# Analyses of crystal field and exchange interaction of $Dy_3Ga_5O_{12}$ under extreme conditions*

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This paper theoretically investigates the effects of crystal field and exchange interaction field on magnetic properties in dysprosium gallium garnet under extreme conditions (low temperatures and high magnetic fields) based on quantum theory. Here, five sets of crystal field parameters are discussed and compared. It demonstrates that, only considering the crystal field effect, the experiments can not be successfully explained. Thus, referring to the molecular field theory, an effective exchange field associated with the Dy–Dy exchange interaction is further taken into account. Under special consideration of crystal field and the exchange interaction field, it obtains an excellent agreement between the theoretical results and experiments, and further confirms that the exchange interaction field between rare-earth ions has great importance to magnetic properties in paramagnetic rare-earth gallium garnets.

**Keywords:** crystal field, exchange interaction, magnetic anisotropy, rare-earth garnet

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## 1. Introduction

Although a lot of work has been devoted to the study of the magnetic properties in rare-earth (Re) garnets, the microscopic essence of the magnetic properties, especially the magnetic anisotropy, is still subjected to debate in the literatures.[1] Remarkably, it is noticed that the anisotropic exchange interaction has made a great contribution to the magnetic and magneto-optical anisotropy in Re iron garnet.[2−5] In comparison with the Re–Fe exchange interaction, the Re–Re exchange interaction between Re ions is relatively weak in Re iron garnets. Thus, correspondingly, general viewpoints show that the exchange interaction can be negligible when analysing the magnetic behaviour in paramagnetic Re gallium garnet.

However, as early as 1930s, van Vleck and Hebb[6] had ever pointed out that Re–Re exchange interaction has great importance to the magnetic properties in the paramagnetic Re fluorides, and, in some compounds, the exchange field also had a demagnetising effect. Also, in Re aluminum garnets, Hastings *et al.*[7,8] discussed the contribution of the dipole–dipole interaction between the Re ions to the magnetic response. In addition, in our previous papers, we have confirmed that the Re–Re exchange interaction is a main factor in the calculations of the magnetisation in ytterbium gallium garnet, especially under high magnetic fields.[9]

To our knowledge, a crystal field analysis on magnetic properties in dysprosium gallium garnet (DyGaG) was reported by Filippi *et al.* where the exchange interaction was negligible.[10] Whereas, it was found that the theoretical results on magnetisation curves could not completely explain the experiments by only considering the crystal field effect, especially when the external magnetic field is applied along the [011] direction. Meanwhile, they also proposed that the susceptibility could be well interpreted when the Dy–Dy exchange interaction field was taken into account in DyGaG. On the other hand, recently, a semi-classical phenomenological theory has been applied to interpret the magnetic behaviours of DyGaG where two magnetic sublattices are suggested, and the corresponding magnetic properties of the two magnetic sublattices are discussed. However, the contribution of the crystal field to the magnetic properties of DyGaG can not be explored by semi-classical theory.[11] Now, in this paper, to further illustrate the effects of crystal field and exchange interaction field on the magnetic characteristics in DyGaG, a quantum theoretical calculation on magnetisation curves is carried out.

First, it is the fact that, to understand the exchange interaction field more clearly, it is necessary to study the crystal field in gallium garnet. As is

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known, a lot of theoretical and experimental work on the crystal field interaction of the heavy Re $Dy^{3+}$ ion in DyGaG has been performed, and several sets of crystal field parameters have been given in the past decades.[12−14] Now, in view of the above work on crystal field interaction and Filippi's experimental results, the crystal field effect on the magnetic properties is also analysed by considering the different sets of crystal field parameters in DyGaG. Then, on the basis of the crystal field calculations, the contribution of the exchange interaction field to the anisotropic magnetisation is discussed when the crystal is magnetised along [001], [011] and [111] directions. Referring to the molecular field theory, we can express the Hamiltonian of the exchange interaction field as $\hat{H}_{\rm ex} = 2\mu_{\rm B}\boldsymbol{S}_z\cdot\boldsymbol{H}_{\rm ex}$, and $\boldsymbol{H}_{\rm ex}$ is the Dy–Dy exchange interaction field. Re the theoretical results are compared with the experimental data.

## 2. Outline of theoretical calculations

It is known that the formula of Re garnets can be expressed as $3Re_2O_3{\cdot}5A_2O_3$ where Re represents a rare-earth ion, and A denotes aluminum, gallium, or iron. Therefore, the formula of dysprosium gallium garnet is $3Dy_2O_3{\cdot}5Ga_2O_3$, and the space group of dysprosium gallium garnet belongs to the cubic space group $Ia3d$ with 48 operations in the point group and eight different non-primitive translations. Meanwhile, in accordance with the crystal structure of neodymium gallium garnet, the gallium ion is on the octahedral and tetrahedral sites in DyGaG, and the trivalent dysprosium ion occupies dodecahedral site where 24 dodecahedral sites with eight-fold oxygen coordination and the point symmetry of the dysprosium site is $D_2$.[15] It is noted that there are six inequivalent crystal sites of dysprosium ion in DyGaG. Hence, the value of the total magnetisation in DyGaG is the average obtained from the calculated results of six sublattices of the $Dy^{3+}$ ions.

The magnetic properties induced by the Re ions of Re gallium garnet originate from the splitting levels of the ground configuration. As to the free $Dy^{3+}$ ion, the ground term is $4f^9$, and in our calculations, the ground multiplet $^6H_{15/2}$ is taken into account, for the energy of the lowest splitting level by crystal field effect of the first excited multiplet $^6H_{13/2}$ is much higher than the highest splitting level of the $^6H_{15/2}$ multiplet. Then, the successive splitting of the ground multiplet of the $Dy^{3+}$ ion in DyGaG induced by crystal field effect, external magnetic field, and Dy–Dy exchange interaction is analysed as follows. Now, we only briefly present the outlines of our theoretical approaches.

First, the crystal field effect in DyGaG is discussed. Here, the crystal field Hamiltonian can be described as

$$\hat{H}_{\rm cf} = \sum_{i=1}^{n}\sum_{km} B_{km}\left[C_m^k\,({\rm i}) + C_{-m}^k\,({\rm i})\right], \tag{1}$$

where $B_{km}$ denote the CF parameters, and $C_m^k$ represent one-electron orbital tensor operators. Meanwhile, the matrix elements of crystal field Hamiltonian are written as

$$\begin{aligned}\left\langle nl^\alpha SLJJ_Z\left\|B_{km}C_m^k\right\|nl^\alpha S'L'J'J'_Z\right\rangle &= B_{km}\delta\left(S,S'\right)\left\langle l\left\|C^k\right\|l'\right\rangle(-1)^{J-J_Z}\begin{pmatrix} J & k & J' \\ -J_Z & m & J'_Z\end{pmatrix}(-1)^{S+L'+J+k}\\ &\times\begin{Bmatrix} J & J' & k \\ L' & L & S\end{Bmatrix}\left[J,J'\right]^{1/2}\left\langle nl^\alpha SL\left\|U^k\right\|nl^\alpha S'L'\right\rangle,\end{aligned} \tag{2}$$

where the reducible matrix element $\langle nl^\alpha SL\|U^k\|nl^\alpha S'L'\rangle$, $3j$ and $6j$ symbols can be found in Refs. [16] and [17], respectively.

Then, the crystal field splitting levels and the corresponding wave functions can be obtained by solving the following secular equation:

$$\left\|\left\langle\phi_i\right|\hat{H}_{\rm c}\left|\phi_j\right\rangle - E_{\rm c}\delta_{ij}\right\| = 0, \tag{3}$$

where $|\phi\rangle$ is the eigenfunction, and $E_{\rm c}$ is the energy level split by the crystal field.

Next, the action of the external magnetic field is considered. And, the corresponding Hamiltonian is written as

$$\hat{H}_{\rm e} = \mu_{\rm B}(\boldsymbol{L}_z + 2\boldsymbol{S}_z)\cdot\boldsymbol{H}_{\rm e}, \tag{4}$$

where $\boldsymbol{L}_z$ and $\boldsymbol{S}_z$ are the components of the orbit and spin angular momenta along the direction of the external magnetic field, $\mu_{\rm B}$ is a Bohr magneton, and $\boldsymbol{H}_{\rm e}$

represents the external magnetic field.

Here, in terms of the transition temperature $T_N = 0.373$ K of the antiferromagnetic ordering,[18] the contribution of the Dy–Dy exchange interaction field in paramagnetic DyGaG at high temperature ($T > 1.15$ K) is evaluated. In terms of the molecular field theory and exchange interaction model,[7,8,19,20] the Hamiltonian of the Dy–Dy exchange interaction can be described as

$$\hat{H}_{\rm ex} = 2\mu_{\rm B}\boldsymbol{S}_z \cdot \boldsymbol{H}_{\rm ex}. \tag{5}$$

where $\boldsymbol{H}_{\rm ex}$ is the Dy–Dy exchange field, $\boldsymbol{H}_{\rm ex} = \lambda \cdot \boldsymbol{M}$. Additionally, as to paramagnetic DyGaG, the magnetisation can be expressed as $\boldsymbol{M} = \chi_{\rm eff} \cdot \boldsymbol{H}_{\rm e}$, so, $\boldsymbol{H}_{\rm ex} = \lambda\chi_{\rm eff} \cdot \boldsymbol{H}_{\rm e}$, in which $\lambda$ is the exchange field parameter and $\chi_{\rm eff}$ is the effective magnetic susceptibility.[10,18] Thus, $\hat{H}_{\rm ex} = 2\mu_{\rm B}\nu\boldsymbol{S}_z \cdot \boldsymbol{H}_{\rm e}$, where $v = \lambda \cdot \chi_{\rm eff}$, which can be named as the effective parameter associated with the exchange field and the magnetic susceptibility.

Therefore, with the actions of crystal field, external magnetic field and Dy–Dy exchange interaction field, the splitting energy levels and wave functions are obtained from the following equation:

$$\left\| \left\langle \psi_i \left| \hat{H}_{\rm c} + \hat{H}_{\rm e} + \hat{H}_{\rm ex} \right| \psi_j \right\rangle - E_{\rm g}\delta_{ij} \right\| = 0, \tag{6}$$

where $|\psi\rangle$ is the eigenfunction, and $E_{\rm g}$ is the splitting energy.

Thus, the average magnetic moment of six Re dysprosium sublattices can be expressed as

$$\bar{m} = -\mu_{\rm B} \sum_{\rm g} \langle \psi_{\rm g} | (L_z + 2S_z) | \psi_{\rm g} \rangle \rho_{\rm g}, \tag{7}$$

where $|\psi_{\rm g}\rangle$ are the wave functions given by Eq. (6), and $\rho_{\rm g}$ is the occupation probability of the ground state,

$$\rho_{\rm g} = {\rm e}^{-E_{\rm g}/kT} / \sum_{\rm g} {\rm e}^{-E_{\rm g}/kT} = \rho_0 {\rm e}^{-E_{\rm g}/kT}. \tag{8}$$

So, from the above theoretical approaches, the magnetisation curves induced by crystal field and exchange interaction field in DyGaG can be given when the external magnetic field is applied along different directions.

## 3. Results and discussion

As mentioned above, the ground multiplet $^6H_{15/2}$ is taken into account and, it is known that $Dy^{3+}$ ion is a Kramers' ion. Thus, the ground multiplet $^6H_{15/2}$ should be split by crystal field into eight doublets. Meanwhile, it should be noted that choosing an appropriate set of crystal field parameters is highly important in the calculation of crystal field effect. Here, to our knowledge, some previous investigations on the crystal field parameters of $Dy^{3+}$ ion in DyGaG have been presented as shown in Refs. [10], [12]–[14]. So, in this paper, the crystal field parameters are obtained from the previous literatures.

However, it is also found that different sets of crystal field parameters are given by different investigators. And, five sets of crystal field parameters, as listed in Table 1, are selected and compared in our calculations. Inserting the crystal field parameters into Eq. (2), we can obtain 16×16 crystal field matrixes. Then, according to Eq. (3), the eight crystal field splitting energies and the corresponding wave functions are calculated. Figure 1 gives the lower four crystal field splitting energies calculated by five different sets of crystal field parameters where a noticeable distinction between them can be found, here, for simplicity, the other four energies are not listed.

**Table 1.** The different sets of crystal field parameters in DyGaG (in $\rm cm^{-1}$).

| No. | $B_{20}$ | $B_{22}$ | $B_{40}$ | $B_{42}$ | $B_{44}$ | $B_{60}$ | $B_{62}$ | $B_{64}$ | $B_{66}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1[12] | 87 | 162 | –235 | 215 | 945 | 67 | –10 | 902 | –200 |
| 2[13] | –22 | 141 | –282 | 181 | 1040 | 36 | –108 | 725 | –57 |
| 3[14] | –34 | 192 | –274 | 195 | 985 | 37 | –104 | 681 | –93 |
| 4[14] | 71 | 175 | –264 | 138 | 1032 | 35 | –113 | 688 | –164 |
| 5[10] | 35 | 80 | –263 | 218 | 1056 | 29 | –147 | 718 | –216 |

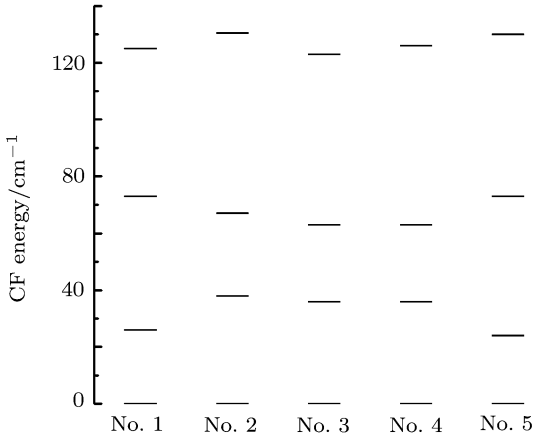



**Fig. 1.** The lower four crystal field splitting energy levels calculated by five different sets of crystal field parameters (in cm$^{-1}$) (supposing the lowest crystal field splitting energy is zero).

Also, our theoretical results show great difference of the wave functions corresponding to the crystal field splitting energy levels calculated by different sets of crystal field parameters. Then, from Eq. (7), for the magnetisation is determined by the splitting energies and the corresponding wave functions, a great disagreement between the magnetisation curves calculated by different sets of crystal field parameters is markedly exhibited. Here, in terms of the No. 1 set of crystal field parameters, Table 2 shows the wave functions and the occupation probabilities corresponding to the lower two energy levels. Apparently, as known from the wave functions, the crystal field splitting energy levels are twofold degenerate, for the $Dy^{3+}$ ion is a Kramer's ion. Also, from Table 2, it is worth noting that nearly all the electrons occupy the lowest level at low temperatures in DyGaG. Although five sets of crystal field parameters are considered, our theoretical calculations indicate that the experiments can not be completely explained by only considering the crystal field effect. Therefore, the contribution of Dy–Dy exchange field is further taken into account.

**Table 2.** The occupation probability ($\rho$) of the lower two crystal field splitting energy levels and the corresponding wave functions ($|J, J_z\rangle$) obtained from the No. 1 set of crystal field parameters at 4.23 K.

| occupation probability | wave functions |
|---|---|
| $0.999999(\rho_1)$ | $\|-0.083\|7.5,-6.5\rangle+0.269\|7.5,-4.5\rangle+0.545\|7.5,-2.5\rangle+0.401\|7.5,-0.5\rangle$ |
| | $+0.510\|7.5,+1.5\rangle+0.428\|7.5,+3.5\rangle+0.099\|7.5,+5.5\rangle-0.096\|7.5,+7.5\rangle$ |
| | $\|-0.096\|7.5,-7.5\rangle+0.099\|7.5,-5.5\rangle+0.428\|7.5,-3.5\rangle+0.510\|7.5,-1.5\rangle$ |
| | $+0.401\|7.5,+0.5\rangle+0.545\|7.5,+2.5\rangle+0.269\|7.5,+4.5\rangle-0.083\|7.5,+6.5\rangle$ |
| $1.17\times10^{-7}(\rho_2)$ | $\|-0.170\|7.5,-7.5\rangle+0.164\|7.5,-5.5\rangle+0.459\|7.5,-3.5\rangle-0.400\|7.5,-1.5\rangle$ |
| | $+0.470\|7.5,+0.5\rangle-0.445\|7.5,+2.5\rangle+0.211\|7.5,+4.5\rangle+0.331\|7.5,+6.5\rangle$ |
| | $\|+0.331\|7.5,-6.5\rangle+0.211\|7.5,-4.5\rangle-0.445\|7.5,-2.5\rangle+0.470\|7.5,-0.5\rangle$ |
| | $-0.400\|7.5,+1.5\rangle+0.459\|7.5,+3.5\rangle+0.164\|7.5,+5.5\rangle-0.170\|7.5,+7.5\rangle$ |

Now, the No. 1 set of crystal field parameters are used in our calculations when considering the actions of the external magnetic field and the Dy–Dy exchange field. From Eq. (6), the splitting energy levels and wave functions induced by crystal field, external magnetic field and exchange interaction field can be secured. Based on the consideration of the Dy–Dy exchange field, comparisons of the magnetisation curves between the theoretical calculations and the experiments are shown in Figs. 2(a)–2(c), where the external magnetic field is applied to parallel [001], [011] and [111] directions, respectively, at low temperatures ($T \leq 4.23$ K). In contrast with the calculated results in Ref. [10], our theory shows much better agreements with the experiments, which further indicates that the Re–Re exchange field has great effects on magnetic properties in Re gallium garnets.

As mentioned above, nearly all the electrons occupy the lowest level at low temperatures in DyGaG. Then, Fig. 3 gives the lowest splitting energies in different magnetic fields for [001], [011] and [111] directions, where it can be obviously found that, under different magnetic fields, the lowest energy levels splitting by crystal field and exchange interaction field are much lower than those splitting by crystal field. So, we suggest that the contribution of the exchange interaction field to the magnetic properties in DyGaG can not be neglected.

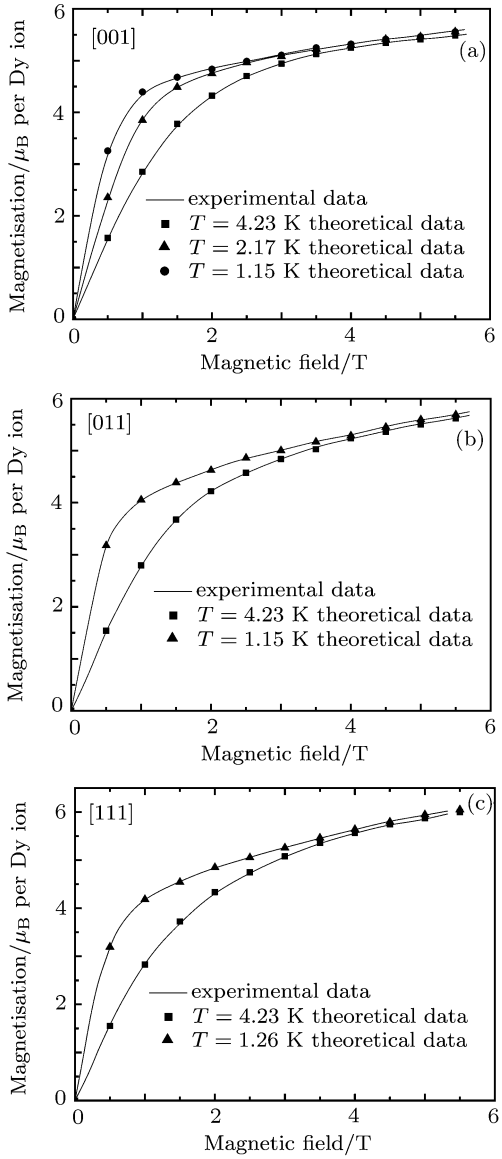



**Fig. 2.** The comparison of magetisation between the theoretical results and the experiments (obtained from Ref. [10]) at different temperatures for [001], [011] and [111] directions. (a) [001], (b) [011] and (c) [111].

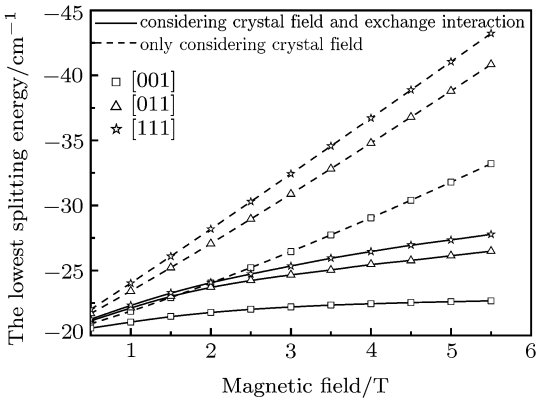



**Fig. 3.** The lowest splitting energies under different magnetic fields by considering crystal field and exchange interaction field for [001], [011] and [111] directions (supposing the average energy of 4f shell is zero).

Meanwhile, the effective parameter $\nu$, associated with the Dy–Dy exchange interaction, is analysed. As to the above three directions, the calculated results of $\nu$ at different temperatures are shown in Figs. 4(a)–4(c).

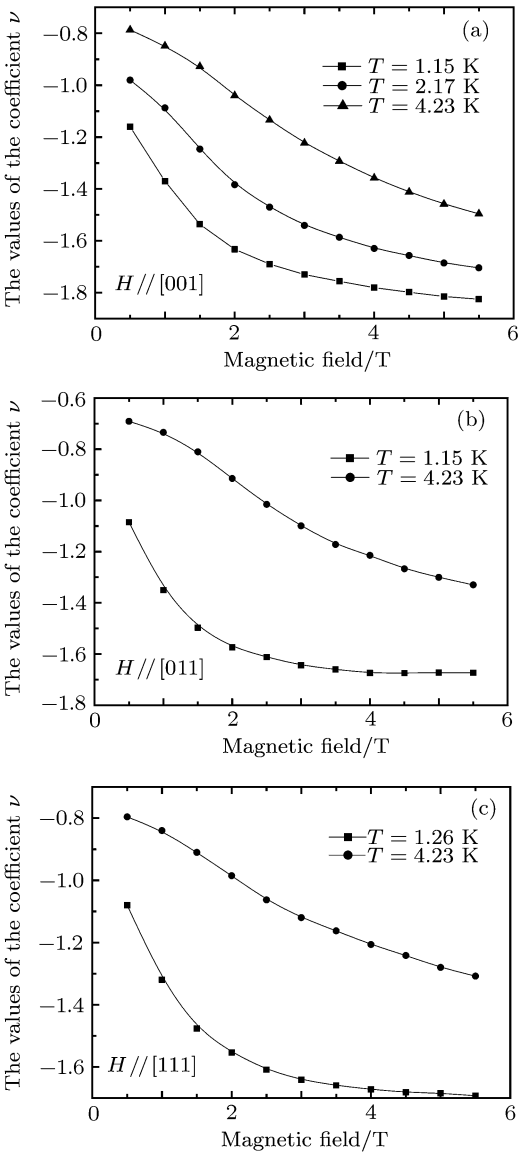



**Fig. 4.** The changes of the effective parameter $\nu$ with the external magnetic fields at different temperatures for [001], [011] and [111] directions ((a) is [001], (b) is [011] and (c) is [111]).

Here, the following characteristics can be concluded: (i) owing to $\chi_{\rm eff} > 0$, it is sure, from our theoretical results, that the exchange field coefficient $\lambda < 0$, which further theoretically confirms the existence of the antiferromagnetic ordering,[18] although Capel had ever predicted that DyGaG was ferrimagnetic at below 0.70–0.77 K or 1.54–2.15 K;[21] (ii) at the same temperatures, a remarkable anisotropy of $\nu$ can be seen. Meanwhile, it is noticeable that $\nu$ is

dependent on the external magnetic field, moreover, decreases with the increase of the external magnetic field. Then, it is obvious that $\nu$ is very sensitive to the temperatures $T$, the external magnetic fields $H_e$ and the magnetisation directions, that is, $\nu$ is the function of $T$ and $H_e$.

Here, it should be noted that, only when detailed experiments on the magnetic susceptibility $\chi$ under different conditions are performed, the characteristic of the Dy–Dy exchange interaction parameters $\lambda$ can be much exactly presented by the above analyses of the effective parameter $\nu$. Referring to our previous studies, we can also propose that the Dy–Dy exchange interaction owns temperature-dependence and anisotropic properties although it is difficult to present the specific values in our calculations. Meanwhile, the conclusion is open to be further studied.

# 4. Conclusion

In this work, the magnetic properties in DyGaG are theoretically analysed in consideration of the effects of crystal field and Dy–Dy exchange interaction field. In the calculations of crystal field, eight twofold degenerate levels are obtained while five sets of crystal field parameters are discussed. Meanwhile, an obvious distinction of the crystal field splitting levels obtained from the five sets of crystal field parameters is described, it further indicates the importance of choosing a suitable set of crystal field parameters. In particular, the Dy–Dy exchange interaction field is evaluated in terms of the molecular field model. According to the analyses of the exchange field parameter, our theory also points out that the Dy–Dy exchange interaction may have temperature-dependence and anisotropic properties. Finally, by the detailed calculations, the theory successfully interprets the experiments when the external magnetic field is applied along [001], [011] and [111] directions.

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