interacting with the field $\theta$, which describes spin waves in the Fe magnetic subsystem. Minimizing $F_0$ with respect to $\theta(y)$, we obtain the distortion in the Fe spin ordering produced by the Tb domain wall, $\theta(y) = (Qg/\sqrt{c(K + h)})e^{-(y/y_0)}$ (Fig. 5a), which reduces the domain wall free energy:

$$F_{DW} = F_{DW}^{(0)} - \frac{g^2}{\sqrt{c(K + h)}}$$

(6)

When $F_{DW}$ becomes negative, the domain walls tend to condense. Their density is, however, limited by the effective long-range repulsion between the domain walls resulting from the exchange of magnons. This interaction is analogous to the pion-mediated Yukawa force between protons and neutrons in nuclei\textsuperscript{18}. The sharp domain walls in the Tb spin subsystem play the role of nucleons, while magnons propagating through the Fe spin subsystem play the role of massive pions. The analogue of the pion mass is a small gap in the magnon spectrum, which limits the range of this interaction by the length $l = \sqrt{c/(K + h)}$, much larger than the lattice constant. This Yukawa-like force attracts equal ‘electric’ charges and repels opposite ones. Because the topological charges of domain walls alternate along the $b$ axis, neighbouring domain walls in a periodic array have opposite ‘electric’ charges, resulting in net repulsion. The interaction between two neighbouring domain walls located at $y_1$ and $y_2$ (Fig. 5b) is

$$U(y_2 - y_1) = \frac{g^2}{\sqrt{c(K + h)}} e^{-|y_2 - y_1|/y_0}$$

(7)

and the total ‘electrostatic’ free energy of an array of domain walls with the charges $Q_n$ alternating along the $b$ axis (including the ‘self-energy’ of the charged surfaces) is given by

$$F_0 = - \sum_{n,m} Q_n U(y_n - y_m)Q_m$$

(8)

where $y_n$ is the position of the $n$th kink. Minimizing the free energy density for an equidistant array of kinks (Fig. 5c), we obtain the optimal period of the incommensurate state. Its temperature dependence fits well the experimental data above 2.8 K, as shown...
in the inset of Fig. 3. The length scale for the period of the IC state, set by \( l \sim 150 \text{ Å} \), is essentially the thickness of the domain wall in the antiferromagnetic ordering of Fe spins, even though such walls are not present in the IC state. Thus the long period of the IC state of Tb spins originates from the large stiffness and low magnetic anisotropy of the Fe magnetic subsystem.

So far in our considerations we have not taken into account crystal imperfections, which result in pinning of the domain walls and destruction of the long-range incommensurate ordering. The inset of Fig. 2c shows that the average distance between the Tb domain walls grows as temperature decreases. This weakens the magnon-mediated interactions between the domain walls and increases the role of disorder. For randomly positioned domain walls the correlation function of the A-type Tb order parameter decays exponentially with the distance: \( \langle A(y)A(0) \rangle \propto e^{-d/\xi} \), where \( d \) is the average distance between the walls, resulting in a broad A-type reflection with the Lorentzian shape, which fits well our neutron data for \( T < 2.8 \text{ K} \) and \( \mu_0 H_c > 0.5 \text{ T} \) (Fig. 2c). This explains the origin of the LT' phase in the experimental phase diagram shown in Fig. 3.

The tantalizing suggestion from our work is that periodic domain wall arrays may be present in other orthoferrites and orthochromites. Lifshitz invariants similar to equation (4) are domain wall arrays may be present in other orthoferrites and orthochromites. Lifshitz invariants similar to equation (4) are

\[ \text{domain wall arrays may be present in other orthoferrites and orthochromites.} \]

in multiferroic materials, such as GdFeO₃, where electric polarization is induced by a transition metal spin order (even under inversion and weakly ferromagnetic) coexisting with a rare-earth spin order odd under inversion'. Long-ranged interactions between domain walls in these two orders resulting from such invariants can have a strong effect on switching of the spontaneous electric polarization with an applied magnetic field and vice versa.

Methods

Single crystals of TbFeO₃ were grown under an oxygen pressure of 4 bar using the crucible-free floating-zone method. Their quality was checked by X-ray diffraction. Neutron diffraction experiments were carried out on a large single crystal of TbFeO₃ at the BER-II reactor of the Helmholtz Zentrum Berlin using the FLEX cold triple-axis spectrometer with collimation of 60°–60°, \( k \sim 1.3 \text{ Å}^{-1} \), and a cooled Be filter positioned in the scattered beam. Further measurements were made also with the E4 two-axis diffractometer with \( l = 2.8 \text{ Å} \). In both cases a magnetic field was applied along the c-axis of the sample using a superconducting horizontal field magnet. Dielectric measurements were performed at the Laboratory for Magnetic Measurements at the Helmholtz–Zentrum Berlin, with temperatures varying between 0.3 K and 15 K and with magnetic fields up to 2 T. Magnetization field and temperature control were provided by an Oxford Instruments 14.5 T cryomagnet equipped with a Heliox ³He insert. An Andeen–Hagerling 2700A Capacitance Bridge was used to measure the capacitance and loss of a disc-shaped sample of TbFeO₃, which was mounted between the electrodes of a parallel plate capacitor.

Received 21 March 2011; accepted 15 June 2012; published online 24 June 2012

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**Acknowledgements**

D.N.A. and S.L. thank the Deutsche Forschung Gemeinschaft for support under contract AR 613/2-1. The neutron scattering work was supported by the Danish National Research Council through DANSCATT. N.P.J. thanks J. B. Hansen, for support and guidance. M.M. was supported by the FOM grant 08.0952.

**Author contributions**

D.N.A. initiated the project, D.N.A. and M.M. interpreted the results and wrote the paper, and M.M. and S.A. developed the theory. N.P.J. and H.N.B. contributed to the interpretation of the experimental results. K.L. and L.T.K. supported the project. Neutron experiments and analysis of these data were conducted by N.P.J., D.N.A., K.P., D.L., V.G.P. and H.N.B. Bulk property and characterization measurements were conducted by S.L., H.R., B.K., S.P. and K.K., and A.M. grew the single crystal. All authors commented on the manuscript.

**Additional information**

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturematerials. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to D.N.A.