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Theory of Faraday rotation and susceptibility of rare-earth trifluorides

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A theoretical investigation on the magneto-optical and magnetic properties of light rare-earth trifluorides CeF_3, PrF_3, and NdF_3 is presented. The 0.6328-μm-wavelength Faraday rotation and susceptibility of these compounds in the temperature range 40–300 K have been calculated based on the quantum theory. The result shows that in the visible region the Faraday rotation is mainly caused by the intraionic electric-dipole transitions between the $4f^n$ and $4f^{n-1}5d$ configurations of rare-earth ions. The Faraday rotation and susceptibility of these compounds depend greatly on the splitting of the ground multiplet of the rare-earth ions in crystal fields. For non-Kramers Pr^{3+} ions in PrF_3, the lowest crystal-field state is a singlet, so at very low temperature the behavior of the Verdet constant and susceptibility of PrF_3 is different from CeF_3 and NdF_3. For CeF_3, the mixed-valent behavior of Ce ions must be taken into account.

I. INTRODUCTION

Many experimental and theoretical investigations have been done on the magneto-optical (MO) properties of magnetic materials. However, most of the theoretical calculations for Faraday or Kerr rotations in magnetic materials are semiempirical.[1] In this paper, the quantum-mechanical calculations of 0.6328-μm-wavelength Faraday rotation (FR) and susceptibility of trifluorides CeF_3, PrF_3, and NdF_3 in the temperature range 40–300 K are presented and the results are compared with the measured results obtained by Leycuras, and Le Gall.[2]

These trifluorides are paramagnetic in the whole temperature range and have a large Faraday rotation in the visible region. The FR induced by Ce ions is larger than that induced by Pr or Nd ions. Similar results have been found for rare-earth (RE) ions substituted iron garnets,[3] and it has been shown that Ce-substituted garnet might be a promising magneto-optical material for application in the region from the visible to the near infrared. Therefore, it is of great importance to study the mechanism of the contribution of the RE ions in such compounds to the magneto-optical effect. The crystal structure of the garnet is more complex than these trifluorides and besides the RE sublattice, the iron sublattices in the garnet will also contribute to the FR. Therefore, it is easier to study the MO effect in these RE trifluorides.

The Ce^{3+} and Nd^{3+} ions are Kramers ions, while the Pr^{3+} ions are not, so the low-temperature behaviors of both the Verdet constant V and magnetic susceptibility χ of CeF_3 and NdF_3 are different from those of PrF_3. Therefore, calculating V and χ of these trifluorides at the same time is helpful for examining the correctness of the theoretical model used in this paper. Furthermore, the electronegativity of fluorine ions is large, the overlap of the $4f$ wave function of the RE ions with the wave function of the fluorine ions is very small. Therefore, different from the garnet, we think that the charge-transfer transition in the trifluorides can be neglected. The magnetic dipole transition is not important in the visible region, comparing with the electric dipole transition. So the MO effect of the trifluorides in the visible region is mainly due to the intraionic parity allowed electric dipole transition between the $4f^n$ and $4f^{n-1}5d$ configurations.

The ground term of the $4f^n$ configuration of the RE ion is split into some multiplets due to the spin-orbit coupling, and the multiplets are split further in a crystal field (CF). In case of the Ce^{3+} and Nd^{3+} ions, the lowest multiplet is split into some degenerate levels. In case of non-Kramers Pr^{3+} ions, the lowest multiplet $^3H_4$ can be split into some singlets and some degenerate levels. The degenerate levels are split into sublevels due to an applied magnetic field. When a plane-polarized electromagnetic wave propagates through the compounds, the transition probabilities for the right- and left-hand circularly polarized light between these sublevels and the $5d$ levels are the same, but the occupation probabilities of these sublevels are different. This results in FR. As for the CF split nondegenerate levels, only the higher-order perturbation of the Zeeman Hamiltonian, which admixes different CF levels, will led to FR. But the FR caused by this mechanism is very small for the paramagnetic materials in a usual magnetic field. So, if the CF ground state of the Pr^{3+} ion is a singlet, the low-temperature MO behavior of the Pr^{3+} ion will be significantly different from that of the Ce^{3+} and Nd^{3+} ions. The susceptibility contributed by the RE ions also comes mainly from the electrons occupying the degenerate levels and is also decided by the splitting of the ground multiplet. So, besides the Verdet constant, the susceptibility has been calculated in the same temperature range as well. We think it is helpful for examining the correctness of the calculation.

The values of the crystal-field parameters and $\langle r \rangle_{4f5d}$

of CeF_3, PrF_3, and NdF_3 are close. So it could be expected that the calculated results would agree with experimental results in the same degree for these compounds. But in fact, only the results for PrF_3 and NdF_3 are in agreement with experiments. It has been found that the valence of the Ce ions in many Ce-based compounds, e.g., $CePd_3$, $CeAl_2$,[4] CeRhIn,[5] $CeSn_3$, $CeBe_3$, $CePb_3$,[6] $CeRhB_2$,[7] CePtSi,[8] is unstable. But to our knowledge, no mixed-valent Nd-based compound has been found up to now, and only very few Pr-based compounds have such behavior. We think that the disagreement of the calculated and measured V and χ of CeF_3 may be canceled by taking the mixed-valent behavior of the Ce ions into account. Such calculation has been carried out and the results are in agreement with experiment.

II. THEORETICAL CALCULATION OF VERDET CONSTANT AND SUSCEPTIBILITY

The contribution of the electric dipole transitions to the FR per unit length is[1]

$$\theta_F=\frac{N\pi e^2}{9\hbar c}\cdot\frac{(\bar{n}^2+2)^2}{\bar{n}}\times\sum_{g,n}\frac{\omega^2}{\omega_{ng}^2-\omega^2}\{|\langle n|V_-|g\rangle|^2-|\langle n|V_+|g\rangle|^2\}\rho_g \tag{1}$$

for each type of ion present in the material, where N is the number of ions per unit volume, $\bar{n}$ the average refractive index of the material, $|g\rangle$ a set of ground states with energy E_g, $|n\rangle$ excited states with energy E_n, ω the angular frequency of the light wave, $\hbar\omega_{ng}=E_n-E_g$, $eV_\pm$ the electric dipole moment operators for right- and left-hand circularly polarized light,

$$eV_\pm=\sum_i e(x(i)\pm jy(i)) , \tag{2}$$

where $\sum_i$ indicates summing over the electric dipole moments of all $4f$ electrons. ρ_g is the occupation probability of the state $|g\rangle$,

$$\rho_g=e^{-E_g/kT}\Big/\left[\sum_g e^{-E_g/kT}\right]=\rho_0 e^{-E_g/kT} . \tag{3}$$

In Eqs. (1) and (3), $\sum_g\sum_n$ indicate summing over the ground states and excited states, respectively. The Verdet constant V is given by

$$V=\frac{\theta_F}{H} , \tag{4}$$

where H is the applied magnetic field.

As mentioned above, in the visible region, the Faraday effect is mainly caused by the intraionic electric dipole transition. So it is necessary to calculate the CF energy levels and corresponding wave functions. The perturbation Hamiltonian of a RE ion in crystals is

$$H'=V_c+\lambda\mathbf{L}\cdot\mathbf{S}+\mu_B(L_z+2S_z)H , \tag{5}$$

where $\lambda\mathbf{L}\cdot\mathbf{S}$ is the spin-orbit coupling, the third term in the right hand is the Zeeman energy, the magnetic field H is supposed to be along the z axis, i.e., the c axis of the fluoride crystals, μ_B is a Bohr magneton, and V_c is the CF energy,

$$V_c=\sum_k\sum_i B_{k,0}C_0^k(i)+\sum_{k,q\neq0}\sum_i B_{kq}[C_{-q}^k(i)+C_q^k(i)] , \tag{6}$$

where B_{kq}'s are CF parameters,

$$C_q^k=\left[\frac{4\pi}{2k+1}\right]^{1/2}Y_{kq} ,$$

Y_{kq}'s are spherical harmonics, and $\sum_i$ indicates summing over the CF energy of all $4f$ electrons. The trifluorides RF_3 have LaF_3 structure, the RE ions are at $2c$ sites.[9] The parameters B_{kq} were calculated by using a point-charge model. The contributions of 23 neighboring F^- ions and 12 neighboring RE^{3+} ions are included in calculating B_{kq}. The values of $\langle r^2\rangle$ $\langle r^4\rangle$, and $\langle r^6\rangle$ of the $4f$ functions of the Pr^{3+} and Nd^{3+} ions have been taken from the paper by Freeman and Watson[10] and from the paper by Starostin for Ce^{3+} ions.[11] The values of nonzero CF parameters are shown in Table I. In the work of Leycuras and Le Gall, the magnetic field used is 20 kOe, so the Zeeman energy is much less than the spin-orbit coupling and CF energy. Therefore, we carried out the perturbation calculations in the order of priorities: $V_c+\lambda L\cdot S$ and $\mu_B(L_z+2S_z)H$. By solving the following secular equation:

$$\|\langle\varphi_i|\lambda L\cdot S+V_c|\varphi_j\rangle-E\delta_{ij}\|=0 , \tag{7}$$

the CF split energy levels $E_g^{(0)}$ and the corresponding wave functions are obtained. In calculating the splitting of the ground configuration, for the Ce^{3+} ion, ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets have been included; for the Pr^{3+} ion, ${}^3H_4$ has been included; for the Nd^{3+} ion, ${}^4I_{9/2}$ has been included. The energy levels obtained are shown in Table II. For the Kramers ions Ce^{3+} and Nd^{3+}, every level is a double degenerate. For the Pr^{3+} ion, multiplet ${}^3H_4$ is split into three singlets and three doublets. The lowest level is a singlet, its wave function is

$$|L=5 ,S=1 ,J=4 ,M_j=0\rangle .$$

The Zeeman Hamiltonian is too small to admix this state with other states. This fact is very important. This state has almost no contribution to the FR or susceptibility.

TABLE I. The parameters of the CF upon RE ions in RE_3 (expressed in cm^{-1}).

Ion and state	B_{20}	B_{40}	B_{60}	B_{66}
Ce^{3+} $(4f)$	−231.2	772.5	224.5	196.1
Ce^{3+} $(5d)$	−1111	12 343		
Pr^{3+} $(4f)$	−225.8	723.5	234.0	206.8
Nd^{3+} $(4f)$	−210.2	631.6	192.1	171.2

TABLE II. The CF energy levels of RE ions in RF_3 (expressed in cm^{-1}).

ion $E(nl)$	$E(cm^{-1})$						
$Ce^{3+}E_g^{(0)}$ $(4f)$	−1413	−1271	−1192	861.3	880.0	1018	1116
$Ce^{3+}E_n$ $(5d)$	46 614	47 418	50 187	51 760	53 296		
$Pr^{3+}E_g^{(0)}$ $(4f)$	−141.7	−75.07	3.738	51.01	60.96	111.4	
$Nd^{3+}E_g^{(0)}$ $(4f)$	−46.16	−32.56	−6.059	−2.921	87.70		

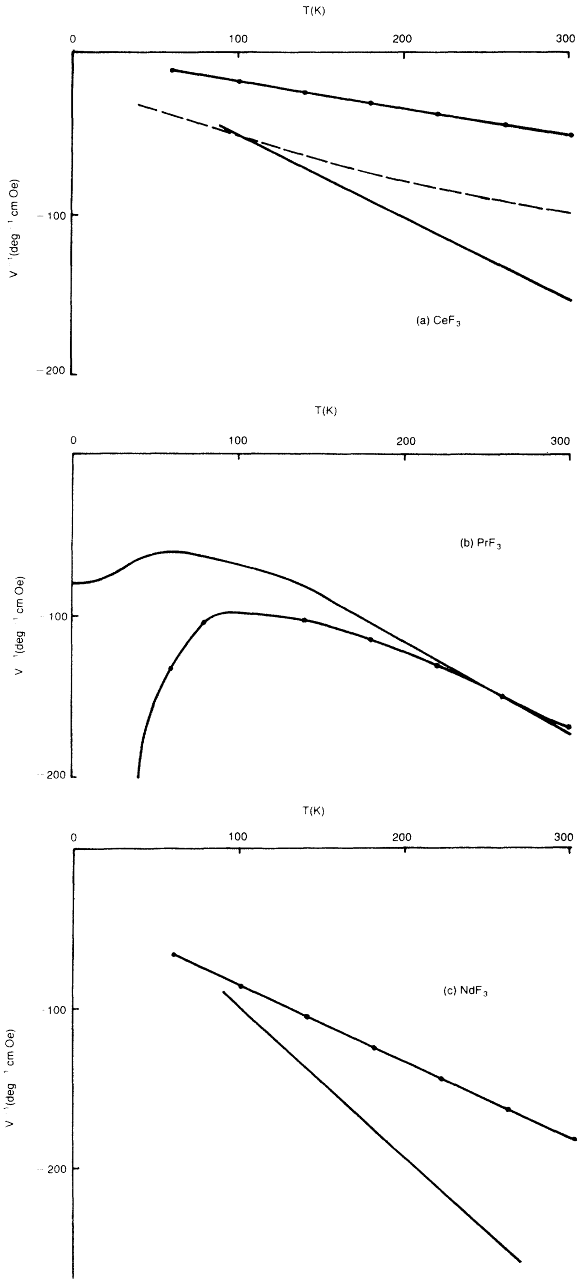

FIG. 1. Inverses of the Verdet constant of CeF_3, PrF_3, and NdF_3 vs temperature at 0.6328-μm wavelength (V is expressed in deg $cm^{-1} Oe^{-1}$). —·—·—· calculated values, —— measured values, — — — calculated values obtained by taking the mixed-valent behavior of the Ce ions into account. (a) CeF_3, (b) PrF_3, and (c) NdF_3.

When the temperature approaches 0 K, nearly all Pr^{3+} ions are in this state. Therefore, the Verdet constant V and susceptibility χ of the PrF_3 crystal are very small at very low temperature. As temperature increases, they increase and after reaching a maximum then decrease, while V and χ of CeF_3 and NdF_3 approach infinity at very low temperature.

The Zeeman Hamiltonian splits the CF double levels into sublevels. To a first approximation, the perturbation energy induced by the Zeeman Hamiltonian can be expressed as

$$E_g^{(1)}=\mu_B H\langle g|(L_z+2S_z)|g\rangle \ . \tag{8}$$

The magnitude of $E_g^{(1)}$ is about 1 cm^{-1} if the magnetic intensity is 20 kOe. For T higher than about 30 K, the occupation probability ρ_g in Eq. (3) can be reduced to

$$\begin{aligned}\rho_g&=\rho_0 e^{-(E_g^{(0)}+E_g^{(1)})/kT}\\&=\rho_0 e^{-E_g^{(0)}/kT}\left[1-\frac{\mu_B H}{kT}\langle g|(L_z+2S_z)|g\rangle\right] \ .\end{aligned} \tag{9}$$

As for the excited states, only the lowest parity allowed configuration $4f^{n-1}5d$ has been included in the calculation. For the Ce^{3+} ion, the splitting of the $5d$ state in the CF has been calculated and the difference between the average energy of the $5d$ states and $4f$ states has been taken to be $E_{5d}-E_{4f}=49\,855$ cm^{-1}.[11] The values of $\langle r^2\rangle$ and $\langle r^4\rangle$ of the $5d$ wave function have also been taken from Ref. 11. For the Pr^{3+} ion, the term energy of the $4f5d$ configuration has been taken from the book by Martin, Zalubas, and Hagan.[12] But the splitting of these terms caused by CF is neglected. For the Nd^{3+} ion, the accurate values of the term energy of the $4f^25d$ configuration are not found. According to the works of Diek and Crosswhite[13] and Kramer and Boyd,[14] we have taken the average energy of the $4f^25d$ configuration as 70 000 cm^{-1}, taking the average energy of the ground configuration as zero. The value of $\langle r\rangle_{4f5d}$ of the Ce^{3+} ion has been taken from Starostin's paper,[11] the value of $\langle r\rangle_{4f5d}$ of the Pr^{3+} ion from Sinha's work.[15] The value of $\langle r\rangle_{4f5d}$ of the Nd^{3+} ion has been estimated from the corresponding values of the Pr^{3+} and Ce^{3+} ion, and has been taken to be 0.377 Å.

The following formula has been used to calculate transitional matrix elements:[16]

$$
\begin{aligned}
&\langle l_1^n \alpha LSJM_J | r^k Y_{kq} | l_1^{n-1} l_2(\alpha' L_1 S_1 l_2) L'S'J'M_J' \rangle \\
&\quad = (-)^{J+J'+L_1+S+l_1+l_2-M_J} \\
&\quad \times \delta_{SS'} \left[\frac{n}{4\pi} [J,J',L,L',l_1,l_2,k] \right]^{1/2} \\
&\quad \times \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & S & J \\ J' & k & L' \end{Bmatrix} \begin{Bmatrix} l_1 & L_1 & L \\ L & k & l_2 \end{Bmatrix} \\
&\quad \times \langle l_1^n \alpha LS \{ | l_1^{n-1} \alpha' S_1 L_1 \rangle \langle l_1 \| r^k \| l_2 \rangle , \qquad (10)
\end{aligned}
$$

where $[J]=2J+1$.

The average magnetic moment of a RE ion is

$$\bar{m} = -\mu_B \sum_g \langle g | (L_z + 2S_z) | g \rangle \rho_g . \qquad (11)$$

Substituting Eq. (9) into Eq. (11), we have the following formula for the susceptibility of RF_3 compounds:

$$\chi = \frac{N\rho_0 \mu_B^2}{kT} \sum_g | \langle g | (L_z + 2S_z) | g \rangle |^2 e^{-E_g^{(0)}/kT} . \qquad (12)$$

Using Eqs. (1) and (12), we have calculated the inverses of the Verdet constant and susceptibility for CeF_3, PrF_3, and NdF_3 in the temperature range 40–300 K. Only a small improvement has been obtained by taking the $4f^2$ $^3H_5$ (for the Pr^{3+} ion) and $4f^3$ $^4I_{11/2}$ (for the Nd^{3+} ion) multiplets into account. The inverses of the Verdet constants of these trifluorides are shown in Fig. 1. The inverses of the susceptibility of them are shown in Fig. 2. The measured values obtained by Leycuras and Le Gall[2] are also shown in these figures for comparison. In cases of PrF_3 and NdF_3, the values improved by taking $^3H_5$ or $^4I_{11/2}$ multiplets into account are given in these figures. It is seen that the calculated results are in agreement with experiments for PrF_3 and NdF_3, but there is a large difference for CeF_3. As mentioned above, this problem can be explained by the mixed-valent behavior of the Ce ions in CeF_3.

III. THE MIXED-VALENT BEHAVIOR OF CeF_3

According to the ionic two-level interconfiguration fluctuation model suggested by Sales and Wohlleben,[17] the susceptibility is given by the following equation:

$$\chi(T) = \frac{N[\mu_n^2 \rho_n(T) + \mu_{n-1}^2(1-\rho_n(T))]}{3k(T+T_{sf})} , \qquad (13)$$

where N is the number of the RE ions per unit volume, n is the number of $4f$ electrons per RE ion, μ_n and μ_{n-1} are the effective Hund's-rule magnetic moments in the two configurations, T_{sf} is the spin-fluctuation temperature, and $\rho_n(T)$ is the fractional occupation of the $4f^n$ configuration. $\rho_n(T)$ is given by the following equation:

$$\rho_n(T) = \frac{2J_n+1}{(2J_n+1)+(2J_{n-1}+1)e^{-E_{ex}/kT}} , \qquad (14)$$

where $2J_n+1$ and $2J_{n-1}+1$ are the degeneracies of the

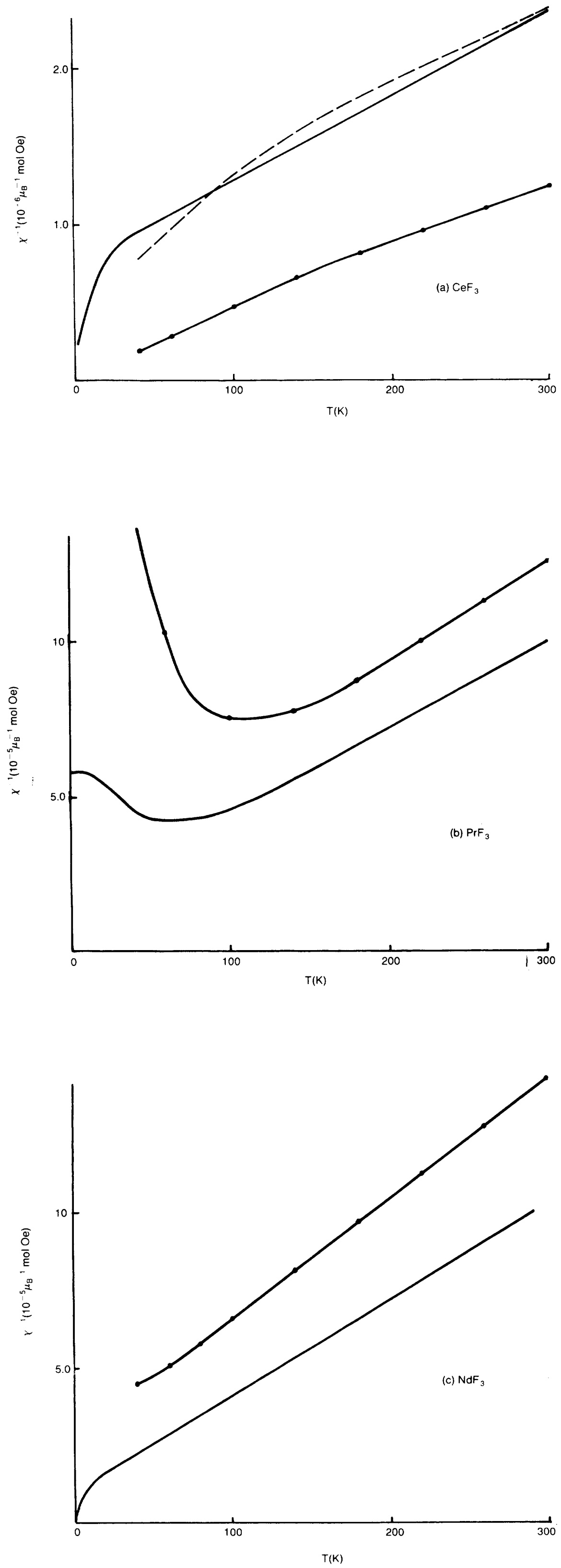

FIG. 2. Inverses of the magnetic susceptibility of CeF_3, PrF_3, and NdF_3 vs temperature (χ is expressed in μ_B mol^{-1}Oe^{-1}). —·—·— calculated values, —— measured values, — — — calculated values obtained by taking the mixed-valent behavior of the Ce ions into account. (a) CeF_3, (b) PrF_3, and (c) NdF_3.

two configurations $4f^n$ and $4f^{n-1}$, and E_{ex} is the interconfiguration excited energy $E_{\text{ex}}=E(4f^{n-1})-E(4f^n)$. $E(4f^{n-1})$ and $E(4f^n)$ are the average energy of the $4f^{n-1}$ and $4f^n$ configurations. Here it is supposed that E_{ex} is very small compared to all multiplet splittings so that only the Hund's-rule ground state of each configuration needs to be taken into account. Note that in this model the fractional occupation numbers $\rho(T)$ do not contain T_{sf} (see also Buschow's paper[6]).

The CF effect is not included in Eq. (13), but in our calculation the CF effect must be included, so we have

$$\chi(T)=\frac{N\mu_B^2}{k(T+T_{\text{sf}})}\sum_g |\langle g|(L_z+2S_z)|g\rangle|^2\rho_0 e^{-E_g^{(0)}/kT} . \tag{15}$$

For the Faraday rotation, similar reform should be done. The reformed equation is

$$\theta_F=\frac{N\pi e^2}{9\hbar c}\,\frac{(\bar{n}^2+2)^2}{\bar{n}}\,\frac{\mu_B H}{k(T+T_{\text{sf}})}\times\sum_{g,n} M_{ng}\langle g|(L_z+2S_z)|g\rangle\rho_0 e^{-E_g^{(0)}/kT} , \tag{16}$$

where

$$M_{ng}=\frac{\omega^2}{\omega_{ng}^2-\omega^2}[|\langle n|V_-|g\rangle|^2-|\langle n|V_+|g\rangle|^2] . \tag{17}$$

It should be noticed that in Eqs. (15) and (16), g should run over ground states of two configurations. The electron configuration of Ce^{4+} is $4f^0$, the moment of Ce^{4+} is zero. Hence, for CeF_3, g can run only over the states of $4f^1$ configuration; but being different from Eq. (3), now ρ_0 should be

$$\rho_0=\frac{1}{\sum_g e^{-E_g/kT}+e^{-E_{\text{ex}}/kT}} . \tag{18}$$

The value of T_{sf} can be determined by the intercept of the extension of the linear part of the measured $\chi^{-1}\sim T$ curve with T axis. It is 120 K for CeF_3. It is very difficult to calculate theoretically the value of E_{ex} now. It is usually obtained by fitting the measured data. The signs of E_{ex} are different for different compounds and even in a certain compound it can be different when the compound is under different pressure. The magnitude of E_{ex} can be smaller than the energy differences between the CF energy levels.[4] In our calculations, the energy of the Ce^{4+} has been taken to be $-1330\ \text{cm}^{-1}$, taking the average energy of Ce^{3+} ions as zero.

The inverses of the Verdet constant and susceptibility of CeF_3 calculated by using Eqs. (15) and (16) are given, respectively, in Figs. 1(a) and 2(a) (dashed curves). They are in agreement with experiment.

IV. DISCUSSION

In this paper, the Verdet constant at 0.6328-μm wavelength and the magnetic susceptibility of CeF_3, PrF_3, and NdF_3 in the temperature range 40–300 K have been calculated based on the quantum theory. If the mixed-valent behavior of the Ce ions in CeF_3 is taken into account, the results are in agreement with experiments for all these trifluorides. Although the calculated curves do not coincide with the measured curves very well, all main features of the FR and susceptibility of these fluorides are explained well. If it is noticed that in the calculation only the value of the interconfiguration excited energy E_{ex} is adjustable, the results can be regarded as good. We think that the difference between the calculated and measured results is caused mainly by the lack of inclusion of magnetic dipole transitions, which are important in the lanthanide $4f$ manifold. As mentioned above, for the PrF_3 crystal, the CF ground state is a singlet, so χ and V would approach zero when temperature T approaches 0 K. But the measured values of χ and V are nonzero at 0 K. We think that they are caused mainly by the magnetic dipole transitions. In CeF_3 and NdF_3, the contribution of this minor origin is covered by the contribution of the main origin. The calculated results can be improved by taking this minor origin into account. As an example, let us consider the verdet constant and susceptibility of PrF_3. The measured value of V^{-1} and χ^{-1} at 0 K are -80 $\text{deg}^{-1}\,\text{cm}\,\text{Oe}$ and $6\times10^5\ \mu_B^{-1}\,\text{mol}\,\text{Oe}$, respectively. The contribution of this minor origin may depend on temperature, but they must have the same sign as at 0 K. So the theoretical curves will move toward the measured curves if the contributions of this minor origin are included. Furthermore, the point-charge model is not a very good approximation. The shielding effect on the $4f$ wave function from the environment by the outer filled $6s$, $5d$ shells and some other causes will change the CF. The calculated results may be improved further by taking these factors into account.

The odd-parity CF are nonzero for the RE ions in RF_3 compounds. So there exist V_{odd}-induced transitions between the $4f^n$ ground states (expressed as $4f_g^n$) and $4f^n$ excited states (expressed as $4f_{\text{ex}}^n$). The matrix elements of these transitions can be expressed as

$$\frac{1}{(E_{4f^{n-1}5d}-E_{4f_{\text{ex}}^n})}\times\langle 4f_{\text{ex}}^n|V_{\text{odd}}|4f^{n-1}5d\rangle\langle 4f^{n-1}5d|V_{\pm}|4f_g^n\rangle .$$

There are many such second-order processes for the RE ions. But according to our estimate, the total contribution of such processes is less than one percent of the contribution of the first-order processes, so it can be neglected.

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