Vol 17 No 8, August 2008
1674-1056/2008/17(08)/3093-04

Chinese Physics B

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Effects of exchange interaction and spin-fluctuation on the magnetic and magneto-optic properties of NdF_3*

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(Received 4 February 2008; revised manuscript received 18 March 2008)

The exchange interaction between the electrons in the different magnetic ions and the spin-fluctuation of the magnetic ions exist in the paramagnetic media NdF_3. The exchange interaction between the electrons in the different magnetic ions may be equivalent to an effective field H_{in} that is in direct proportion to the magnetization $\boldsymbol{M}$. The spin-fluctuation of the magnetic ions leads the coefficient of the effective field to vary with temperature. The effective field is given as $\boldsymbol{H}_{\rm in} = -(0.75 + 0.22{\rm T}) \times 10^{-5} \boldsymbol{M}$ in NdF_3. When the secondary crystal field effect is taken into account, the magnetic susceptibility and Verdet constant are calculated for NdF_3 by means of the effective field $\boldsymbol{H}_{\rm in}$ and the applied field $\boldsymbol{H}_e$. The calculated results are in agreement with the measured ones.

Keywords: exchange interaction, spin-fluctuation, magnetic and MO properties, NdF_3 crystal

PACC: 7820L, 7520

1. Introduction

Since the work of Leycuras and Gall[1] in 1984, many investigators have been interested in the producing mechanism of the magnetic and magneto-optic (MO) properties of NdF_3 crystal. Xu and Duan[2,3] have even calculated the temperature relations of the magnetic and MO properties for RF_3 (R = Ce^{3+}, Pr^{3+}, Nd^{3+}) by using the crystal field (CF) theory. But in their investigations, the secondary CF effect, the exchange interaction between the electrons in the different magnetic ions and the spin-fluctuation of the magnetic ions were not taken into account. Therefore, the calculated results do not accord with the measured values well for the NdF_3 crystal.

According to the extended Curie–Weiss law,[4] the exchange interaction between the electrons in the different magnetic ions is equivalent to an effective field $\boldsymbol{H}_{\rm in}$, which increases in proportion to the magnetization $\boldsymbol{M}$. The action of the spin-fluctuation of the magnetic ions may be equivalent to the variation of coefficient of effective field with temperature .On the basis of the idea, the form of the effective field containing the two factors can be set up. The magnetic and MO properties for NdF_3 crystal are calculated, and the calculated results are in agreement with the experimental ones.

2. Calculation of CF-split levels of ground state for Nd^{3+} ions

The CF Hamiltonian of Nd^{3+} ions in NdF_3 crystal is

$$\hat{H}_{\rm C} = \sum_{k,q} A_{k,q} \left\langle r^k \right\rangle Y_{k,q}(\theta, \varphi), \tag{1}$$

where $A_{k,q} \left\langle r^k \right\rangle$ are the CF parameters, $\left\langle r^k \right\rangle$ the average values of r^k, and $Y_{k,q}$ the spherical harmonic functions.

The NdF_3 crystal has a LaF_3 structure, Nd^{3+} ions are at $2c$ sites, and the site symmetry of the Nd^{3+} ions is C_{3V}.[5] So expression (1) may be simplified into (for a 4f configuration)

$$\begin{aligned}\hat{H}_{\rm C} = & \sum_{k=2,4,6} A_{k,0} r^k Y_{k,0} \\ & + \sum_{k=4,6} r^k (A_{k,3} Y_{k,3} + A_{k,-3} Y_{k,-3}) \\ & + r^6 (A_{6,6} Y_{6,6} + A_{6,-6} Y_{6,-6}).\end{aligned} \tag{2}$$

With the CF parameters calculated by point charge model,[2,3] the CF-split levels and the corresponding wavefunctions of Nd^{3+} ions can be obtained

*Project supported by the Science and Technology Foundation of China University of Mining and Technology (Grant No OK061066).
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by solving the following secular equation:

$$\left\| \left\langle \varphi_a \left| \hat{H}_c \right| \varphi_b \right\rangle - E_g^{(0)} \delta_{ab} \right\| = 0, \tag{3}$$

where $\langle \varphi_a|$ and $\langle \varphi_b|$ are the wavefunctions corresponding to the free Nd^{3+} ions. The values of the CF-split levels for the 4f configuration of Nd^{3+} ions in NdF_3 are shown as follows: -46.155, -32.569, -6.056, -2.917 and $87.698\,cm^{-1}$, separately.

3. Calculation of Zeeman energy levels and magnetic susceptibility

The magnetic susceptibility for NdF_3 crystal follows the Curie–Weiss law[1]

$$\chi = C/\left(T - T_\theta\right), \tag{4}$$

where C is the Curie constant, and T_θ the Curie temperature. The fact implies that there exit an exchange interaction between the electrons in the different magnetic ions and the spin-fluctuation of the magnetic ions in the crystal.[4] The spin-fluctuation has an important influence on the magnetic properties of the crystal, which depends on the temperature.[6] According to the extended Curie–Weiss law,[4] the exchange interaction and the spin-fluctuation can be represented by an effective field $\boldsymbol{H}_{\rm in}$, i.e.

$$\boldsymbol{H}_{\rm in} = (\alpha + \beta T)\boldsymbol{M}, \tag{5}$$

where $\boldsymbol{M}$ is the magnetization caused by an applied field $\boldsymbol{H}_e$, α and β are the constants whose values are determined by fitting the measured data. So the total field $\boldsymbol{H}_a$ acting on the magnetic ions is the sum of the applied field $\boldsymbol{H}_e$ and the effective field $\boldsymbol{H}_{\rm in}$, i.e.

$$\boldsymbol{H}_a = \boldsymbol{H}_e + \boldsymbol{H}_{\rm in} = [1 + (\alpha + \beta T)\chi]\boldsymbol{H}_e, \tag{6}$$

where χ is the susceptibility. For the NdF_3 crystal, the optimum values of α and β are fitted by the measured data.[1] They are $\alpha = -6.0 \times 10^{-4}\mu_{\rm B}^{-1}{\rm mol}\cdot{\rm A}\cdot{\rm m}^{-1}$ and $\beta = -1.76 \times 10^{-4}\mu_{\rm B}^{-1}K^{-1}\cdot{\rm mol}\cdot{\rm A}\cdot{\rm m}^{-1}$. Therefore, the Zeeman effect Hamiltonian is given by

$$\hat{H}_m = \mu_{\rm B}[H_e(\hat{L}_z + 2\hat{S}_z) + H_{\rm in}2\hat{S}_z], \tag{7}$$

where $\mu_{\rm B}$ is the Bohr magneton.

By solving the following secular equation:

$$\left\| \langle \varphi_i|\, \hat{H}_m\, |\varphi_j\rangle - E_g^{(1)}\delta_{ij} \right\| = 0, \tag{8}$$

the Zeeman splitting of the CF energy levels caused by the magnetic field $\boldsymbol{H}_a$ can be obtained. The $\langle \phi_i|$ and the $\langle \phi_j|$ are the wavefunctions corresponding to CF -split energy levels $E_g^{(0)}$. The value of the external magnetic field is taken as $1.6 \times 10^6\,{\rm A/m}$.[1]

The average magnetic moment of a Nd^{3+} ion is

$$\bar{m} = -\mu_{\rm B} \sum_g \langle g|\left(L_z + 2S_z\right)|g\rangle \rho_g, \tag{9}$$

where $\langle g|$ is the wavefunction corresponding to the Zeeman-split level $E_g^{(1)}$ and $E_g^{(1)} \ll E_g^{(0)}$, $\bar{M} = N\bar{m}$. When the temperature T is higher than 30 K i.e. $T > 30\,{\rm K}$, the occupation probability ρ_g in expression (9) can be reduced to

$$\begin{aligned} \rho_g &= \rho_0 {\rm e}^{-E_g/kT} \\ &= \rho_0 {\rm e}^{-\left(E_g^{(0)} + E_g^{(1)}\right)/kT} \\ &= \rho_0 {\rm e}^{-E_g^{(0)}/kT}\left(1 - \frac{\mu_{\rm B}}{kT}\langle g|\left(H_e(\hat{L}_z + 2\hat{S}_z)\right.\right. \\ &\quad \left.\left. + H_{\rm in}2\hat{S}_z\right)|g\rangle\right), \end{aligned} \tag{10}$$

where k is the Boltzmann constant. The reciprocal susceptibility of NdF_3 crystal may be expressed as

$$\begin{aligned} \chi^{-1} &= \frac{H_e}{M} = \frac{H_a - (\alpha + \beta T)M}{M} \\ &= \chi_p^{-1} - (\alpha + \beta T), \end{aligned} \tag{11}$$

where $\chi_p^{-1} = H_a/M$ is the inverse of the paramagnetic susceptibility that obeys the Curie law. χ_p can be calculated from the following formula that contains the secondary CF effect:

$$\chi_p = N\sum_i \left\{ \left(B_i^{(1)}\right)^2 / \kappa T - 2B_i^{(2)} \right\} \cdot \rho_g, \tag{12}$$

where,

$$B_i^{(1)} = \mu_{\rm B}\left\langle \varphi_i \right| \hat{L}_z + 2\hat{S}_z \left| \varphi_i \right\rangle,$$

and

$$B_i^{(2)} = \mu_{\rm B}^2 \sum_{j \neq i} \frac{\left\langle \varphi_i \right| \hat{L}_z + 2\hat{S}_z \left| \varphi_j \right\rangle^2}{E_{gi}^{(0)} - E_{gj}^{(0)}}.$$

with $E_{gi}^{(0)}$ and $E_{gj}^{(0)}$ being the ith and jth CF-split levels, respectively. By using expressions (11) and (12), the reciprocal susceptibility of the NdF_3 crystal is obtained and shown in Fig.1, in which the measured values obtained by Leycuras and Gall[1] and the calculated values obtained by Xu and Duan[2] are both shown for comparison. It can be seen that our calculated results are in good agreement with the measured ones from Fig.1.

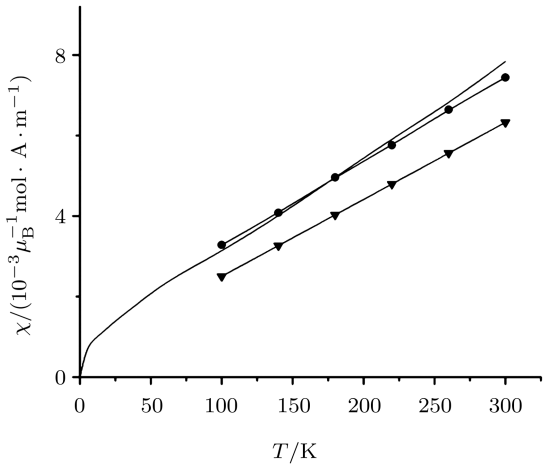


Fig.1. Variation of inverse magnetic susceptibility of NdF_3 with temperature (χ is expressed in $\mu_B\cdot\mathrm{mol}^{-1}\cdot\,\mathrm{A}\cdot\mathrm{m}^{-1}$, where — denotes measured values,[1] —▶— calculated values with the secondary CF effect taken into account, —●— calculated values considering the secondary CF effect, the exchange interaction and the spin-fluctuation.

4. Calculation of Verdet constant

The MO effect of the NdF_3 crystals in a visible region is mainly due to the intraionic parity allowed electric dipole transition between the $4f^3$ and $4f^25d$ configurations. The contribution of the electric dipole transitions to the Faraday rotation (FR) per unit length is[7]

$$\theta_{\mathrm{F}} = \frac{N\pi e^2}{9\hbar c}\frac{\left(\bar{n}^2+2\right)^2}{\bar{n}}\sum_{g,n}\frac{\omega^2}{\omega_{ng}^2-\omega^2} \times\left\{\left|\langle n|\,V_-\,|g\rangle\right|^2-\left|\langle n|\,V_+\,|g\rangle\right|^2\right\}\rho_g. \quad (13)$$

Here N is the number of ions per unit volume, $\bar{n}$ the average refractive index of NdF_3, ω the angular frequency of the light wave, $\langle g|$ a set of ground states with energy E_g, $|n\rangle$ the exciting states with energy E_n, $\hbar\omega_{ng}=E_n-E_g$, $eV_\pm$ the electric dipole moment operators for the right- and left-hand circularly polarized light, expressed as

$$eV_\pm = e(x\pm\mathrm{i}y), \quad (14)$$

and ρ_g the occupation probability of the state $|g\rangle$.

The Verdet constant V is given by

$$V=\frac{\theta_{\mathrm{F}}}{H_e}. \quad (15)$$

Substituting expression (6) into expression (15), the Verdet constant can be rewritten as

$$V=\frac{\theta_{\mathrm{F}}[1+(\alpha+\beta T)\chi]}{H_a}. \quad (16)$$

Because the accurate values of the terms of the $4f^25d^1$ configuration for the free Nd^{3+} ions are not found, according to the work of Dieke and Crosswhite,[8] the average energy of the $4f^25d$ configuration is taken as $7000\,\mathrm{cm}^{-1}$, and the splittings of these terms corresponding to $4f^25d$ configuration caused by CF is neglected. The value of $\langle r\rangle_{4f5d}$ of the Nd^{3+} ion is taken as 0.0377 nm.[2]

By using expressions (13) and (16), the inverse of the Verdet constant can be calculated for NdF_3 in a 100–300 K temperature range at a 0.6328 μm wavelength. The calculated results are shown in Fig.2. The measured values obtained by Leycuras and Gall[1] and the calculated values without considering the exchange interaction by Xu and Duan[2] are also shown in Fig.2 for comparison. It may be seen from Fig.2 that our calculated results are better than those given by Xu and Duan.[2]

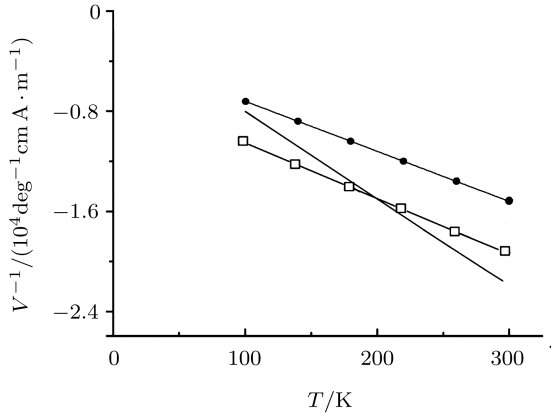


Fig.2. Variation of inverse Verdet constant of NdF_3 with temperature (V is expressed in $\mathrm{deg}\cdot\mathrm{cm}^{-1}\cdot\,\mathrm{A}^{-1}\cdot\mathrm{m}$, where — denotes measured values,[1] —●— calculated values,[2] —□— calculated values with the secondary CF effect, the exchange interaction and the spin-fluctuation taken into account.

5. Conclusion and discussion

In this paper, the magnetic susceptibility and Verdet constant of NdF_3 crystals at a 0.6328 μm wave length in a 100–300 K temperature range have been calculated based on the quantum theory. The calculations show the characteristics as follows:

(1) The contribution of the secondary CF effect to the magnetic susceptibility of NdF_3 crystal is approximately 6.8 percent of the first-order processes at 300 K, while the contribution in CeF_3 crystal is less than one percent of the first-order processes at

300 K.[4] It appears that the secondary CF effect increases with the increase of atomic number of Kramers ions in the rare-earth trifluorides.

(2) There exist the exchange interaction between the electrons in the different magnetic ions and the spin-fluctuation of the magnetic ions in the neodymium trifluoride. The exchange interaction may be represented by an effective field $\boldsymbol{H}_{\rm in}$ in proportion to the magnetization $\boldsymbol{M}$, and the spin-fluctuation may be equivalent to the variation of the coefficient of effective field with temperature. The effective field together with the applied field $\boldsymbol{H}_e$ causes the splitting of the ground state. The occupation probability of an electron in the ground state is affected by the energy separation between the ground levels.

(3) It can be seen from Figs.1 and 2 that the calculated results of the magnetic susceptibility of NdF_3 in a 100–300 K temperature range are in good agreement with the measured values. While the calculated values of Verdet constant cannot accord with the measured values well. The difference in Verdet constant between the calculated and the measured results arises mainly from the lack of the term values of the $4f^25d^1$ configuration and the corresponding splitting in the CF.

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