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Experimental and theoretical investigations of the magnetic susceptibility and anisotropy of $Nd(OH)_3$

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Measurements are reported on the magnetic susceptibilities and anisotropies of single crystals of $Nd(OH)_3$ in the temperature range between 300 and 77 K. The intermediate-coupling scheme with J mixing under the crystal field of C_{3h} symmetry is used to obtain the crystal-field energy levels and their eigenfunctions. Matrix elements of the Coulomb, spin-orbit, and crystal-field interactions within the f^3 configuration are calculated. The g values are found to be $g_{\parallel}=3.65\pm0.01$ and $g_{\perp}=1.95\pm0.01$ in close agreement with the experimental values quoted by P. D. Scott (Ph.D. dissertation, Yale University, 1970). The calculated crystal-field splitting explains successfully the temperature dependence of the specific heat as observed by Chirico and Westrum [J. Chem. Thermodyn. **12**, 311 (1980)] in the temperature range between 350 and 20 K. Saturated magnetizations parallel and perpendicular to the applied magnetic field are found to be 271 and 145 emu/cm^3, respectively.

I. INTRODUCTION

Neodymium is the most abundant rare earth. The absorption spectra of a number of its salts has been the field of research of many physicists.[1–9] Earlier investigations were not very reliable due to not very pure material, insufficient spectral resolution, and not well-developed theory. Satten's investigation of the spectrum of $Nd(BrO_4)_3\cdot9H_2O$ provided for the first time a sound basis for its interpretation.[1] Theoretical investigations were reported by Judd.[2] Free-ion energies and the wave functions were calculated by Wybourne[3] and Carlson and Dieke.[4,5] Some additional measurements of the infrared-absorption spectrum have been reported by Varsanyi and Dieke.[6] Eisenstein carried out crystal-field (CF) calculations for the energy levels of Nd^{3+} in $LaCl_3$.[7] Gruber and Satten investigated both theoretically and experimentally the CF energy levels of Nd^{3+} ion in neodymium ethylsulfate nonahydrate crystals.[8] Wong calculated the Taylor series expansion of the intermediate-coupling (IC) energy levels for Nd^{3+} in

TABLE I. Experimental and calculated Stark splitting and the g values of the ground $^4I_{9/2}$ term of Nd^{3+} ion in different lattices.

System	2μ	Experimental positions of energy levels (cm^{-1})	Calculated energy levels (cm^{-1})	$g_{\parallel}$ values expt.	calc.	$g_{\perp}$ values expt.	calc.
NES[a]	5	−178	−178	3.535±0.001	3.52	2.072±0.001	2.27
	3	−29	−29				
	1	−24	−24				
	7	101	102				
	9	133	129				
Nd:$LaCl_3$[b]	5	−146.47	−146.02	3.996±0.001	4.10	1.763±0.001	1.86
	1	−31.08	−31.93				
	3	−23.26	−21.39				
	7	97.93	96.01				
	9	102.88	103.34				
Nd:$Y(OH)_3$[c]	5		−183.25	3.63±0.03	3.59	1.95±0.03	2.22
	3		−37.72				
	1		−10.06				
	7		104.78				
	9		126.25				

[a] Reference 8; NES denotes neodymium ethylsulfatenonahydrate.
[b] Reference 7.
[c] Reference 12.

$NdCl_3$.[9] Detailed work on magnetothermodynamics of NES have been published by Fisher *et al.*[10,11] The g values were reported as $g_{\parallel}=3.594\pm0.001$ and $g_{\perp}=2.039\pm0.001$. Scott studied electron paramagnetic resonance (EPR) spectroscopy with diluted $Nd(OH)_3$ crystals and obtained $g_{\parallel}=3.63\pm0.03$ and $g_{\perp}=1.95\pm0.03$.[12] Eisenstein reported the same for Nd:$LaCl_3$ as $g_{\parallel}=3.996\pm0.001$ and $g_{\perp}=1.763+0.001$.[7] It is noticeable that the neodymium hydroxide g values are intermediate between those observed for the ethylsulfate and $LaCl_3$ lattices (Table I). Meissner has measured the heat capacities of $Nd(OH)_3$ from 0.62 to 18 K.[13] Heat capacities from 11.4 to 350 K have been reported by Chirico and Westrum.[14] By the application of lattice heat-capacity approximation method, Chirico and Westrum obtained a Schottky curve in agreement with the calorimetrically obtained curve below 150 K. The deviations were considerably large at higher temperatures. None of the optical or magnetic measurements has been reported with $Nd(OH)_3$ pure crystals as yet.

In spectral study by optical absorption experiments, Nd^{3+} has several cases where two levels come very close together and no reliable results can be expected unless J mixing is taken into consideration.[8] Scott estimated the crystal-field parameters (CFP) of Nd:$Y(OH)_3$ to be equal to those determined for Tb:$Y(OH)_3$ and calculated the g values by CF model.[15] It is seen that the value of $g_{\parallel}(=3.59)$ is in agreement with the experiment $(=3.63\pm0.03)$, but $g_{\perp}(=2.22)$ is quite off the resonance value $(=1.95\pm0.03)$. To obtain a good matching with the experiment, I varied the different CFP values and carried out CF calculations and found that it was not possible to obtain $g_{\perp}$ in agreement with the experimental value, not affecting $g_{\parallel}$ adversely, without J mixing. It shows that the required lowering of $g_{\perp}$ definitely comes from the CF mixing of the J states. This is evident because the J multiplets are comparatively close in Nd^{3+} ion. It is well established that the EPR results only by themselves are totally inadequate to fix the crystal electric field correctly. Hence, the CFP based on them should be checked by some other means such as optical spectroscopy or magnetic or thermal study.[16]

II. EXPERIMENTAL

Well-developed thin needle-shaped crystals of neodymium hydroxide of length ~0.4 cm are available for experiment. The mass of the biggest crystal is 4.835 mg. In the bimolecular unit cell, the molecules have C_{3h} point-group symmetry with the trigonal axis along the C axis. The C axis developed along the needle axis is prominent. The mounting of the crystals can be done very accurately with the help of a microscope. The error in mounting is well within 0.1°. It crystallizes with two magnetically equivalent Nd^{3+} ions per unit cell. The crystalline anisotropy $\chi_c-\chi_a$ is the same as the molecular or gram-ionic anisotropy $K_{\parallel}-K_{\perp}$. The anisotropy $(K_{\parallel}-K_{\perp})$ is measured between 300 to 77 K by suspending the crystal with a quartz fibre in a homogeneous magnetic field such that the C axis moves freely in a horizontal plane.[17] The thermal variation of $K_{\perp}$ is measured in the same temperature region by suspending a crystal vertically in a horizontal gradient using Faraday method.[18] The experimental data are shown in Fig. 1. Accuracy of the results is high, $\leq 0.1\%$.

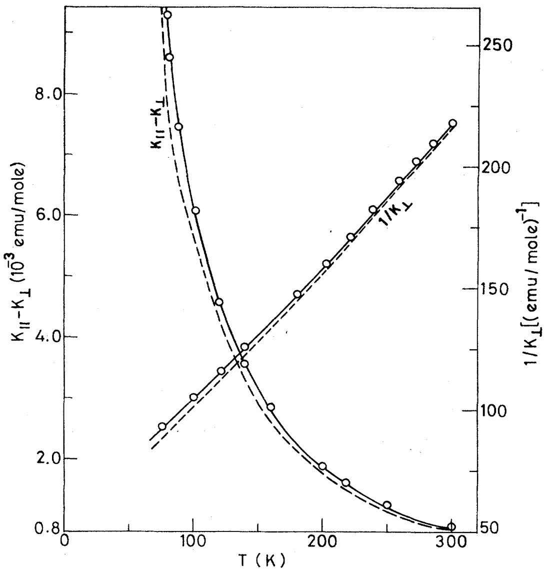

FIG. 1. Thermal variation of $(K_{\parallel}-K_{\perp})$ and inverse of $K_{\perp}$ from 300 to 77 K. The broken and solid lines indicate the calculated values using the CFP of Scott (Ref. 12) and this work, respectively. ○ represents the experimental points.

III. RESULTS AND DISCUSSION

The effect of intermediate coupling is sufficient to strongly mix states of different L and S. The intermediate-coupled wave functions are determined by the direct diagonalization of IC matrices with the values of the free-ion parameters given by Gruber and Satten for neodymium ethylsulfate, viz., the electrostatic parameters $F_2=331.330$, $F_4=47.956$, and $F_6=5.313$ and the spin-orbit coupling parameter $\zeta=880.11$, all in cm^{-1}. Other interactions, such as, configuration interaction are not considered. The IC wave functions thus obtained are slightly different from those given by Wybourne which, in fact, referred to Nd^{3+} in $LaCl_3$, correspondingly, the electrostatic parameters (F_2, F_4, F_6), and ζ were slightly different from this case.

The effective Hamiltonian for the IC calculation is

$$H_{IC}=\sum_{\substack{i,j\\i<j}}\frac{e^2}{r_{ij}}+\zeta\sum_i \mathbf{l}_i\cdot\mathbf{s}_i \, .$$

The diagonalization of the matrix H_{IC} yields IC wave functions and their eigenvalues. It is sufficient to determine the four IC wave functions and their eigenvalues corresponding to $J=\frac{9}{2}, \frac{11}{2}, \frac{13}{2}$, and $\frac{15}{2}$. Other levels lie too high to give any significant contribution. The energy levels for $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ are found to be at 1867.7, 3856.2, and 5921.4 cm^{-1}, respectively, above the ground state. The crystal-field interaction is given by

$$H_c=\sum -|e|(B_{20}V_2^0+B_{40}V_4^0+B_{60}V_6^0+B_{66}V_6^6)\, .$$

The best set of CFP to fit the experimental anisotropy and susceptibility data from 300 to 77 K is found to be as follows:

$$B_{20}=186.5\ \mathrm{cm}^{-1}\ ,$$

$$B_{40}=-70.6\ \mathrm{cm}^{-1}\ ,$$

$$B_{60}=-50.7\ \mathrm{cm}^{-1}\ ,$$

$$B_{66}=615.0\ \mathrm{cm}^{-1}\ .$$

Using these values of the parameters, the diagonalization of the matrix H_c yields ten zeroth-order CF states comprising of five doublets and the first-order energy corrections (Table II).

Now, the effect of J mixing is taken into account. The states, correct to first order, is given by

$$\phi_i=N\left[\phi_i^{(0)}-\sum_{\psi_j}\frac{\langle\psi_j\,|\,H_c\,|\,\phi_i^{(0)}\rangle}{E_{\psi_j}^{(0)}}\,|\,\psi_j\rangle\right]\ ,$$

where ϕ_i and ψ_j are the CF and IC wave functions, respectively, and $j=2,3,4$. $E_{\psi_1}^{(0)}$ is the zero of the energy scale. N is the normalization factor so that $\langle\phi_i\,|\,\phi_i\rangle=1$. The CF energy, correct to second order, is

TABLE II. Crystal-field splitting of the ground $^4I_{9/2}$ term of Nd^{3+} in $\mathrm{Nd(OH)_3}$.

2μ	Energy eigenvalues (cm^{-1})	Wave functions
5	-199.3519	$0.9233\,|\pm\frac{7}{2}\rangle+0.3842\,|\pm\frac{5}{2}\rangle$
3	-31.7552	$0.8374\,|\pm\frac{9}{2}\rangle+0.5466\,|\pm\frac{3}{2}\rangle$
1	-17.1480	$|\pm\frac{1}{2}\rangle$
7	118.6824	$0.3842\,|\pm\frac{7}{2}\rangle-0.9233\,|\pm\frac{5}{2}\rangle$
9	129.5727	$0.5466\,|\pm\frac{9}{2}\rangle-0.8374\,|\pm\frac{3}{2}\rangle$

$$E_i=E_i^{(1)}-\sum_{\psi_j}\frac{|\langle\psi_j\,|\,H_c\,|\,\phi_i^{(0)}\rangle|^2}{E_{\psi_j}^{(0)}}\ .$$

The number of matrix elements in the above two sums are considerably reduced by the application of selection rules.

A significant contribution to the magnetic susceptibility comes from the lowest group of ten CF states forming five doublets. The general expression for the gram-ionic paramagnetic susceptibility is given by

$$K_\alpha=\frac{N\sum_{m,n}[(W_{m,n,\alpha}^{(1)})^2/k_BT-2W_{m,n,\alpha}^{(2)}]\exp(-W_{m,n}^{(0)}/k_BT)}{\sum_{m,n}\exp(-W_{m,n}^{(0)}/k_BT)}\ ,$$

where $W_{m,n,\alpha}^{(1)}H$ and $W_{m,n,\alpha}^{(2)}H^2$ are the first- and second-order energy corrections when the magnetic field H is applied along the direction α and $W_{m,n}^{(0)}$ is the unperturbed energy in the zero magnetic field.

The thermal variation of magnetic anisotropy as well as the susceptibility in a direction perpendicular to the applied magnetic field is shown in Fig. 1. The experimental points lie quite close to the calculated curve. The magnetic anisotropy is found to be 847×10^{-6} emu/mole at 300 K. With the decrease of temperature, it increases slowly up to 200 K. The increase is very sharp below 200 K. It becomes 9345×10^{-6} emu/mole at 77 K, i.e., 11 times its value at 300 K. The gram-molar susceptibility in a direction perpendicular to the applied magnetic field is found to be 0.004 578 emu/mole at 300 K and increases to a value of 0.010 753 emu/mole at 77 K, which is about 2.4 times its value at 300 K.

The thermal variation of magnetic moments in directions parallel and perpendicular to the applied magnetic field and their effective values are shown in Fig. 2, in Bohr magneton. With the increase of temperature, the magnetic moments and hence their effective values increase rapidly up to 140 K. Above this temperature, the rate of increase in the values of $p_\perp$ and p_{eff} become slow but $p_{\|}$ starts decreasing slowly from 220 K.

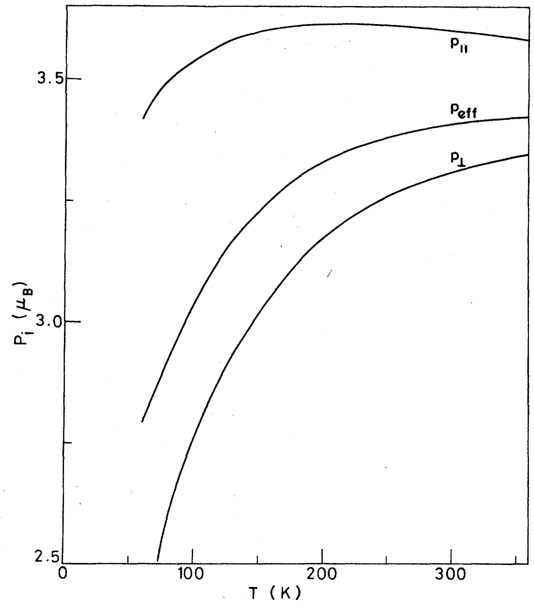

FIG. 2. Thermal variation of $p_{\|}$, $p_\perp$, and p_{eff} in Bohr magnetons (μ_B).

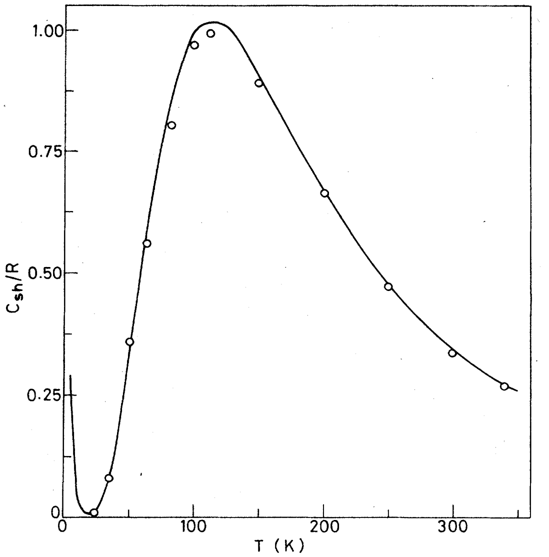

FIG. 3. Thermal variation of the Schottky specific heat obtained by calculation. ○ represents the experimental values reported by Chirico and Westrum (Ref. 14). R is the universal gas constant.

To understand the various magnetic phenomena in systems [such as $\mathrm{Nd(OH)_3}$] which has completely isolated ground doublet (other levels lying above 167 cm^{-1}), it is convenient to utilize the formalism of the effective spin-$\frac{1}{2}$ Hamiltonian. When a large magnetic field is applied, the saturated magnetization of such a doublet at liquid-helium temperatures is given by

$$M_{\mathrm{sat},\alpha}=Ng_J\mu_B\langle s_g\,|\,J_\alpha\,|\,s_g\rangle\ ,$$

where N is the number of spins per cm^3 and α is the x, y, or z direction. $\langle s_g\,|\,J_\alpha\,|\,s_g\rangle$ is the expectation value of J_α in the ground doublet. Utilizing the ground-state wave function given in Table II, the saturated magnetization parallel and perpendicular to the C axis was found to be 271 and 145 $\mathrm{emu/cm^3}$, respectively.

Without a knowledge of the ground-state wave function, the saturated magnetization can also be calculated from the experimental values of $g_{\parallel}$ and $g_{\perp}$, utilizing the formula $M_{\mathrm{sat}}=\frac{1}{2}N\mu_B g_\alpha$, obtaining $M_{\mathrm{sat},\parallel}=269$ and $M_{\mathrm{sat},\perp}=145$ $\mathrm{emu/cm^3}$, in excellent agreement with the values obtained above.

The g values calculated including the effect of IC of the J states into the ground term are $g_{\parallel}=3.65\pm0.01$ and $g_{\perp}=1.96\pm0.01$, in excellent agreement with the experimental values of Scott as expected that the g values would not vary appreciably for the concentrated solution. Thus, the CF obtained in the present study solves the difficulty encountered by Scott in explaining his EPR spectroscopic data, especially, the perpendicular component of the g value.

The thermal variation of the Schottky specific heat is plotted in Fig. 3. The circles showing the experimental (calorimetric) Schottky contributions reported by Chirico and Westrum lie quite close to the curve obtained by calculation with the present CF. The agreement between the experiment and the calculated curve is reasonably good throughout the entire range of measurement. The discrepancy observed by Chirico and Westrum[14] in the high-temperature region above 150 K is removed by the use of the exact crystal field for $\mathrm{Nd(OH)_3}$.

IV. CONCLUSION

While comparing the present set of CFP with the one postulated by Scott, viz., $B_{20}=189.1\pm2.6$, $B_{40}=-69.1\pm1.5$, $B_{60}=-45.7\pm1.0$, and $B_{66}=606\pm9$, all in cm^{-1}, it is seen that the B_{20}, B_{40}, and B_{66} values lie within the limit of their experimental errors. The value of B_{60} is varying from that prescribed by Scott for $\mathrm{Nd{:}Y(OH)_3}$, the variation being 7%. The percentage variation in the value of B_{60} is not much, yet, the present set of CFP gives an elegant match with the experimental values of the susceptibilities, their anisotropies over a large temperature region from 300 to 77 K and of the EPR spectroscopic data. It explains successfully the thermal variation of the Schottky heat capacity in the 350- to 20-K temperature range. This study will enable us to construct the crystal-field spectra of the excited states which can be verified by optical spectroscopy. Single crystals of neodymium hydroxide are found to be chemically stable with good optical properties. They find applications in magneto-optic devices.

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