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Quantitative analyses of magnetic and magneto-optical properties in cerium trifluoride

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We first consider the effects of the crystal field on both the $4f$ ground state and the $5d$ excited state of a Ce^{3+} ion in the paramagnetic medium CeF_3, and further take account of the splitting of the crystal-field ground-state levels caused by the effective superexchange field H_v and the applied field H_e; then, with a model of a double transition that includes ground-state splitting, we calculate quantitatively the specific Faraday rotation θ_F, the Verdet constant V, the magnetic susceptibility χ, and their temperature dependences in CeF_3. Theoretical calculations show that the magneto-optical effect and its temperature dependence in CeF_3 are closely related to the superexchange interaction between Ce^{3+} ions. V^{-1} is linearly dependent on T and $V/\chi = -18\,353(1+63.01/T)$ in the temperature range $60 < T \leq 300$ K. The theory is in good agreement with the experimental results.

I. INTRODUCTION

Up to now, most paramagnetic media with large Verdet constants V, such as the Faraday Hoya FR glasses, contain rare-earth elements. These media can be used in many magneto-optical (MO) devices, such as optical isolators, optical modulators and so further research, especially the calculation of the effects of the rare-earth elements on the MO effect seems very important.

In 1934, the experiment of Van Vleck and Hebb showed that in the paramagnetic rare-earth compounds, V exhibits the same temperature dependence as does the magnetic susceptibility χ.[1] This was also shown by the MO theory of paramagnetic media.[2,3] In 1984, Leycuras *et al.* found that in many rare-earth compounds, the temperature dependence of V is quite complicated. For NdF_3 and PrF_3, V/χ depend linearly on the temperature T, and in CeF_3 depends linearly on $1/T$.[4] These phenomena cannot be explained by the previous MO theory.

In our opinion, the shortcoming of the previous theory is that many interactions in paramagnetic media, especially the (super-)exchange interaction between electron spins and the crystal field, have not been taken into account. The (super-)exchange interaction can be equivalent to an effective field H_v. This field causes the splitting of the ground state together with the applied field H_e. Electron transitions from the two split levels of the ground state ought to have contributions to the MO effect. From this point of view, the complicated temperature dependence of the MO rotation θ and the Verdet constant V have been calculated.[5] It has been shown that the work of Leycuras *et al.* is correct. In this paper, calculation of some MO properties in the paramagnetic medium CeF_3 has been made. We first consider the effect of the crystal field on both the $4f$ ground state and the $5d$ excited state of the Ce^{3+} ion in CeF_3, and further take account of the splitting of the ground state in the crystal field caused by both H_v and H_e, and then using the model of the double transition with the splitting of the ground state, calculate the specific Faraday rotation θ_F, V, χ and their temperature dependence in CeF_3. The calculations are compared with the experiments in detail. The important contribution of the superexchange interaction to the MO effect is pointed out.

II. THE LEVEL SPLITTING AND WAVE FUNCTION OF THE Ce^{3+} ION IN THE CRYSTAL FIELD

In the paramagnetic crystal CeF_3, the Hamiltonian of the Ce^{3+} ion is

$$\begin{aligned} H &= H_0 + H_{LS} + H_c \\ &= H_0 + \zeta(r)\mathbf{L}\cdot\mathbf{S} + \sum_{k=0}^{\infty}\sum_{m=-k}^{k} B_{k,m} Y_{k,m}(\theta,\phi) , \end{aligned} \tag{1}$$

where $H_0 + H_{LS}$ is the Hamiltonian of the free Ce^{3+} ion, H_{LS} the spin-orbital (L-S) interaction energy, H_c the crystal field. The crystal-field parameter $B_{k,m}$ is

$$B_{k,m} = \frac{4\pi e r^k}{2k+1} \sum_j \frac{q_j}{R_j^{k+1}} Y^*_{k,m}(\theta_j,\phi_j) \tag{2}$$

where the Ce^{3+} ion of interest is at the origin, and the coordinates of the electron and the jth neighboring Ce^{3+} ion are (r,θ,ϕ) and (R_j,θ_j,ϕ_j), respectively, q_j is the electric charge of the jth neighboring ion, $Y_{k,m}(\theta,\phi)$ is the spherical harmonics function. In real crystals, because of the restrictions of parity and symmetry, only some spherical harmonics contribute. The crystal field in CeF_3 has the symmetry of C_{3h}, so for $4f$ and $5d$ electrons, H_c can be expressed as

TABLE I. The crystal field parameters of Ce^{3+} in CeF_3 (cm^{-1}).

CFP[a]	$B_{2,0}$	$B_{4,0}$	$B_{6,0}$	$B_{4,\pm 3}$	$B_{6,\pm 3}$	$B_{6,\pm 6}$
$4f$	-150	1500	2500	0	0	0
$5d$	23000	3000	—	0	—	—

[a] CFP means the crystal-field parameters.

$$H_{c,4f}=B_{0,0}Y_{0,0}+B_{2,0}Y_{2,0}+B_{4,0}Y_{4,0}+B_{4,3}Y_{4,3}+B_{4,-3}Y_{4,-3}+B_{6,0}Y_{6,0}+B_{6,3}Y_{6,3}+B_{6,-3}Y_{6,-3}+B_{6,6}Y_{6,6}+B_{6,-6}Y_{6,-6} \tag{3a}$$

$$H_{c,5d}=B_{0,0}Y_{0,0}+B_{2,0}Y_{2,0}+B_{4,0}Y_{4,0}+B_{4,3}Y_{4,3}+B_{4,-3}Y_{4,-3}\ . \tag{3b}$$

In the crystal field, the levels are splittings. For rare-earth ions $H_{LS}>H_c$ thus H_c can be taken as the perturbation. The splittings of $4f$ and $5d$ levels and their eigenfunctions can be calculated from following secular equation:

$$\|\langle\phi_i|H_c+H_{LS}|\phi_j\rangle-E^{(0)}\delta_{23}\|=0\ , \tag{4}$$

where $|\phi_i\rangle, |\phi_j\rangle$ are the eigenfunctions of H_0+H_{LS}, and $E^{(0)}=E_a^{(0)}$ is the shift of the ground level caused by the L-S interaction and the crystal field. $E^{(0)}=E_{b'}^{(0)}$ is the shift of the excited level resulting from both the L-S interaction and the crystal field. $E_b^{(0)}$ is the energy of the excited state. We take the lowest level of the ground state as zero. Then the lowest level of the excited state is 39 900 cm^{-1}.[6] Because either the $4f$ or the $5d$ level has only one electron, according to Kramers law, each split level is double, degenerate. The L-S interaction does not disturb the time-reversal symmetry of the Hamiltonian, so it will not lift the Kramers degeneracy.

Before Eq. (4) can be solved, $\zeta(r)$ and $B_{k,m}$ in H_c must be calculated. The values of $\langle r^k\rangle$ and $\langle\zeta(r)\rangle$ can be found in Ref. 7. For $4f$ level, $\langle\zeta(r)\rangle=644\ cm^{-1}$ and for $5d$ level, $\langle\zeta(r)\rangle=1000\ cm^{-1}$, $B_{k,m}$ can be calculated from the levels of the $4f$ and $5d$ states reported in Ref. 6. The crystal-field parameters are shown in Table I.

From Eq. (4) and Table I we can get the energy levels and wave functions of the $4f$ and $5d$ states of Ce^{3+} ion in CeF_3. Table II gives the split levels of the $4f$ and $5d$ states.

III. THE EFFECT OF THE EFFECTIVE FIELD ON THE GROUND LEVEL

The magnetic susceptibility χ in CeF_3 conforms to the Curie-Weiss law,[4]

$$\chi=\frac{c}{T-\Theta_p}\ . \tag{5}$$

This signifies that there is a superexchange interaction between the spins of the Ce^{3+} ions. Suppose that the superexchange interaction in CeF_3 is isotropic; it can be equivalent to an effective field,[5]

$$H_v=vM=v\chi H_e\ , \tag{6}$$

where M is the magnetization, and the coefficient $v=\Theta_p/c$. Equation (5) can be written in another form:

$$\chi^{-1}=\frac{H_i}{M}-v\ . \tag{7}$$

Here the effective field $H_i=H_e+H_v$. H_i/M is the reciprocal of the susceptibility χ_p which obeys the formal Curie law. According to the quantum theory of paramagnetism, we have

$$\chi_p=\frac{N}{kT}\sum_a|\langle\psi_a|(L_z+2S_z)\mu_B|\psi_a\rangle|^2\frac{\exp(-E_a^{(0)}/kT)}{\sum_a\exp(-E_a^{(0)}/kT)}\ . \tag{8}$$

Under the effect of both H_v and H_e, all the crystal-field levels of $4f$ and $5d$ states will be split again. Because the splitting is much smaller than that caused by the crystal field, a wave function which corresponds with a crystal-field level may be used as a base function to calculate the splitting of the level caused by H_i.

As the superexchange interaction only acts on the spins, the perturbation Hamiltonian is

$$\begin{aligned}H_i&=\mu_BH_e(L_z+2S_z)+\mu_BH_v2S_z\\&=\mu_BH_e[(L_z+2S_z)+2v\chi S_z]\ .\end{aligned} \tag{9}$$

According to the degenerate perturbation theory, the secular equation can be solved and, in first approximation, the splitting of the crystal-field ground-level of Ce^{3+} ion resulting from H_i is given by

$$E_a^{(1)}=\mu_BH_e[\langle\psi_a|L_z+2S_z|\psi_a\rangle+2v\chi\langle\psi_a|S_z|\psi_a\rangle]\ , \tag{10}$$

where $|\psi_a\rangle$ is the wave function of each $4f$ level calculated by Eq. (4).

At room temperature, $KT\approx 200\ cm^{-1}$. Obviously, there are certain electron-distribution probabilities on the first, second, and third ground levels in Table II. When we calculate θ_F and V, the three levels must be taken into consideration. Because each level of the ground state is doublet, these three levels will be split into six nondegenerated levels by H_i, which are labeled by a_i ($i=1,2,\ldots,6$). From Eq. (10) we get the six split levels, as shown in Table III, and the wave functions of the ground state. χ can be calculated from Eqs. (7) and (8). v is obtained from the experimental curve of χ^{-1} vs T, and $v=-0.65\times10^6\ \mu_B^{-1}$ Oe mol.

The difference between the excited-state levels is much larger than the splitting of the excited-state caused by H_i

TABLE II. The split levels of $4f$ and $5d$ states of Ce^{3+} in CeF_3 (cm^{-1}).

$4f$	1	2	3	4	5	6	7
$H_a^{(0)}$	0	154	282	2133	2392	2569	2868
$H_b^{(0)}$	39900	42365	46115	47942	50620	—	—

TABLE III. The energy levels of Ce^{3+} under the influence of H_i.

a_i	E_{ai} $(cm^{-1})^{a}$
a_1	$0 \quad +\mu_B H_e(-1.3076+0.2870 v\chi)$
a_2	$0 \quad +\mu_B H_e(1.3076-0.2870 v\chi)$
a_3	$154+\mu_B H_e(-0.2105+0.5566 v\chi)$
a_4	$154+\mu_B H_e(0.2105-0.5566 v\chi)$
a_5	$282+\mu_e H_e(-2.1680+0.6640 v\chi)$
a_6	$282+\mu_B H_e(2.1680-0.6640 v\chi)$

[a] $E_{ai}=E_{ai}^{(0)}+E_{ai}^{(1)}$.

and the splitting of the excited-state resulting from the superexchange interaction has no contribution to the MO effect,[8] so the influence of H_i on the levels and wave functions of the excited state can be neglected.

IV. THE SPECIFIC FARADAY ROTATION Θ_F AND THE VERDET CONSTANT V

The MO effect in CeF_3 is caused by $4f-5d$ electric-dipole transitions in Ce^{3+} ion. Neglecting the linewidth Γ_{ab}, θ_F is given by[5,9]

$$\theta_F=\frac{\omega_p^2\omega^2}{4nc}\sum_{a,b}\frac{\beta_a}{\omega_{ab}(\omega_{ab}^2-\omega^2)}(f_{ab}^{+}-f_{ab}^{-}) , \tag{11}$$

where $\omega_p^2=4\pi Ne^2/m$, N is the number of ions per unit volume, n the average index of refraction, ω the frequency of the incident light, $\hbar\omega_{ab}$ the energy-level separation between the excited state b and the ground state a. The oscillator strengths are

$$f_{ab}^{\pm}=\frac{m\omega_{ab}}{\hbar e^2}|P_{ab}^{\pm}|^2 . \tag{12}$$

The matrix elements of the $4f-5d$ electric-dipole transitions excited by left- and right-handed circularly polarized light are

$$\begin{aligned} P_{ab}^{\pm}&=\langle\psi_{ai}|e(x\pm jy)|\psi_b\rangle\\ &=(8\pi/3)^{1/2}e\langle n'l'|r|nl\rangle\langle l'm_l'|Y_{1,\pm1}|lm_l\rangle\\ &\quad\times\delta_{ss'}\delta_{m_s m_s'} \end{aligned} \tag{13}$$

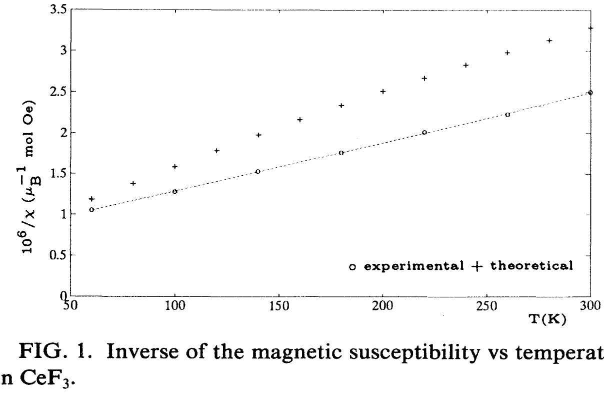

FIG. 1. Inverse of the magnetic susceptibility vs temperature in CeF_3.

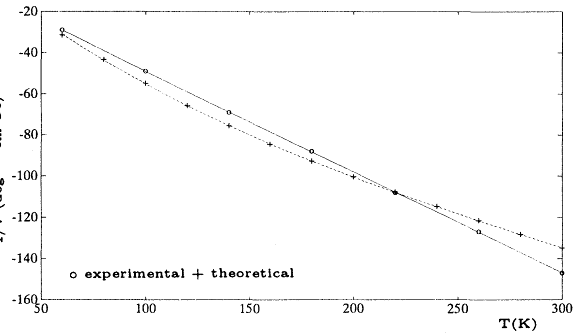

FIG. 2. Inverse of the Verdet constant as a function of temperature in CeF_3 at 0.6328 μm wavelength.

where $\langle n'l'|r|nl\rangle=\langle r\rangle$ can be found in Ref. 7, $\langle l'm_l'|Y_{1,\pm1}|lm_l\rangle$ is calculated according to the Winger-Eckart law. From all of the hundred and twenty matrix elements of the transitions calculated by Eq. (13), it can be seen that the probabilities of the electric-dipole transitions excited by left- and right-handed circularly polarized light are equal. From Eq. (11), the main reason for resulting in the Faraday rotation in CeF_3 is that the occupation probabilities of an electron in the two split levels of the ground state caused by H_i are not the same. The probability β_{ai} of an electron lying in the split level a_i as shown in Table III is given as

$$\begin{aligned} \beta_{ai}&=\frac{\exp[-(E_{ai}^{(0)}+E_{ai}^{(1)})/kT]}{\sum_{i=1}^{6}\exp(-E_{ai}/kT)}\\ &\approx\frac{\exp(-E_{ai}^{(0)}/kT)}{\sum_{i=1}^{6}\exp(-E_{ai}^{(0)}/kT)}\\ &\quad\times[1-(\mu_B H_e/kT)(\langle\psi_{ai}|L_z+2S_z|\psi_{ai}\rangle\\ &\qquad+v\chi\langle\psi_{ai}|2S_z|\psi_{ai}\rangle)] . \end{aligned} \tag{14}$$

On the basis of Table III, we can get β_{ai} of the six split levels of the ground state. Substituting the calculated values of Eqs. (12) and (14) into Eq. (11), and basing on $V=\theta_F/H_e$ we get the values of θ_F and V at different temperatures. The relevant parameters in Eq. (11) are obtained from Ref. 10. Figures 1 and 2 show the theoretical and experimental curves of χ^{-1} vs T and V^{-1} vs T, respectively.

V. DISCUSSION

The calculations show the following characteristics.

(1) In the temperature region for 60–300 K, χ^{-1} and V^{-1} in CeF_3 are linearly dependent on T. This is in good agreement with experimental results.[4]

(2) It has been proved by both the theory and the experiment that the temperature dependence of V/χ in CeF_3 fits[4,5]

$$V/\chi=A(1+B/T) . \tag{15}$$

Substituting two arbitrary sets of values of χ and V, such as the two sets at $T=60$ K and $T=160$ K, into Eq. (15), we get $A=-18353$, $B=63.0$. This is in accord with the experimental results $A=-13706$, $B=75.9$ quite well.

(3) The theoretical values of V and V/χ conform to the experimental results so well that, it is again proved that the three-level transition model (i.e., the double transition model with ground state splitting) is correct. That is, the two split levels of ground state caused by both the effective (super-)exchange field and the applied field ought to have contributions to the MO effect. This also is the internal cause that the MO effect in some paramagnetic media has complicated temperature dependence.

It must be emphasized that the superexchange interaction only acts on the electron spins, not on the orbitals directly. If we assume arbitrarily that an effective field acts not only on the spins but also on orbitals, the theoretical values of χ, V, and V/χ will be far from the experimental results.

(4) It can be shown by analyzing Eqs. (11) and (14) that the stronger the (super-) exchange interaction in paramagnetic media is, the larger is the probability β_{ai} ($i=1$, 3, and 5) of an electron stayed in the lower split level of the ground state for crystal CeF_3 and both the specific Faraday rotation θ_F and the Verdet constant V increase with H_i.[5] When the temperature becomes higher, the probability β_{ai} ($i=2$, 4, and 6) of an electron staying in the upper split level of the ground state for CeF_3 becomes larger too, and β_{ai} of an electron staying in the lower split level becomes correspondingly smaller. This makes θ_F and V decline. For CeF_3, raising the density of Ce^{3+} ions cannot only increase the value of ω_p^2 but also enhance the superexchange interaction between Ce^{3+} ions. So raising the density of Ce^{3+} ions suitably is a valid way to strengthen the MO effect.

The influence of the superexchange interaction on the MO effect in ferromagnetic, ferrimagnetic, and antiferromagnetic media has been initially approached by the quantum theory.[11,12] Our research shows that besides the L-S interaction, the (super-)exchange interaction has a remarkable contribution to the MO effect and its properties concerned. So to thoroughly study the (super-)exchange interaction in every kind of magnetic medium and the influence of impurity on (super-)exchange interaction is an important way to find a medium which has large specific Faraday rotation.

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