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Importance of magnetically derived crystal-field parameters in estimation of some properties of $Dy_2Ge_2O_7$

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Results of measurements of magnetic susceptibilities and anisotropies of $Dy_2Ge_2O_7$ (DyPG) between 300 and 23 K are reported here. Crystal-field (CF) analysis under D_{5h} site symmetry was performed to explain the magnetic results. With use of the parametrized CF interaction and intermediate-coupling formalism, the positions of different spectral lines were calculated and matched with earlier observations. At low temperature DyPG behaves almost like an Ising $S=\frac{1}{2}$ system with $g_\parallel=1.293\pm0.01$ and $g_\perp=10.301\pm0.02$. The calculated values of saturated magnetization along the D_{5h} symmetry axis and its perpendicular were found to be 82.58 and 659.41 emu/cm^3, respectively. The nuclear hyperfine field and quadrupole interactions (associated with strong asymmetric CF) give rise to appreciable nuclear hyperfine splitting for DyPG. More hyperfine lines than usual were predicted in the Mössbauer spectra.

I. INTRODUCTION

Dysprosium pyrogermanate ($Dy_2Ge_2O_7$) belongs to an isomorphous series of tetragonal crystal with space group $P4_12_12$, the unit cell of which has 4 formula units with eight Dy atoms.[1] The coordination polyhedron of each Dy^{3+} ion is a distorted pentagonal bipyramid, having D_{5h} symmetry. Due to this unique symmetry, optical and magnetic susceptibility properties of the pyrogermanate (PG) system are expected to be interesting. Optical investigation[2] on DyPG at 1.8 K has revealed prominent effects of the crystal field (CF) of D_{5h} symmetry on Dy^{3+} spectra. This paper reports the results of measurements of magnetic susceptibilities and their anisotropies between 300 and 23 K and investigates the effect of this symmetry of the coordination polyhedron on the magnetic, optical, and other properties of DyPG. In this temperature range, the CF effect acts as a major perturbation and hence a parametral fitting of accurate experimental results with the corresponding theoretical expressions provides a set of crystal-field parameters (CFP). Generally, CFP values thus obtained are more accurate than those obtained from spectral analysis because the latter is difficult due to configuration interaction and *jj* mixing[3] of spectral lines of Dy compounds. On the other hand, magnetic susceptibility properties involve only the ground term $^6H_{15/2}$, which is free from such effects, because the first excited term $^6H_{13/2}$ is 3300 cm^{-1} above. In the present work, magnetic data for Dy^{3+} in a pyrogermanate lattice were used to determine accurately the multiplet pattern of $^6H_{15/2}$ as well as the corresponding eigenstates of each of the multiplet levels. These results were next used to determine the *g* values of the lowest level, saturated magnetization values at low temperature, and also the crystal-field components of the optical levels.

II. EXPERIMENT

Single crystals of this magnetically concentrated compound were grown for the first time from a flux of Dy_2O_3, PbO, PbO_2, GeO_2, and PbF.[4] For DyPG, lattice constants are $a=6.828\pm0.005$ Å and $c=12.43\pm0.01$ Å.[2] Crystals used in the experiments were in the form of platelets, having the *c* axis perpendicular to the principal face. In DyPG, the D_{5h} symmetry axis nearly coincides with the tetragonal *c* axis, so that the experimentally measured crystalline susceptibilities $\chi_\parallel$ and $\chi_\perp$ give directly the molecular susceptibilities for each Dy ion, i.e., $K_\parallel$ and $K_\perp$, respectively, being numerically half of the measured $\chi_\parallel$ and $\chi_\perp$.[5]

The static torque method[6] was used for measuring the magnetic crystalline anisotropy ($\Delta\chi=\chi_\parallel\sim\chi_\perp$) between 300 and 23 K. Crystals were freely suspended using a fine quartz fiber with the *c*-axis lying in the horizontal plane inside a uniform horizontal magnetic field. These crystals are very hard, hence, $\chi_\perp$ instead of $\bar{\chi}$ was measured using the Faraday method in a sensitive Curie-type balance.[7] While measuring $\Delta\chi$, it was observed that in the entire experimental temperature range, $\chi_\perp$ pointed along the magnetic-field direction, implying $\chi_\perp>\chi_\parallel$ (or $K_\perp>K_\parallel$). Experimental results of thermal variations for $\Delta\chi$, $1/\chi_\perp$, and $1/\chi_\parallel$ have been shown in Fig. 1. The calculated values of $\Delta\chi$ using the CF parameters reported earlier from optical work have also been shown by the dashed curve. At 300 K, $\Delta\chi$ was observed to be very large (41.280×10^{-6} emu/mol or 0.5185×10^{-6} m^3/mol in SI units), which was 59.6% of $\bar{\chi}$. On cooling, $\chi_\perp$ increased at a much faster rate than $\chi_\parallel$, causing $\Delta\chi$ to be very large at low temperatures. This is consistent with the fact that DyPG is magnetically denser along the *a*

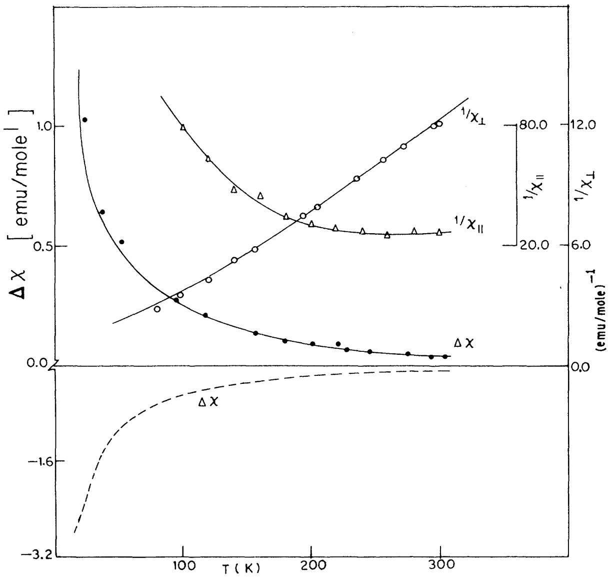

FIG. 1. Thermal variations of $\Delta\chi$, $1/\chi_\perp$, and $1/\chi_\parallel$, represented respectively by ●, ○, and △; solid and dashed curves correspond to calculated values using CFP's from this work and earlier optical studies, respectively.

axis. The accuracy of the results of $\Delta\chi$ and $\chi_\perp$ was better than 0.1%. As in most rare earth (RE) insulators, the $1/\chi_\perp$ vs T curve appeared to be a reasonably straight line between 300 and 90 K, suggestive of Curie-Weiss-type behavior. The Curie constant C and average effective moment $\bar{\mu}_{\rm eff}$ for single $\rm Dy^{3+}$ were found to be 11.23 K emu/mol and 9.47 BM, respectively. These are appreciably smaller than the free-ion values due to strong CF effects in the PG lattice.

III. THEORETICAL CONSIDERATION

The crystal-field potential V_c at the RE site possessing D_{5h} site symmetry is expressed in a polynomial series:

$$V_c = A_2^0 V_2^0 + A_4^0 V_4^0 + A_6^0 V_6^0 + A_6^5 (V_6^5 - V_6^{-5}) \ . \qquad (1)$$

V_k^q are irreducible tensor operators and A_k^q are even-parity CF parameters[8] which are usually determined from the fitting of experimental results of optical spectra, magnetic susceptibility, specific heat, and from other experiments.[9] The general matrix elements of the tensor operators and the reduced matrix elements were obtained employing the tensor operator technique. Under this crystalline electric field, the ground multiplet arising from the $4f^9\ {}^6H_{15/2}$ state of $\rm Dy^{3+}$ splits into eight Kramers doublets; the positions of these levels are expressed in terms of the above four CFP's, which are assumed to be temperature independent. The first- and second-order Zeeman energies were next calculated with magnetic perturbation $g_L' \mu_\beta H \cdot J$, where g_L' is the effective Landé splitting factor. The principal magnetic susceptibilities at different temperatures were then obtained using Van Vleck's formula,[10] denoting the principal molar susceptibilities for each Dy atom as $K_\parallel$ and $K_\perp$ corresponding respectively to an external magnetic field parallel and perpendicular to the symmetry axis of the $\rm Dy^{3+}$ site.

IV. DISCUSSIONS

A. Magnetic susceptibilities

Magnetic susceptibilities $K_\parallel$ and $K_\perp$ for DyPG were expressed in terms of the four CF parameters: A_2^0, A_4^0, A_6^0, and A_6^5, which were varied using computer programming to obtain the best set of CF parameters to fit the experimental data of $\chi_\perp$, $\chi_\parallel$, $\bar{\chi}$, and $\Delta\chi$. While varying the CFP, the following interesting facts were noted.

(a) There was a sensitive dependence of the anisotropy value on the electronic pattern of the ground multiplet as also observed in other studies.[11] This was because the principal susceptibilities $K_\perp$ and $K_\parallel$, and hence their difference, depend not only on the lowest level but also on the relative positions and the nature of the eigenstates of the excited levels of the ground multiplet. Thus, the thermal characteristics of $K_\parallel$, $K_\perp$, and ΔK depend sensitively on the four CF parameters.

(b) The sign and the absolute value of $\Delta\chi$ at 300 K depend strongly on A_2^0. For example, a change of $\pm 1\ \rm cm^{-1}$ in the value of A_2^0, the rest being the same as given in Table I, caused $\Delta\chi$ to vary by 209×10^{-6} emu/mol, which was much larger than the experimental accuracy.

The best set of CFP's along with the corresponding Stark energies and eigenstates are listed in Table I. It may be remarked that any other values of the parameters beyond the error limit would not explain the experimental results as satisfactorily.

Inspection of Table I shows that the CF splitting of ${}^6H_{15/2}$ of DyPG is 610 $\rm cm^{-1}$, which is much larger than that observed in $\rm Dy(OH)_3$ or $\rm DyCl_3$.[12] It is relevant to mention here that the CF was also found to be strong in other RE pyrogermanates.[13] The first excited state ($\mu = \frac{3}{2}$) lies at 111.4 $\rm cm^{-1}$ above the ground doublet ($\mu = \frac{1}{2}$). Thus, magnetic behavior below liquid-$\rm N_2$ temperature is expected to be decided by the ground state only. It may be mentioned here that on substituting the optically obtained CFP, the calculated value of $K_\perp - K_\parallel$ was negative between 300 and 23 K. This implied that $\chi_\parallel$ (or $K_\parallel$) ought to align along the applied field direction, which was contrary to the observation as described earlier. Furthermore, the thermal characteristics of $K_\parallel$ and $K_\perp$ differed from our observed results (not shown in Fig. 1); thus, the optically derived parameters do not explain the magnetic results, whereas it was found that the magnetically derived parameters can account for the observed spectra within the limitations as is discussed in Sec. IV C. Hence the CFP values obtained from magnetic studies can be considered to be more accurate.

B. *g* values

The *g* values are spectroscopic splitting factors and depend on the orientation of the external magnetic field with respect to the symmetry axis of the crystalline electric field. For the ground CF level in DyPG, the *g* tensor is found to be quite anisotropic, having $g_{\parallel}$ (or $2g_L'\langle\psi_g|J_z|\psi_g\rangle$)$=1.293$ and $g_{\perp}$ (or $2g_L'\langle\psi_g|J_x|\psi_g\rangle$) $=10.301$. Whereas in most Dy compounds studied to date, $g_{\perp}=0$ so that direct measurements of g values were not possible by the EPR method.

The two related conditions in DyPG, i.e., the high anisotropic g tensor and large spin lattice relaxation time, give rise to low-temperature paramagnetic hyperfine (HF) interactions involving only the ground Kramers doublet (the first excited level being 111.4 cm^{-1} above). These HF interactions can be estimated by certain important HF quantities, i.e., the effective magnetic field H_{eff},[14] which is related to the g values and the electric field gradient (EFG) produced at the nucleus. The latter is expected to be strong due to high CF asymmetry. These quantities and also the HF splitting of the RE nucleus in the particular compound are generally studied from Mössbauer spectra and can also be calculated with the CF parameters and CF wave functions. Thus using our CF energy pattern of the ground term, the quadrupole interaction parameters P and p' for ^{161}Dy (19% abundance) were calculated for the ground and the first excited nuclear levels by the standard method.[15,16] They were found to be temperature dependent but attained constant values of 6.3 and 6.2, respectively (all in 10^{-4} cm^{-1}), below 4 K. The magnetic HF interaction energy $g_N\beta_N H_{\text{eff}}$ was found to be 809.3 MHz with $H_{\text{eff}}=5.8$ MG, being close to the values reported for other Dy compounds.[17] The ground nuclear level ($I=\frac{5}{2}$) splits into five doublets and two singlets with a total splitting 0.086 cm^{-1}. Similarly, the first excited nuclear level ($I'=\frac{5}{2}$), being 26 keV above, splits into five doublets and two singlets with a total width of 0.112 cm^{-1}. The allowed Mössbauer transition lines between these HF levels in DyPG are found to be 19 in number, whereas only 16 lines are allowed in other Dy compounds, studied earlier. This unique feature is a consequence of the nonzero value of $g_{\perp}$ and therefore a Mössbauer experiment on DyPG is welcome.

TABLE I. Crystal-field splitting (in cm^{-1}) of the ground and excited terms in DyPG [crystal-field parameters (in cm^{-1}): $A_2^0=600\pm0.5$, $A_4^0=2750\pm2$, $A_6^0=-1100\pm2$, $A_6^5=-190\pm5$]. CF levels inside the first bracket are due to Ref. 2, all of which have been observed. IC constants are given inside the third bracket.

LS states	μ	Energy levels	Wave functions
$^6H_{15/2}$	$\frac{1}{2}$	0.00	$0.025\|\pm\frac{11}{2}\rangle+0.999\|\pm\frac{1}{2}\rangle$ $-0.021\|\mp\frac{9}{2}\rangle$
	$\frac{3}{2}$	111.95	$0.039\|\pm\frac{13}{2}\rangle+0.999\|\pm\frac{3}{2}\rangle$ $-0.019\|\mp\frac{7}{2}\rangle$
	$\frac{5}{2}$	250.73	$0.985\|\pm\frac{15}{2}\rangle+0.173\|\pm\frac{5}{2}\rangle$
	$\frac{5}{2}'$	299.51	$0.173\|\pm\frac{15}{2}\rangle-0.985\|\pm\frac{5}{2}\rangle$
	$\frac{3}{2}'$	447.44	$-0.999\|\pm\frac{13}{2}\rangle+0.039\|\pm\frac{3}{2}\rangle$ $-0.007\|\mp\frac{7}{2}\rangle$
	$\frac{3}{2}''$	489.83	$-0.006\|\pm\frac{13}{2}\rangle+0.0197\|\pm\frac{3}{2}\rangle$ $+0.999\|\mp\frac{7}{2}\rangle$
	$\frac{1}{2}'$	598.02	$-0.999\|\pm\frac{11}{2}\rangle+0.024\|\pm\frac{1}{2}\rangle$ $-0.026\|\mp\frac{9}{2}\rangle$
	$\frac{1}{2}''$	610.12	$-0.026\|\pm\frac{11}{2}\rangle+0.022\|\pm\frac{1}{2}\rangle$ $+0.999\|\mp\frac{9}{2}\rangle$
$^6F_{9/2}$	$\frac{7}{2}$	9 377.23	(9 342)
	$\frac{5}{2}$	9 392.58	(9 391)
	$\frac{3}{2}$	9 419.45	(9 420)
	$\frac{9}{2}$	9 441.96	(9 469)
	$\frac{1}{2}$	9 523.73	(9 521)
$^6H_{5/2}$	$\frac{1}{2}$	10 326.36	(10 328)
[0.946,0.952]	$\frac{5}{2}$	10 524.19	(10 472)
	$\frac{3}{2}$	10 595.45	(10 647)
$^6F_{7/2}$	$\frac{5}{2}$	11 194.00	(11 198)
[1.39,0.91,0.90]	$\frac{3}{2}$	11 304.44	(11 289)
	$\frac{3}{2}'$	11 323.34	(11 310)
	$\frac{1}{2}$	11 338.69	(11 364)
$^6F_{5/2}$	$\frac{3}{2}$	12 604.20	(12 598)
[1.69,1.00]	$\frac{5}{2}$	12 684.80	(12 663)
	$\frac{1}{2}$	12 704.95	(12 729)
$^6F_{3/2}$	$\frac{1}{2}$	13 453.55	(13 452)
	$\frac{3}{2}$	13 474.45	(13 475)

C. Magnetic saturations

At a very low temperature (say 4 K), the ground doublet ($\mu=\frac{1}{2}$) can be regarded as a totally isolated one and the saturated magnetization can be easily calculated like an ideal Ising system ($S=\frac{1}{2}$) using the relation

$$M_{\text{sat}}=Ng_L'\mu_B\langle\psi_g|J_1|\psi_g\rangle\ , \tag{2}$$

where $N=1.38\times10^{22}$ ions per cm^3 in DyPG, $g_L'=1.293$, and the rest have their usual meanings.[18] Values of magnetic saturations in the directions parallel and perpendicular to the symmetry axis were found to be 82.58 and 659.41 emu/cm^3, respectively. Hence in this highly magnetic anisotropic system, the magnetic moments are constrained to lie in the plane perpendicular to the symmetry axis. Similar characteristics were also observed in DyVO_4 and DyAsO_4.[19] It is relevant to mention here that magnetic ordering[20] was detected near 2.15 K in DyPG, however, details are not available. Few Dy compounds having similar tetragonal symmetry are found to order antiferromagnetically at very low temperature (like 0.58 K).[21] We do not have the facility for measurements of susceptibility at such low temperatures. It has been observed for some $R(\text{OH})_3$, in which magnetic ordering due to dipolar and nondipolar interactions occurs below 4 K, the interaction constants could be estimated knowing the ground CF level and its g values.[19] Hence results from this study can also contribute substantially for future analyses of ordering in DyPG.

D. Optical spectra

Crystal-field parameters had been obtained earlier from the analysis of the optical absorption lines in the visible and infrared region of Dy^{3+} spectra corresponding to different transitions within the configuration of $4f^9$. Wardzynska and Wanklyn recorded[2] the optical transitions to $^6F_{9/2}$, $^6H_{5/2}$, $^6F_{7/2}$, $^6F_{5/2}$, and $^6F_{3/2}$ manifolds from the lowest CF level $\mu=\frac{1}{2}$ of $^6H_{15/2}$ (Table I), which is the only populated level at 1.8 K. Thus, the absorption lines give directly the positions of CF levels of excited manifolds. Being anhydrous, DyPG is expected to give sharp lines with greater freedom from superimposed molecular and crystal vibrations. However, the excited states of Dy^{3+} are heavily mixed, mainly due to the pronounced effect of intermediate coupling (IC). Hence to refine our CF calculations for excited states ^6F and ^6H, the IC eigenfunctions for each were taken as basis states[3] and IC constants for different terms were determined using the following form of relation:

$$\text{IC for } V_K^q \text{ term} = \frac{\langle {}^6F'_{5/2} | V_K | {}^6F'_{5/2} \rangle}{\langle \text{Pure } {}^6F_{5/2} | V_K^q | \text{Pure } {}^6F_{5/2} \rangle}\ , \tag{3}$$

where

$$\begin{aligned} {}^6F'_{5/2} = {} & -0.9557|{}^6F\rangle + 0.14|{}^4_5D_{20}\rangle - 0.1386|{}^4_5D_{21}\rangle \\ & + 0.0914|{}^4_3D_{20}\rangle - 0.1531|{}^4_5F_{21}\rangle + 0.0928|{}^4_3F_{10}\rangle\ . \end{aligned}$$

Matrix elements were calculated in the usual manner.[9] Table I includes the CF splittings for different manifolds along with the assigned crystal quantum number (μ) and the IC constants. $^6F_{9/2}$ and $^6H_{7/2}$ overlap completely, showing considerable *jj* mixing in CF, thereby introducing several more parameters.[22] This needs more of an *ab initio* calculation and for the present paper it was avoided.

It is to be noted that effects due to intermediate coupling for $^6F_{3/2}$ were found to be zero and, using the parameter A_2^0 from optical work, the CF splitting (ΔE) for $^6F_{3/2}$ comes out to be 14 cm^{-1} as compared to the observed value of 24 cm^{-1}. On substituting the magnetically derived value for A_2^0, ΔE is found to be 21 cm^{-1}. Moreover, the sign of A_2^0 decides which of the CF components of $^6F_{3/2}$ (i.e., $\mu=\frac{3}{2}$ or $\frac{1}{2}$) lie lower. In our case $\mu=\frac{1}{2}$ lies lower so that transition $^6H_{15/2} \rightarrow {}^6F_{3/2}$ is at a lower energy with higher intensity (since $\Delta\mu=0$), which is consistent with the observed results. Thus, the splitting of the $^6F_{3/2}$ term is better matched using magnetically obtained parameters. A reasonable good matching for other terms is also obvious from Table I. Inspection of Table I shows that, in general, the fitting was satisfactory, yet in some cases the positions of the observed and calculated spectral lines differ appreciably when the values for optical or magnetic CF parameters are substituted. It should be emphasized that, due to shifts introduced by *J*-mixing effects of the crystal field, the fitted free-ion energies are not, in general, the same as the centers of gravity of the manifolds. In DyAlG (Ref. 23) and in other RE spectra[24] there are indications of variations of CFP's from term to term for configuration interactions or phonon-phonon interactions.

V. CONCLUSIONS

(1) The magnetic method provides very accurate results on CFP.

(2) DyPG has been shown to be highly anisotropic below 4 K, with a large component of magnetization in the *c* plane.

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