THERMODYNAMIC AND HIGH-FREQUENCY PROPERTIES OF A PARAMAGNET WITH NEGATIVE ANISOTROPY CONSTANT AT LOW TEMPERATURES

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It is shown that for a uniaxial paramagnet with negative anisotropy, placed in a magnetic field directed along the chosen axis, at low temperatures, the temperature correction to the magnetization oscillates with field for fields such that $\mu H < 2\alpha s$ (here μ is the Bohr magneton, α is the anisotropy constant (with the dimensions of energy), and s is the spin of the paramagnetic ion). A classical treatment does not lead to oscillations; the temperature correction is always negative. The high-frequency susceptibility tensor is calculated.

It is known[1] that if the spin-orbit interaction is small in comparison with the interaction of the paramagnetic ion with the crystalline field, then a paramagnet is described sufficiently well by means of an effective spin Hamiltonian. In the case in which the crystalline field possesses axial symmetry, in an external magnetic field directed along the axis of symmetry, the effective spin Hamiltonian of the paramagnet has the form

$$\mathcal{H}_N = \alpha \sum_{n=1}^{N} (s_n^z)^2 - \mu H \sum_{n=1}^{N} s_n^z, \quad (1)$$

where α is the anisotropy constant (with the dimensions of energy), μ is the Bohr magneton, H is the external magnetic field, s_n^z is the operator of the projection of the spin of the n-th ion along the chosen axis of the crystal, and N is the number of particles.

The present paper investigates the low-temperature thermodynamic and high-frequency properties of a paramagnet that is described by the Hamiltonian (1).

1. Because of the absence in (1) of interaction between the paramagnetic ions, it is possible to consider the one-particle problem with the Hamiltonian

$$\mathcal{H} = \alpha s_z^2 - \mu H s_z. \quad (2)$$

The energy levels are expressed directly in terms of the eigenvalues σ of the operator s_z:

$$E_\sigma = \alpha\sigma^2 - \mu H\sigma = -\frac{\mu^2 H^2}{4\alpha} + \alpha\left(\sigma - \frac{\mu H}{2\alpha}\right)^2,$$

where $\sigma = -s, -s+1, \ldots, s$; s is the spin of the paramagnetic ion.[1)]

It is seen from the expression (3) that if $\alpha < 0$ (positive anisotropy), then for any positive value of the field H, the ground state corresponds to $\sigma = s$; that is, for arbitrary field the magnetization in the ground state is the intrinsic magnetization.

The situation is different in the case $\alpha > 0$ (negative anisotropy). As is seen from the second equation (3), the ground state corresponds to the smallest value of the quantity $(\sigma - \mu H/2\alpha)^2$. If $\mu H > 2\alpha s$, then the ground state is reached at $\sigma = s$, and its energy is[2)]

$$E_s = \alpha s^2 - \mu H s.$$

For $\mu H < 2\alpha s$, the ground state corresponds to the value $\sigma = \sigma_0$ nearest to $\mu H/2\alpha$ (from the left or from the right). If $\sigma_0 < \mu H/2\alpha$, then the energy of the first excited state is

$$E_{\sigma_0+1} = \alpha(\sigma_0+1)^2 - \mu H(\sigma_0+1), \quad (4)$$

but if $\sigma_0 > \mu H/2a$, then the first excited state has the energy

$$E_{\sigma_0-1} = \alpha(\sigma_0-1)^2 - \mu H(\sigma_0-1). \quad (5)$$

In other words, for $\mu H < 2\alpha s$ there occurs, with increase of the magnetic field, a reorganization of the ground state, which manifests itself in a stepwise increase of σ_0 with field. It will be shown below that in consequence of this, the change with field of the temperature correction to the magnetization of the paramagnet has an oscillatory character at low temperatures ($\alpha/T \gg 1$). At such temperatures, it is in general sufficient, for calculation of thermodynamic quantities, to consider only the ground state and the first excited state; a necessary condition for this is satisfaction of the inequality $\beta|2\alpha\sigma_0 - \mu H| \gg 1$. Then the partition function is

$$Z = \exp(-\beta E_{\sigma_0}) + \exp(-\beta E_{\sigma_0+1}) \quad \text{for} \quad \sigma_0 < \mu H/2\alpha,$$

$$Z = \exp(-\beta E_{\sigma_0}) + \exp(-\beta E_{\sigma_0-1}) \quad \text{for} \quad \sigma_0 > \mu H/2\alpha; \quad \beta = 1/T.$$

Calculation of the magnetization[3)] by the formula $M = \beta^{-1} Z^{-1} \partial Z/\partial H$ gives, to within exponentially small terms,

$$M = \mu\sigma_0 - \frac{\mu}{\exp\{\beta[\mu H - (2\sigma_0 - 1)\alpha]\} + 1}, \quad \mu H < 2\alpha\sigma_0, \quad (6)$$

$$M = \mu\sigma_0 + \frac{\mu}{\exp\{\beta[(2\sigma_0+1)\alpha - \mu H]\} + 1}; \quad \mu H > 2\alpha\sigma_0. \quad (7)$$

[1)]The energy levels of a spin Hamiltonian with the field oriented arbitrarily with respect to the chosen axis were calculated in references [2,3] by perturbation theory. The anisotropy energy was treated as the perturbation.

[2)]The anisotropy constant α in order of magnitude amounts to several degrees, which corresponds to fields of order 10^4 Oe.

[3)]By "magnetization" is understood the magnetic moment of the paramagnet referred to one particle.

In the case $\beta[\mu H - (2\sigma_0 - 1)\alpha] \gg 1$ or $\beta[2\sigma_0 + 1)\alpha - \mu H] \gg 1$, we have respectively

$$M = \mu\sigma_0 - \mu \exp\{-\beta[\mu H - (2\sigma_0 - 1)\alpha]\}, \quad \mu H < 2\alpha\sigma_0, \qquad (6')$$

$$M = \mu\sigma_0 + \mu \exp\{-\beta[(2\sigma_0 + 1)\alpha - \mu H]\}, \quad \mu H > 2\alpha\sigma_0. \qquad (7')$$

As is seen from the expressions (6′) and (7′), the temperature correction to the magnetization has different signs according to whether σ_0 lies to the left or to the right of $\mu H/2\alpha$, and it has an order of magnitude $\mu \exp(-\beta\alpha)$ if only $\mu H/2\alpha$ is not too close to $\sigma_0 - {}^1/_2$ or to $\sigma_0 + {}^1/_2$, respectively.

If $\mu H/2\alpha$ is close to $\sigma_0 - {}^1/_2$ or to $\sigma_0 + {}^1/_2$, so that $\beta[\mu H - (2\sigma_0 - 1)\alpha] \ll 1$ or $\beta[(2\sigma_0 + 1)\alpha - \mu H] \ll 1$, then

$$M = \mu\left(\sigma_0 - \frac{1}{2}\right) + \frac{\mu\beta}{4}[\mu H - (2\sigma_0 - 1)\alpha], \quad \mu H < 2\alpha\sigma_0, \qquad (6'')$$

$$M = \mu\left(\sigma_0 + \frac{1}{2}\right) - \frac{\mu\beta}{4}[(2\sigma_0 + 1)\alpha - \mu H], \quad \mu H > 2\alpha\sigma_0. \qquad (7'')$$

In this case, as follows from (6″) and (7″), the role of the magnetization in the ground state is played by the quantity $\mu(\sigma_0 - {}^1/_2)$ or $\mu(\sigma_0 + {}^1/_2)$, and the temperature correction to the magnetization obeys Curie's law.

Now let $\mu H/2\alpha = \sigma_0 + {}^1/_2$. Then the ground state, and also excited states for which the values of σ are equally distant from $\sigma_0 + {}^1/_2$, are doubly degenerate. As a result, the contributions of such excited states to the magnetization at low temperatures compensate each other. The last compensated contributions are made by the level with $\sigma = s$ and the level for which σ is located symmetrically with s with respect to the point $\sigma_0 + {}^1/_2$; that is, $\sigma = 2\sigma_0 - s + 1$. Therefore the first uncompensated state corresponds to $\sigma = 2\sigma_0 - s$. As a result, the temperature correction is negative, and

$$M|_{\mu H = \alpha(2\sigma_0+1)} = \mu\left(\sigma_0 + \frac{1}{2}\right) - \frac{\mu}{4}[2(s - \sigma_0) + 1] \times \exp\{-\beta\alpha(s - \sigma_0)(s - \sigma_0 + 1)\}. \qquad (8)$$

An analogous result is obtained when $\mu H/2\alpha = \sigma_0 - {}^1/_2$. The case in which $\mu H/2\alpha$ is close to σ_0, that is $\beta|2\alpha\sigma_0 - \mu H| \ll 1$, is also peculiar. Then it can be shown that the magnetization, to within terms of higher order, is

$$M = \mu\sigma_0 + 2\mu\beta(2\sigma_0\alpha - \mu H)e^{-\beta\alpha}. \qquad (9)$$

The magnetization at $\mu H/2\alpha = \sigma_0$, as can be easily shown, is

$$M|_{\mu H = 2\alpha\sigma_0} = \mu\sigma_0 - \mu(s - \sigma_0 + 1) \times \exp\{-\beta\alpha(s - \sigma_0 + 1)^2\}, \quad \sigma_0 > 0. \qquad (10)$$

It is seen from formulas (9) and (10) that the absolute values of the temperature corrections at the points $\mu H/2\alpha = \sigma_0$ and $\mu H/2\alpha = \sigma_0 + {}^1/_2$ are larger, the larger σ_0.

Finally, if $\mu H/2\alpha > s$, then, as has already been pointed out, the ground state will be that with $\sigma_0 = s$, and the moment at low temperatures has the form

$$M = \mu s - \mu \exp\{-\beta[\mu H - \alpha(2s - 1)]\}. \qquad (11)$$

Thus if $\mu H < 2\alpha s$, the temperature correction to the magnetization at zero temperature changes nonmonotonically with the field. It oscillates, taking alternatively now positive and now negative values. The values of field at which it vanishes are close to the values determined by the equalities $\mu H/2\alpha = \sigma_0$ and $\mu H/2\alpha = \sigma_0 \pm {}^1/_2$; the zeroes are closer to these points, the smaller σ_0. At fields for which $\mu H/2\alpha > s$, the correction is negative and tends exponentially to zero with increase of field. This behavior of the magnetization with field is a direct consequence of the reorganization of the quantum ground state with change of the magnetic field within the field range from zero up to $2\alpha s/\mu$. When $\mu H > 2\alpha s$, the ground state is fixed, and therefore the temperature correction to the magnetization changes monotonically with field.

2. A classical treatment does not lead to oscillations of the temperature correction. If we treat the spin of the paramagnetic ion as a c-number, then the thermodynamic properties are described by the (single-particle) partition function

$$Z = \exp\left\{\beta\alpha\left(\frac{\mu H}{2\alpha}\right)^2\right\} \int_0^\pi \exp\left\{-\beta\alpha\left(s\cos\theta - \frac{\mu H}{2\alpha}\right)^2\right\} \sin\theta\, d\theta.$$

From this is derived the following expression for the magnetization:

$$M = \frac{\mu^2 H}{2\alpha} - \frac{2\mu}{\sqrt{\pi\beta\alpha}} \frac{\mathrm{sh}(\beta\mu H s)\exp\{-\beta\alpha s^2[1 + (\mu H/2\alpha s)^2]\}}{\Phi[s\sqrt{\beta\alpha}(1 + \mu H/2\alpha s)] + \Phi[s\sqrt{\beta\alpha}(1 - \mu H/2\alpha s)]} \qquad (12)$$

where

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

is the error function.

It follows from formula (12) that for $\mu H < 2\alpha s$ and for temperatures approaching zero, the magnetization M approaches $M_0 = \mu^2 H/2\alpha$, which agrees with the result of a minimization of the classical energy of the paramagnetic ion with respect to the angle between the moment and the field. The second term in (12) gives the temperature correction to the magnetization, which, as is clear, is negative for any temperature and for any fields $\mu H < 2\alpha s$. In the case $\mu H \geq 2\alpha s$, the magnetization at zero temperature is equal to its intrinsic value μs, and the temperature correction of course is negative.

For comparison with the quantum results, we give the asymptotic expressions for the magnetization at low temperatures ($\beta\alpha \gg 1$) for fields $\mu H < 2\alpha s$ and $\mu H > 2\alpha s$:

$$M = \frac{\mu^2 H}{2\alpha} - \frac{\mu}{\sqrt{\pi\beta\alpha}} \mathrm{sh}(\beta\mu H s)\exp\left\{-\beta\alpha s^2\left[1 + \left(\frac{\mu H}{2\alpha s}\right)^2\right]\right\}, \quad \mu H < 2\alpha s, \qquad (13)$$

$$M = \mu s \frac{\mu H\,\mathrm{ch}(\beta\mu H s) + 2\alpha s\,\mathrm{sh}(\beta\mu H s)}{\mu H\,\mathrm{sh}(\beta\mu H s) + 2\alpha s\,\mathrm{ch}(\beta\mu H s)}, \quad \mu H > 2\alpha s. \qquad (14)$$

Thus the classical results for the system we have considered differ qualitatively from the quantum: the quantum treatment leads to oscillations of the temperature correction to the magnetization in the field range $\mu H < 2\alpha s$, whereas the classical leads to a negative correction at all fields.

3. We now consider the behavior of a paramagnet described by the Hamiltonian (2) in a high-frequency magnetic field h_t, polarized perpendicular to the z axis. If $\mathcal{H}_t = -\mu(h_t^x s_x + h_t^y s_y)$ is the Hamiltonian of interaction of the paramagnetic ion with the high-frequency field, then the mean value of the circular projection $s_+ \equiv s_x + is_y$ of the spin is given by the formula[4]

$$\langle s_+\rangle = \frac{i}{\hbar} \int_0^\infty d\tau\, \mathrm{Sp}\, \rho_0[\mathcal{H}_{t-\tau}\, s_+(\tau)]. \qquad (15)$$

Here ρ_0 is the equilibrium Gibbs distribution, $s_+(\tau)$ is the Heisenberg representation of the operator s_+ with the Hamiltonian (2), and the square brackets denote the commutator. On taking into account that the terms in the Hamiltonian (2) commute, we can write

$$s_+(\tau) = e^{i\mathcal{H}\tau/\hbar} s_+ e^{-i\mathcal{H}\tau/\hbar} = e^{-i\mu H\tau/\hbar}\tilde{s}_+(\tau),$$

where

$$\tilde{s}_+(\tau) = \exp(i\alpha s_z^2\tau/\hbar)s_+\exp(-i\alpha s_z^2\tau/\hbar).$$

For the operator $\tilde{s}_+(\tau)$ we easily obtain the equation

$$i\hbar\dot{\tilde{s}}_+ = -\alpha(\tilde{s}_+s_z + s_z\tilde{s}_+),$$

solution of which gives

$$\tilde{s}_+(\tau) = \exp\left(\frac{i\alpha s_z\tau}{\hbar}\right)s_+\exp\left(\frac{i\alpha s_z\tau}{\hbar}\right).$$

Hence we find

$$\mathrm{Sp}\{\rho_0\mathcal{H}_{t-\tau}s_+(\tau)\} = \exp\left(-\frac{i\mu H\tau}{\hbar}\right)Z^{-1}$$
$$\times\,\mathrm{Sp}\left\{\exp(-\beta\mathcal{H})\mathcal{H}_{t-\tau}\exp\left(\frac{i\alpha s_z\tau}{\hbar}\right)s_+\exp\left(\frac{i\alpha s_z\tau}{\hbar}\right)\right\}$$
$$= \exp\left(\frac{i}{\hbar}(\alpha-\mu H)\tau\right)Z^{-1}\mathrm{Sp}\left\{\exp\left(-\beta\mathcal{H}+\frac{2i\alpha s_z}{\hbar}\tau\right)\mathcal{H}_{t-\tau}s_+\right\}.$$

As a result, the following expression is obtained for $\langle s_+\rangle$:

$$\langle s_+\rangle = \frac{i\mu}{2\hbar}Z^{-1}\int_0^\infty d\tau h^+_{t-\tau}\exp\left(-\frac{i\mu H\tau}{\hbar}\right)\mathrm{Sp}\exp\left(\frac{2i\alpha s_z}{\hbar}\tau-\beta\mathcal{H}\right)$$
$$\times\left\{s_+s_-\exp\left(-\frac{i\alpha\tau}{\hbar}\right)-s_-s_+\exp\left(\frac{i\alpha\tau}{\hbar}\right)\right\}, \tag{16}$$

where $Z = \mathrm{Sp}[\exp(-\beta\mathcal{H})]$, $h_t^+ \equiv h_t^x + ih_t^y = h_0^+\exp(-i\omega+\nu)t$; ω is the frequency of the field, and $\nu > 0$ is an imaginary correction to the frequency that takes account of the adiabaticity of the process of turning on the field. In the final formulas, the quantity ν can be regarded as an effective time, related to various relaxation processes.

Finally we find[4)]

$$\langle s^+\rangle = -\frac{i\mu}{2\hbar}h_0^+e^{-i\omega t}Z^{-1}\sum_{\sigma=-s}^{s}e^{-\beta E_\sigma}\left\{\frac{s(s+1)-\sigma^2-\sigma}{\nu-i(\omega-\Omega_{\sigma1})}\right.$$
$$\left.-\frac{s(s+1)-\sigma^2+\sigma}{\nu-i(\omega-\Omega_{\sigma2})}\right\}, \tag{17}$$

whereas $\langle s^-(\omega)\rangle = \langle s^+(-\omega)\rangle^*$. Here E_σ is the energy level (3), and $\Omega_{\sigma1}$ and $\Omega_{\sigma2}$ are given respectively by

$$\hbar\Omega_{\sigma1} = \mu H-(2\sigma+1)\alpha,\quad \hbar\Omega_{\sigma2} = \mu H-(2\sigma-1)\alpha. \tag{18}$$

From formulas (17) follow the expressions for the components of the complex magnetic-susceptibility tensor:

$$\chi_{xx} = \chi_{yy} = \frac{\mu^2}{4\hbar}Z^{-1}\sum_{\sigma=-s}^{s}e^{-\beta E_\sigma}\left\{[s(s+1)-\sigma^2-\sigma]\left(\frac{1}{\omega-\Omega_{\sigma1}+i\nu}\right.\right.$$
$$\left.\left.-\frac{1}{\omega+\Omega_{\sigma1}+i\nu}\right)+[s(s+1)-\sigma^2+\sigma]\left(\frac{1}{\omega+\Omega_{\sigma2}+i\nu}-\frac{1}{\omega-\Omega_{\sigma2}+i\nu}\right)\right\}, \tag{19}$$

$$\chi_{xy} = -\chi_{yx} = \frac{i\mu^2}{4\hbar}Z^{-1}\sum_{\sigma=-s}^{s}e^{-\beta E_\sigma}\left\{[s(s+1)-\sigma^2-\sigma]\left(\frac{1}{\omega-\Omega_{\sigma1}+i\nu}\right.\right.$$
$$\left.\left.+\frac{1}{\omega+\Omega_{\sigma1}+i\nu}\right)-[s(s+1)-\sigma^2+\sigma]\left(\frac{1}{\omega+\Omega_{\sigma2}+i\nu}+\frac{1}{\omega-\Omega_{\sigma2}+i\nu}\right)\right\} \tag{20}$$

Formulas (19) and (20) show that the paramagnet we are considering has $2(3s+1)$ resonance frequencies. Each such frequency corresponds on the absorption curve to a peak, whose height and width (for given σ) depend on the temperature.

At low temperatures ($1 \ll \beta\alpha$), the magnetic susceptibility is basically determined by those terms of the sum that correspond to the ground state of the Hamiltonian (2). The result, just as above, depends significantly on whether the Zeeman energy μH is larger or smaller than $2\alpha s$.

If $\mu H > 2\alpha s$, then in expressions (19) and (20) the term corresponding to the ground state is that with $\sigma = s$. Then for $\beta\alpha \gg 1$ we have

$$\chi_{xx} = -\frac{\mu^2 s}{\hbar}\frac{\Omega_{s2}}{\omega^2-\Omega_{s2}^2+2i\omega\nu}, \tag{19'}$$

$$\chi_{xy} = -\frac{i\mu^2 s}{\hbar}\frac{\omega+i\nu}{\omega^2-\Omega_{s2}^2+2i\omega\nu}. \tag{20'}$$

If $\mu H < 2\alpha s$ and if, for given H, $\sigma = \sigma_0$ corresponds to the ground state, then for $1 \ll \alpha\beta$

$$\chi_{xx} = \frac{\mu^2}{2\hbar}\left\{\frac{s(s+1)-\sigma_0(\sigma_0+1)}{\omega^2-\Omega_{\sigma_01}^2+2i\omega\nu}\Omega_{\sigma_01}+\frac{s(s+1)-\sigma_0(\sigma_0-1)}{\omega^2-\Omega_{\sigma_02}^2+2i\omega\nu}\Omega_{\sigma_02}\right\}; \tag{19''}$$

$$\chi_{xy} = \frac{i\mu^2}{2\hbar}\left\{\frac{s(s+1)-\sigma_0(\sigma_0+1)}{\omega^2-\Omega_{\sigma_01}^2+2i\omega\nu}-\frac{s(s+1)-\sigma_0(\sigma_0-1)}{\omega^2-\Omega_{\sigma_02}^2+2i\omega\nu}\right\}(\omega+i\nu). \tag{20''}$$

From formulas (19′), (19″), (20′), and (20″) it is seen that when $\mu H > 2\alpha s$ there is a single resonance peak, whereas when $\mu H < 2\alpha s$ there are two peaks. This follows also from the selection rules for the magnetic quantum number σ. These rules allow a transition $\sigma \to \sigma \pm 1$. When $\mu H < 2\alpha s$, transitions are possible into the states σ_0+1 and σ_0-1; but when $\mu H > 2\alpha s$, a transition is possible only into the state $s-1$.

Let the frequency ω of the alternating field be close to one of the resonance frequencies $\Omega_{\sigma j}$ (j equal to 1 or 2), with $\sigma \neq \sigma_0$. Then for $1 \ll \beta\alpha$, it is necessary in the tensor χ_{ik}, in general, to take into account, besides the term with $\sigma = \sigma_0$, the resonance term; that is, the one for which $|\omega-\Omega_{\sigma j}| \ll \nu$. If, for example, $\mu H > 2\alpha s$ and ω is close to $\Omega_{\sigma1}$, then

$$\chi_{xx} = -\frac{\mu^2 s}{\hbar}\frac{\Omega_{s2}}{\omega^2-\Omega_{s2}^2+2i\omega\nu}$$
$$+\frac{\mu^2}{4\hbar}\exp\{-\beta(E_\sigma-E_s)\}\frac{s(s+1)-\sigma(\sigma+1)}{\omega-\Omega_{\sigma1}+i\nu}$$

and analogously for the other components.

The contribution of the second term in the last formula depends on the behavior of the relaxation frequency ν at low temperature. If at low temperature the frequency ν either is independent of temperature or depends on it according to a power law, then the second term makes an exponentially small contribution. Consequently, in order that the resonance peak may become

[4)]The expression (17) is similar to the formula for the cross section for absorption of γ-quanta in the theory of the Mössbauer effect [5].

accentuated with lowering of the temperature, it is necessary that ν depend exponentially on temperature.

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