

Crystal field and magnetism with Wannier functions: rare-earth doped aluminum garnets

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Abstract: Using the recently developed method we calculated the crystal field parameters in yttrium and lutetium aluminum garnets doped with seven trivalent Kramers rare-earth ions. We then inserted calculated parameters into the atomic-like Hamiltonian taking into account the electron-electron, spin-orbit and Zeeman interactions and determined the multiplet splitting by the crystal field as well as magnetic \hat{g} tensors. We compared calculated results with available experimental data. Very good agreement with the spectroscopic data and qualitative agreement with experimental \hat{g} tensors was found.

Keywords: crystal field; *ab initio* calculations; garnets; rare earths

To explain certain optical and magnetic properties of rare-earth (R) materials, determination of crystal field parameters (CFP) is essential. When sufficient experimental data are available CFP are usually determined by the least squares fit. Since the number of nonzero CFP depends on the site symmetry and may be as high as 27, such method often ends up being ambiguous. As a result, there has been a continuous effort to estimate CFP theoretically (for the review of various methods, see Refs. [1,2]).

Recently, a novel theoretical approach to calculate CFP has been proposed^[3]. An original motivation of the work was to explain the magnetic properties of rare-earth cobaltites RCoO_3 where available experimental data do not suffice to estimate CFP. The method starts with the density functional theory (DFT) based band structure calculation, followed by a transformation of the Bloch to Wannier basis. The local Hamiltonian is then expanded in terms of the spherical tensor operators. Resulting CFP are inserted in an atomic-like Hamiltonian involving the crystal field, 4f–4f correlation, spin-orbit coupling and Zeeman interaction. The method does not suffer from the 4f electron self-interaction (the difficult problem of DFT *ab initio* methods). The hybridization of the 4f states with other valence orbitals is taken into account *via* hybridization parameter Δ , a single parameter of the method. In the recent paper^[4], a relatively simple way allowing to estimate this parameter was suggested and applied to the R:LaF_3 system.

The method has been extensively tested for rare-earth doped aluminates $\text{YAlO}_3\text{:R}^{3+}$ with orthorhombic perovskite structure^[3]. Remarkable agreement of calculated and ex-

perimental data was achieved. Application to gallates RGaO_3 and cobaltites RCoO_3 ^[5] as well as manganites RMnO_3 ^[6] followed. Even in these cases calculations provide a fair agreement with experimental data.

Rare-earth doped aluminum garnets are widely used as laser materials and scintillators due to which extensive experimental data are available. In recent years magneto-optical properties of some non-Kramers ions in garnet hosts have been studied. High magneto-optical activity observed in some cases is of interest in microwave amplifiers and generators. Magneto-optics of Tb^{3+} and Tm^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) is studied in Refs. [7,8] and Ref. [9], respectively. Magneto-optics of Eu^{3+} in various garnets is reported in Refs. [10,11] and that of Pr^{3+} in YAG in Ref. [12].

In this work we apply the new CFP method to rare-earth doped aluminum garnets. After reviewing the theory and computational procedure, the next section is devoted to analysis of the problem of determination of the parameter Δ in more detail compared to Ref. [4]. In the following section we calculate crystal field parameters. We show examples of multiplet splitting by the crystal field. We focus on Kramers ions and calculation of their magnetic g factors, yet more crystal-field sensitive quantities, and compare them with experimental data.

1 Theoretical approach and computational details

The effective Hamiltonian describing 4f states can be written as

$$\hat{H}_{\text{eff}} = \hat{H}_A + \hat{H}_Z + \hat{H}_{\text{CF}} \quad (1)$$

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where \hat{H}_A is the spherically symmetric, free ion atomic-like Hamiltonian (for details see Ref. [13]), while \hat{H}_Z and \hat{H}_{CF} are the Zeeman interaction and crystal field Hamiltonian, respectively. In the Wybourne notation^[14] \hat{H}_{CF} has the form

$$\hat{H}_{CF} = \sum_{k=2,4,6} \sum_{q=-k}^k B_q^{(k)} \hat{C}_q^{(k)} \quad (2)$$

where $\hat{C}_q^{(k)}$ is a spherical tensor operator of rank k acting on the 4f electrons of the R ion. The coefficients $B_q^{(k)}$ are the crystal field parameters. Hermiticity of \hat{H}_{CF} requires that $(B_{-q}^{(k)}) = (-1)^q B_q^{(k)}$.

Calculation of crystal field parameters consists of four steps:

(1) Standard selfconsistent band calculation with 4f states included in the core. The results yield the crystal field potential, subsequently used in the next step.

(2) The 4f as well as oxygen 2p and 2s states are treated as the valence states in a nonselfconsistent calculation, all other states are moved away using the orbital shift operator. Relative position of 4f and oxygen states is adjusted using the *hybridization* parameter Δ (a single parameter of the method).

(3) The 4f band states are transformed to Wannier basis using the wien2wannier^[15] and wannier90^[16] packages.

(4) Local 4f Hamiltonian in the Wannier basis is extracted and expanded in a series of spherical tensor operators. The coefficients of expansion are the crystal field parameters.

To perform the band structure calculations in steps (1) and (2) we used the WIEN2k package^[17] with implemented augmented plane waves + local orbital method. For the exchange correlation functional we applied the generalized-gradient approximation form^[18]. We used experimental lattice parameters of $Y_3Al_5O_{12}$ (YAG) and $Lu_3Al_5O_{12}$ (LuAG)^[19], but the atomic positions within the unit cell were optimized for each R substitution by minimizing the atomic forces. The unit cell in our calculations consisted of 80 atoms. The eigenvalue problem was solved in five points of the irreducible Brillouin zone and the number of basis functions was ~ 7700 (corresponding to the parameter $RK_{\max}=6.5$). The calculations were non-spin polarized. The atomic radii of R (Y,Lu), Al and O were 2.3, 1.7 and 1.55, respectively.

Once the crystal field parameters were determined we used the modified lanthanide package^[20] to solve the eigenproblem for the Hamiltonian Eq. (1). The results provide the multiplet splitting by the crystal field. From the energy dependence on external magnetic field one extracts the \hat{g} tensor (for more details see Refs. [3,5]).

2 Hybridization parameter

The parameter Δ appears due to hybridization between

the rare-earth 4f states and the valence states of its ligands. Our treatment of hybridization is briefly described in Ref. [3]. In the R containing orthorhombic perovskites^[3,5,6] remarkable agreement between experimentally obtained spectroscopic data and the calculation was obtained by fixing the value of Δ at 0.6 Ry. With the same Δ also the magnetism was calculated and compared with experiment. However, less experimental data were available and the agreement, though still satisfactory, was not as good as in case of spectroscopy. In R:LaF₃ very good agreement between optical data and calculation was obtained for $\Delta=0.4Ry$ ^[4]. In the same paper Δ was estimated using a charge transfer energy

$$\Delta \cong E_{\text{tot}}(4f^{(n+1)}, N_{\text{val}}-1) - E_{\text{tot}}(4f^n, N_{\text{val}}) \quad (3)$$

where $E_{\text{tot}}(4f^n, N_{\text{val}})$ is the total energy of the ground state of the system (n_{4f} electrons in 4f shell of R ion and N_{val} electrons in the valence band), while $E_{\text{tot}}(4f^{(n+1)}, N_{\text{val}}-1)$ corresponds to the excited state in which one of the valence electrons was transferred in the 4f electron shell. The hybridization parameter thus can be calculated by performing two calculations with 4f electrons treated as the core states – the first one with $4f^n, N_{\text{val}}$, the second with $4f^{(n+1)}, N_{\text{val}}-1$ electron configurations.

Using the above equation we calculated Δ for the R in question in both YAG and LuAG. The results, together with the data for R:LaF₃ and orthorhombic perovskites RMnO₃, are shown in Fig. 1.

There are several problems connected with the above method. The first one is connected with the multiplet splitting of the 4f levels, which is not provided by the DFT calculation. In principle this splitting may be obtained by the atomic-like program we are using. However, there is a problem of double counting of the electron-electron correlation, which would be difficult to overcome. We can only estimate that corresponding uncertainty of Δ is on the order of the crystal field splitting i.e. less than ~ 0.1 eV and it will change with R. Such scatter will become relatively more important in R:YAG

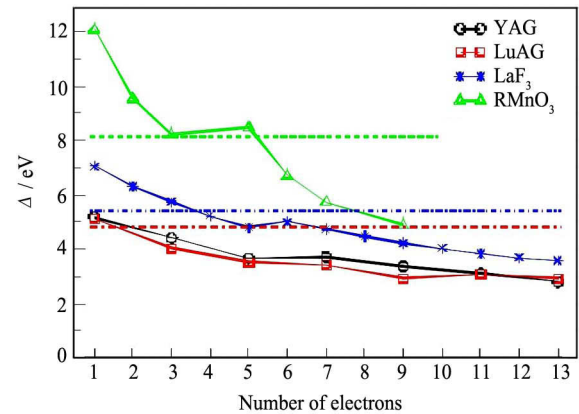


Fig. 1 Dependence of the hybridization parameter Δ on number of the 4f electrons calculated using Eq. (3). Dashed and dash-and-dotted lines correspond to the Δ values, which were adopted for calculations in RmnO₃ and R:LaF₃, respectively.^[4,6]

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