Faraday Rotation of Rare-Earth Ions. I. Theory*

Y. R. SHEN
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts
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A general expression for the complex Faraday rotation is obtained by generalizing the Kramers-Heisenberg dispersion formula. It shows that the pure rotation is proportional to the sum of circular dichroism in in all resonance transitions weighted by the appropriate resonance-dispersion factors. The cases of free ions and rare-earth ions in solids are discussed. It is shown how Gd^{3+} and Eu^{2+}, having the same electronic structure, may possess very different rotatory powers in a given frequency range through the difference in their optical spectra. The formula for the anomalous rotatory dispersion about sharp lines is also given.

I. INTRODUCTION

THE most concise expression for the Faraday rotation in the absence of damping is the one given by Kramers.[1] When the Lorentz-Lorenz correction[2] is incorporated, his result has the form

$$\phi=[2\pi\omega(\langle n\rangle^2+2)^2/9\langle n\rangle c](\chi_--\chi_+)\,, \tag{1}$$

where ϕ is the angle of rotation per unit length, $\langle n\rangle$ is the average index of refraction, and $\chi_\pm$ are the electric susceptibilities for the right and left circularly polarized waves. For a system of N atoms per unit volume, $\chi_\pm$ are given by the Kramers-Heisenberg dispersion relation[3]

$$\chi_\pm=N\sum_{a,b}[(\rho_b{}^0-\rho_a{}^0)/\hbar(\omega_{ab}-\omega)]\langle a|er_\pm|b\rangle\langle b|er_\mp|a\rangle\,,$$
$$r_\pm=x\pm iy\,, \tag{2}$$

$\rho_i{}^0$ being the Boltzmann factor.

The rotation arises as a result of the difference between χ_- and χ_+ induced by the steady magnetic field, which lifts the degeneracy of the resonance frequencies, redistributes the populations among the ground levels, and changes the matrix elements.

Equations (1) and (2) show that the rotation is connected only to electric-dipole transitions in the medium. But from the general point of view, we should expect to find contributions to the rotation from all types of transitions. An obvious example is the microwave Faraday rotation in ferrites. Here, the rotation is mainly due to magnetic-dipole transitions between the ground states. Hougen[4] has also considered the effect of magnetic-dipole transitions in order to explain the observed rotatory dispersion in oxygen. It seems desirable, therefore, to generalize the Kramers formula for the rotation to include all types of transitions.

In the following section, such a general formula is obtained by generalizing the Kramers-Heisenberg dispersion formula [Eq. (2)]. The density matrix method is used for the derivation and the effect of damping is included. The rotation is proportional to the sum of circular dichroism in all transitions weighted by the appropriate resonance-dispersion frequency factors.

The applications of this formula to rare-earth ions in crystals are discussed in the remainder of the paper. Special emphasis is given to situations far away from or very near to optical absorption lines and to the S-state ions Eu^{2+} and Gd^{3+} in sites of cubic symmetry.

II. GENERAL EXPRESSION FOR THE FARADAY ROTATION

The field potentials $\mathbf{A}$ and ϕ obey the wave equations

$$\left(\nabla^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\begin{pmatrix}\mathbf{A}\\ \phi\end{pmatrix}=-\frac{4\pi}{c}\left\langle\begin{matrix}\mathbf{j}(\mathbf{r},t)\\ cq(\mathbf{r},t)\end{matrix}\right\rangle. \tag{3}$$

The current density $\langle\mathbf{j}(\mathbf{r},t)\rangle$ is usually written in terms of multipole moments,

$$\langle\mathbf{j}(\mathbf{r},t)\rangle=\mathbf{j}_{\text{cond}}+\frac{\partial}{\partial t}\langle\mathbf{P}\rangle+c\nabla\times\langle\mathbf{M}\rangle-\frac{\partial}{\partial t}\nabla\cdot\langle\mathbf{Q}\rangle+\cdots. \tag{4}$$

The Kramers formula, Eq. (1), was derived under the assumption that $\langle\mathbf{P}\rangle$ is the only nonzero component in Eq. (4) However, in general, we must take all the components into consideration. In fact, the expansion in Eq. (4) is meaningless if the wavelength of the propagating waves is small compared with the dimension of the medium.[5] It is more appropriate to treat the current density as a single quantity.

In the presence of classical radiation fields, the nonrelativistic Hamiltonian of the atomic system is $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{\text{int}}$.

$$\mathcal{H}_0=(1/2m)\mathbf{\Pi}^2+V(\mathbf{r})\,,\quad \mathcal{H}_0|a\rangle=E_a|a\rangle$$
$$\mathcal{H}_{\text{int}}=(e/2mc)(\mathbf{\Pi}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{\Pi})+(e\hbar/mc)\mathbf{S}\cdot\nabla\times\mathbf{A}$$
$$+(e^2/2mc^2)\mathbf{A}\cdot\mathbf{A}+e\phi\,, \tag{5}$$
$$\mathbf{\Pi}=\mathbf{p}+(e/c)\mathbf{A}_0\,,$$

$\mathbf{A}_0$ being the vector potential for the dc magnetic field and $V(\mathbf{r})$ the electrostatic field.

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[2] H. A. Lorentz, Wiedem Ann. **9**, 641 (1880); L. Lorenz, Wiedem Ann. **11**, 70 (1881).

[3] H. A. Kramers and W. Heisenberg, Z. Physik **31**, 681 (1925); M. Born, W. Heisenberg, and P. Jordan, Z. Physik, **35**, 570 (1926).

[4] J. T. Hougen, J. Chem. Phys. **32**, 1122 (1960); dissertation, Harvard University, 1960 (unpublished).

[5] L. D. Landau and E. M. Lifshitz, *Electrodynamics in Continuous Media* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959), p. 252.

The corresponding current and charge density operators are[6]

$$\mathbf{j}(\mathbf{r}_0,t)=-\frac{e}{2mc}\left\{\left[\delta(\mathbf{r}-\mathbf{r}_0)\left(\mathbf{\Pi}+\frac{e}{c}\mathbf{A}\right)+\left(\mathbf{\Pi}+\frac{e}{c}\mathbf{A}\right)\delta(\mathbf{r}-\mathbf{r}_0)\right]\right.$$
$$\left.+2i[\delta(\mathbf{r}-\mathbf{r}_0)(\mathbf{p}\times\mathbf{s})-(\mathbf{p}\times\mathbf{s})\delta(\mathbf{r}-\mathbf{r}_0)]\right\}, \quad (6)$$
$$q(\mathbf{r}_0,t)=-e\delta(\mathbf{r}-\mathbf{r}_0)$$

with the statistical averages given by[7]

$$\left\langle\begin{matrix}j\\q\end{matrix}\right\rangle=\sum_{a,b}\left(\begin{matrix}j\\q\end{matrix}\right)_{ab}\rho_{ba}, \quad (7)$$

The density matrix operator ρ obeys the equation of motion

$$\frac{\partial}{\partial t}\rho=\frac{1}{i\hbar}[\mathcal{H}_0+\mathcal{H}_{\text{int}},\rho]+\left(\frac{\partial}{\partial t}\rho\right)_{\text{damping}}. \quad (8)$$

We shall assume that the system relaxes to time-independent thermal equilibrium, and the off-diagonal density matrix has a damping term[8]

$$[(\partial/\partial t)\rho_{ab}]_{\text{damping}}=-\tfrac{1}{2}\Gamma_{ab}\rho_{ab}. \quad (9)$$

These assumptions are well met for dilute spin systems in the optical frequency range.[9]

Equations (3), (6), (7), and (8) should be solved simultaneously. However, for weak interaction, the waves can be approximated as free waves with $\phi=0$ and $\nabla\cdot\mathbf{A}=0$ in calculating the current density. A monochromatic incoming wave is represented by

$$\mathbf{A}=(c/i\omega)\mathbf{E}(\mathbf{k},\omega)\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]. \quad (10)$$

Then, the Fourier components of the current density operator in the k space, defined as $\mathbf{j}(\mathbf{k}',t)=\int d^3r\times\exp(-i\mathbf{k}'\cdot\mathbf{r})\mathbf{j}(\mathbf{r},t)$, has the matrix elements

$$(\mathbf{j}(\mathbf{k}',t)_{ab}$$
$$=(-e/m)\langle a|\exp(-i\mathbf{k}'\cdot\mathbf{r})\left(\mathbf{\Pi}+\frac{e}{c}\mathbf{A}-i\hbar\mathbf{s}\times\mathbf{k}'\right)|b\rangle \quad (11)$$
$$\equiv(\mathbf{j}_0(\mathbf{k}'))_{ab}+(\mathbf{j}_1(\mathbf{k}',\omega))_{ab}e^{-i\omega t}, \quad (12)$$

where, in general, $|\mathbf{j}_1(\mathbf{k},\omega)|\ll|\mathbf{j}_0(\mathbf{k})|$.

By iteration, the steady-state solution of Eq. (8) for the density matrix can be expanded into a Fourier series in the frequency space. Consequently, $\langle\mathbf{j}(\mathbf{k}',t)\rangle$ can also be written as a Fourier series. We shall, for the present, be interested only in the linear response, $\langle j(\mathbf{k},\omega)\rangle$, to the incoming radiation given by (10); the nonlinear response is treated elsewhere.[9] We then find

$$\langle\mathbf{j}(\mathbf{k},\omega)\rangle=\left\{\sum_{a,b}\frac{(\rho_b{}^0-\rho_a{}^0)}{\hbar(\omega_{ab}-\omega-i\frac{1}{2}\Gamma_{ab})}\right.$$
$$\times\langle b|\frac{e}{m}\exp(-i\mathbf{k}\cdot\mathbf{r})(\mathbf{\Pi}-i\hbar\mathbf{s}\times\mathbf{k})|a\rangle$$
$$\left.\times\langle a|\frac{e}{im\omega}(\mathbf{\Pi}+i\hbar\mathbf{s}\times\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r})|b\rangle+\frac{Ne^2}{im\omega}\right\}$$
$$\cdot\mathbf{E}(\mathbf{k},\omega). \quad (13)$$

The linear conductivity tensor for N atomic systems per unit volume is defined as

$$\boldsymbol{\sigma}(\mathbf{k},\omega)=N\langle\mathbf{j}(\mathbf{k},\omega)\rangle/E(\mathbf{k},\omega). \quad (14)$$

If we define a generalized electric polarization by $\langle\mathbf{P}'(\mathbf{k},\omega)\rangle=i\langle\mathbf{j}(\mathbf{k},\omega)\rangle/\omega$, the corresponding generalized electric susceptibility tensor is

$$\chi'(\mathbf{k},\omega)=i\boldsymbol{\sigma}(\mathbf{k},\omega)/\omega. \quad (15)$$

This susceptibility tensor is then put back into Eq. (1) to yield the general formula for the complex Faraday rotation.

$$\phi=\frac{\pi\omega e^2N(\langle n\rangle^2+2)^2}{mc9\langle n\rangle}\sum_{a,b}\left[\frac{(\omega+i\frac{1}{2}\Gamma_{ba})/\omega_{ba}}{(\omega_{ba}{}^2-\omega^2+\frac{1}{4}\Gamma_{ba}{}^2)-i\omega\Gamma_{ab}}\right]$$
$$\times(f_{ba}{}^+-f_{ba}{}^-), \quad (16)$$

where $f_{ab}{}^\pm$ are the oscillator strengths of the transitions $\langle b|$ to $\langle a|$ for the two circular waves.

$$f_{ba}{}^\pm=(2m\omega_{ba}/\hbar e^2)|\langle b|(e/m\omega)(\mathbf{\Pi}-i\hbar\mathbf{s}\times\mathbf{k})_\pm$$
$$\times\exp(-i\mathbf{k}\cdot\mathbf{r})|a\rangle|^2\rho_a{}^0. \quad (17)$$

It is easy to see that the pure rotation (the real part of ϕ) is proportional to the sum of circular dichroism in all transitions weighted by the resonance-dispersion frequency factors. If the factor $\exp(-i\mathbf{k}\cdot\mathbf{r})$ in Eq. (18) is expanded into a power series of $\mathbf{k}\cdot\mathbf{r}$, we should find,

$$f_{ba}{}^\pm=(2m\omega_{ba}/\hbar e^2)|\langle b|(e/m\omega)\{im\omega_{ba}r_\pm-\tfrac{1}{2}m\omega_{ba}(i\mathbf{k}\cdot\mathbf{r})$$
$$-\tfrac{1}{2}i\hbar[(l+2\mathbf{s})\times\mathbf{k}]_\pm+\cdots\}|a\rangle|^2\rho_a{}^0. \quad (18)$$

Here, the electric-dipole, electric-quadrupole, and magnetic-dipole terms have been written out explicitly. Equation (16) is generally valid for all cases. In the case of semiconductors, the summation over states should be replaced by an integration over bands, and the Boltzmann distribution by the Fermi distribution. In this paper, we are mainly interested in rare-earth ions.

III. FREE IONS AND RARE-EARTH IONS IN SOLIDS

In the free-ion case, the electric-dipole transitions are only allowed between states in different electronic

[6] See, for example, A. Messiah, *Quantum Mechanics* (Interscience Publishers, Inc., New York, 1961).
[7] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).
[8] See, for example, A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961).
[9] N. Bloembergen and Y. R. Shen, Phys. Rev. Phys. Rev. **133**, A37 (1964).

configurations, whereas the magnetic-dipole and electric-quadrupole transitions are allowed between states in the same configuration. The latter type of transitions have much smaller oscillator strengths than the former, and in most cases, will contribute to the optical rotation only when the frequency is close to resonance for these transitions. Therefore, at frequencies far away from resonance, the rotation is determined by the electric-dipole transitions to a good approximation. Then, Eq. (17) reduces to the Kramers formula.

The Faraday rotation depends to a large extent on the populations in the ground states. We can always write

$$\phi=\sum_{a,b}\sum_{\mu_a,\mu_b>0}\{A_{a\mu_a-b\mu_b}(\rho_{a\mu_a}{}^0-\rho_{a-\mu_a}{}^0)+B_{a\mu_a-b\mu_b}(\rho_{a\mu_a}{}^0+\rho_{a-\mu_a}{}^0)\}\,, \quad (19)$$

μ being the magnetic quantum number. The two terms in the bracket may be classified as the paramagnetic and the diamagnetic rotations, respectively.

For small magnetic perturbation on the J multiplet of a free ion, the states can be written as

$$\langle a|=\langle\gamma,J,m|+\sum_{J_1\neq J}\sum_{m_1}\frac{\langle\gamma,J,m|\beta\mathbf{H}\cdot\mathbf{S}|\gamma,J_1,m_1\rangle}{\hbar\omega_{\gamma J-\gamma J_1}}\times\langle\gamma,J_1,m_1|\,, \quad (20)$$

$$\langle b|=\langle\gamma',J',m'|+\sum_{J_2\neq J'}\sum_{m_2}\frac{\langle\gamma',J',m'|\beta\mathbf{H}\cdot\mathbf{S}|\gamma',J_2,m_2\rangle}{\hbar\omega_{\gamma' J'-\gamma' J_2}}\times\langle\gamma',J_2,m_2|\,,$$

and the resonance frequencies are given by (Fig. 1)

$$\omega_{\gamma' J' m'-\gamma J m}=\omega_{\gamma' J'-\gamma J}+\Delta\omega_{m' m}\,,$$
$$\Delta\omega_{m' m}=-\Delta\omega_{-m'-m}=(-m'g_{J'}+mg_J)\beta H\,. \quad (21)$$

For $|\Delta\omega_{m' m}|\ll\omega_{\gamma' J'-\gamma J}$, we have

$$\frac{(\omega_{\gamma' J' m'-\gamma J m})^2}{(\omega_{\gamma' J' m'-\gamma J m})^2-\omega^2}\cong\frac{(\omega_{\gamma' J'-\gamma J})^2}{(\omega_{\gamma' J'-\gamma J})^2-\omega^2}\times[1+O(\Delta\omega_{m' m})]\,. \quad (22)$$

If the Zeeman perturbation in Eqs. (20) and (22) is neglected, we then find[10,11]

$$\phi\equiv\phi_P=\sum_{\gamma,\gamma',J,J'}A(\gamma,J;\gamma',J')\sum_m m\rho_{\gamma J m}{}^0\,, \quad (23)$$

which is the paramagnetic rotation. It is strictly proportional to the magnetization if only the ground J multiplet is occupied.

The Zeeman perturbation on the states and on the frequencies[12] together gives a diamagnetic rotation

$$\Delta\phi\equiv\phi_D=\sum_{\substack{\gamma,J,m\\ \gamma',J',m'}}B(\gamma,J,m;\gamma',J',m')\times H(\rho_{\gamma J m}{}^0+\rho_{\gamma,J,-m}{}^0)\,. \quad (24)$$

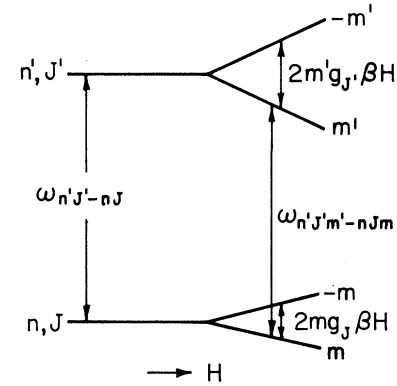

FIG. 1. Resonance frequencies of a free ion with small magnetic perturbation.

For rare-earth ions in solids, the states in the ground $(4f)^n$ configuration are only slightly perturbed by a crystal field of even symmetry. The magnetic degeneracy of the J states is being partially lifted, but the mixing between different J multiplets is small, so that γ and J are still good quantum numbers. The states can be written as

$$\langle\gamma,J,\mu|+\sum_{\gamma',J'\neq J}\sum_{\mu'}\frac{\langle\gamma,J,\mu|(V^e+\beta\mathbf{H}\cdot\mathbf{S})|\gamma',J',\mu'\rangle}{\hbar\omega_{\gamma J-\gamma' J'}}\times\langle\gamma',J',\mu'|\,, \quad (25)$$

μ being the symmetric quantum number.[13]

The effect of the crystal field on the excited configurations, $(4f)^{n-1}(5d)$, etc., is presumably strong, and in general, J is no longer a good quantum number. However, it is very likely that the quantum numbers L and S are not badly spoiled. These excited states can then be represented by $\langle\gamma',\zeta',\mu'|$. Let us write

$$\omega_{\gamma'\zeta'\mu'-\gamma J\mu}=\langle\omega_{\gamma'-\gamma J}\rangle+\Delta\omega_{\zeta'\mu'-\mu}\,, \quad (26)$$

where $\langle\omega_{\gamma'-\gamma J}\rangle$ is the average separation between the ζ' multiplets and the ground J multiplet. Under the condition

$$|\Delta\omega_{\zeta'\mu'-\mu}|\ll|\langle\omega_{\gamma'-\gamma J}\rangle-\omega|\,, \quad (27)$$

we can expand the frequency factors in the Kramers formula into a power series of $\Delta\omega_{\zeta'\mu'-\mu}$. In the zeroth-order approximation, we take only the term independent of $\Delta\omega_{\zeta'\mu'-\mu}$, and neglect the mixing of states among different J and ζ multiplets due to crystal field and Zeeman perturbations. The rotation reduces to the form of Eq. (23).[10] In the first-order approximation, the term linear in $\Delta\omega_{\zeta'\mu'-\mu}$ and the first-order mixing of states among different J and ζ multiplets are considered.

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[11] N. Bloembergen, P. S. Pershan, and L. R. Wilcox, Phys. Rev. **120**, 2014 (1960).
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A small diagmagnetic rotation then arises from the Zeeman perturbation and a small paramagnetic rotation from the crystal field perturbation.[14] For rare-earth ions in solids, electric-dipole transitions between states within the $(4f)^n$ configuration are no longer strictly forbidden because of the odd crystal-field perturbation and the electron-phonon interaction.[15] The oscillator strengths for these intraconfiguration transitions become somewhat larger than in the free-ion case. However, they are still much weaker than the electric-dipole transitions between states in different configurations, and their contribution to the rotation at frequencies far away from resonance can usually be neglected.

The above discussion applies very well to the case of trivalent rare-earth ions. For divalent rare-earth ions, the strong electric-dipole transitions appear in the visible, and the condition (27) is no longer satisfied at light frequencies. The optical rotation is often greatly enhanced through the resonance effect. In general, the principal paramagnetic rotation can no longer be proportional to the magnetization even if only the ground J multiplet is occupied. Nevertheless, Eu^{2+}, an S-state ion, turns out to be an exception, if it is situated at a cubic site.

IV. Eu^{2+} AT CUBIC SITES

For a free S-state ion, the allowed electric-dipole transitions are of the form $S_J \rightarrow P_{J-1}, P_J, P_{J+1}$. If the incident light frequency is far removed from all levels of the P_J multiplet,

$$|\Delta\omega_{J'm'-Jm}| \ll |\langle\omega_{\gamma'-\gamma}\rangle - \omega|\,, \tag{28}$$

$\langle\omega_{\gamma'-\gamma}\rangle = \omega_{\gamma'J'm'-\gamma Jm} - \Delta\omega_{J'm-Jm}$ being the average resonance frequency for the $S \rightarrow P$ transitions, then the rotation is nearly proportional to the orbital momentum $\langle L_z\rangle$, and hence vanishingly small for S-state ions.[16] This has been verified experimentally for[17] Gd^{3+} and[18] Mn^{2+}. The small residual paramagnetic rotation, however, is still proportional to the magnetization.

In solids, the Stark effect of the crystal field on the P_J levels is very small, if the S-state ion is at a cubic site.[19] Here, the cubic field can split the P term only in higher order perturbation through the interplay with the spin-orbit coupling, and the splittings are of the order of 10 cm^{-1}. The quantum number J, therefore, remains approximately valid.

When the light frequency is much closer to one of the P_J levels so that (28) is not satisfied, and, on the other hand, it is sufficiently removed from that P_J level so that

$$|\Delta\omega_{\mu'\mu}| \ll |\langle\omega_{\gamma'J'-\gamma J}\rangle - \omega|$$
$$\omega_{\gamma'J'\mu'-\gamma J\mu} = \langle\omega_{\gamma'J'-\gamma J}\rangle + \Delta\omega_{\mu'\mu}\,, \tag{29}$$

then the rotation of the S-state ion can be very large but still proportional to the magnetization. This happens in the case of $CaF_2:Eu^{2+}$ at visible frequencies. If in the ground states, the crystal-field and Zeeman splittings are small compared to kT, or the Zeeman splittings are much larger than the crystal-field splittings, the magnetization of Eu^{2+} is given by the Brillouin function $B_{J=7/2}(g\beta H/kT)$. The above discussion also applies to the case of Gd^{3+} at frequencies close to its uv absorption bands.

The experimental observation[20] of the existence of proportionality between rotation and magnetization in the case of $CaF_2:Eu^{2+}$ proves that the excited states in the strong transitions are of the P_J character. It also supports the conjecture of L and S being good quantum numbers in the excited configurations, $(4f)^6(5d)$, etc. Wood and Kaiser[21] suggested decoupling of the $(5d)$ electron from the $(4f)$ electrons for the $(4f)^{n-1}(5d)$ states in order to explain the observed spectrum of $CaF_2:Sm^{2+}$, but the spectrum can be explained equally well as arising from $F-D$ transitions.

V. ANOMALOUS ROTATORY DISPERSION ABOUT SHARP LINES

Owing to the resonance-dispersion effect, the rotation varies rapidly as the frequency is swept over an absorption line or lines. This is known as the anomalous rotatory dispersion.

Express the deviation of ω from the resonance frequency ω_0 in terms of the linewidth by introducing a dimensionless quantity α,

$$\omega = \omega_0 + \alpha\Gamma\,.$$

If $(\Gamma/2\omega_0) \ll |\alpha| \ll (2\omega_0/\Gamma)$, the anomalous rotation due to this particular absorption line is

$$\phi_A = \frac{\pi\omega e^2 N(\langle n\rangle^2+2)^2}{mc9\langle n\rangle}\frac{\omega_0\Gamma(-2\alpha+i)}{(2\alpha\omega_0\Gamma)^2+\omega^2\Gamma^2}(f^+-f^-)\,, \tag{30}$$

where f^+ and f^- are given by Eq. (17).

It is seen that the pure anomalous rotation, $\mathrm{Re}\,\phi_A$, has the typical S-shaped dispersion. In general, the observed spectral line does not have a Lorentzian shape. However, if the line can be approximated by a Lorentzian curve, we may still use Eq. (30) in an approximate sense. At $|\alpha| = \frac{1}{2}$, the pure anomalous rotation, $|\mathrm{Re}\phi_A|$, is a maximum.

$$|\mathrm{Re}\phi_A|_{\max} = \frac{\pi e^2 N}{mc\omega_0}\frac{(\langle n\rangle^2+2)^2}{9\langle n\rangle}\frac{\omega_0}{2\Gamma}(f^+-f^-)\,. \tag{31}$$

This shows that the maximum anomalous rotation is

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[18] J. Becquerel, W. J. de Haas, and J. van den Handel, Commun. Kamerlingh Onnes Lab. Univ., Leiden **218**; or Proc. Acad. Sci. Amsterdam **34**, 1231 (1931).
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[20] Y. R. Shen and N. Bloembergen, Phys. Rev. **133**, A515 (1964), following paper.
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proportional to the circular dichroism in the line and inversely proportional to the linewidth.

More generally, an absorption line (or group of lines) can be approximated by several Lorentzian curves. The anomalous rotation is obtained by summing over contributions from all the Lorentzian components.

VI. CONCLUSION

The generalization of the linear electric susceptibility leads to a general formula for the Faraday rotation which takes all multipole transitions into account. Under electric-dipole approximation, it reduces to the well-known Kramers formula. The S-state ion of Eu^{2+} is investigated. It is found that the rotation of Eu^{2+} which comes mainly from $S_J((4f)^7) \rightarrow P_{J'}[(4f)^6(5d)$, etc.] transitions, can be very large while still proportional to the magnetization. The anomalous rotatory dispersion about sharp lines can also be obtained directly from the general formula.

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Faraday Rotation of Rare-Earth Ions in CaF_2. II. Experiments*

Y. R. SHEN AND N. BLOEMBERGEN
Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts
(Received 17 June 1963)

The complex rotatory power of several rare-earth ions in the CaF_2 lattice has been observed. Measurements on anomalous rotatory dispersion and concomitant circular dichroism about some spectral lines in CaF_2:Nd^{3+} and CaF_2:Er^{3+} crystals agree well with the theory of the preceding paper. The rotatory power of Gd^{3+} in CaF_2 in the visible range is very small. By contrast, the rotation in (Eu^{2+}, Eu^{3+}) doped CaF_2 crystals is very large and stems from the Eu^{2+} ions. The rotatory dispersion measurements show that the strong absorption lines and bands of Eu^{2+} in the visible region are responsible for the large optical rotatory power of Eu^{2+}. Gd^{3+} and Eu^{2+} are isoelectronic in structure, but the difference in their optical spectra gives rise to a significant difference in their optical rotatory power. This assertion is supported by experimental observations.

I. INTRODUCTION

THE Faraday rotation in a Eu^{3+}-doped CaF_2 crystal has been measured by Chang and Burgess.[1] They found that the crystal possessed an appreciable rotatory power, and the rotation versus magnetic field curve appeared to have some saturation effect. Since the Eu impurities in the crystal were presumably all in the trivalent state, they ascribed the rotation to the trivalent Eu ions. The ground state of Eu^{3+} is, however, a singlet $^7F_0$ state, and the ion has zero paramagnetic rotation. Its diamagnetic rotation arises from the Zeeman perturbation on the resonance frequencies, and on the transition matrix elements. Therefore, the observed rotation should be small, independent of temperature, and have no saturation effect.

From many reports and our own experience in growing Eu-doped CaF_2 crystals, it became apparent that the Eu impurities in the CaF_2 lattice usually exist in both the trivalent and the divalent states. The ratio of the Eu^{3+} concentration to the Eu^{2+} concentration depends on the growing conditions, but can never be either zero or infinity. The rotation observed by Chang and Burgess might well have been caused by a residual portion of Eu^{2+} in the crystals. In this case, the Eu^{2+} ion must possess a very large rotatory power. Experiments reported in this paper confirm this. According to the theory,[2] Eu^{2+} may indeed have a large rotatory power in the visible range, although its structure is isoelectronic with Gd^{3+}.

The observed anomalous rotatory dispersions about sharp spectral lines of rare-earth ions in CaF_2 crystals agree very well with the theory.[2] Such anomalous rotations were observed in metal vapors at the end of the last century.[3] No quantitative result on anomalous rotatory dispersion in solids has been reported, although J. Becquerel made an early attempt on rare-earth salts.[4] There are of course numerous experiments on paramagnetic rotation in concentrated salts in nonabsorbing regions of the spectrum, notably by the Leiden

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