Chirality and Magnetocaloricity in GdFeTeO$_6$ as Compared to GdGaTeO$_6$

Elena Zvereva $^{1,*}$, Tatyana Vasilchikova $^{1,}$, Maria Evstigneeva $^{2}$, Angelica Tyureva $^{2}$, Vladimir Nalbandyan $^{2,\dagger}$, Joào Gonçalves $^{3,\ddagger}$, Paolo Barone $^{4}$, Alessandro Stroppa $^{5}$ and Alexander Vasiliev $^{1,6,*}$

1 Department of Low Temperature Physics and Superconductivity, Physics Faculty, Lomonosov Moscow State University, 119991 Moscow, Russia; t_vasilchikova@yahoo.com
2 Department of Chemistry, Southern Federal University, 344090 Rostov-on-Don, Russia; maevstigneeva@gmail.com (M.E.); tyureva.likia@mail.ru (A.T.); vbn@sfsedu.ru (V.N.)
3 Department of Physics and CICECO, University of Aveiro, 3810-193 Aveiro, Portugal; joaonsg@ua.pt
4 Consiglio Nazionale delle Ricerche, Institute for Superconducting and Innovative Materials and Devices (CNR-SPIN), Area della Ricerca di Tor Vergata, Via del Fosso del Cavaliere 100, I-00133 Rome, Italy; paolo.barone@spin.cnr.it
5 Consiglio Nazionale delle Ricerche, Institute for Superconducting and Innovative Materials and Devices (CNR-SPIN), c/o Department of Physical and Chemical Sciences, University of L’Aquila, Via Vetoio Coppito, I-67100 L’Aquila, Italy; alessandro.stroppa@spin.cnr.it
6 Quantum Functional Materials Laboratory, National University of Science and Technology “MISIS”, 119049 Moscow, Russia
* Correspondence: anvas2000@yahoo.com
† Deceased.

Abstract: GdFeTeO$_6$ and GdGaTeO$_6$ have been prepared and their structures refined by the Rietveld method. Both are superstructures of the rosiaite type (space group $P\bar{F}Ic$). Their thermodynamic properties have been investigated by means of magnetization $M$ and specific heat $C_p$ measurements, evidencing the formation of the long-range antiferromagnetic order at $T_N=2.4$ K in the former compound and paramagnetic behavior down to 2 K in the latter compound. Large magnetocaloric effect allows considering GdFeTeO$_6$ for the magnetic refrigeration at liquid hydrogen stage. Density functional theory calculations produce estimations of leading Gd$-$Gd, Gd$-$Fe and Fe$-$Fe interactions suggesting unique chiral 120° magnetic structure of Fe$^{3+}$ ($S=5/2$) moments and Gd$^{3+}$ ($I=7/2$) moments rotating in opposite directions (clockwise/anticlockwise) within weakly coupled layers of the rosiaite type crystal structure.

Keywords: chirality; magnetocaloricity; metaloxide

1. Introduction

Both classical and quantum spin systems of reduced dimensionality host a plethora of exotic magnetic ground states, including spin liquids and peculiar long-range ordered patterns [1,2]. The layered crystal structure of the rosiaite type, AB$_2$O$_6$, can be considered as an ideal playground to study the low-dimensional and frustrated magnetism. It is organized by diluted triangular $A$ and dense honeycomb $B$ layers alternating along the trigonal axis $c$ [3]. In case of the $A$ position being occupied by the divalent transition metal ions ($M=$ Mn, Co, Ni), the long-range antiferromagnetic (AFM) order takes place at low temperatures in both MA$_2$O$_6$ arsenates [4] and MSb$_2$O$_6$ antimonates [5]. Exceptionally, CuSb$_2$O$_6$ [5] does not order down to 1.5 K, while PdAs$_2$O$_6$ orders at an unusually high Néel temperature 140 K [6]. The couple of pentavalent cations in the $B$ layer can be substituted by a combination of tetravalent and hexavalent cations, as is the case of MnSnTeO$_6$ [7]. The $A$ position in the rosiaite structure can be taken also by a trivalent rare-earth ion [8–13] or bismuth [14]. Simultaneously, in accord with charge compensation, half of $B$ positions can be occupied by a trivalent cation (e.g., Cr$^{3+}$ or Fe$^{3+}$), and another half by Te$^{6+}$.
ions. Concerning magnetic properties, it is known that all $RCrTeO_6$ studied ($R = Y, La, Tb, Er, Gd,$ and Bi) experience the antiferromagnetic transition at low temperatures [11,12,14]. Paramagnetic behavior down to 3 K was observed in $LaFeTeO_6$ [10] and $GdFeTeO_6$ [13], albeit in the latter case it has been anticipated that this compound experiences ferrimagnetic order at lower temperature.

It is well known that in two dimensions, the triangular lattice antiferromagnet in the Ising limit remains disordered at all temperatures. In the Heisenberg limit, the problem of frustration is lifted by $120^\circ$ arrangement of magnetic moments, which is the essence of Yafet–Kittel model [15]. The magnetic subsystem of $GdFeTeO_6$ is comprised by basically isotropic $Gd^{3+}$ ($J = 7/2$) and $Fe^{3+}$ ($S = 5/2$) ions. It opens the way to unique clockwise/anticlockwise $120^\circ$ antiferromagnetic structure in case of appreciable $f–d$ interaction. The reported bond lengths in $GdFeTeO_6$ [13] differ from the corresponding sums of ionic radii [16] by 0.16, 0.24 and 0.29 Å for $Gd–O$, $Fe–O$ and $Te–O$, respectively. We report here the preparation, correctly refined crystal structure and detailed experimental and theoretical study of magnetic properties of $GdFeTeO_6$ in comparison with its analogue containing diamagnetic $Ga^{3+}$ in place of $Fe^{3+}$.

2. Experimental

2.1. Sample Preparation, Phase Analysis and Structural Studies

Polycrystalline samples of $GdFeTeO_6$ and $GdGaTeO_6$ were prepared by solid-state reactions (see Electronic Supplementary Material, ESM, for details). Reasonable agreement of the hexagonal lattice parameters for $GdFeTeO_6$ prepared by different methods, even in the presence of foreign phases (Table S1 of ESM), suggests that the compound does not have any extended homogeneity range.

XRD studies were performed in CuK$_\alpha$ radiation using an ARL X'tra diffractometer, Thermo Scientific, Switzerland, in the Bragg–Brentano geometry, equipped with a solid-state Si(Li) detector. Lattice parameters were refined using CELREF 3 (J. Laugier and B. Bochu), with angular corrections by corundum (NIST SRM 676) as an internal standard. To reduce effect of grain orientation, the samples for the XRD profile analysis were mixed with amorphous powder (instant coffee). The structures were refined with the GSAS + EXPGUI suite [17,18].

2.2. Physical Measurements

Magnetization $M$ and specific heat $C_p$ were studied using various options of Physical Properties Measurements System PPMS–9T, Quantum Design, San Diego, CA, USA.

3. Results and Discussion

3.1. Crystal Structures of $GdMTeO_6$ ($M = Fe, Ga$)

For the structure analysis, we used a single-phase light yellow $GdFeTeO_6$ powder prepared by solid-state reaction at a final temperature of 830 °C and white $GdGaTeO_6$ powder prepared at 950 °C. The latter contained trace amounts of $Ga_2O_3$ and an unknown phase, and this may explain somewhat lower accuracy of its structural data (see below). The crystal structures were successfully refined starting from the structural model of $LaFeTeO_6$ [10].

Experimental and calculated XRD profiles are compared in Figure 1; experimental and refinement details, crystallographic data, atomic coordinates and displacement parameters are reported in Tables S2–S4 and Figure S2 of ESM, and bond lengths, bond angles and bond valence sums (BVS), in Table 1. The Crystallographic information files (CIF) are supplied as Supplementary Material. The data for $GdFeTeO_6$ have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2002460.
lengths, bond angles and bond valence sums (BVS), in Table 1. The Crystallographic information files (CIF) are supplied as Supplementary Material. The data for GdFeTeO₆ have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2002460.

For the Fe compound, possible Te/Fe inversion was investigated, but the refined degree of inversion, 0.02, was within experimental accuracy and, therefore, was neglected. The structures are very similar and Figure 2 effectively represents both of them. Bond lengths agree with the corresponding sums of ionic radii (less accurately for M = Ga), and calculated BVS are also reasonable. Each oxygen anion has an almost planar environment, with the sum of the three bond angles being close to 360° (Table 1).

Figure 1. Results of the Rietveld refinement for GdFeTeO₆ (top) and GdGaTeO₆ (bottom). Crosses, experimental data; red line, calculated profile; bottom blue line, difference profile; vertical bars, Bragg angles.

Table 1. Lattice parameters, bond lengths (Å), sums of ionic radii [16], bond valence [19] sums (BVS) and bond angles in GdMTeO₆ (M = Fe, Ga).

|          | GdFeTeO₆       | GdGaTeO₆       |
|----------|----------------|----------------|
| a, Å     | 5.16556(5)     | 5.11096(6)     |
| c, Å     | 9.8523(11)     | 9.9192(17)     |
| c/a      | 1.907          | 1.941          |
| Distances/sum of radii/BVS |       |               |
| Gd-O     | 2.3283(10) × 6/2.30/2.73 | 2.280(10) × 6/2.30/3.06 |
| M-O      | 2.014(10) × 6/2.003/3.01 | 1.929(10) × 6/1.98/3.43 |
| Te-O     | 1.930(1) × 6/1.92/5.88 | 2.029(10) × 6/1.92/5.02 |
| O: BVS   | 1.94           | 1.92           |
| Angles (°) |       |               |
| Gd-O-Te  | 130.31(4)      | 126.8(5)       |
| Te-O-M   | 98.22(4)       | 96.4(4)        |
| M-O-Gd   | 125.78(4)      | 132.4(5)       |
For the Fe compound, possible Te/Fe inversion was investigated, but the refined degree of inversion, 0.02, was within experimental accuracy and, therefore, was neglected. The structures are very similar and Figure 2 effectively represents both of them. Bond lengths agree with the corresponding sums of ionic radii (less accurately for M = Ga), and calculated BVS are also reasonable. Each oxygen anion has an almost planar environment, with the sum of the three bond angles being close to 360° (Table 1).

### Table 1. Cont.

|                  | GdFeTeO₆ | GdGaTeO₆ |
|------------------|----------|----------|
| Sum for O        | 354.3    | 355.6    |
| O-Gd-O          | 88.0–92.0| 86.2–93.8|
| O-M-O           | 79.7–94.2| 86.2–91.7|
| O-Te-O          | 83.9–92.1| 81.0–94.3|

Figure 2. Upper panel: Polyhedral presentation of the crystal structure of GdFeTeO₆, Violet, green, grey and black spheres are Gd, Fe, Te and O ions, respectively. Lower panel: magnetoactive layer of Fe and Te ions, and Gd layer. A three-dimensional visualization system VESTA [20] for electronic and structural analysis has been used for the presentation of crystal structure.

3.2. Basic Properties

The temperature dependences of magnetic susceptibility $\chi = M/B$ in both GdFeTeO₆ and GdGaTeO₆ taken at $B = 0.1$ T are shown in the left panel of Figure 3. Note that no difference between data obtained within field-cooled and zero-field-cooled protocols has been observed signaling absence of any impurity-driven or spin-glass effects. In a wide temperature range, both compounds evidence paramagnetic behavior following basically the Curie law $\chi = C/T$. The Curie constants $C$ are 11.96 emu K/mol for GdFeTeO₆ and 7.58 emu K/mol for GdGaTeO₆ in full correspondence with expectations for Gd$^{3+}$ ($S = 5/2$) and Fe$^{3+}$ ($S = 5/2$) magnetic moments. Straight inverse susceptibility curves, $\chi^{-1}(T)$, point to the absence of any magnetic frustration effects inherent to triangular systems. While GdGaTeO₆ remains paramagnetic down to 2 K, the $\chi(T)$ curve in GdFeTeO₆ evidences the kink ascribed to antiferromagnetic phase transition at $T_N = 2.4$ K. This part of the $\chi(T)$ curve is enlarged in the inset to the left panel of Figure 3. The kink at 2.4 K is readily suppressed by an external magnetic field. The field dependences of magnetization $M(B)$ in GdFeTeO₆ and GdGaTeO₆ taken at 2 K are shown in the right panel of Figure 3. In
both compounds, the magnetization reaches the saturation values, albeit the shape of $M(B)$ curve in GdFeTeO$_6$ differs from that in GdGaTeO$_6$, presumably due to $f$–$d$ interactions which result in magnetic long-range order.

Figure 3. (a) The temperature dependences of magnetic susceptibility $\chi$ in GdFeTeO$_6$ and GdGaTeO$_6$ at $B = 0.1$ T (left ordinate) and inverse susceptibility $1/\chi$ (right ordinate). The inset enlarges the low temperature part of $\chi(T)$ curve for GdFeTeO$_6$. (b) The field dependences of magnetization $M(B)$ in GdFeTeO$_6$ and GdGaTeO$_6$ at 2 K.

The evidence for the magnetic phase transition in GdFeTeO$_6$ was further obtained from the specific heat data, as shown in the left panel of Figure 4. The $C_p(T)$ curve taken in the absence of magnetic field evidences sharp $\lambda$-type anomaly at $T_N = 2.4$ K. The data well above the transition temperature were used to estimate the phonon background $C_{\text{lattice}}$ in GdFeTeO$_6$ using the Debye model, as shown by the solid line in Figure 4. No such anomaly has been detected down to 2 K in GdGaTeO$_6$; however, a slight upturn of specific heat at lowest temperatures should be noted which can be considered as an indication for the forthcoming low-temperature magnetic phase transition. An external magnetic field rapidly suppresses the $\lambda$-peak in $C_p(T)$ curve, but the Schottky-type anomaly appears at elevated temperatures. This anomaly is associated with the Zeeman splitting of magnetic levels in both gadolinium and iron ions. It shifts to higher temperatures with increasing magnetic field. Similarly, the Zeeman splitting of gadolinium levels in GdGaTeO$_6$ results in the appearance of pronounced Schottky anomaly, as shown in the right panel of Figure 4.

Figure 4. The temperature dependences of the specific heat $C_p$ in GdFeTeO$_6$ (a) and GdGaTeO$_6$ (b). The solid lines represent the Debye fitting of the phonon contributions. The insets show $C_p(T)$ curves taken in various magnetic fields.
3.3. Magnetocaloric Effect

The magnetocaloric effect in GdFeTeO$_6$ was estimated from the specific heat $C_p(T, B)$ at various magnetic fields. The lattice contribution $C_{\text{lattice}}$ has been subtracted from the total specific heat $C_p(T, B)$ to estimate the magnetic entropy $S_m(T)$, as shown in the left panel of Figure 5. The magnetic entropy change $\Delta S_m(T, \Delta B)$ has been calculated as $\Delta S_m(T, \Delta B) = S_m(T, B) - S_m(T, 0)$. The adiabatic change of the magnetic field from $B_1$ to $B_2$ causes not only change in the magnetic entropy, but also alteration of the sample temperature $\Delta T_{\text{ad}} = T_2 - T_1$, which can be determined by the adiabatic condition $S(T, B_1) = S(T + \Delta T, B_2)$. Thus, $\Delta T_{\text{ad}}$ has been calculated from the zero-field $C_p(T)$ and $\Delta S_m(T, \Delta B)$ data with the use of equation:

$$\Delta T(T, \Delta B) = T \left[ \exp \left( -\frac{dS_m(T, \Delta B)}{C_p(T, 0)} \right) - 1 \right]$$  \hspace{1cm} (1)

Figure 5. The temperature dependence of the magnetic entropy $S_M$ in various magnetic fields. The inset shows the field dependences of the refrigerant capacity $RC$ and the relative cooling power $RCP$ (a). The magnetic entropy $\Delta S_m$ and adiabatic temperature change $\Delta T_{\text{ad}}$ (b).

Right panels of Figure 5 show both $\Delta S_m$ and $\Delta T_{\text{ad}}$ sets of data in GdFeTeO$_6$ as a function of temperature for the various external magnetic fields. These curves demonstrate a broad peak for both quantities, with the width increasing at higher magnetic fields. The maximum value $-\Delta S_m^{\text{max}}$ is 35.3 J/kg K for the field change of 0–9 T. This result agrees with the previous data for $\Delta S_m(T, \Delta B)$ derived from an isothermal process of magnetization using the Maxwell relations. The temperature change, $\Delta T_{\text{ad}}$, is 27 K at 9 T reaching liquid hydrogen temperatures.

The magnetocaloric study is completed by the estimation of refrigeration properties for GdFeTeO$_6$. The results for the refrigerant capacity (RC) and the relative cooling power (RCP) vs. applied magnetic field are shown in the inset to the right panel of Figure 5. The RC and the RCP are defined as

$$RC = \int_{T_1}^{T_2} |\Delta S_M dT|, \hspace{0.5cm} RCP = |\Delta S_M^{\text{max}}| \times |\delta T_{\text{FWHM}}|$$  \hspace{1cm} (2)

where $T_1$ and $T_2$ represent the temperatures corresponding to the half maximum of $\Delta S_M(T)$ curve, $\Delta S_M^{\text{max}}$ is the maximum of $\Delta S_M$ value, and $\delta T_{\text{FWHM}}$ is the width at half maximum.
(FWHM) of $\Delta S_M(T)$ curve. Note that similarly large magnetocaloric effect has been recently reported for another $f$-$d$ oxide of rosiaite-type GdCrTeO$_6$ [12].

3.4. Density Functional Calculations

Density functional theory calculations [21,22] were performed to study the magnetic interactions by determining the exchange interactions. We considered both Perdew–Burke–Ernzerhof (PBE + U) [23,24] and Heyd–Scuseria–Ernzerhof (HSE) [25,26] exchange correlation functionals. For the PBE + U calculations, the choice of $U$ for the $f$ electrons is subtle since different values have been deemed a reasonable choice for each specific material. For example, in elemental Gd [27] and Gd monopnictides [28], a $U_{\text{eff}} = U - J$ value of 6 eV has been used, but in some transition metal oxides a lower value of 4 eV has been found more appropriate for the $f$ electrons of Gd and Dy [29,30]. In the previous study for this compound, a value of $U_{\text{Gd}} = 6$ eV has been used [13]. However, we found that the energy difference between different magnetic configurations is very sensitive to $U_{\text{Gd}}$. Therefore, previous calculations for similar compounds must be considered with care with respect to the choice of the $U$ parameter. In order to avoid ambiguities in the choice of $U$ correction, we have used the HSE functional calculations as a benchmark. The energy differences are more sensitive to $U_{\text{Gd}}$, with a value $U_{\text{Gd}}$ close to 2.09 eV needed, but much less sensitive to $U_{\text{Fe}}$, with $4U_{\text{Fe}} = 5$ eV producing similar energy differences. Nevertheless, there is no single combination of $U$ values which can reproduce all the HSE energy differences between magnetic states, which prompted us to adopt the latter approach also in the estimate of exchange interactions. This is probably due to the fact that while HSE affects both $p$- and $d$-states, the $U$ correction affects mainly the $d$-states [31].

We considered the $2 \times 1 \times 1$ supercell in order to estimate the pairwise exchange interactions. Four Gd and four Fe atoms are considered, hence 9 possible AFM states, since both Fe and Gd can have three different AFM spin arrangements. We considered the FM, the nine AFM states and five additional FiM states, both for HSE and PBE + U, with $U_{\text{Gd}} = 2.09$, $U_{\text{Fe}} = 5$ eV, which was found to be a reasonable compromise to reproduce the HSE energies. We evaluated the exchange interactions by mapping the first-principles magnetic energies to the Heisenberg model:

$$H = \frac{1}{2} \sum_{i,j} J_{ij} \vec{S}_i \vec{S}_j$$

and performing multiple linear regression with least-squares fitting. Gd–Gd interactions were found to be negligible, and the magnetic energies can be well reproduced in a minimal model comprising only Fe–Fe and nearest-neighbor Gd-Fe interactions. The third nearest-neighbor out-of-plane Fe–Fe interaction was found to be important for improving the linear regression, even though the distance between involved Fe atoms is quite large; this exchange is in fact mediated by the same bridging atoms involved in the other Fe–Fe exchanges, occurring on a Fe–O–Gd–O–Fe path. The estimated values of the exchange interactions for PBE + U and HSE approaches are shown in Table 2. The interactions within HSE are generally reduced in comparison with PBE + U, with the main difference being a much smaller Fe–Fe in-plane interaction, and the sign of the next-nearest-neighbor $J_{\text{Fe–Fe}}^{\text{out–of–plane}}$, which turned out to be the only ferromagnetic interaction at the HSE or PBE + U levels. The in-plane AFM Fe–Fe interaction is known to lead to a (classical) co-planar three-sublattice “120-degree” state within each Fe-layer, while the Gd–Fe AFM interaction, mediating an inter-layer coupling between Fe layers, would instead promote a ferrimagnetic state with antiparallel Fe and Gd spins, and the third nearest-neighbor $J_{\text{Fe–Fe}}^{\text{ann–out–of–plane}}$ would instead favor AFM configurations of Fe spins. Such a fierce competition of magnetic exchange interactions combined with their weakness in magnitude is compatible with the low critical temperature observed in the system. Indeed, we used the estimated interactions to predict the critical temperature within a classical Monte Carlo approach. Using a Metropolis algorithm for an $18 \times 18 \times 12$ cell, we found cusps in the specific heat and magnetic
susceptibility signaling a transition at $T_N \sim 2.6$ K (5 K) for exchange parameters evaluated within the HSE (PBE + U) approach, with no net magnetization developing in the ordered phase, in good agreement with the experimental estimates.

Table 2. Effective and renormalized (with $J_{Gd} = 7/2$, $S_{Fe} = 5/2$) exchange constants (meV) obtained by fitting to the PBE + U ($U_{Gd} = 2.09$, $U_{Fe} = 5$ eV) and HSE energies.

| Effective Exchange $J_{ij}^*$ | $J_{ij}$ for $J_{Gd} = 7/2$, $S_{Fe} = 5/2$ (meV) |
|-------------------------------|-----------------------------------------------|
| $J_{Fe-Fe, \text{in-plane}}$ | PBE + U | HSE | PBE + U | HSE |
| $J_{Fe-Fe, \text{out-of-plane}}$ | $-0.4883$ | $-0.0356$ | $-0.0749$ | $-0.0057$ |
| $J_{Fe-Gd}$ | $-0.0263$ | $0.0169$ | $-0.0042$ | $0.0027$ |
| $J_{\text{nnn, out-of-plane}}$ | $-0.0382$ | $-0.0993$ | $-0.0044$ | $-0.0113$ |
| $J_{\text{nn, out-of-plane}}$ | $-0.1831$ | $-0.1182$ | $-0.0293$ | $-0.0189$ |

The HSE (PBE + U) calculated local magnetic moments have absolute values of approximately 6.92, 4.25, 0.00, and 0.10 (6.97, 4.29, 0.01, and 0.09) $\mu_B$, for Gd, Fe, Te, and O, respectively, irrespective of the magnetic order considered, consistent with Gd$^{3+}$ ($J = 7/2$) and Fe$^{3+}$ ($S = 5/2$) ions, in agreement with the susceptibility measurements.

3.5. Discussion

The crystal structure of both GdFeTeO$_6$ and GdGaTeO$_6$ is a superstructure (space group $P\overline{3}1c$) of the rositaite $AB_2O_6$ [3] due to the doubling of the $c$ parameter associated with the alternating Fe/Te or Ga/Te along the principal axis. Thermodynamic measurements evidence the long-range magnetic order at $T_N = 2.4$ K in GdFeTeO$_6$ and paramagnetic behavior down to 2 K in GdGaTeO$_6$. GdFeTeO$_6$ possesses excellent magnetocaloric properties. For a magnetic field change of 9 T at 2 K, the values of entropy change $-\Delta S_M(T) = 35.3$ J/kg K and adiabatic temperature alteration $\Delta T_{ad} = 27$ K are obtained, as well as relative cooling power 580 J/kg and refrigerant capacity 465 J/kg. This makes GdFeTeO$_6$ attractive for the working body of low-temperature magnetic refrigerator devices. With the intensification of research at helium temperatures, the problem of cooling the current leads of superconducting solenoids and reaching ultralow temperatures becomes increasingly urgent [32–37].

The presence of gadolinium in the structure of GdFeTeO$_6$ precludes determination of its magnetic structure using neutron scattering methods. However, the absence of the magnetic order in GdGaTeO$_6$ evidences the weakness of the Gd–Gd interactions. Moreover, no long-range order has been detected in LaFeTeO$_6$, pointing to the weakness of interlayer Fe–Fe interactions [10]. GdFeTeO$_6$ represents a unique system which orders due to interlayer f–d interactions. The absence of spontaneous magnetization in the magnetically ordered phase of this compound excludes any ferrimagnetic arrangement of Gd$^{3+}$ and Fe$^{3+}$ magnetic moments [13]. The only solution compatible with the absence of any frustration effects in magnetic susceptibility seems to be 120$^\circ$ structure of iron moments within B layers (say, clockwise) and 120$^\circ$ structure of gadolinium moments within A layers (say, anticlockwise), as shown in Figure 6. In the first principle calculations, this structure is of the lowest energy, but the energy difference with other configurations is very small, about 0.01 meV per formula unit. In our knowledge, the proposed chiral–antichiral magnetic structure is unique, deserving some kind of experimental verification.
Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/ma14205954/s1, Figure S1. Comparison of the two XRD patterns of nominal “GdFeTeO₆” taken in CuKα radiation. Upper panel: Relatively pure phase prepared from oxides for 48 h at 700 °C [5]. Lower panel: mixed phase prepared by the semi-wet method for 56 h at 750 °C with three intermediate re-grindings (this work), Figure S2. Correlation between crystal radii [6] of RE³⁺ and hexagonal subcell parameters of REFeTeO₆. Red diamonds, a; blue triangles, c/2; RE = La [1, 3, 4], Pr, Nd, Sm [4], and Gd (this work); green circles, same from Reference [5], Figure S3. (a) Effect of changing UGd (eV) for the energy differences of one AFM and 3 FiM states with respect to the FM state. Changes of Gd UGd in the legend, with fixed UFe = 4 eV. (b) Energy difference between FiM1 and FM states. Effect of changing UGd and UFe, and comparison with HSE calculations (black line), Figure S4. The comparison of Monte-Carlo calculations (solid lines) with the experimental temperature dependencies of magnetic susceptibility χ(T) (left panel) and specific heat Cp(T) (right panel), Table S1. Phase analysis results and hexagonal lattice parameters of GdFeTeO₆ samples prepared by various methods, Table S2. Details of the data collection and structure refinement, Table S3. Atomic coordinates and displacement parameters in GdFeTeO₆, space group P31c, Table S4. Atomic coordinates and displacement parameters in GdGaTeO₆, space group P31c.

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Figure 6. The ball-and-stick representation [20] of the crystal structure of GdFeTeO₆. Purple, green, gray and black spheres are Gd, Fe, Te and O ions, respectively. Blue and pink arrows highlight the clockwise and anticlockwise arrangements of spins in different magnetoactive layers.
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