THE SHAPE OF EPR LINE IN MAGNETS WITH STRONG CRYSTALLINE FIELD ANISOTROPY

By J. Czakon

Institute of Physics, Silesian University, Katowice *

The method of orthogonal operators has been applied in the investigation of the EPR line shape for the case of magnets with strong crystalline field anisotropy $JD^{-1} \ll 1$. The behaviour of the resonance line in the vicinity of the transition point is considered. The parameters of the line shape depend on temperature and are expressed in terms of thermo-dynamical correlation functions. The results for magnets with arbitrary value of spin S in the molecular field approximation are given and compared with those of the Tanaka and Kondo theory.

1. Introduction

The shape of the EPR line in magnets for the case when the crystalline field anisotropy of the type $-D \sum_f (S_f^z)^2$ is stronger than the exchange interaction has been investigated by several authors [1, 2]. The absorption EPR line is usually observed in an external magnetic field in which the rotating component can be determined. The shape and intensity of the line can be represented as a function of temperature, constant magnetic field, frequency ω and parameters of internal interactions. A well-known expression can be used [3]

$$\chi''(\omega) = \text{th} \frac{\beta\omega}{2} \int\limits_{-\infty}^{\infty} G(t) \cos \omega t dt, \tag{1.1}$$

where $G(t)$ stands for the thermodynamical correlation function of spin operators

$$G(t) = \tfrac{1}{2} \langle S^+(t)S^- + S^- S^+(t) \rangle, \tag{1.2}$$

and $\langle ... \rangle$ denotes average over the great canonical ensemble. When the resonance is observed at temperatures higher than the temperature of magnetic phase transition, we can calculate the correlation function (1.2) with the use of Hamiltonian either in the approximation of noninteracting spin [1] or in the molecular field approximation.

* Address: Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40-007 Katowice, Poland.

The aim of the present work is to show how the existence of the transition point in correlation functions describing the line shape can be taken into account for the case when the magnet contains ions with an arbitrary value of spin S. The method of orthogonal operators [4] which has been used in the thermodynamical description of the spin system with exchange interaction and with the crystalline field-type anisotropy $-D \sum_f (S_f^z)^2$ [5] will be applied here for the calculation of the correlation functions describing the line shape. The numerical results for the case of $S = 1$ and $S = \frac{3}{2}$ for the Tanaka and Kondo and molecular field approximations will be given in the form of appropriate graphs for the intensity and for the parameters by which its shape is characterized.

2. The method of orthogonal operators

Now the method of calculation for function $G(t)$ defined by (1.2) for the case of an arbitrary spin value will be formulated [3]

$$S^+(t) = \sum_f S_f^+(t) = \sum_f e^{i(H_0 + H_I)t} S_f^+ e^{-i(H_0 + H_I)t}, \tag{2.1}$$

where

$$H_0 = -\mu g_0 h_0 \sum_f S_f^z - D \sum_f (S_f^z)^2,$$

$$H_I = -\sum_{fg} J_{fg}(S_f^+ S_g^- + S_f^z S_g^z). \tag{2.2}$$

H_0 contains the Zeeman interaction of spins with the external magnetic field and the crystalline field anisotropy and H_I describes the exchange interaction among spins. Further, H_I will be considered in (2.1) as a small perturbation. Let us focus our attention on the lower order terms of the $S_f^+(t)$ expansion

$$S_f^+(t) = e^{iH_0^x t} S_f^+ + i \int_0^t dt' [H_I(t' - t), e^{iH_0^x t} S_f^+]$$

$$- \int_0^t dt' \int_0^{t'} dt'' [H_I(t' - t), [H_I(t'' - t), e^{iH_0^x t} S_f^+]], \tag{2.3}$$

where

$$H_I(\tau) = e^{iH_0^x \tau} H_I, \quad H_0^x \dots = [H_0, \dots]. \tag{2.4}$$

All expressions in (2.3) can be calculated easily if one expresses S_f^+ in terms of $L_{\alpha,\beta}^f$ operators [5] i. e.

$$S_f^+ = \sum_{\alpha=-S}^{S-1} C_\alpha^S L_{\alpha+1,\alpha}^f, \quad (S_f^z)^N = \sum_{\alpha=-S}^{S} \alpha^N L_{\alpha,\alpha}^f,$$

$$C_\alpha^S = \sqrt{S(S+1) - \alpha(\alpha+1)}. \tag{2.5}$$

We shall make use of the commutations rules for $L^f_{\alpha,\beta}$

$$[L^f_{\alpha,\beta}, L^g_{\mu,\nu}] = \delta_{fg}(\delta_{\beta\mu}L^f_{\alpha,\nu} - \delta_{\alpha\nu}L^f_{\mu,\beta})$$

and of the relation

$$H^x_0 L^f_{\alpha+1,\alpha} = \varepsilon_\alpha L^f_{\alpha+1,\alpha}, \tag{2.6}$$

where

$$\varepsilon_\alpha = -\mu g_0 h_0 - D(2\alpha+1). \tag{2.7}$$

The expansion (2.3) takes the form

$$S^+_f(t) = \sum_{\alpha=-S}^{S-1} C^S_\alpha e^{i\varepsilon_\alpha t}\{L^f_{\alpha+1,\alpha} + i\int_0^t dt'[H_I(t'-t), L^f_{\alpha+1,\alpha}]$$

$$- \int_0^t dt' \int_0^{t'} dt''[H_I(t'-t), [H_I(t''-t), L^f_{\alpha+1,\alpha}]]\}. \tag{2.8}$$

Using (2.6) and (2.7) $H_I(\tau)$ can be given as

$$H_I(\tau) = -\sum_{fg} J_{fg}(\sum_{\alpha=-S}^{S-1} (C^S_\alpha)^2 L^f_{\alpha+1,\alpha}L^g_{\alpha,\alpha+1} + \sum_{\alpha,\beta=-S}^{S} \alpha\beta L^f_{\alpha,\alpha}L^g_{\beta,\beta})$$

$$-\sum_{fg} J_{fg} \sum_{\varrho=1}^{2S-1} \sum_{\alpha=-S}^{S-\varrho-1} C^S_{\alpha+\varrho}C^S_\alpha(L^f_{\alpha+1,\alpha}L^g_{\alpha+\varrho,\alpha+\varrho+1}e^{-2iD\varrho\tau} + L^f_{\alpha+\varrho+1,\alpha+\varrho}L^g_{\alpha,\alpha+1}e^{2iD\varrho\tau}), \tag{2.9}$$

or equivalently

$$H_I(\tau) = \sum_{\varrho=-2S+1}^{2S-1} H^\varrho e^{2iD\varrho\tau}. \tag{2.10}$$

For $G(t)$ we get

$$G(t) = G_0(t) + G_1(t) + G_2(t), \tag{2.11}$$

where

$$G_0(t) = \sum_{\alpha=-S}^{S-1} I_\alpha e^{i\varepsilon_\alpha t},$$

$$G_1(t) = it \sum_{\alpha=-S}^{S-1} I_\alpha e^{i\varepsilon_\alpha t}\sigma^1_\alpha,$$

$$G_2(t) = -\sum_{\alpha=-S}^{S-1} I_\alpha e^{i\varepsilon_\alpha t} \sum_{\varrho=-2S+1}^{2S-1} \sigma^2_{\alpha,\varrho}\int_0^t d\tau(t-\tau)e^{2iD\varrho\tau}, \tag{2.12}$$

and the functions of the line shape will be defined by

$$\sigma^1_\alpha = \langle\{[L_{\alpha+1,\alpha}, H^0], L_{\alpha,\alpha+1}\}\rangle,$$

$$\sigma^2_{\alpha,\varrho} = \langle\{[[L_{\alpha+1,\alpha}H^\varrho], H^{-\varrho}], L_{\alpha,\alpha+1}\}\rangle,$$

$$I_\alpha = \langle\{L_{\alpha+1,\alpha}, L_{\alpha,\alpha+1}\}\rangle,$$

$$\langle\{A, B\}\rangle = \tfrac{1}{2}\langle AB+BA\rangle. \tag{2.13}$$

. In (2.12) an approximation based on neglecting the term proportional to ε_α^{-1} and ε_α^{-2} was made and in $G_1(t)$ the expressions with ϱ different from zero were neglected [1]. The values of σ_α^1, $\sigma_{\alpha,\varrho}^2$ and I_α can be calculated if one assumes that the correlations between different sites vanish above the transition point

$$\langle A_f B_g \rangle_{f \neq g} = \langle A_f \rangle \langle B_g \rangle. \tag{2.14}$$

The above approximation is valid in the molecular field theory. From (2.13) the line shape parameters can be derived explicitly

$$\sigma_\alpha^1 = zJ[2 \sum_{\nu=-S}^{S} \nu L_\nu + (C_\alpha^S)^2 (L_\alpha - L_{\alpha+1})], \tag{2.15}$$

$$\sigma_{\alpha,\varrho}^2 = z(z-1)J^2 (C_{\alpha+\varrho}^S)^2 (C_\alpha^S)^2 (L_\alpha - L_{\alpha+1})(L_{\alpha+\varrho} - L_{\alpha+\varrho+1})$$

$$+ zJ^2 \{ (C_{\alpha+\varrho}^S)^2 (C_\alpha^S)^2 (L_{\alpha+\varrho} + L_{\alpha+\varrho+1})$$

$$+ (C_{\alpha+1}^S)^2 (C_{\alpha-\varrho+1}^S)^2 L_{\alpha-\varrho+2} + (C_{\alpha-1}^S)^2 (C_{\alpha-\varrho-1}^S)^2 L_{\alpha-\varrho-1} \}, \tag{2.16}$$

$$\sigma_{\alpha,0}^2 = z(z-1)J^2 [2 \sum_{\nu=-S}^{S} \nu L_\nu + (C_\alpha^S)^2 (L_\alpha - L_{\alpha+1})]^2$$

$$+ zJ^2 [(C_{\alpha+1}^S)^4 L_{\alpha+2} + (C_\alpha^S)^4 (L_\alpha + L_{\alpha+1}) + (C_{\alpha-1}^S)^4 L_{\alpha-1}]$$

$$+ 4zJ^2 [\sum_{\nu=-S}^{S} \nu^2 L_\nu + (C_\alpha^S)^2 (\alpha L_\alpha - (\alpha+1)L_{\alpha+1})], \tag{2.17}$$

$$I_\alpha = \tfrac{1}{2} N (C_\alpha^S)^2 (L_\alpha - L_{\alpha+1}) \operatorname{cth} \frac{\varepsilon_\alpha}{kT}, \tag{2.18}$$

where

$$L_\alpha = \langle L_{\alpha,\alpha}^f \rangle, \quad \alpha = -S, ..., S$$

can be calculated from [5]

$$L_S = \left(1 + \sum_{k=1}^{2S} \prod_{i=1}^{k} \frac{\phi_{S-i}}{1+\phi_{S-i}} \right)^{-1},$$

$$L_\alpha = L_S \prod_{i=\alpha}^{S-1} \frac{\phi_i}{1+\phi_i}, \quad \alpha = -S, ..., S-1. \tag{2.19}$$

Functions ϕ_α are given by

$$\phi_\alpha = (e^{-\beta\omega_\alpha} - 1)^{-1}, \quad \beta = (kT)^{-1}. \tag{2.20}$$

In the approximation of noninteracting spins (high temperatures) ω_α equals

$$\omega_\alpha = \varepsilon_\alpha = -\mu g_0 h_0 - D(2\alpha+1). \tag{2.21}$$

In the molecular field approximation one should assume

$$\omega_\alpha = -\mu g_0 h_0 - D(2\alpha+1) - 2zJ \sum_{v=-S}^{S} v L_v. \tag{2.22}$$

In both (2.21) and (2.22) $G(t)$ can be approximated [1] by

$$G(t) = \sum_{\alpha=-S}^{S-1} \tilde{I}_\alpha \exp\left[i(\omega_\alpha + \Delta\omega_\alpha)t\right] \exp\left[-\tfrac{1}{2}\sigma_{\alpha,0}^2 t^2\right] + g_S(t), \tag{2.23}$$

where $\Delta\omega_\alpha$ and $\tilde{I}_\alpha$ are modified position and intensity of the resonance lines

$$\Delta\omega_\alpha = -\sigma_\alpha^1 - \sum_{\substack{\varrho=-2S+1 \\ \varrho \neq 0}}^{2S-1} \frac{\sigma_{\alpha,\varrho}^2}{2\varrho D}, \tag{2.24}$$

$$\tilde{I}_\alpha = I_\alpha\left(1 - \sum_{\substack{\varrho=-2S+1 \\ \varrho \neq 0}}^{2S-1} \frac{\sigma_{\alpha,\varrho}^2}{4\varrho^2 D^2}\right), \tag{2.25}$$

and $g_S(t)$ describes the satellite lines with the values of $\varepsilon_\alpha + 2D\varrho$ independent of temperature and spin correlations

$$g_S(t) = \sum_{\alpha=-S}^{S-1} I_\alpha \sum_{\substack{\varrho=-2S+1 \\ \varrho \neq 0}}^{2S-1} \frac{\sigma_{\alpha,\varrho}^2}{4\varrho^2 D^2} \exp\left[i(\varepsilon_\alpha + 2D\varrho)t\right]. \tag{2.26}$$

The absorption line χ'' calculated from (2.23) on the basis of (1.1) takes the form

$$\chi''(\omega) = \text{th}\,\frac{\beta\omega}{2}\left[I_0(\omega) + I_S(\omega)\right], \tag{2.27}$$

where

$$I_0(\omega) = \sum_{\alpha=-S}^{S-1} \tilde{I}_\alpha \sqrt{\frac{\pi}{2\sigma_{\alpha,0}^2}} \exp\left[-(\omega_\alpha + \Delta\omega_\alpha + \omega)^2 / 2\sigma_{\alpha,0}^2\right] \tag{2.28}$$

describes the line shape and

$$I_S(\omega) = \sum_{\alpha=-S}^{S-1} \sum_{\substack{\varrho=-2S+1 \\ \varrho \neq 0}}^{2S-1} I_\alpha \frac{\sigma_{\alpha,\varrho}^2}{4\varrho^2 D^2} \delta(\omega + \varepsilon_\alpha + 2D\varrho), \tag{2.29}$$

describes the satellite part. The results obtained concern arbitrary spin values and enable us to calculate the parameters of the line shape σ_α^1, $\sigma_{\alpha,\varrho}^2$ in the molecular field approximation.

3. Numerical results and discussion

Formulas (2.27) and (2.28) can be used for the investigation of the dependence of χ'' on the parameters and temperature. Let us start by stating that the shape of the absorption line depends strongly on parameter JD^{-1}, which determines the ratio of exchange interaction and uniaxial anisotropy. At high temperatures even small changes of this parameter (e. g. from 0.05 to 0.08 and 0.1) cause significant changes in the line shape including the disappearance of the lateral maxima (Fig. 1). We have assumed $S = \frac{3}{2}$ to make it more
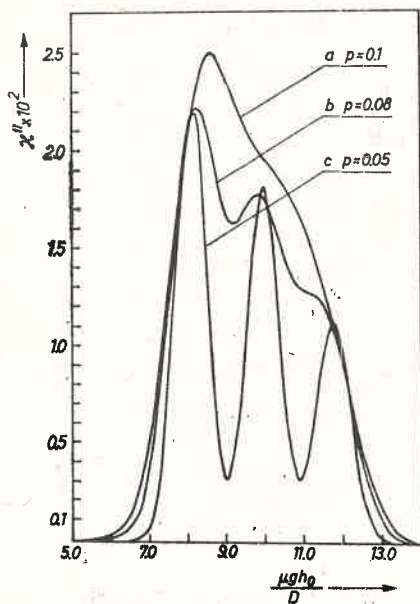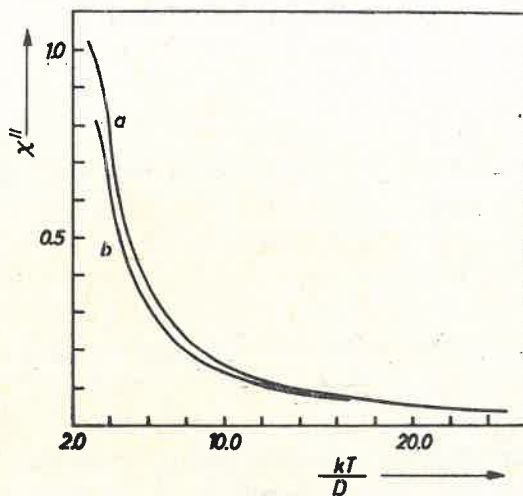

Fig. 1
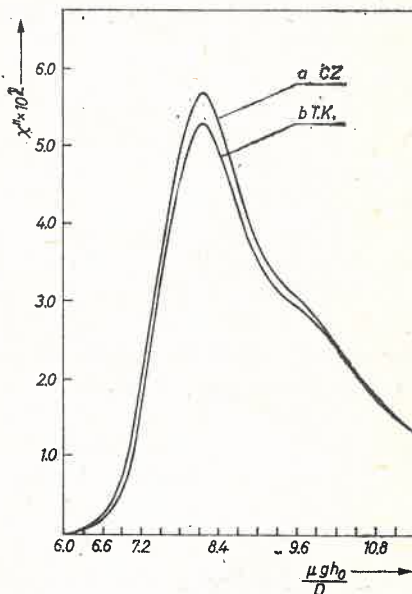
Fig. 2

Fig. 3

visible. This has been derived in the molecular field approximation but we have found the same behaviour in the Tanaka and Kondo approximation. In the absolute scale the absorption lines derived in the molecular field approximation are narrower and lower than those from the Tanaka and Kondo approximation (Fig. 2, $S = 1$) and in the relative scale (the line normalized to unity) they are always narrower, independent of the spin value. We have also found that as a function of temperature takes on higher values in the molecular field approximation for the arbitrary magnetic field (Fig. 3, $\mu g_0 h_0/D = 8.1$).

The position of the main maximum $(\omega_{max})_{MFA}$ also is a function of temperature (Fig. 4); up to temperature $kT/D = 8.1$ it is shifted toward higher fields and at temperatures above that value it is shifted toward lower magnetic fields with respect to the values
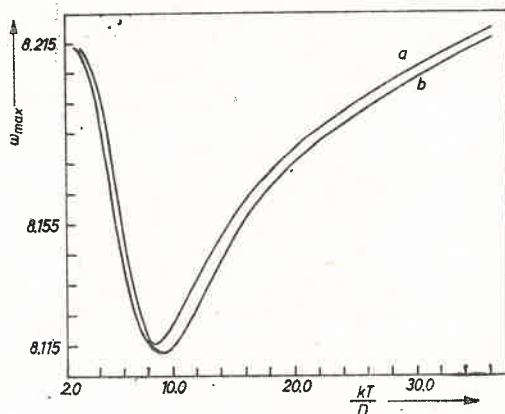

Fig. 4

calculated without taking into account the existence of the phase transition point. This is due to a change of parameters $\Delta\omega_\alpha$, $\sigma^2_{\alpha,0}$. It is visible in Figs. 5 and 6 where the behaviour of $\Delta\omega_{-\frac{3}{2}}$ and $\sigma^2_{-\frac{3}{2},0}$ versus temperature is shown ($\mu g_0 h_0/D = 8.1$). $\Delta\omega_{-\frac{1}{2}}$, $\Delta\omega_{\frac{1}{2}}$ and $\sigma^2_{-\frac{1}{2},0}$, , $\sigma^2_{\frac{1}{2},0}$ for different values of the magnetic field behave similarly and the curves derived within the MFA always lie below those of the Tanaka and Kondo approximation.

In the recapitulation we can say that in the EPR theory taking the molecular field approximation into account for the case of magnets with $JD^{-1} \ll 1$ causes the resonance lines to change their shape and position. The line becomes narrower and the difference between theory and experiment [6] should be attributed to the fact that an important dipole-dipole interaction has not been taken into account.

The limiting values of the line shape parameters σ^1_α and $\sigma^2_{\alpha,0}$ do not depend on taking or not taking the molecular field into account. For example, when $T \to 0$, L_α determined by equations (2.19) takes the values

$$L_S = 1, \quad L_{S-1} = \ldots = L_{-S} = 0, \tag{3.1}$$

and

$$\sigma^1_{S-1} = 0, \quad \sigma^1_{S-2} = \ldots = \sigma^1_{-S} = 2zJS, \tag{3.2}$$

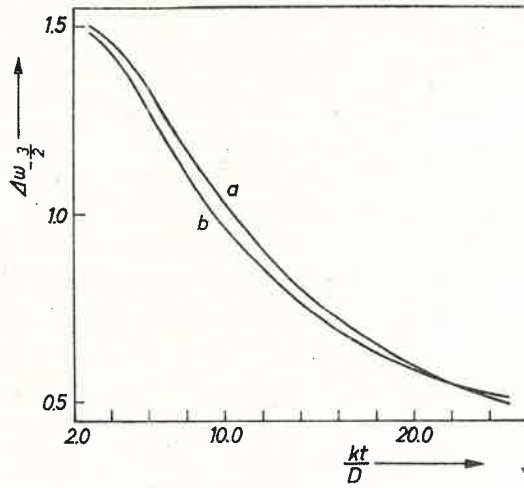$$\sigma^2_{S-1,0} = 0, \quad \sigma^2_{S-2,0} = \ldots = \sigma^2_{-S,0} = z(z+1)(2JS)^2. \tag{3.3}$$

Fig. 5

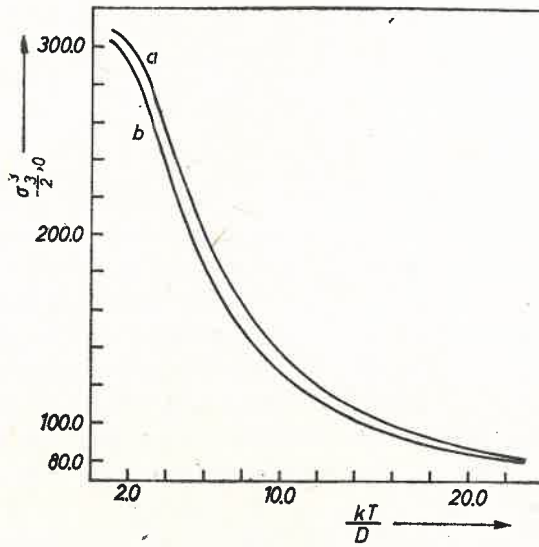

Fig. 6

At high temperatures we get

$$L_S = L_{S-1} = \dots = L_{-S} = \frac{1}{2S+1}, \tag{3.4}$$

$$\sigma_\alpha^1 = 0, \quad \alpha = -S, \dots, S-1, \tag{3.5}$$

and

$$\sigma^2_{\alpha,0} = \frac{zJ^2}{2S+1}\left[(C^S_{\alpha+1})^4 + 2(C^S_\alpha)^4 + (C^S_{\alpha-1})^4 - 4(C^S_\alpha)^2\right.$$

$$\left. + \frac{4S(S+1)(2S+1)}{3}\right], \quad \alpha = -S, ..., S-1. \tag{3.6}$$

The results which we have obtained are a generalization of the results of Tanaka and Kondo for the case of arbitrary spin value S. The existence of the molecular field in a magnet has also been taken into account.

REFERENCES

[1] M. Tanaka, Y. Kondo, *J. Phys. Soc. Jap.* **40**, 35 (1976).
[2] M. McMillan, W. Opechowski, *Can. J. Phys.* **38**, 1168 (1960); **39**, 1369 (1961); A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford 1970.
[3] R. Kubo, K. Tomita, *J. Phys. Soc. Jap.* **9**, 1539 (1954).
[4] S. B. Haley, P. Erdos, *Phys. Rev.* **B5**, 1106 (1972).
[5] J. Czakon, *Acta Phys. Pol.* **53A**, 57 (1978).
[6] I. Svare, G. Seidel, *Phys. Rev.* **134A**, 172 (1964).