Nonlinear Phenomenon of Longitudinal Magnetization of a Uniaxial Paramagnet by a Transverse High-Frequency Magnetic Field

L. D. Filatova and V. M. Tsukernik
Kharkov State University
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It is shown that because of the presence of anisotropy, there occurs in a uniaxial paramagnet a nonvanishing constant component of longitudinal magnetization, induced by a transverse high-frequency magnetic field. This occurs even in the absence of a longitudinal constant field. The dependence of the magnetization on the amplitude and frequency of the alternating field is investigated.

It is well known that if the interaction of the paramagnetic ions with the crystalline field is much larger than the spin-orbit interaction, then a paramagnet can be described quite well by means of an effective spin Hamiltonian[1]. When the crystalline field has axial symmetry (a uniaxial crystal), the effective spin Hamiltonian for an individual paramagnetic ion can be written[1)]

$$\mathscr{H}_0 = \alpha S_z^2 - g_{\parallel}\mu H S_z, \tag{1}$$

where α is the anisotropy constant, $g_{\parallel}$ is the longitudinal g-factor, μ is the Bohr magneton, S_z is the operator of the projection of the spin along the anisotropy axis, and H is the external magnetic field, directed along this axis. In the linear approximation, a weak alternating transverse field affects only the components of the magnetization transverse to the anisotropy axis. In this case the high-frequency magnetic susceptibility tensor is described by the well known resonance formulas[1]. Here we shall consider the effect of a transverse alternating magnetic field on the magnetization along the chosen axis, not assuming smallness of the field[2)].

Let the paramagnet be in thermodynamic equilibrium, which is described by the Gibbs distribution ρ_0 for a gas of particles with the Hamiltonian (1). Then at the instant t = 0 an alternating magnetic field h ($h_0 \cos \omega t, -h_0 \sin \omega t, 0$) is applied, and the behavior of the system for t > 0 is described by a density matrix $\rho(t)$ that satisfies the equation

$$i\hbar \partial\rho / \partial t = [\mathscr{H}, \rho] \tag{2}$$

with the Hamiltonian

$$\mathscr{H} = \alpha S_z^2 - g_{\parallel}\mu H S_z - g_{\perp}\mu h_0 (S_x \cos \omega t - S_y \sin \omega t) \tag{3}$$

($g_{\perp}$ is the transverse g-factor). What interests us is the longitudinal magnetization, which is determined by the mean value of the operator S_z ($\langle S_z \rangle = \mathrm{Sp}\, \rho S_z$). We go over to a rotating system of coordinates by means of the unitary transformation

$$U = \exp (i\omega S_z t). \tag{4}$$

The corresponding density matrix $\tilde{\rho}$ is connected with ρ by the relation

$$\tilde{\rho} = U^{-1} \rho U. \tag{5}$$

From (2), (4), and (5) follows the equation for $\tilde{\rho}$:

$$i\hbar \partial\tilde{\rho} / \partial t = [\tilde{\mathscr{H}}, \tilde{\rho}], \tag{6}$$

$$\tilde{\mathscr{H}} = \alpha S_z^2 - \Delta H \cdot S_z - h_0 S_x, \tag{7}$$

where $\Delta H = H - \hbar\omega$. Here and hereafter we assume $g_{\parallel}\mu = 1$ and $g_{\perp}\mu = 1$. In transformation to the usual dimensions, it is necessary to multiply H and ΔH by $g_{\parallel}\mu$, h_0 by $g_{\perp}\mu$.

Since the Hamiltonian (7) does not contain the time explicitly, the solution of equation (6) that reduces at the initial instant to the Gibbs distribution ρ_0 has the form

$$\tilde{\rho} = \exp (-i\tilde{\mathscr{H}} t / \hbar)\, \rho_0 \exp (i\tilde{\mathscr{H}} t / \hbar). \tag{8}$$

Hence, by taking into account that the operator (4) commutes with S_z, we find

$$\langle S_z \rangle = \mathrm{Sp}\, [\exp (i\tilde{\mathscr{H}} t / \hbar) S_z \exp (-i\tilde{\mathscr{H}} t / \hbar)\, \rho_0]. \tag{9}$$

The further calculations are carried out for spin unity. We assume that the results thus obtained are qualitatively retained for an arbitrary spin greater than one half[3)]. The obtaining of quantitative results for the general case involves great computational difficulties. We choose as a complete set the eigenfunctions of the operator $\tilde{\mathscr{H}}$:

$$\tilde{\mathscr{H}} \psi^{(i)} = E^{(i)} \psi^{(i)}, \quad i = 1, 2, 3.$$

In a representation in which the matrix S_z is diagonal, the components of each of the functions $\psi^{(i)}$ satisfy the system of equations

$$\begin{aligned} (\alpha + \Delta H) \psi_{-1}^{(i)} - 2^{-1/2} h_0 \psi_0^{(i)} &= E^{(i)} \psi_{-1}^{(i)}, \\ -2^{-1/2} h_0 (\psi_{-1}^{(i)} + \psi_1^{(i)}) &= E^{(i)} \psi_0^{(i)}, \\ -2^{-1/2} h_0 \psi_0^{(i)} + (\alpha - \Delta H) \psi_1^{(i)} &= E^{(i)} \psi_1^{(i)}. \end{aligned} \tag{10}$$

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1)We neglect interaction between the paramagnetic ions. This, in any case, is correct for magnetically dilute crystals that are obtained by replacement of some of the diamagnetic ions by paramagnetic. For example, in the crystal $K_2Zn(SO_4)_2 \cdot 6H_2O$) in the zinc ion Zn^{2+} may be replaced by the copper ion Cu^{2+}.

2)At sufficiently low temperatures and at sufficiently high frequency ω of the alternating field, the condition $\omega\tau_{sp} \gg 1$ is satisfied, where τ_{sp} is the spin-phonon relaxation time. The effect considered below becomes noticeable at a temperature $T \lesssim \alpha \approx 1°$K. At such a temperature. $\tau_{sp} \sim 10^{-2}$sec, so that the condition $\omega\tau_{sp} \gg 1$ is satisfied even at comparatively low frequencies. We suppose hereafter that this condition is fulfilled; this permits us to disregard spin-phonon interaction.

3)For S = 1/2, the anisotropy-energy operator reduces to the unit operator.

Hence is obtained the equation for the eigenvalues of $\epsilon = \alpha - E$:

$$\varepsilon^3 - \alpha\varepsilon^2 - (h_0^2 + (\Delta H)^2)\varepsilon + \alpha(\Delta H)^2 = 0. \quad (11)$$

The density matrix ρ_0 in the case under consideration, S = 1, can be described in the form

$$\rho_0 = I + S_z e^{-\beta\alpha}\,\mathrm{sh}\,\beta H + S_z^2(e^{-\beta\alpha}\,\mathrm{ch}\,\beta H - 1). \quad (12)$$

Then

$$\langle S_z\rangle = Z^{-1}\Big[(e^{-\beta\alpha}\,\mathrm{ch}\,\beta H - 1)\sum_{i,j=1}^{3}(S_z)_{ij}(S_z^2)_{ji}\cos\omega_{ij}t + e^{-\beta\alpha}\,\mathrm{sh}\,\beta H\cdot\sum_{i,j=1}^{3}(S_z)_{ij}^2\cos\omega_{ij}t\Big], \quad (13)$$

Explicit expressions for the matrix elements and frequencies that enter in (13) can be found only in limiting cases. But the longitudinal magnetization, averaged over a time long in comparison with the characteristic periods, can be calculated for arbitrary values of the parameters α, h_0, and ΔH. From (13) we find[4)]

$$\sigma = \overline{\langle S_z\rangle} = Z^{-1}\Big[(e^{-\beta\alpha}\,\mathrm{ch}\,\beta H - 1)\sum_{i=1}^{3}(S_z)_{ii}(S_z^2)_{ii} + e^{-\beta\alpha}\,\mathrm{sh}\,\beta H\cdot\sum_{i=1}^{3}(S_z)_{ii}^2\Big] \quad (14)$$

where the bar means a time average. The matrix elements that enter in (14) are expressed as follows in terms of the components of the wave functions $\psi^{(i)}$:

$$(S_z)_{ii} = (\psi_1^{(i)})^2 - (\psi_{-1}^{(i)})^2, \quad (S_z^2)_{ii} = (\psi_1^{(i)})^2 + (\psi_{-1}^{(i)})^2 = 1 - (\psi_0^{(i)})^2.$$

If we use the orthogonality and normalization relations for the functions $\psi^{(i)}$,

$$\psi_l^{(1)}\psi_m^{(1)} + \psi_l^{(2)}\psi_m^{(2)} + \psi_l^{(3)}\psi_m^{(3)} = \delta_{lm}, \quad l, m = -1, 0, 1$$

we can obtain the following expression:

$$\begin{aligned}\sigma = 2Z^{-1}\{&(e^{-\beta\alpha}\,\mathrm{ch}\,\beta H - 1)[\psi_0^{(1)}\psi_0^{(2)}(\psi_{-1}^{(1)}\psi_{-1}^{(2)} - \psi_1^{(1)}\psi_1^{(2)})\\ &+ \psi_0^{(2)}\psi_0^{(3)}(\psi_{-1}^{(2)}\psi_{-1}^{(3)} - \psi_1^{(2)}\psi_1^{(3)}) + \psi_0^{(3)}\psi_0^{(1)}(\psi_{-1}^{(3)}\psi_{-1}^{(1)} - \psi_1^{(3)}\psi_1^{(1)})]\\ &+ e^{-\beta\alpha}\,\mathrm{sh}\,\beta H[1 - (\psi_1^{(1)}\psi_1^{(2)} - \psi_{-1}^{(1)}\psi_{-1}^{(2)})^2 - (\psi_1^{(2)}\psi_1^{(3)} - \psi_{-1}^{(2)}\psi_{-1}^{(3)})^2\\ &- (\psi_1^{(3)}\psi_1^{(1)} - \psi_{-1}^{(3)}\psi_{-1}^{(1)})^2]\}.\end{aligned} \quad (15)$$

Each of the components of the wave functions $\psi^{(i)}$ is a solution of the system (10) and cannot be expressed rationally in terms of the parameters α, h_0, and ΔH, because the characteristic equation (11) is cubic. From the system (10) and the normalization condition it follows that

$$\psi_{-1}^{(i)} = -\frac{h_0}{\sqrt{2}}\frac{\psi_0^{(i)}}{\varepsilon_i + \Delta H}, \quad \psi_1^{(i)} = -\frac{h_0}{\sqrt{2}}\frac{\psi_0^{(i)}}{\varepsilon_i - \Delta H},$$

$$(\psi_0^{(i)})^2 = \frac{[\varepsilon_i^2 - (\Delta H)^2]^2}{h_0^2[\varepsilon_i^2 + (\Delta H)^2] + [\varepsilon_i^2 - (\Delta H)^2]^2}.$$

Hence it is clear that the right side of (15) is a rational symmetric function of the roots ϵ_1, ϵ_2, and ϵ_3 of the characteristic equation (11) and, according to a well-known theorem of algebra about symmetric functions[2], can be expressed rationally in terms of the coefficients of equation (11). As a result, we obtain the following expression for the magnetization of the paramagnetic ion:

$$\sigma = \sigma_0\Big(1 - \frac{L(\alpha, h_0, \Delta H)}{D(\alpha, h_0, \Delta H)}\Big) + \frac{e^{-\beta\alpha}\,\mathrm{ch}\,\beta H - 1}{2e^{-\beta\alpha}\,\mathrm{ch}\,\beta H + 1}\,\frac{2\alpha\Delta H h_0^2[h_0^2 - 8(\Delta H)^2]}{D(\alpha, h_0, \Delta H)} \quad (16)$$

where

$$\sigma_0 = \frac{2e^{-\beta\alpha}\,\mathrm{sh}\,\beta H}{2e^{-\beta\alpha}\,\mathrm{ch}\,\beta H + 1}$$

is the static magnetization in a constant longitudinal field H, and where the polynomials L and D are

$$\begin{aligned}L &= h_0^2\{4\alpha^2(\Delta H)^2 + \alpha^2h_0^2 + 4[(\Delta H)^2 + h_0^2]^2\},\\ D &= 4(\Delta H)^2[(\Delta H)^2 - \alpha^2]^2 + h_0^2[12(\Delta H)^4 + 12(\Delta H)^2h_0^2\\ &\quad + 20(\Delta H)^2\alpha^2 + h_0^2\alpha^2 + 4h_0^4].\end{aligned} \quad (17)$$

We notice that the polynomial D coincides with the discriminant of equation (11). From the expression (16) for σ it is seen that the first term, which is proportional to σ_0, vanishes with H, whereas the second remains finite even for H = 0. Hence it follows that for $\alpha \neq 0$, there exists a possibility of longitudinal magnetization of a paramagnet by a high-frequency magnetic field polarized in a plane perpendicular to the anisotropy axis; for H = 0 we have

$$\sigma = \frac{e^{-\beta\alpha} - 1}{2e^{-\beta\alpha} + 1}\,\frac{2\alpha\Delta H h_0^2[h_0^2 - 8(\Delta H)^2]}{D(\alpha, h_0, \Delta H)}. \quad (18)$$

From (17) and (18) it follows that σ for H = 0 is an odd function of ΔH. Furthermore, as is seen from (18), σ changes sign at $\Delta H = \pm h_0/2\sqrt{2}$. It can be shown that this result is retained for arbitrary spin, at least if α is sufficiently small. Since σ vanishes both for $h_0 = 0$ and for $h_0 = \infty$, there is a value of the amplitude for which σ reaches a maximum. This is true also of the dependence of σ on ΔH.

If the amplitude h_0 is small in comparison with ΔH or α, then from (18) we find

$$\sigma = \frac{e^{-\beta\alpha} - 1}{2e^{-\beta\alpha} + 1}\,\frac{4\alpha h_0^2\Delta H}{((\Delta H)^2 - \alpha^2)^2}$$

an expression that can be obtained directly by means of perturbation theory. But if the difference $(\Delta H)^2 - \alpha^2$ is small, which corresponds to a transition frequency in the paramagnet[3], then perturbation theory with respect to h_0 is inapplicable, and the result depends on the order of the approach of h_0 to zero and of ΔH to $\pm\alpha$ (see footnote 4). If initially $h_0 \to 0$, then, of course, $\sigma \to 0$. Therefore we consider the case in which $\Delta H \to \alpha$ and h_0 is small, using perturbation theory for the case of degeneracy. The following result is obtained:

$$\sigma = \frac{e^{-\beta\alpha} - 1}{2e^{-\beta\alpha} + 1}\Big\{\frac{1 - \cos th_0\sqrt{2}}{2} - \Big(\frac{h_0}{8\alpha}\Big)^2(17 - \cos th_0\sqrt{2})\Big\}$$

(we have set h = 1). For $t \ll 1/h_0\sqrt{2}$, we find from this that $\sigma \sim h_0^2$, while for $t \gg 1/h_0\sqrt{2}$ we get, as the result of the time-averaging,

$$\sigma = \frac{1}{2}\,\frac{e^{-\beta\alpha} - 1}{2e^{-\beta\alpha} + 1} + O(h_0^2).$$

This means that for $\Delta H = \pm\alpha$, a high-frequency field of arbitrarily small amplitude produces, after a sufficiently long time, a finite value of the magnetization, which at T = 0 is equal to ½. There is also degeneracy in the case that ΔH and h_0 approach zero. For $\Delta H \ll h_0 \ll \alpha$, we have

4)Equation (14) follows from (13) under the condition that all the frequencies ω_{ij} are different from zero for $i \neq j$; that is, in the absence of multiple roots of equation (11). It can be shown that this is always so except in two cases: $h_0 = \Delta H = 0$ and $h_0 = 0$, $\Delta H = \pm\alpha$. These cases we shall discuss separately.

$$\sigma = \frac{e^{-\beta\alpha} - 1}{2e^{-\beta\alpha} + 1} \frac{2\Delta H}{\alpha} \left\{ 4 \frac{h_0^2}{\alpha^2} - \left(1 - \cos \frac{h_0^2}{\alpha} t \right) \right\}.$$

In conclusion, we present exact expressions for the transverse components of the magnetization in the special case $\Delta H = 0$, with arbitrary values of the other parameters. For $\Delta H = 0$, as is seen from (10) and (11), the eigenvalues and eigenfunctions of the Hamiltonian (7) can be found explicitly. As a result, the following expression is obtained for the cyclic component of the transverse magnetization:

$$\langle S_+ \rangle \equiv \langle S_x \rangle + i \langle S_y \rangle = 2Z^{-1} e^{-iHt} \sin \varphi \sin \Omega t \times [(1 - e^{-\beta\alpha} \operatorname{ch} \beta H) \cos \varphi \sin \Omega t + i e^{-\beta\alpha} \operatorname{sh} \beta H \cos (\alpha t / 2)], \quad (19)$$

where

$$Z = 1 + 2e^{-\beta\alpha} \operatorname{ch} \beta H, \quad \operatorname{tg} \varphi = 2h_0 / \alpha, \quad \Omega = (\alpha^2 / 4 + h_0^2)^{1/2}.$$

Here, as also above, we set h = 1. For small values of the amplitude, the transverse components of the magnetization are linear with respect to h_0, as they should be, whereas the longitudinal component is quadratic.

[1]G. E. Pake, Paramagnetic Resonance, W. A. Benjamin, New York, 1962.
[2]A. G. Kurosh, Kurs vyssheĭ algebry (Course of Higher Algebra), Nauka, 1968.
[3]L. D. Filatova and V. M. Tsukernik, Zh. Eksp. Teor. Fiz. **56**, 1290 (1969) [Sov. Phys.-JETP **29**, 694 (1969)].

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