THE PHENOMENOLOGICAL THEORY OF THE VOIGT EFFECT IN PARAMAGNETICS

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A macroscopic calculation of the Voigt effect for centimeter waves in paramagnetic media is presented.

1. Ordinary double refraction in gyrotropic media denotes that radiation traversing such substances splits into two waves with mutually perpendicular magnetic (and electric) vectors and propagating in different directions. In the special case represented by the Voigt effect the gyration vector is perpendicular to the direction of propagation of the incident wave. The original linearly polarized radiation then splits into two waves which propagate in the same direction with different velocities and at different rates of absorption. These waves interfere at each point of the medium; the original linear polarization becomes elliptic and the ellipse rotates as the radiation passes through the medium.

In the present paper we attempt to construct a phenomenological theory of paramagnetic rotation through the Voigt effect for centimeter waves. The paramagnetic substance is assumed to be electrically isotropic with magnetic anisotropy caused by a static external magnetic field.[1]

2. We must first derive the magnetic susceptibility tensor for arbitrary relative orientation of the external static magnetic field $\mathbf{H}_0$ and the external oscillating magnetic field $\boldsymbol{\eta}$ of the radio wave. Hitherto[2,3] phenomenological theories of paramagnetic relaxation effects have considered only two special orientations, with $\mathbf{H}_0$ and $\boldsymbol{\eta}$ either mutually parallel or perpendicular.

To obtain the magnetic susceptibility tensor we use the general equations that describe the magnetization of a normal paramagnetic with pure spin magnetism in an oscillating field.[2] The equation for the time dependence of the magnetization $\mathbf{M}$ is[2]

$$\dot{\mathbf{M}} = -\varkappa\{\partial\Phi/\partial\mathbf{M}\} + g\{[\mathbf{M}\times\mathbf{H}]\}, \qquad (1)$$

where

$$\Phi = -b/2T - \mathbf{HM} + \mathbf{M}^2 T/2C \qquad (2)$$

is the nonequilibrium thermodynamic potential. Here $\mathbf{H} = \mathbf{H}_0 + \boldsymbol{\eta}$ is the total external magnetic field with a dc component $\mathbf{H}_0$ and an rf component $\boldsymbol{\eta}$; T is the temperature of the spin system; b is the magnetic specific heat constant; C is the Curie constant; g is the gyromagnetic ratio; κ in the phenomenological theory is an unknown function of H_0 and of the (assumed constant) lattice temperature T_0. The curly brackets in (1) denote that the quantities within them are linearized with respect to the small quantities $\theta = T - T_0$, the components of $\boldsymbol{\eta}$ and the variable part of the magnetization $\boldsymbol{\xi} \equiv \mathbf{M} - \mathbf{M}_0$, where $\mathbf{M}_0 \equiv (C/T_0)\mathbf{H}_0$.

We use (1) and the first law of thermodynamics for the spin system, as in reference 2. Instead of κ we introduce the isothermal spin relaxation time of the magnetization, $\tau_s = c/T_0\kappa$;[4] instead of the coefficient of thermal conductivity between the spin system and the lattice, α, which appears in the first law and remains an unknown function of T_0 and H_0 in the phenomenological theory, we introduce the spin-lattice relaxation time $\tau_e = (b + cH_0^2)/\alpha T_0$.[3] After linearization we arrive at the following basic equation for ξ:

$$(i\omega + \tau_s^{-1})\boldsymbol{\xi} + \frac{i\omega(1-\gamma)}{(i\omega\gamma + \tau_e^{-1})\tau_s}(\mathbf{l}_0\boldsymbol{\xi})\mathbf{l}_0 + \omega_0[\mathbf{l}_0\times\boldsymbol{\xi}] = \chi_0\tau_s^{-1}\boldsymbol{\eta} + \chi_0\omega_0[\mathbf{l}_0\times\boldsymbol{\eta}], \qquad (3)$$

where $\mathbf{l}_0$ is a unit vector in the direction of the constant field $\mathbf{H}_0$; $\chi_0 = c/T_0$ is the equilibrium isothermal magnetic susceptibility; $\gamma = [1 + H_0^2(c/b)]^{-1} = C_M/C_H$ is the ratio of specific heats of the spin system for constant magnetization and a static field; ω is the oscillating field frequency (in deriving (3) it was assumed that the time dependence of ξ and θ is given, as for η, by the factor $\exp(i\omega t)$, since steady conditions are being considered) and $\omega_0 = gH_0$. It is found easily and directly that the solution of (3) is given by

$$\boldsymbol{\xi} = \chi_\perp\boldsymbol{\eta} + i[\boldsymbol{\delta}\times\boldsymbol{\eta}] + (\chi_\parallel - \chi_\perp)(\mathbf{l}_0\boldsymbol{\eta})\mathbf{l}_0. \qquad (4)$$

Here $\chi_\parallel$ and $\chi_\perp$ represent the susceptibility of the paramagnetic in parallel and perpendicular fields, respectively (obtained in reference 2) and $\boldsymbol{\delta}$ is the gyration vector (obtained in reference 1), which is parallel to $\boldsymbol{l}_0$. Substituting (4) into (3) we obtain the complex magnetic susceptibility tensor

$$\chi = \begin{pmatrix} \chi_\perp & -i\delta & 0 \\ i\delta & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix}. \quad (5)$$

3. In order to obtain the refractive index of a wave traversing a paramagnet we now make use of Maxwell's equations

$$\mathrm{curl}\,\mathbf{E} = -\dot{\mathbf{B}}/c, \qquad \mathrm{curl}\,\mathbf{H}' = \dot{\mathbf{D}}/c. \quad (6)$$

Here $\mathbf{H}'$ is the magnetic field in the material. Since the specimen is regarded as electrically isotropic we have

$$\mathbf{D} = \varepsilon\mathbf{E}. \quad (7)$$

We denote by $\boldsymbol{\eta}'$ and $\mathbf{b}$ the variable parts of $\mathbf{H}'$ and $\mathbf{B}$, so that $\mathbf{b} = \boldsymbol{\eta}' + 4\pi\boldsymbol{\xi}$. In paragraph 2 it was shown that $\boldsymbol{\xi} = \chi\boldsymbol{\eta}$; since paramagnets are only weakly polarizable we shall assume that $\boldsymbol{\xi} = \chi\boldsymbol{\eta}'$. Equation (4) then gives

$$\mathbf{b} = (1 + 4\pi\chi_\perp)\,\boldsymbol{\eta}' + 4\pi\,[\boldsymbol{\delta}\times\boldsymbol{\eta}'] + 4\pi\,(\chi_\parallel - \chi_\perp)\,(\mathbf{l}_0\boldsymbol{\eta}')\,\mathbf{l}_0. \quad (8)$$

Substituting (7) into (6), eliminating $\mathbf{E}$ and making use of (8), we obtain the wave equation for $\boldsymbol{\eta}'$, which for a plane wave is represented by

$$(\varepsilon n^2)^{-1}\,[\mathbf{k}_0(\mathbf{k}_0\boldsymbol{\eta}') - \boldsymbol{\eta}'] + (1 + 4\pi\chi_\perp)\,\boldsymbol{\eta}' + 4\pi i\,[\boldsymbol{\delta}\times\boldsymbol{\eta}'] + 4\pi\,(\chi_\parallel - \chi_\perp)\,(\mathbf{l}_0\boldsymbol{\eta}')\,\mathbf{l}_0 = 0, \quad (9)$$

where n is the index of refraction and $\mathbf{k}_0$ is a unit vector in the direction of wave propagation.

We now consider a wave propagating in the x direction. Projecting (9) on the coordinate axes, we obtain a set of homogeneous equations for the vector components of $\boldsymbol{\eta}'$, the solution of which gives two values for the index of refraction. Thus two waves are possible in the x direction. From the solution we find that one of these waves possesses the index of refraction

$$n_\parallel = \sqrt{\varepsilon(1 + 4\pi\chi_\parallel)} \quad (10)$$

and a magnetic vector parallel to $\boldsymbol{l}_0$ (so that $\eta'_x = n'_y = 0$, $n'_z \neq 0$). For the other wave we have the refractive index

$$n_\perp = \{\varepsilon\,[(1 + 4\pi\chi_\perp) - 16\pi^2\delta^2/(1 + 4\pi\chi_\perp)]\}^{1/2} \quad (11)$$

and a magnetic vector lying in a plane perpendicular to $\boldsymbol{l}_0$ (so that $\overline{\eta}_z = 0$). The second wave is elliptically polarized with the following relation between η'_x and η'_y:

$$\eta_x'^{(0)} = i4\pi\delta\eta_y'^{(0)}/(1 + 4\pi\chi'_\perp), \quad (12)$$

which shows that the x component of $\boldsymbol{\eta}'$ is considerably smaller than the y component, since $\chi_\perp$ and δ are of the order of $\chi_0 \sim 10^{-6}$ (see reference 1).

4. Let us now consider the interference of the waves indicated by (10) and (11) inside the paramagnetic. An rf wave impinges at the point x = 0 on a plane-parallel paramagnetic plate which is perpendicular to the x axis. The magnetic field of the wave is linearly polarized in the yz plane with the components

$$\eta_z = (\eta_0 \cos\alpha)\,e^{i\omega t}, \qquad \eta_y = (\eta_0 \sin\alpha)\,e^{i\omega t}, \quad (13)$$

where α is the angle between $\mathbf{H}_0$ and $\boldsymbol{\eta}$. Taking the boundary conditions into account and ignoring reflection of the incident wave (since we are interested only in the change of polarization but not of intensity), we obtain at a point x inside the plate the two waves:

$$\eta'_z = \eta_0 \cos\alpha \exp\{i\omega\,(t - n_\parallel x/c)\}, \quad (14)$$

$$\eta'_y = \eta_0 \sin\alpha \exp\{i\omega\,(t - n_\perp x/c)\},$$

$$\eta'_x = i\frac{4\pi\delta}{1 + 4\pi\chi_\perp}\,\eta'_y, \quad (15)$$

the complex refractive indices of which are given by

$$n_\parallel = n'_\parallel - in''_\parallel, \qquad n_\perp = n'_\perp - in''_\perp. \quad (16)$$

To investigate the interference of waves (14) and (15) it is sufficient to obtain the results in the yz plane, since the x component of the magnetic field disappears when the combined oscillations emerge from the plate. Introducing the notation

$$a_1 = \eta_0 \sin\alpha \exp\left(-\frac{\omega}{c}\,n''_\perp x\right), \qquad \delta_1 = -\frac{\omega}{c}\,n'_\perp x,$$

$$a_2 = \eta_0 \cos\alpha \exp\left(-\frac{\omega}{c}\,n''_\parallel x\right), \qquad \delta_2 = -\frac{\omega}{c}\,n'_\parallel x \quad (17)$$

and eliminating the time t from η'_y and η'_z, we obtain the equation of an ellipse:

$$(\eta'_y/a_1)^2 + (\eta'_z/a_2)^2 - 2\,(\eta'_y\eta'_z/a_1a_2)\cos\delta = \sin^2\delta, \quad (18)$$

where $\delta = \delta_2 - \delta_1$. This ellipse is rotated with respect to the coordinate axes through an angle which is the sum of α and the angle of paramagnetic rotation β, by which we mean the angle between η in the incident wave and the major semi axis of the polarization ellipse of the emerging wave. The ellipse can be put into canonical form by a transformation of the axes, and for the angle of rotation $\varphi = \alpha + \beta$ we obtain

$$\tan 2\varphi = 2a_1a_2\cos\delta/(a_2^2 - a_1^2); \quad (19)$$

it is evident that we have $\varphi = \alpha$ at x = 0, as is to be expected. We now take the very small susceptibility of paramagnets ($\chi_0 \sim 10^{-6}$) into account. Since $\chi_\perp$, $\chi_\parallel$ and δ in (10) and (11) are of the order of χ_0 (see reference 1), we can extract approximate values of the square roots in (10) and (11) and obtain corresponding approximations for $\cos\delta$ and for the exponentials in a_1 and a_2. Equation (19) then gives

$$\alpha + \beta = \tan^{-1}\left\{\frac{\sin\alpha}{\cos\alpha}\left[1 - \frac{\omega}{c}(n''_\perp - n''_\parallel)x\right]\right\}. \quad (20)$$

Considering also that the investigated effect is very small in paramagnets, in virtue of which we may assume $\sin\beta \sim \beta$ and $\cos\beta \sim 1$, we finally obtain from (20):

$$\beta = -(\pi\sqrt{\varepsilon}\omega/c)(\chi''_\perp - \chi''_\parallel)(\sin 2\alpha)x, \quad (21)$$

where χ'' is the imaginary part of the susceptibility.

It is evident from (21) that the angle of rotation depends in first approximation only on the difference between the absorptions of the waves corresponding to (10) and (11). This angle also exhibits periodic dependence on α, vanishing at $\alpha = 0$, $\pi/2$, π . . . . The angle of rotation also depends on the frequency of the oscillating field and the magnitude of the dc field.

5. In experiments on paramagnetic rotation it is customary to determine the dependence of the angle of rotation on the static field for a constant radiation frequency. To plot the $\beta(H_0)$ curve we must use the expressions[2]

$$\chi''_\perp = \chi_0 \frac{[1 + \tau_s^2(\omega_0^2 + \omega^2)]\tau_s\omega}{[1 + \tau_s^2(\omega_0^2 - \omega^2)]^2 + 4\tau_s^2\omega^2}, \quad (22)$$

$$\chi''_\parallel = \chi_0 \frac{(F\tau_e + \tau_s)\omega + (1 - F)^2\tau_e^2\tau_s\omega^3}{[1 - (1 - F)\tau_e\tau_s\omega^2]^2 + (\tau_e + \tau_s)^2\omega^2}, \quad (23)$$

where $F = 1 - \gamma$ increases monotonically from 0 to 1 as H_0 increases.

All the rotation experiments known to us were performed at frequencies for which $\tau\omega$ was very close to unity and $\tau_e\omega$ was so large that spin-lattice relaxation was practically absent. For $\tau_e\omega \gg 1$, Eq. (23) then gives

$$\chi''_\parallel = \chi_0(1 - F)^2\tau_s\omega / [1 + (1 - F)^2\tau_s^2\omega^2]. \quad (24)$$

It is evident from (22) and (24) that the static field H_0 enters into the expression for β both directly through ω_0 and F and through the isothermal spin relaxation time τ_S. For some paramagnets experimental data have recently been obtained[5] on spin absorption in parallel fields which may possibly indicate that τ_S is dependent on the external field (although this is still unaccounted for) or perhaps that the theory of reference 2 is inadequate for these cases. However, a number of investigations[1,6] show that the theory of Shaposhnikov[2] is applicable with τ_S independent of H_0 for a large number of paramagnets over broad frequency and temperature ranges.

When this is so, Eqs. (21), (22), and (23) give a very definite dependence of β on H_0. The shape of the $\beta(H_0)$ curve can, of course, differ depending on the substance. In some substances $\chi''_\parallel$ is very weakly dependent on H_0;[6] the curve $\beta = f(H_0)$ is then similar in shape to the absorption curve in perpendicular fields (22), with the single difference that since $\chi''_\perp$ and $\chi''_\parallel$ are equal at $H_0 = 0$ the rotation curve starts at the coordinate origin (which is physically expected, since with $H_0 = 0$ there is no gyrotropy and there can be no rotation). We also note from an analysis of the rotation curve given by (21), (22), and (24) with τ_S independent of H_0 that except for $H_0 \to \infty$ and $H_0 = 0$ the rotation either vanishes nowhere or vanishes twice.

6. Not much experimental information has been published concerning the effect that we are considering. So far as we know the first such data were given in reference 7 for powdered $MnSO_4 \cdot H_2O$ at about 9.4 × 10^9 cps at room temperature. In this paper the experimental curve $\beta = f(H_0)$ was given for H_0 ranging from about 2.7 × 10^3 to 4.7 × 10^3 oersteds, with a maximum for H_0 at about 3.4 × 10^3 oersteds and with no intersection of the horizontal axis. The review article by Gozzini[8] gives the curve in reference 7 together with a curve for $MnSO_4 \cdot H_2O$ (communicated privately) obtained under the same conditions but carried to about 5.8 × 10^3 oersteds for H_0, as well as measurements of the given effect in certain radicals. The curves given in reference 8 possess a single maximum but do not intersect the horizontal axis. Hedvig[3] gives experimental results for the dependence of the rotation angle on the angle α between the static and oscillating fields for the organic free radical diphenylpicrylhydrazyl at about 9.4 × 10^9 cps at room temperature; this relation can apparently be characterized by $\sin 2\alpha$. Battaglia et al and Hedvig note especially that the sign of the effect does not change. In these papers the experimental results are not discussed from a theoretical point of view.

A recent paper by Imamutdinov, Neprimerov and Shekun[10] gives the experimental $\beta(H_0)$ curve for powdered $MnCl_2 \cdot 4H_2O$ at room temperature at about 9.4 × 10^9 cps with some theoretical discussion.

The rotation curve given in reference 10 begins at zero, has a sharp maximum in the positive region, passes through zero again at $H_0 = 4 \times 10^3$ oersteds, has a very indistinct minimum in the negative region and then monotonically approaches the horizontal axis slowly from below. The theoretical discussion is as follows. In (21) (given in reference 10 without derivation) the expressions

$$\chi''_{\perp} = \frac{\chi_0\omega}{2\tau}\left[\frac{1}{(\omega_0-\omega)^2+\tau^{-2}}+\frac{1}{(\omega_0+\omega)^2+\tau^{-2}}\right], \quad (25)$$

$$\chi''_{\parallel} = (\chi_0\omega/\tau)/(\omega^2+\tau^{-2}), \quad (26)$$

are substituted. It is stated[10] that for lack of a satisfactory theory of the complex paramagnetic susceptibility of solids these expressions were obtained by using the theory for a paramagnetic gas consisting of identical particles with spin $\frac{1}{2}$. It is then stated that if we assume the relaxation time τ in (25) and (26) to increase with H_0 these equations "describe the experimental results well both qualitatively and quantitatively." Regarding the postulated increase of τ with the field the writers refer to Gorter's book[3] and Kurushin's papers.[6] It is also stated that the phenomenological theory of Shaposhnikov[3] likewise apparently leads to (25) and (26).

7. A comparison of the experimental data from references 7 — 9 (in Sec. 6) with the discussion of the theoretical rotation curve given by (21), (22), and (24) (Sec. 5) indicates agreement between these experimental results and our theory. The following must be stated concerning the experimental rotation curve given in reference 10. For powdered $MnCl_2 \cdot 4H_2O$ at room temperature and at a frequency very close to that used in reference 7, Kurushin obtained the experimental curves of $\chi''_{\perp}(H_0)$ and $\chi''_{\parallel}(H_0)$ using the same apparatus that he had described in an earlier paper.[6] These results, which will be published in the near future, show without any doubt that up to H_0 of the order 6×10^3 oersteds the $\chi''_{\parallel}(H_0)$ curve is everywhere below the $\chi''_{\perp}(H_0)$ curve. It follows (see (21)) that in the given region of field values the rotation curve $\beta(H_0)$ can become zero nowhere except at the origin $H_0 = 0$; however, the experimental curve in reference 7 passes through zero for $H_0 = 4 \times 10^3$ oersteds. It must be added that for $MnCl_2 \cdot 4H_2O$ under the given conditions many experiments[1,6] support Shaposhnikov's theory with τ_s independent of H_0; but in this case, as was noted at the end of Sec. 5, an analysis of the $\beta(H_0)$ curve shows that except for $H_0 = 0$ the curve has either no zero or two zeros, in agreement with the experimental results of Kurushin that have just been mentioned.

With regard to the theoretical discussion in reference 10 we may state the following. Although (25) and (26) are actually derived from the general equations of Karplus and Schwinger[11] for the complex susceptibility of an ideal gas in the special case of spin $\frac{1}{2}$ and perpendicular and parallel fields, we believe it would be incorrect to use (25) and (26) in the theoretical explanation of the experimental rotation curve given in reference 10. Under the given experimental conditions the spin system of the paramagnetic is practically isolated from the lattice, since $\tau_e\omega \gg 1$. Therefore for $\chi''_{\parallel}$ we must use an expression that corresponds to adiabatic spin-spin relaxation in the absence of spin-lattice relaxation, as we did in Sec. 5 [see Eq. (24)]. It is also evident from (22) that $\chi''_{\perp}$ does not contain τ_e at all. A comparison of (25) and (26) with (22) and (24) shows that when $\tau = \tau_s$ (25) coincides with (22); however, (26) is not transformed into (24), which corresponds to adiabatic spin-spin relaxation and is obtained from (23) for $\tau_e\omega \to \infty$, but (26) does correspond to isothermal spin-spin relaxation and is obtained from (23) for $\tau_e\omega \to 0$. We also note that if we follow the authors of reference 10 by accepting (25) and (26), we cannot fully check their statement that theory and experiment are in good qualitative and quantitative agreement for τ increasing with H_0 since the specific dependence of τ_0 on H is not given. We must add that if in (25) and (26) we understand τ to mean τ_s [which is required if (25) is to agree with (22)], then we are not in accord with the reference to Gorter and to Kurushin[6] with regard to the dependence of τ_s on H_0. In our opinion Gorter's results cannot be used for any definite general conclusions regarding the dependence of τ_s on H_0, while the cited papers of Kurushin indicate that τ_s is independent of H_0.

8. We have plotted the $\beta(H_0)$ curve given by (21), (22), and (24) for $MnCl_2 \cdot 4H_2O$ under the experimental conditions of reference 10 with τ_s taken as 0.24×10^{-9} sec (see reference 6). The curve starts at zero and remains entirely in the positive region with one maximum, after which it drops monotonically and practically reaches the horizontal axis for H_0 of the order 8×10^3 oersteds. This rotation curve agrees with the experimental curves of $\chi''_{\perp}(H_0)$ and $\chi''_{\parallel}(H_0)$ that were obtained by Kurushin (see Sec. 7).

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281