First-principles insights into f magnetism, a case study on some magnetic pyrochlores

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First-principles calculations are performed to investigate f magnetism in $A_2T_2O_7$ ($A=$Eu, Gd, Tb, Dy, Ho, Er, Yb) magnetic pyrochlore oxides. The Hubbard $U$ parameter and the relativistic spin orbit correction is applied for more accurate description of the electronic structure of the systems. It is argued that the main obstacle for first-principles study of these systems is the multi-minima solutions of their electronic configuration. Among the studied pyrochlores, Gd$_2$Ti$_2$O$_7$ shows the least multi-minima problem. The crystal electric field theory is applied for phenomenological comparison of the calculated spin and orbital moments with the experimental data.

I. INTRODUCTION

Magnetic pyrochlore oxides [1] with chemical formula $A_2B_2O_7$ have rich physics and exotic magnetic properties (such as magneticty [2]) caused by geometrical frustration. In these materials, A and B are usually trivalent rare-earth and trivalent transition metal ions, respectively, which form a network of corner sharing tetrahedral on the fcc Bravais lattice (Fig. 1). This geometrical feature is known to be the origin of the magnetic frustration of the system. Among these materials, $A_2T_2O_7$ ($A=$Eu, Gd, Tb, Dy, Ho, Er, Yb) are the most studied compounds [3], and exhibit various magnetic phenomena including spin ice behavior in Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ [1], spin liquid behavior in Tb$_2$Ti$_2$O$_7$ [4, 5] and Yb$_2$Ti$_2$O$_7$ [6], and order by disorder phenomena in Er$_2$Ti$_2$O$_7$ [1, 7, 8]. Gd$_2$Ti$_2$O$_7$, as a controversial case, is assumed to be a classical Heisenberg antiferromagnet [3].

Theoretical investigations on magnetic pyrochlores are mainly based on model Hamiltonians, involving Heisenberg exchange, dipole-dipole interactions, and single ion anisotropy, which are parametrized by using experimental data [1]. The lack of modern ab initio calculations on these materials prevents microscopic understanding of these magnetic model Hamiltonians. To our knowledge, ab initio calculations on magnetic pyrochlore oxides are limited to nonmagnetic properties [10, 11] or those compounds with no active f electrons [12]. It is due to the fact that the partially filled 4f orbital of the rare earth ions involves strongly correlated and localized electrons which cause serious difficulties in finding the true ground state of the system within density functional theory (DFT) computations [13]. It is well understood that conventional local functionals give rise to wrong ground states for these strongly correlated systems. The usual solution for correct description of the coulomb interaction between 4f electrons is applying orbital dependent approaches including hybrid functionals [14] and the Hubbard based DFT+U technique. An important challenge in first-principles calculation of the systems with 4f electrons within orbital dependent functionals is sensitivity of the final results to the initial electronic configuration of the 4f shell. Moreover, close energy local minima are serious obstacles to achieve convergency in first-principles calculation of the 4f electron systems.

Our specific aim in this work is employing DFT+U approach for first-principles calculation and investigation of f magnetism in $A_2T_2O_7$ ($A=$Eu, Gd, Tb, Dy, Ho, Er, Yb) compounds. After brief explanation of our computational method, the obtained results are presented in section III. In section IV, our conclusions are presented.

II. COMPUTATIONAL METHOD

Our electronic structure calculations are performed by using Fleur [15] computer code, which solves Kohn-Sham single particle equations by using the full-potential linearized augmented plane wave (FP-LAPW) method [16]. The muffin-tin radii of A, Ti, and O atoms were set to 2.75, 2.0, and 1.35 bohr, respectively. The Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient functional (GGA) is used in this work [17]. We used the GGA+U approximation for better description of the Coulomb interaction between f electrons. The adapted values of $U$ for $A_2T_2O_7$ are given in table [1] while the value of on-site Hund’s exchange, $J_H$, is set to

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TABLE I: Hubbard U parameters used in this work (taken from Ref. [15]), calculated band gap (this work), lattice constant (a), and structural internal parameter of oxygen (x) [10] in the studied titanate pyrochlore oxides. The available experimental values of the band gaps are given in the parenthesis.

| Material         | U (eV) | gap (eV) | a (Å)  | x    |
|------------------|--------|----------|--------|------|
| Er₂Ti₂O₇         | 10.14  | 2.1 (2.5 [20]) | 10.194 | 0.327|
| Gd₂Ti₂O₇         | 11.48  | 3.0 (3.2 [21]) | 10.186 | 0.326|
| Tb₂Ti₂O₇         | 5.00   | 2.4      | 10.159 | 0.328|
| Dy₂Ti₂O₇         | 5.68   | 1.9 (2.4 [22]) | 10.124 | 0.328|
| Ho₂Ti₂O₇         | 6.82   | — (3.2 [23]) | 10.104 | 0.329|
| Er₂Ti₂O₇         | 6.80   | 3.0      | 10.071 | 0.328|
| Yb₂Ti₂O₇         | 6.00   | 0.6      | 10.325 | 0.331|

1 eV. The spin-orbit coupling (SOC) is very important in the systems with heavy 4f elements, hence we considered this relativistic interaction in our calculations.

A 4 × 4 × 4 Monkhorst-Pack k mesh was used for Brillouin zone integration. The lanthanide 4f electrons were treated as valence states while their 5s²5p⁶ electrons as well as the Ti 3s²3p⁶ electrons were considered as semicore states. The cut-off of wave function expansion in the interstitial region was set to 3.8 (a.u)⁻¹. We adapted experimental lattice parameters of A₂Ti₂O₇, given in Table I, for our calculations. The space group of A₂Ti₂O₇ is Fd₃m, with the following Wyckoff positions for A and Ti atoms, respectively: 16d (1/2,1/2,1/2), Ti: 16c (0,0,0).

Unfortunately the calculations for Er₂Ti₂O₇ and Ho₂Ti₂O₇ were unstable and we could not achieve their converged electronic structure within GGA+U+SOC. Hence in the case of Er₂Ti₂O₇, we report our previous converged results [21] within LDA+U+SOC and muffin-tin radii 2.5, 2, 1.5 bohr for Er, Ti, and O, respectively. While for Holmium Titanate, we could converge its electronic structure within GGA+U to determine its band gap and spin moment.

III. RESULTS

As it was mentioned, the multi minima problem is a serious challenge in first-principles investigation of 4f electron systems. In order to see the existence of this problem, we performed some test calculations on Tb₂Ti₂O₇ within GGA+U, by starting from three different initial states. In these preliminary calculations, we omitted the SOC interaction, while other parts of our study involves this relativistic correction. At the end of calculations, we reached to three different electronic band structures, presented in Fig. 2. The top band structure is obtained by using the full symmetry (Fd₃m) of the system during the computations, while the middle band structure is calculated without using any symmetry. It is clearly visible that in the resulted band structure after low symmetry calculations, the narrow occupied and unoccupied f bands are slightly separated from the valence and conduction bands. The bottom band structure was calculated by using the full symmetry of the structure and the converged metallic electronic structure of the system within GGA as the starting point of GGA+U calculation. In this way, the GGA+U calculation is converged to a metallic electronic structure.

As it was mentioned, GGA predicts a wrong metallic state for most of the 4f compounds, while GGA+U opens a gap between f states and make A₂Ti₂O₇ insulators. The calculated band gap of these compounds within GGA+U+SOC are given in Table I along with the available experimental data. The good agreement observed between computed and measured band gaps confirms the selected U parameters for these materials. The obtained orbital resolved Density of State (DOS) of the studied systems are shown in Fig. 3. As it was mentioned in Computational method, there are two kinds of oxygen atoms in the systems. The first kind of O atoms connect the neighboring Ti⁴⁺ ions displayed in Fig. 1 and hence, a good hybridization happens between d-orbital of Ti and p-orbital of these O atoms (Fig. 3). The sec-
FIG. 3: Calculated partial density of states (DOS) of the studied titanate pyrochlore $A_2\text{Ti}_2\text{O}_7$ ($A=$Eu, Gd, Tb, Dy, Yb) by GGA+U+SOC. The Fermi energies are set to zero.

The second kind of O atoms (O') are inside tetrahedrons of $A^{3+}$ ions, hence their p orbital DOS are compared with the f orbital DOS of A atoms in Fig. 3. The hybridization between these orbitals is clearly weak, which is likely due to the localized nature of f states. However, in the case of Tb, Dy, and Yb based pyrochlores, the contribution of f states in the valence shell is high, showing the importance of valence treatment of f electrons for ab initio calculation of these systems. It is seen that among $A_2\text{Ti}_2\text{O}_7$, Gd$_2$Ti$_2$O$_7$ exhibits the lowest contribution of f states in the valence shell, which is due to the half-filling of f orbital in Gd. As a result of that, there is only one set of possible occupation numbers in Gd$_2$Ti$_2$O$_7$ and this helps the ab initio calculations to easily converge to its global minima.

The calculated spin, orbital, and total magnetic moments of the studied $A_2\text{Ti}_2\text{O}_7$ pyrochlores obtained from collinear GGA+U+SOC calculations are given in Table I. These moments are calculated inside Muffin-tin spheres. The spin quantization axis is set to the z direction. The experimental values of total magnetic moments are also reported for comparison. The calculated effective magnetic moment of Eu$_2$Ti$_2$O$_7$ is about 4.9 $\mu_B$, which shows large deviation from the experimental value of 0.6$\mu_B$ [25]. In contrast, the calculated energy gap of this system is close to the experimental value (Table I). In the case of Gd$_2$Ti$_2$O$_7$ we got a magnetic moment of 7.0$\mu_B$, in good agreement with the measured value of 7.7$\mu_B$ [4]. The Gd$^{3+}$ ion with a valence shell of $(4f^7)$ has a spin of $S=7/2$ with no orbital magnetic moment, giving rise to an effective moment of $g \times \sqrt{S(S+1)} = 7.9$ ($g=2$), in good agreement with the experimental moment. The GGA band gap of Gd$_2$Ti$_2$O$_7$ is found to be about 2.7 eV, in agreement with Xiao et al. [26]. This compound is the only titanate pyrochlore with a band gap within GGA. This observation provides further evidence for the fact that this system easily converges to its true ground state during ab initio calculations. It should be admitted that the true ground state of this system, as well as other magnetic pyrochlores, may be a non-collinear antiferromagnetic state. Our preliminary calculations confirm the non-collinear ground state of Gd$_2$Ti$_2$O$_7$, however accurate determination of this ground state requires comprehensive ab initio calculations which is out of the scope of this paper. It should be noted that non-collinear calculations for other pyrochlores are much more complicated.

In Tb$_2$Ti$_2$O$_7$, GGA+U+SOC gives a total moment of about 7.2$\mu_B$, which is larger than the measured value of 5.1$\mu_B$ [4]. On the other hand, the calculated total moment of Dy$_2$Ti$_2$O$_7$ (8.2$\mu_B$) is lower than the experimental moment of 10$\mu_B$ [1]. In the case of Yb$_2$Ti$_2$O$_7$, our ab initio calculation predicts a moment of 2.4$\mu_B$ which is about twice the experimental value of about 1.1$\mu_B$ measured by single-crystal neutron diffraction method below 0.2 K [6]. As it was mentioned in Computational method, we could not converge our GGA+U+SOC calculations for Er$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$. The total moment of Erbium Titanate within LDA+U+SOC was found to be 8.8$\mu_B$, which is larger than the experimental value [8]. The spin moment of Ho$_2$Ti$_2$O$_7$ within GGA+U was found to be about 3.8$\mu_B$.

For more accurate comparison of the experimental and computational values of magnetic moments, we used the crystal electric field theory to decompose experimental moments into spin and orbital contributions. Applying crystal electric field theory to the experimental neutron spectra, the magnetic ground-state wave function of $A_2\text{Ti}_2\text{O}_7$ ($A=$Eu, Gd, Tb, Dy, Ho, Er, Yb) pyrochlore compounds, except Gd$_2$Ti$_2$O$_7$ and Eu$_2$Ti$_2$O$_7$ are determined in terms of $|j, m_j\rangle$ basis set [27], where $j$ and $m_j$ are total angular momentum and magnetic quantum number, respectively. We used Clebsch-Gordan coefficients to decompose $|j, m_j\rangle$ to $|m_l, m_s\rangle$ states, where $m_l$ and $m_s$ are orbital and spin magnetic quantum num-
TABLE II: Magnetic properties of titanate pyrochlore, L,S,J: orbital, spin, and total angular momentum, $\mu_S$, $\mu_L$ ($\mu_B$): Calculated spin and orbital magnetic moments, The values in the parenthesis are estimated from crystal field analysis. $\mu_{tot}$ (\mu_B): Calculated total magnetic moment, The values in the parenthesis are available measured data, collected from references [11][11][11][11][11][11][11]

|             | L  | S   | J   | $\mu_S$ | $\mu_L$ | $\mu_{tot}$ |
|-------------|----|-----|-----|---------|---------|------------|
| Eu$_2$Ti$_2$O$_7$ | 3  | 3   | 0   | 6.1     | -1.1    | 4.9 (0.6)  |
| Gd$_2$Ti$_2$O$_7$ | 0  | 7/2 | 7/2 | 7.0     | 0.0     | 7.0 (7.7)  |
| Tb$_2$Ti$_2$O$_7$ | 3  | 3   | 6   | 6.0     | 3.3     | 9.3 (5.1)  |
| Dy$_2$Ti$_2$O$_7$ | 5  | 5/2 | 15/2| 5.0     | 3.3     | 8.2 (10.0) |
| Ho$_2$Ti$_2$O$_7$ | 6  | 2   | 8   | 3.8     | -5.8    | -2.0 (10.0)|
| Er$_2$Ti$_2$O$_7$ | 6  | 3/2 | 15/2| 3.0     | 5.9     | 8.8 (3.2)  |
| Yb$_2$Ti$_2$O$_7$ | 3  | 1/2 | 7/2 | 0.9     | 1.5     | 2.4 (1.1)  |

numbers, respectively. The resulting magnetic ground-state wave functions in terms of $|m_l,m_s\rangle$ states are given in appendix A and the obtained orbital and spin moments are presented in Table III. The observed consistency between crystal field spin and orbital moments and measured total moments confirms the obtained magnetic ground state wave functions. It is seen that the calculated orbital moment of Tb$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$ are about 30% smaller than the crystal field orbital moment, while the calculated orbital moment of Er$_2$Ti$_2$O$_7$ and Yb$_2$Ti$_2$O$_7$ are significantly higher than the crystal field values. On the other hand, the calculated spin moments show generally more agreement with the corresponding crystal field values. The obtained spin moments of Dy$_2$Ti$_2$O$_7$, Ho$_2$Ti$_2$O$_7$ are very close to the crystal field data while in the case of Tb$_2$Ti$_2$O$_7$, Er$_2$Ti$_2$O$_7$, and Yb$_2$Ti$_2$O$_7$ significant difference is visible between first-principles and crystal field spin moments.

IV. CONCLUSIONS

The electronic structure and magnetic properties of A$_2$Ti$_2$O$_7$ (A=Eu, Gd, Tb, Dy, Ho, Er, Yb) magnetic pyrochlores were investigated by using full-potential density functional calculations within GGA+U scheme and relativistic spin orbit coupling (SOC). The calculated band gaps are in good agreement with the available measured values. We used Tb$_2$Ti$_2$O$_7$ compound to show the possible multi-minima solutions of the electronic structure of these magnetic pyrochlores. It was argued that the half filling of the 4f shell of Gd significantly decreases the contribution of f electrons in the valence shell of Gd$_2$Ti$_2$O$_7$ and hence facilitates the electronic structure calculation of this system to converge to its global minima. The calculated spin, orbital, and total magnetic moments of the systems within GGA+U+SOC calculations were presented and compared with the available measured total magnetic moments. The best agreement was observed in Gd$_2$Ti$_2$O$_7$, while Eu$_2$Ti$_2$O$_7$ and Er$_2$Ti$_2$O$_7$ compounds showed the highest deviation from experiment. The phenomenological magnetic ground state wave function of Tb$_2$Ti$_2$O$_7$, Dy$_2$Ti$_2$O$_7$, Ho$_2$Ti$_2$O$_7$, Er$_2$Ti$_2$O$_7$, and Yb$_2$Ti$_2$O$_7$ compounds were determined in the framework of crystal electric field theory for decomposition of the measured total magnetic moments into spin and orbital contributions. Comparing the calculated and the crystal field spin and orbital moments shows more accuracy of the calculated spin moments.

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Appendix A: Crystal field analysis

The magnetic ground-state wave function of A$_2$Ti$_2$O$_7$ (A=Eu, Gd, Tb, Dy, Yb) pyrochlore compounds in terms of $|j,m_j\rangle$ states are as follows [27]:

$$|\phi_g^{Tb}\rangle = +0.96|± 4\rangle ± 0.13|± 1\rangle ± 1\rangle$$

$$-0.12|± 2\rangle ± 0.23|± 5\rangle$$

$$|\phi_g^{Dy}\rangle = +0.981|± 15\rangle ± 0.190|± 9\rangle$$

$$+0.022|± 3\rangle ± 0.037|± 7\rangle$$

$$+0.005|± 9\rangle ± 0.001|± 15\rangle$$

$$|\phi_g^{Ho}\rangle = -0.979|± 8\rangle ± 0.189|± 5\rangle$$

$$-0.014|± 2\rangle ± 0.070|± 1\rangle$$

$$-0.031|± 4\rangle ± 0.005|± 7\rangle$$

$$|\phi_g^{Yb}\rangle = +0.376|± 7\rangle ± 0.922|± 1\rangle$$

$$-0.093|± 5\rangle$$
these magnetic ground-state wave functions in terms of $|m_l, m_s\rangle$ states:

$$|\phi^T_D\rangle = + 0.46| - 3, -1\rangle + 0.71| - 2, -2\rangle + 0.46| 1, -3\rangle - 0.04| 1, -2\rangle - 0.08| 0, -1\rangle - 0.08| 0, 1\rangle - 0.04| 2, +1\rangle - 0.01| 2, -3\rangle - 0.01| 3, 2\rangle - 0.02| 3, -1\rangle - 0.06| 2, 0\rangle - 0.08| 1, 1\rangle - 0.06| 0, 2\rangle - 0.02| - 1, 3\rangle + 0.16| 3, 2\rangle + 0.16| 2, 3\rangle$$

$$|\phi^T_{\text{Yb}}\rangle = + 0.37| 3, 1\rangle + 0.70| 0, 1\rangle + 0.60| 1, 1\rangle - 0.03| 3, 1\rangle - 0.09| 2, 1\rangle$$

$$|\phi^D_{\text{Er}}\rangle = + 0.21| 6, 2\rangle + 0.42| 5, 2\rangle + 0.04| 5, 3\rangle + 0.16| 4, 2\rangle + 0.31| 3, 2\rangle + 0.25| 2, 2\rangle - 0.16| 2, 3\rangle + 0.38| 0, 3\rangle - 0.20| 1, 3\rangle - 0.12| 1, 3\rangle + 0.17| 2, 1\rangle + 0.11| 3, 2\rangle + 0.04| 4, 3\rangle + 0.37| 4, 3\rangle + 0.28| 5, 2\rangle + 0.08| 6, 2\rangle$$

$$|\phi^H_{\text{Ho}}\rangle = - 0.9790| 6, 2\rangle + 0.1184| 3, 2\rangle + 0.1290| 4, 1\rangle + 0.0670| 5, 0\rangle + 0.0160| 6, 0\rangle - 0.0047| 0, 2\rangle - 0.0088| 1, 1\rangle - 0.0080| 2, 0\rangle - 0.0046| 3, 1\rangle - 0.0012| 4, 2\rangle + 0.0098| 3, 2\rangle + 0.0300| 2, 1\rangle + 0.0450| 1, 0\rangle + 0.0040| 0, 1\rangle + 0.0180| 1, 2\rangle - 0.0007| 6, 2\rangle - 0.0050| 5, 1\rangle - 0.0210| 3, 1\rangle - 0.0160| 2, 2\rangle - 0.0140| 4, 0\rangle + 0.0025| 6, 1\rangle + 0.0043| 5, 2\rangle$$

We used Clebsch-Gordan coefficients to represent these magnetic ground-state wave functions in terms of $|m_l, m_s\rangle$ states:

For calculating the spin and orbital magnetic moments from the above wave functions, one should take into account that the Tb$_2$Ti$_3$O$_7$, Dy$_2$Ti$_3$O$_7$, Ho$_2$Ti$_3$O$_7$, and Yb$_2$Ti$_3$O$_7$ are Ising like systems while Er$_2$Ti$_3$O$_7$ adopts XY model magnetism. For Ising like systems, $g_l\langle L_z \rangle$ and $g_s\langle S_z \rangle$ are calculated as orbital and spin moments of the magnetic atom of the systems, while in XY-like systems, $\langle S_{z\pm}\rangle$ and $\langle L_{z\pm}\rangle$, therefore $g_l\langle L_{z\pm}\rangle = L_{z\pm} \pm i L_y g_l = 1$ and $g_s\langle S_{z\pm}\rangle = L_{z\pm} \pm i L_y g_s = 2$ are calculated as orbital and spin moments, respectively.
[1] J. S. Gardner, M. J. Gingras, and J. E. Greedan, Reviews of modern Physics 82, 53 (2010).
[2] S. Bramwell, S. Giblin, S. Calder, R. Aldus, D. Prabhakaran, and T. Fennell, Nature 461, 956 (2009).
[3] O. Petrenko, M. R. Lees, and G. Balakrishnan, Journal of Physics: Condensed Matter 23, 164218 (2011).
[4] J. Gardner, B. Gaulin, A. Berlinsky, P. Waldron, S. Dunsiger, N. Raju, and J. Greedan, Physical Review B 64, 224416 (2001).
[5] J. Gardner, S. Dunsiger, B. Gaulin, M. Gingras, J. Greedan, R. Kiefl, M. Lumsden, W. MacFarlane, N. Raju, J. Sonier, et al., Physical review letters 82, 1012 (1999).
[6] J. Hodges, P. Bouville, A. Forget, A. Yaouanc, P. D. De Reotier, G. Andre, M. Rams, K. Krolas, C. Ritter, P. Gubbens, et al., Physical review letters 88, 077204 (2002).
[7] S. Bramwell, M. Field, M. Harris, and I. Parkin, Journal of Physics: Condensed Matter 12, 483 (2000).
[8] A. Poole, A. Wills, and E. Leilievre-Berna, Journal of Physics: Condensed Matter 19, 452201 (2007).
[9] N. Raju, M. Dion, M. Gingras, T. Mason, and J. Greedan, Physical Review B 59, 14489 (1999).
[10] H. Xiao, X. T. Zu, F. Gao, and W. J. Weber, Journal of Applied Physics 104, 073503 (2008).
[11] H. Xiao, Advances in Condensed Matter Physics 2013 (2013).
[12] V. Nemoshkalenko, S. Borisenko, V. Uvarov, A. Yaresko, A. Vakhney, A. Senkevich, T. Bondarenko, and V. Borisenko, Physical Review B 63, 075106 (2001).
[13] B. Dorado, M. Freyss, B. Amadon, M. Bertolus, G. Jonard, and P. Garcia, Journal of Physics: Condensed Matter 25, 333201 (2013), URL http://stacks.iop.org/0953-8984/25/i=33/a=333201.
[14] A. D. Becke, The Journal of Chemical Physics 98, 1372 (1993).
[15] FLEURgroup, http://www.flapw.de/.
[16] E. Wimmer, H. Krakauer, M. Weinert, and A. Freeman, Physical Review B 24, 864 (1981).
[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996), URL http://link.aps.org/doi/10.1103/PhysRevLett.77.3865.
[18] S. Sann, Ph.D. thesis, University of Paderborn (2007).
[19] J. Lian, J. Chen, L. Wang, R. C. Ewing, J. M. Farmer, L. A. Boatner, and K. Helean, Physical Review B 68, 134107 (2003).
[20] A. Pandit, T. Ansari, R. Singh, R. Singh, and B. Wanklyn, Journal of materials science 27, 4080 (1992).
[21] K. Parida, A. Nashim, and S. K. Mahanta, Dalton Transactions 40, 12839 (2011).
[22] A. Pandit, T. Ansari, R. Singh, and B. Wanklyn, Materials Letters 11, 52 (1991), ISSN 0167-577X, URL http://www.sciencedirect.com/science/article/pii/0167577X91901.
[23] S. T. Bramwell and M. J. Gingras, Science 294, 1495 (2001).
[24] E. Khorasani, N. Deylinazar, M. Alaei, F. Shahbazi, and AWTAG, Iranian Journal of Physics Research 14 (2014).
[25] P. Dasgupta, Y. Jana, A. Nag Chattopadhyay, R. Higashinaka, Y. Maeno, and D. Ghosh, Journal of Physics and Chemistry of Solids 68, 347 (2007).
[26] H. Xiao, L. Wang, X. Zu, J. Lian, and R. C. Ewing, Journal of Physics: Condensed Matter 19, 346203 (2007).
[27] A. Bertin, Y. Chapuis, P. D. de Réotier, and A. Yaouanc, Journal of Physics: Condensed Matter 24, 256003 (2012).