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First principles results on $\text{TbAl}_3(\text{BO}_3)_4$: A promising magneto-optical material

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The electronic and optical properties of $\text{TbAl}_3(\text{BO}_3)_4$ are determined using density functional theory. The calculated total magnetic moment of $5.96 \mu_B$ is close to the expected moment of Tb^{3+} . The frequency dependent dielectric function, refractive index, extinction coefficient, absorption, optical reflectivity, and energy loss function are explained in terms of the transitions between the valence and conduction bands. We find very high Kerr angles for ultraviolet light and potential for extension, even into the visible range by band structure design. © 2011 American Institute of Physics. [doi:10.1063/1.3662176]

I. INTRODUCTION

Borates are used in a vast number of applications, ranging from glass to fibers and flame retardants. Interestingly, a non-centrosymmetric geometry appears to be typical for borate structures.¹ The compounds consequently have attracted much attention by outstanding (non-)linear optical properties, which are useful in magnetic devices for optical communication and measurement technology.^{2–5} Comparison of experimental as well as theoretical results for this class of materials indicates that the planar $[\text{BO}_3]^{3-}$ group gives larger non-linear optical contributions than the tetrahedral $[\text{BO}_4]^{5-}$ group.⁶ The Kerr and Faraday rotations in borate glasses have been addressed in Ref. 7.

Borates can be doped by rare earth ions for using them as magneto-optical materials.⁸ The iron-based rare earth borates $\text{RFe}_3(\text{BO}_3)_4$ ($\text{R} = \text{Nd}, \text{Ho}, \text{Gd}, \text{Tb}, \text{and Y}$) are interesting because of a large magneto-electric effect and non-centrosymmetric geometry, which makes them candidates for application in (non-)linear optical and magneto-optical devices.^{9–18} In rare earth iron borates, the exchange interaction between the Fe 3d electrons gives rise to antiferromagnetic ordering. Coupling of the Fe moments to the rare earth moments with a strong single-ion anisotropy results in complex magnetic phases, spin reorientation phase transitions, and (non-)collinear magnetism, as discovered by neutron scattering.^{19–22} The complexity of the magnetic structures associated with the d and f electrons makes it difficult to understand the microscopic details of the magneto-electric effect. Moreover, Fe does not play an important role for the large magneto-electric effect in rare earth iron borates.²³

The magnetic complexity can be reduced by substituting Fe by Al, which results in a new class of isostructural borates without d valence electrons, $\text{RAl}_3(\text{BO}_3)_4$. A lot of experimental studies on the spectroscopic and optical properties of these materials have been performed, while a theoretical treatment is lacking in the literature.^{23–35} Recently,

Chaudhury *et al.*²³ have studied the magneto-electricity and magneto-striction in $\text{TmAl}_3(\text{BO}_3)_4$ and concluded that the magneto-electricity is related to the piezoelectric effect of the non-centrosymmetric structure. The giant magneto-electric effect in $\text{HoAl}_3(\text{BO}_3)_4$ has been found to increase with decreasing magnetic anisotropy.²⁴ Moreover, the optical absorption edges of undoped and Sm^{3+} doped $\text{YAl}_3(\text{BO}_3)_4$ have been studied in the vacuum ultraviolet spectral region.²⁵

Since $\text{TbAl}_3(\text{BO}_3)_4$ has potential in laser applications,^{26–30} its optical absorption and luminescence have been measured by Kellendonk *et al.*³¹ and later by Couwenberg *et al.*,³² who found that the crystal field parameters are comparable with those of Eu^{3+} -doped $\text{GdAl}_3(\text{BO}_3)_4$.³³ The structural and optical properties of $\text{TbAl}_3(\text{BO}_3)_4$ single crystals have been studied in Ref. 34. The $4f^n \rightarrow 4f^{n-1}5d$ absorption plays a central role for the optical and magneto-optical properties.³⁵

II. METHODOLOGY

In this work, we investigate the electronic structure of $\text{TbAl}_3(\text{BO}_3)_4$ and interrelate it with the optical and magneto-optical properties of the compound, due to its potential in (non-)linear optical devices. We study the band structure (BS) and density of states (DOS) in order to explain the optical conductivity and complex Kerr spectra in terms of electronic transitions. Our calculations are based on density functional theory, using the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code.³⁶ We have performed spin-polarized calculations, including spin-orbit coupling (SOC), with the magnetization along the (001) direction. We use the local spin density approximation plus onsite Coulomb interaction (LSDA+U) method and apply the exchange-correlation potential parameterization of von Barth and Hedin.³⁷ This approach describes the ground state of the present compound with high accuracy.^{38,39} On the other hand, calculation of optical spectra, in principle, involves excited states. Thus, additional approximations have to be introduced, which, however, do not compromise the following line of reasoning,

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as they are only gradual and not qualitative.⁴⁰ The generalized gradient approximation (GGA) is used to compare the results to the isostructural compound $\text{TbFe}_3(\text{BO}_3)_4$.⁴¹

The crystal structure of $\text{TbAl}_3(\text{BO}_3)_4$ has a trigonal symmetry with space group R32 (No. 155). The cell parameters are $a = b = 9.2933 \text{ \AA}$ and $c = 7.2496 \text{ \AA}$.³⁴ The O–B–O bond angle is 120° and the B–O bond distance is $1.383 \text{ \AA}$. In the FP-LAPW method, the unit cell is divided into two parts: non-overlapping atomic spheres centered at the atomic sites and the interstitial region. The convergence parameter $R_{\text{mt}}K_{\text{max}}$, where K_{max} is the plane-wave cut-off and R_{mt} is the smallest of all atomic sphere radii, controls the size of the basis. It is set to $R_{\text{mt}}K_{\text{max}} = 7$ with $G_{\text{max}} = 18$. Convergence tests have shown that 63 k-points in the irreducible wedge of the Brillouin zone are sufficient, as more k-points give no appreciable change in energy or properties. A dense mesh of 174 uniformly distributed k-points is required in the optical calculations. Self-consistency is assumed for a total energy convergence of less than 10^{-5} Ry .

The LSDA+ U approach allows us to overcome the shortcoming of the LSDA that the Tb 4*f* states appear at the Fermi level and are partially occupied, contradicting an atomic-like nature. A finite U results in a Hubbard splitting of the occupied and empty Tb 4*f* states. We use $U_{\text{eff}} = 5 \text{ eV}$, as suggested in Ref. 42. Our LSDA+ U calculations yield a total magnetic moment of $5.96 \mu_B$, in good agreement with the $6 \mu_B$ expected for Tb^{3+} ions. A small amount of the magnetic moment ($0.05 \mu_B$) comes from the interstitial region, while negligible contributions arise from B, O, and Al ($< 0.004 \mu_B$).

III. RESULTS AND DISCUSSION

The calculated LSDA+ U BS and DOS are shown in Figs. 1 and 2, respectively. We find $\text{TbAl}_3(\text{BO}_3)_4$ to be a wide bandgap insulator with a bandgap of 3.3 eV . The flat bands around 4 eV are due to empty Tb 4*f* states. These states are shifted deep inside the valence band as compared to the LSDA results (not shown). The DOS plots reveal the majority spin Tb 4*f* states mainly between -7 and -2 eV , while the minority spin states are almost empty, except for a sharp peak close to the Fermi energy. Below the Fermi energy, the valence band maximum mainly originates from the O 2*p* states with small contributions of B 2*p* and Al 3*p*, which are similar to those observed in other borates.⁴⁶ The empty Tb 4*f* states give rise to strong peaks for the minority spin, while the majority spin DOS is very small in this energy range (see the inset in Fig. 2). Above 5 eV , the unoccupied states are due to the Tb 5*d* bands with small B 2*p* and Al 3*p* contributions. No appreciable changes appear in the electronic structure when Fe is replaced by Al, except for the fact that the Fe 3*d* states lie near the Fermi energy in the valence band of $\text{TbFe}_3(\text{BO}_3)_4$.⁴¹ The energy level positions of the Tb 4*f* states remain unchanged for GGA and GGA + SOC calculations. In the LSDA+ U approach, these states shift off the Fermi energy, as expected.

Comparison of our GGA results with calculations for $\text{TbFe}_3(\text{BO}_3)_4$ (Ref. 41) indicate that the ferroelectric polarization of $\text{TbFe}_3(\text{BO}_3)_4$ is largely due to the absence of

FIG. 1. BS of $\text{TbAl}_3(\text{BO}_3)_4$ as obtained from LDA+ U calculations.

inversion symmetry in the crystal structure and is only weakly affected by the antiferromagnetic ordering. Therefore, Fe plays kind of no role for the optical and magneto-optical properties, but increases the magnetic complexity.

Figure 3 shows the calculated real, $\text{Re}[\epsilon]$, and imaginary, $\text{Im}[\epsilon]$, parts of the frequency-dependent dielectric function of $\text{TbAl}_3(\text{BO}_3)_4$. $\text{Im}[\epsilon]$ reveals a threshold energy of 3.3 eV followed by two peaks at 8.5 and 15 eV , which are due to transitions from occupied O 2*p* and Tb 4*f* states to unoccupied Tb 5*d* states. Furthermore, there are oscillating structures in the energy range from 10 to 15 eV , followed by a drop toward higher energy. $\text{Re}[\epsilon]$ shows a pronounced peak at 6.5 eV and a shallow minimum around 17 eV with a negative value. The structures around 18 eV trace back to transitions between occupied Tb 4*f* and unoccupied Tb 5*d* states. They are not sensitive to U , since the onsite interaction influences only the Tb 4*f* states. The static dielectric constant equals $\text{Re}[\epsilon(0)] = 3.15$.

Figure 4 addresses the calculated frequency-dependent refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption $\alpha(\omega)$, energy loss function $L(\omega)$, as well as reflectivity $R(\omega)$ of $\text{TbAl}_3(\text{BO}_3)_4$. We obtain $n(0) = 1.78$, which is very close to the value (1.75) reported for $\text{GdAl}_3(\text{BO}_3)_4$ (Ref. 33) and, as expected, clearly less than found for $\text{YAl}_3(\text{BO}_3)_4$.^{43,44} For $n(\omega)$ and $k(\omega)$, we have maxima at 6 and 15.5 eV , respectively. The maximal reflectivity (minimal absorption) is found near 22 eV . The maximal absorption, on the other hand, occurs in the low energy range, due to the large number of bands just below the Fermi energy. A similar behavior has been reported for the absorption spectrum of $(\text{Li/Cs})\text{B}_3\text{O}_5$ (see Ref. 45 and the references given therein).

FIG. 2. (Color online) Total DOS and projected DOS of the Al 3*p*, Tb 4*f*, and Tb 5*d* orbitals separated in majority and minority spin contributions. The inset magnifies the majority spin Tb 4*f* DOS from 0 to 6 eV.

FIG. 3. (Color online) Real and imaginary components of the dielectric tensor of TbAl₃(BO₃)₄ along the perpendicular (xx) and parallel (zz) directions.

FIG. 4. (Color online) Refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption $\alpha(\omega)$, energy loss function $L(\omega)$, and reflectivity $R(\omega)$.

FIG. 5. (Color online) Diagonal (σ_{xx}) and off-diagonal (σ_{xy}) optical conductivities, Kerr rotation (θ_K) and ellipticity (ϵ_K), as well as Faraday rotation (θ_F) and ellipticity (ϵ_F).

The energy loss of fast electrons traversing the material, $L(\omega)$, shows a distinct maximum near 22 eV, associated with plasma oscillations. At this energy, $\text{Im}[\epsilon]$ is small (see Fig. 3). The structures present in the optical spectra between 6 and 15.5 eV originate mainly from transitions from the top of the valence band to unoccupied Tb 5d states.

To understand the relationship between the optical conductivity and the Kerr spectra, we have calculated the magneto-optical properties, which have been measured by Sawannobori.⁴⁷ The frequency-dependent diagonal and off-diagonal components of the optical conductivity tensor are shown in Fig. 5. A broadening of 0.1 eV is employed to simulate the experimental finite lifetime. $\text{Re}[\sigma_{xx}]$ and σ_{xy} almost vanish up to 3.3 eV, which equals the energy gap, while $\text{Im}[\sigma_{xx}]$ shows structures in the whole energy range. $\text{Re}[\sigma_{xx}]$ exhibits a peak conductivity of $4.5 \times 10^{15} \text{ s}^{-1}$ at 8.5 eV, while $\text{Im}[\sigma_{xx}]$ shows a deep minimum around 7 eV. $\text{Im}[\sigma_{xy}]$ has a maximum at 9.5 eV and a minimum at 7.5 eV. $\text{Re}[\sigma_{xy}]$, on the other hand, has a maximum at 9 eV and a minimum at 7.5 eV. The structure present in the low energy range (around 4 eV) can be explained by transitions from O 2p and Al 2p to Tb 5d states. The higher energy structures are due to transitions from Tb 4f to Tb 5d states.

The Kerr rotation θ_K and ellipticity ϵ_K as well as the Faraday rotation θ_F and ellipticity ϵ_F are displayed in Fig. 5. Both θ_K and ϵ_K are characterized by various peaks above 5 eV. The maxima of θ_K (-2.1°) and θ_F (-20°) appear in the region where $\text{Re}[\sigma_{xx}]$ and $\text{Re}[\sigma_{xy}]$ have the largest magnitude. In contrast, ϵ_K (1.6°) and ϵ_F (9°) have pronounced peaks where $\text{Im}[\sigma_{xx}]$ and $\text{Im}[\sigma_{xy}]$ are maximal, respectively. Our results show that the magneto-optical Kerr and Faraday effects strongly depend on the diagonal and off-diagonal components of the optical conductivity tensor. The fact that $\text{Re}[\sigma_{xx}]$ is directly linked to the optical transitions, i.e., the electronic states, is fruitful for magneto-optical engineering. The electronic structure can be tuned in such a way that the

maximum of $\text{Re}[\sigma_{xx}]$ shifts toward the visible region. This is achieved by alloying to reduce the energy gap. The observed energy dependence of θ_K and ϵ_K makes $\text{TbAl}_3(\text{BO}_3)_4$ directly suitable for application in ultraviolet magneto-optical laser devices.

IV. CONCLUSION

In conclusion, we have discussed first principles findings on $\text{TbAl}_3(\text{BO}_3)_4$ obtained from density functional theory. The Tb total magnetic moment is found to be $5.94 \mu_B$, in agreement with previous experiments and calculations. We observe a wide direct bandgap of 3.3 eV. The DOS shows that the Tb 4f states lie deep inside the valence band, similar to $\text{TbFe}_3(\text{BO}_3)_4$. We have analyzed the frequency-dependent dielectric function $\epsilon(\omega)$, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption $\alpha(\omega)$, energy loss function $L(\omega)$, and reflectivity $R(\omega)$ along the *a* and *c*-axes. The static refractive index $n(0)$ is close to that of $\text{GdAl}_3(\text{BO}_3)_4$. The Kerr and Faraday rotations are very large, amounting to -2.1° and -20° at ~ 9 eV (ultraviolet), respectively. In particular, $\text{TbAl}_3(\text{BO}_3)_4$ paves the way for a systematic tailoring of the magneto-optical properties according to technological needs by suitable dopants.

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