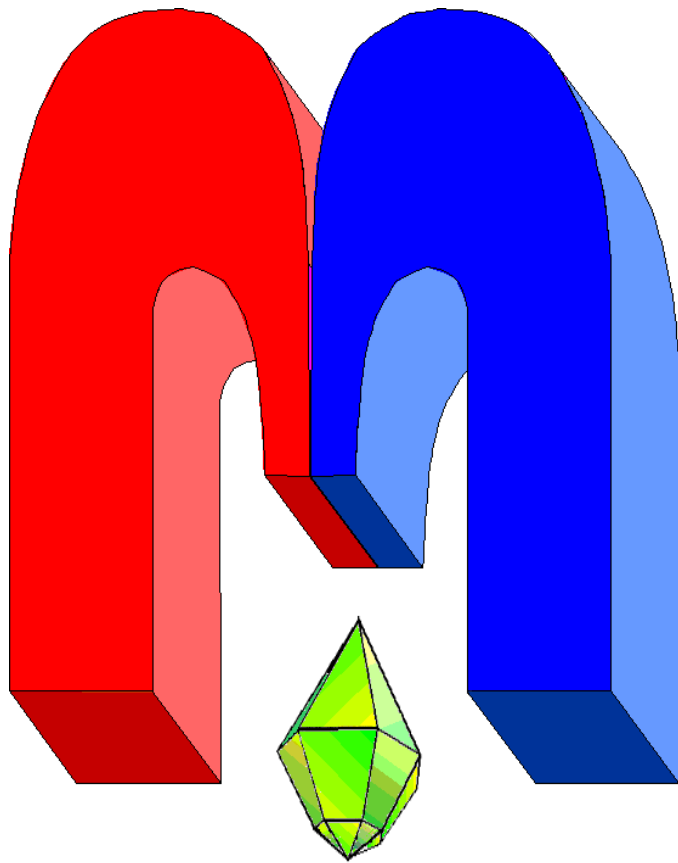


ISSN 2072-5981  
doi: 10.26907/mrsej



***Magnetic  
Resonance  
in Solids***

Electronic Journal

*Volume 26*

*Issue 2*

*Article No 24203*

*1-5 pages*

*June, 6*

**2024**

doi: 10.26907/mrsej-24203

<http://mrsej.kpfu.ru>  
<https://mrsej.elpub.ru>



Established and published by Kazan University\*  
Endorsed by International Society of Magnetic Resonance (ISMAR)  
Registered by Russian Federation Committee on Press (#015140),  
August 2, 1996  
First Issue appeared on July 25, 1997

© Kazan Federal University (KFU)†

*"Magnetic Resonance in Solids. Electronic Journal" (MRSej)* is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by  
*Web of Science (ESCI, Clarivate Analytics, from 2015), Scopus (Elsevier, from 2012), RusIndexSC (eLibrary, from 2006), Google Scholar, DOAJ, ROAD, CyberLeninka (from 2006), SCImago Journal & Country Rank, etc.*

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† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

‡ Dedicated to Professor Boris Z. Malkin on the occasion of his 85th birthday

# Crystal structure of impurity centers $\text{Eu}^{3+}$ and $\text{Dy}^{3+}$ in $\text{Re}_2\text{Ti}_2\text{O}_7$ ( $\text{Re}=\text{Gd},\text{Tb}$ ) crystals: ab initio calculation<sup>†</sup>

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(Received March 30, 2024; accepted May 30, 2024; published June 6, 2024)

Within the framework of the DFT approach, with a hybrid functional PBE0 that takes into account the contribution of nonlocal exchange in the Hartree-Fock formalism, the structure of impurity centers  $\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$ ,  $\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Dy}^{3+}$  and  $\text{Tb}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$  was calculated. It has been shown that there is practically no lattice distortion in these impurity centers.

**PACS:** 61.50.Ah, 63.20.dk

**Keywords:** DFT, Hybrid functionals, Pyrochlores, Impurity centers

## 1. Introduction

Rare earth oxides with a pyrochlore structure ( $\text{A}_2\text{B}_2\text{O}_7$ , where  $\text{A}=\text{Y}, \text{La-Lu}$ ,  $\text{B}=\text{Ti}, \text{Zr}, \text{Sn}, \text{Ge}, \dots$ ) attract attention due to their optical, magnetic, and electrical properties. They have potential applications as heat-protective ceramic barriers [1], solid electrolytes [2], as materials of immobilization of actinides [3]. Interest to the optical properties of rare earth pyrochlores has increased recently [4–6]. The electronic structure of the rare earth ion  $\text{RE}^{3+}$  included in the regular sublattice of rare earth titanates  $\text{RE}_2\text{Ti}_2\text{O}_7$  has been studied in detail [7]. The electronic structure of rare-earth impurity centers in yttrium titanate  $\text{Y}_2\text{Ti}_2\text{O}_7$  has been studied also [6]. Recently experimental work has appeared devoted to the study of the optical properties of rare earth titanates activated by other rare earth ions –  $\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Dy}^{3+}$  [8],  $\text{Tb}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$  [9],  $\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$  [10]. It is of interest to study lattice distortion near to impurity ion in crystals  $\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$ ,  $\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Dy}^{3+}$ ,  $\text{Tb}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$  within the framework of the ab initio approach. Information about lattice distortions near an impurity ion can be useful when calculating the crystal field on the impurity ion.

## 2. Calculations

Calculations were performed in the framework of the density functional theory (DFT). Hybrid functionals, that take into account non-local exchange at Hartree-Fock (HF) formalism, were used [11]. Currently, there is no universal DFT functional that would describe all compounds equally well. Therefore, test calculations were carried out with various hybrid functionals. The most tested and well-known functionals – B3LYP, PBE0, WC1LYP were used. These functionals take into account local contributions to exchange and correlations at the level of the generalized gradient approximation. They have different contributions of nonlocal exchange, calculated in the Hartree-Fock formalism (20, 25, and 16 percent accordingly). The functionals are implemented in the CRYSTAL17 code [12]. The program CRYSTAL is designed for modeling periodic structures using density functional theory and Hartree-Fock methods within the framework of the MO LCAO approach. For oxygen all electron basis set of TZVP type was used [13]. For titanium, pseudopotential HAYWSC was used to replace the electrons of the first and second layers ( $n - 1, 2$ ). Electrons  $3s^23p^6$ , involved in chemical bond were de-

<sup>†</sup>This paper is dedicated to Professor Boris Z. Malkin, who made a significant contribution to the field of magnetic radio spectroscopy in Kazan University, on the occasion of his 85th birthday.

scribed using one-electron wave functions. Oxygen basis and the pseudopotential for titanium are available on website of CRYSTAL program. Quasi-relativistic pseudopotential ECP52MWB, ECP53MWB, ECP55MWB were used for Eu, Gd and Tb. In this abbreviation '52', '53', '55' is the number of internal electrons replaced by the pseudopotential. Thus the inner shells of the rare-earth ion were replaced by a pseudopotential on the  $4f$  inclusive. The outer shells,  $5s^25p^6$ , involved in the chemical bonds, were described by valence basis sets ECPnMWB-I of TZVP type. These pseudopotentials and valence basis sets are available on the Stuttgart website <http://www.tc.uni-koeln.de/PP/clickpse.en.html>. The work also carried out a test calculation for  $\text{Eu}^{3+}$ , when the  $4f$  shell was not replaced by a pseudopotential, but was taken into account explicitly, i.e. was part of the valence basis set. Pseudopotential ECP28MWB has been used for this purpose. The accuracy of self-consistent system of Kohn-Sham equations was set at  $10^{-10}$  a.u. The accuracy of the calculation of the two-electron integrals was no less than  $10^{-8}$  a.u. The Monkhorst-Pack mesh was  $8 \times 8 \times 8$ .

### 3. Results and discussion

The results of calculating the crystal structure and band gap value of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  with various DFT functionals are given in Table 1. The functionals WC1LYP, B3LYP, PBE0 have a part of non-local HF -exchange 16%, 20%, 25% respectively. It can be seen that the higher part of HF exchange, the better the crystal structure is reproduced. The crystal structure is best reproduced by PBE0 functional. Table 1 shows the band gap value. This is «HOMO-LUMO» estimate based on the calculations. Calculations show that the larger the part of HF exchange in functional, the greater the overestimation of the gap relative to experiment. The band gap value that is closest to the experiment is reproduced by functional WC1LYP (Table 1). If we reduce the part of HF exchange in the PBE0 functional to 11 percent, we can reproduce a band gap value that practically coincides with the experiment. However, such a reduction will be a fitting and will not make sense. Thus, we cannot describe both the crystalline and band structure of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  with the same functional. The crystal structure is well reproduced with functional PBE0. For the band structure, functional WC1LYP gives an acceptable result. Similar calculations for  $\text{Tb}_2\text{Ti}_2\text{O}_7$  are presented in Table 2. The best agreement for the crystal structure of  $\text{Tb}_2\text{Ti}_2\text{O}_7$  is also given by the functional PBE0. Therefore, in this work, functional PBE0 was used to calculate the crystal structure of impurity centers.

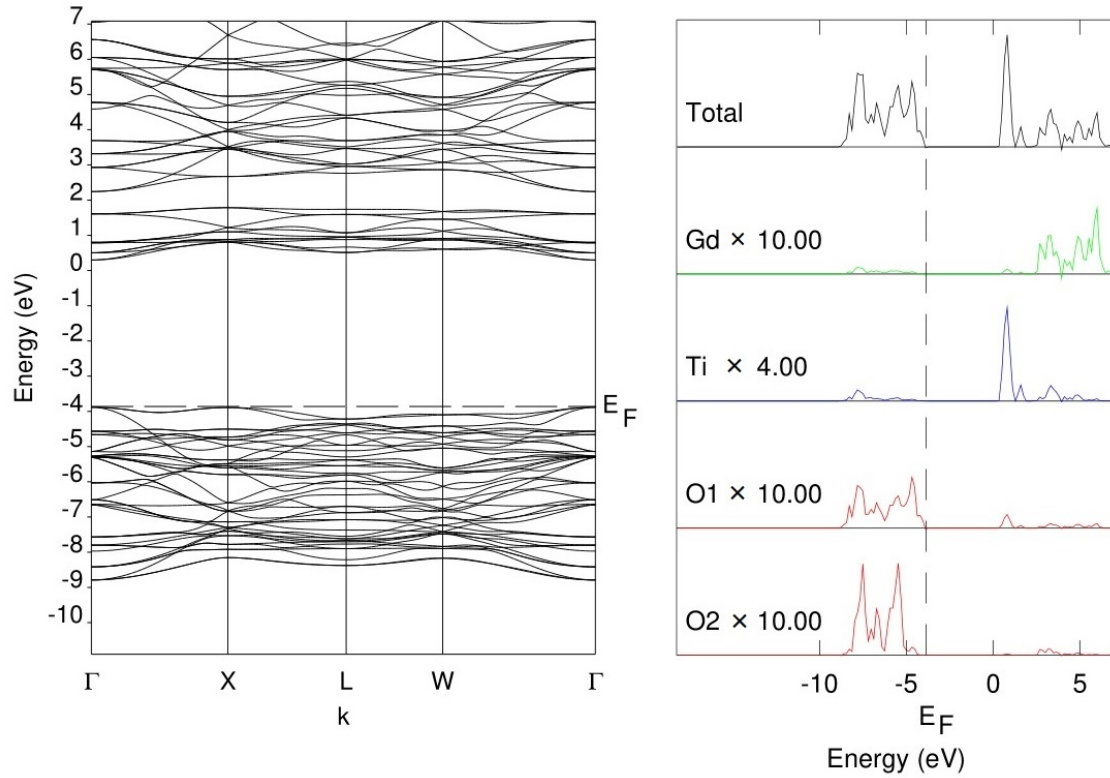
**Table 1.**  $\text{Gd}_2\text{Ti}_2\text{O}_7$ . Lattice constant and band gap value.

DFT functional	Lattice constant, Å	$x$ , rel. un.	Band gap, eV
B3LYP	10.291	0.327	4.52
PBE0	10.199	0.327	5.05
WC1LYP	10.243	0.327	4.18
PBE0 (11% HF)	10.250	0.328	3.73
Exp.	10.196 [14]	0.322 [15]	3.68 [4]

To test the approach, the band structure of a crystal with functional WC1LYP was calculated (Fig. 1). As can be seen from the figure, oxygen orbitals give the main contribution to states near to top of the valence band. Titanium orbitals give the main contribution to states near to bottom of the conduction band. Therefore, we can reproduce the value of band gap even if we do not directly take into account the  $4f$  state of the rare earth ion ( $4f$  state of gadolinium are replaced by the pseudopotential in this calculation). The band structure of the  $\text{Gd}_2\text{Ti}_2\text{O}_7$

**Table 2.**  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . Lattice constant and band gap value.

DFT functional	Lattice constant, Å	$x$ , rel.un.	Band gap, eV
B3LYP	10.261	0.328	4.52
PBE0	10.172	0.328	5.05
WC1LYP	10.214	0.328	4.18
PBE0 (11% HF)	10.221	0.328	3.73
Exp.	10.155 [14]	—	—

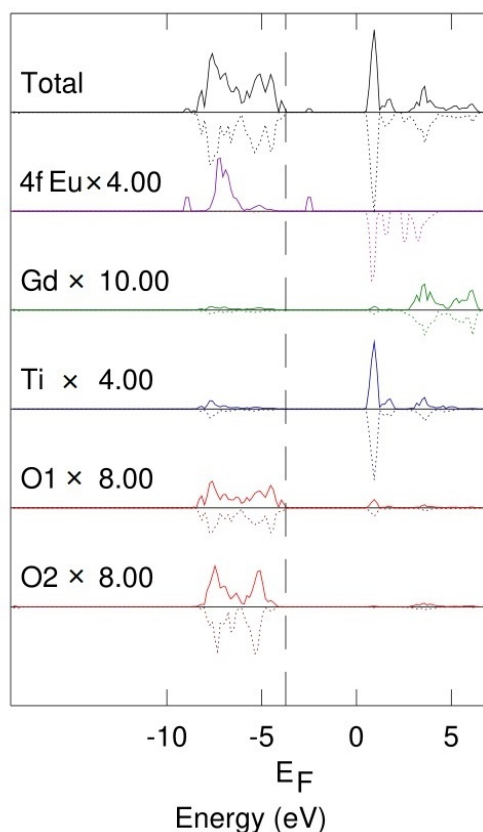
**Figure 1.** Band structure of crystal  $\text{Gd}_2\text{Ti}_2\text{O}_7$ .

crystal doped by europium  $\text{Eu}^{3+}$  was calculated also (Fig. 2). Moreover, for europium in this calculation, a short pseudopotential was used, replacing electrons only of the first three layers ( $n = 1 - 3$ ). The  $4f$  shell of europium was taken into account explicitly in this calculation, using one-electron functions. The  $4f$  shell of gadolinium was replaced by a pseudopotential, as in the previous calculation, to save computer costs.

**Table 3.**  $\text{Gd}_2\text{Ti}_2\text{O}_7$ . The distance to neighbors in a pure lattice and impurity centers, Å.

Coordination sphere	Distance to ions	$\text{Gd}_2\text{Ti}_2\text{O}_7$	$\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$	$\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Dy}^{3+}$
1	$R - \text{O1}$ (6)	2.5195	2.5239	2.5103
1	$R - \text{O1}$ (2)	2.2082	2.2190	2.1861
2	$R - \text{Ti}$ (6)	3.6060	3.6083	3.6012

The calculation of the crystal structure of impurity centers was carried out with functional PBE0, while for all rare earth ions pseudopotentials were used that replaced the inner electron shells  $4f$  inclusive (Table 3, 4). As predicted by calculations, when gadolinium is replaced by



**Figure 2.** Density of states of crystal  $\text{Gd}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$ .  $4f$  shell is taken into account only for Europium.

**Table 4.**  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . The distance to neighbors in a pure lattice and impurity centers, Å.

Coordination sphere	Distance to ions	$\text{Tb}_2\text{Ti}_2\text{O}_7$	$\text{Tb}_2\text{Ti}_2\text{O}_7:\text{Eu}^{3+}$
1	$R - \text{O}1$ (6)	2.5084	2.5170
1	$R - \text{O}1$ (2)	2.2022	2.2240
2	$R - \text{Ti}$ (6)	3.5962	3.6006

**Table 5.**  $\text{BaF}_2$ . The distance to neighbors in a pure lattice and impurity centers, Å. PBE0 calculation.

Coordination sphere	Distance to ions	$\text{BaF}_2$ pure	$\text{BaF}_2:\text{Eu}^{3+}$
1	$R - \text{F}$ (8)	2.6904	2.3963
2	$R - \text{Ba}$ (12)	4.3935	4.3502

europium or dysprosium in  $\text{Gd}_2\text{Ti}_2\text{O}_7$ , the distances to the ligands change little (within 0.01 angstroms). The distances to the ions of the second coordination sphere (cations) change even less. Thus, impurity centers  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  practically do not distort the crystal lattice of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  (Table 3). Also, the impurity center  $\text{Eu}^{3+}$  practically does not distort the crystal lattice of  $\text{Tb}_2\text{Ti}_2\text{O}_7$  (Table 4). For comparison, we calculated the impurity center  $\text{BaF}_2:\text{Eu}^{3+}$  (Table 5). The replacement of  $\text{Ba}^{2+}$  ion by  $\text{Eu}^{3+}$  is non-isovalent. Calculations predict a strong change in the distance to the ligands (0.2 angstroms).

#### 4. Summary

DFT calculations of impurity centers were carried out. Calculations predict that impurity centers  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  practically do not distort the lattice of  $\text{Gd}_2\text{Ti}_2\text{O}_7$ . Calculations predict that

impurity center  $\text{Eu}^{3+}$  practically do not distort the lattice of  $\text{Tb}_2\text{Ti}_2\text{O}_7$ . The results obtained can be useful for calculating the crystal field on these impurity ions.

## Acknowledgments

This study was supported by the Ministry of Education and Science of the Russian Federation (project No. FEUZ-2023-0017)

## References

1. Pan W., Phillpot S. R., Wan C., Chernatynskiy A., Qu Z., *MRS Bulletin* **37**, 917 (2012).
2. Wuensch B. J., Eberman K. W., Heremans C., Ku E. M., Onnerud P., Yeo E. M. E., Haile S. M., Stalick J. K., Jorgensen J. D., *Solid State Ionics* **129**, 111 (2000).
3. Sickafus K. E., Minervini L., Grimes R. W., Valdez J. A., Ishimaru M., Li F., McClellan K. J., Hartmann T., *Science* **289**, 748 (2000).
4. Masud A., Singh B. K., J.Lahiri, Das N. K., Himanshu A. K., *AIP Conference Proceedings* **2995**, 020059 (2024).
5. Liao J., Kong L., Wang Q., Li J., Peng G., *Journal of Advanced Optics and Photonics* **1**, 95 (2018).
6. Batulin R. G., Cherosov M. A., Gil'mutdinov I. F., Khaliulin B. F., Kiiamov A. G., Klekovkina V. V., Malkin B. Z., Mukhamedshin I. R., Mumdzhi I. E., Nikitin S. I., Rodionov A. A., Yusupov R. V., *Physics of the Solid State* **5**, 818 (2019).
7. Malkin B. Z., Lummen T. T., van Loosdrecht P. H., Dhahlenne G., Zakirov A. R., *Journal of Physics: Condensed Matter* **22**, 276003 (2010).
8. Berwal U., Singh V., Sharma R., *Ceramics International* **49**, 8897 (2023).
9. Singh P., Pal A., Gangwar V. K., Ghosh S., Singh R. K., Ghosh A. K., Chatterjee S., *Journal of Magnetism and Magnetic Materials* **490**, 165512 (2019).
10. Kuo-Min L., Chih-Cheng L., Yuan-Yao L., *Nanotechnology* **17**, 1745 (2006).
11. Arbuznikov A. V., *Journal of Structural Chemistry* **48**, S1 (2007).
12. Dovesi R., Saunders V. R., Roetti C., Orlando R., Zicovich-Wilson C. M., Pascale F., Civalieri B., Doll K., Harrison N. M., Bush I. J., D'Arco P., Llunel M., Causa M., Noel Y., Maschio L., Erba A., Rerat M., Casassa S., *CRYSTAL17 User's Manual. Gruppo di Chimica Teorica, Dipartimento di Chimica* (2017).
13. Peintinger M. F., Oliveira D. V., Bredow T. J., *Journal of Computational Chemistry* **34**, 451 (2012).
14. Li Q. J., Xu L. M., Fan C., Zhang F. B., Lv Y. Y., Ni B., Zhao Z. Y., Sun. X., *Journal of Crystal Growth* **377**, 96 (2013).
15. Subramanian M., Aravamudan G., Rao G. S., *Progress in Solid State Chemistry* **15**, 55 (1983).