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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.
Anisotropic exchange and effective crystal field parameters
for low dimensional systems, EPR data*

R.M. Eremina
Zavoisky Physical-Technical Institute, Sibirskii trakt, 10/7, Kazan 420029, Russia
Kazan Federal University, Kremlevskaya, 18, Kazan 420008, Russia
E-mail: RRerema@yandex.ru

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We review some aspects of the electron paramagnetic resonance (EPR) studies in quasi-one-dimensional inorganic compounds with special emphasis on the angular dependencies of g-factors, linewidth and the information they reveal about the physical system. In particular, we employ for the analysis of the data the method of moments and outline the expressions for the second and the fourth moments which is related to different spin-spin interactions.

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1. Introduction

Quantum phenomena in low-dimensional magnets continue to attract an interest in condensed matter physics. For example, several inorganic quasi-one-dimensional spin Heisenberg antiferromagnets do not show a three-dimensional magnetic order, but exhibit a spin-Peierls transition into a singlet ground state characterized by the dimerization of neighboring spins as in CuGeO$_3$ [1]. Recently a quasi-one-dimensional (1D) chain compound LiCuVO$_4$ gained interest as a real material with a low magnetic ordering temperature $T_N$ due to weak inter-chain interaction [2]. In this particular compound, magnetic frustration is formed due to competition between ferromagnetic intra-chain nearest-neighbor $J_{NN}$ and antiferromagnetic next-nearest-neighbor $J_{NNN}$ exchange interactions an incommensurate helix structure of the magnetic Cu$^{2+}$ moments with $S = \frac{1}{2}$. In addition, the magnetic structure at $T_N$ is accompanied by the ferroelectric order with spontaneous polarization at the same temperature.

Electron paramagnetic resonance (EPR) is a convenient method to probe anisotropic spin-spin interactions. The EPR linewidth displays the average amplitude of the fluctuating field on the magnetic ion, which can be directly related to the parameters of the anisotropic spin-spin interactions. The EPR signal of this system consists of a single exchange-narrowed resonance line. The theory of the EPR linewidth is still under debate in current literature (see [3, 4] and Refs. therein).

Two reviews about EPR in inorganic quasi-one dimensional system were published with the accent made on the experimental data [5, 6]. Here we focus mainly on the problem how to extract the spin-Hamiltonian parameters from the angular dependencies of the EPR frequencies and the linewidth.

This article is a brief review of relevant expressions which are obtained for the second and the fourth moments of the EPR line in limit of high temperatures. These formulas can be used for the analysis of the angular dependence of EPR linewidth. In particular, measuring EPR linewidth in three mutually orthogonal planes $(ab)$, $(ac)$ and $(bc)$ one is able to obtain a complete information about the anisotropic exchange parameters. Few examples of such kind of studies will be shortly described.

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2. Anisotropic symmetric exchange interaction

The theory of the EPR linewidth, as a rule based on momentum method. It has been shown that in the case of sufficiently strong exchange interaction the EPR spectrum is narrowed into a single Lorentz line. Assuming that the EPR line is Lorentzian, the linewidth $\Delta H$ is given by

$$\Delta H = \frac{\pi}{\sqrt{3}} \left( \frac{M_2^2}{M_4} \right)^{1/2},$$

where $M_2$ and $M_4$ are the second and fourth moments of the EPR line, respectively. Both moments can be expressed in terms of the microscopic parameters of the Hamiltonian of the spin system using expressions

$$M_2 = \frac{\left\langle \left[ H_{an}, S^+ \right] \left[ S^- , H_{an} \right] \right\rangle}{\hbar^2 \left\langle S^+ S^- \right\rangle},$$

$$M_4 = \frac{\left\langle \left[ H_{ex} \left[ H_{an}, S^+ \right] \right] \left[ S^- , H_{an} \right] , H_{ex} \right\rangle}{\hbar^4 \left\langle S^+ S^- \right\rangle}.$$  

Here, $H_{an}$ contains all anisotropic exchange interactions, crystal field, dipole-dipole and anisotropic Zeeman terms, $H_{ex}$ is the isotropic Heisenberg exchange $H_{ex}^{ij} = J S_i S_j$ between neighboring spins $S_i$ and $S_j$, $\left\langle \right\rangle$ means thermodynamic averaging, $S^+$ and $S^-$ are the raising and lowering spin operators, respectively. In a high-temperature approximation ($kT >> J$) the details of calculations of the second and the fourth moments are described in Ref. [7]. There is a wide temperature range in the paramagnetic state where antiferromagnetic correlations have to be taken into account.

The exchange interactions of the spin in the chain are not necessarily inversely symmetric, i.e. interactions to the left and to the right neighbours in a chain may not be identical [8] (see Fig. 1).

In this case one has the spin Hamiltonian

$$H = J_{ll} S_i S_j + \sum_{a,\beta=x,y,z} J_{ll}^{\alpha\beta} S_i^\alpha S_j^\beta + J_{lr} S_i S_r + \sum_{a,\beta=x,y,z} J_{lr}^{\alpha\beta} S_i^a S_r^\beta.$$  

Here $J_{ll}$, $J_{ll}^{\alpha\beta}$ are the parameters of the isotropic and anisotropic exchange interactions with the left ($l$) nearest neighbour spins of magnetic ion, and $J_{lr}$, $J_{lr}^{\alpha\beta}$ are the parameters of the isotropic and anisotropic exchange interactions with the right ($r$) nearest neighbor spins of magnetic ions, respectively. For brevity, the summation over the spins of the chain (orange colors in Fig. 1) is not indicated. The interaction of spins with an external magnetic field is written as:

$$H_z = \sum_{a,\beta=x,y,z} g_\beta \mu_B H_a S_\beta.$$  

The summation over all spins of the chain is not indicated. In a coordinate system with the z-axis directed along the external magnetic field, the second and fourth moments of the EPR line are calculated as follows [8]:

$$M_2 = \frac{S(S+1)}{3} \left[ B(J_{ll}) + B(J_{lr}) \right].$$

Figure 1. The quasi-one dimensional spin-system with alternating isotropic exchange interaction.
\[ M_4 = \frac{N(6N-7)}{30} \left[ J_{ii}^z B(J_{ii}) + J_{ii}^y B(J_{ii}) \right] + \frac{N^2}{9} \left[ J_{ii}^x B(J_{ii}) + J_{ii}^y B(J_{ii}) \right] \]
\[ + \frac{N^2 J_{ii}^z}{9} \left[ (2J_{ii}^z - J_{ii}^x - J_{ii}^y) \left( 2J_{ii}^y - J_{ii}^x - J_{ii}^y \right) + (J_{ii}^x - J_{ii}^y) \left( J_{ii}^x - J_{ii}^y \right) \right] + 10J_{ii}^x J_{ii}^y + 10J_{ii}^y J_{ii}^x + 4J_{ii}^x J_{ii}^y, \]  
where \( N = S(S+1), \)
\[ B(J_{ii}) = \left( 2J_{ii}^z - J_{ii}^x - J_{ii}^y \right)^2 + \left( J_{ii}^x - J_{ii}^y \right)^2 + 10 \left( J_{ii}^x \right)^2 + 10 \left( J_{ii}^y \right)^2 + 4 \left( J_{ii}^z \right)^2. \]

The quantities \( J_{ii}^{\alpha \beta \eta} \) (where \( \alpha, \beta = x, y, z; \) and \( \eta = l, r \)) are determined in a local coordinate system with \( z \)-axis being parallel to the external magnetic field. However, it is important to bear in mind that the number of independent parameters of the anisotropic symmetric exchange is less if one works in the crystallographic coordinate system. Therefore, it is useful to express the relevant combinations of quantities \( J_{ii}^{\alpha \beta \eta} \) via its values in crystallographic coordinate system \((a, b, c)\). Performing the necessary rotation, the following relation can be written as:
\[ J_{1q}^{yz} = (J_{bb} - J_{aa}) \cos \beta \sin \alpha \cos \alpha + J_{ab} \cos \beta \cos 2 \alpha + J_{ac} \sin \beta \sin \alpha - J_{bc} \sin \beta \cos \alpha, \]  
\[ J_{1q}^{zx} = (J_{cc} \cos^2 \alpha + J_{bc} \sin^2 \alpha - J_{cc} \sin 2 \alpha + J_{bc} \cos 2 \alpha) \cos \beta \sin \beta + (J_{ac} \cos \alpha + J_{bc} \sin \alpha \cos \alpha) \cos 2 \beta, \]  
\[ J_{1q}^{zy} = (J_{bb} - J_{aa}) \sin \beta \cos \alpha \sin \alpha + J_{ab} \sin \beta \cos 2 \alpha - J_{ac} \cos \beta \sin \alpha + J_{bc} \cos \beta \cos \alpha, \]  
\[ J_{1q}^{xy} = J_{1q}^{yx} = (J_{cc} \cos^2 \beta \cos^2 \alpha - 2 \cos \beta \cos \alpha \sin \alpha) + J_{bb} \left( \cos^2 \beta \sin^2 \alpha - \cos^2 \alpha \right) + J_{bc} \sin^2 \beta \]
\[ + J_{ab} \sin 2 \alpha \left( \cos^2 \beta + 1 \right) - J_{ac} \sin 2 \beta \cos \alpha - J_{bc} \sin 2 \beta \sin \alpha, \]  
\[ 2J_{1q}^{xz} - J_{1q}^{yz} = J_{cc} \left( 3 \cos^2 \beta \cos^2 \alpha - 1 \right) + J_{bb} \left( 3 \sin^2 \beta \cos^2 \alpha - 1 \right) + J_{bc} \left( 3 \sin^2 \beta \sin^2 \alpha - 1 \right) \]
\[ + 3J_{ab} \sin^2 \beta \sin 2 \alpha + 3J_{ac} \sin 2 \beta \cos \alpha + 3J_{bc} \sin 2 \beta \sin \alpha, \]
where
\[ \cos \alpha = \frac{A}{\sqrt{A^2 + B^2}}, \]  
\[ \cos \beta = \frac{C}{\sqrt{A^2 + B^2 + C^2}}, \]
\[ A = g_{aa} \sin \theta \cos \phi + g_{ab} \sin \theta \sin \phi + g_{ac} \cos \theta, \]  
\[ B = g_{bb} \sin \theta \cos \phi + g_{bc} \sin \theta \sin \phi + g_{bc} \cos \theta, \]  
\[ C = g_{cc} \sin \theta \cos \phi + g_{ac} \sin \theta \sin \phi + g_{bc} \cos \theta. \]  
\[ g = \sqrt{A^2 + B^2 + C^2}. \]

The angles \( \theta \) and \( \phi \) are the magnetic field orientation with respect to the crystallographic axes. The quantities \( J_{z\zeta}^{\xi}, g_{z\zeta}^{\xi} \) \((\zeta, \xi = a, b, c)\) are parameters of anisotropic exchange interaction and \( g \)-tensor in crystallographic coordinate system, respectively. It is assumed, that in the coordinate system \((x', y', z')\), with \( z' \)-axis is directed along the chain, the symmetric intra-chain anisotropic exchange interaction between two neighbouring spins \( S_i \) and \( S_j \) can be written as
Anisotropic exchange and effective crystal field parameters for low dimensional systems, EPR data

$$H_{\text{AEX}} = J_{x'x'} S_i^x S_j^x + J_{y'y'} S_i^y S_j^y + J_{z'z'} S_i^z S_j^z,$$  (16)

where is assumed that $J_{x'x'} + J_{y'y'} + J_{z'z'} = 0$. The values of the anisotropic exchange interaction for the left and right neighbour spins in the chain may differ, therefore the magnitudes of $J_{\zeta \xi}$ ($\zeta, \xi = a, b, c$) in the crystallographic coordinate system for the neighbour spins to the right and to the left may have different values. Also the $g$-tensor in the crystallographic coordinates is obtained from its counterpart in local coordinates ($x''$, $y''$, $z''$), where $g$-tensor have only diagonal components $g_{xx''}$, $g_{yy''}$, $g_{zz''}$, by means of a rotation.

Interesting example of such EPR studies is CuTe$_2$O$_5$ single crystal. At temperatures of 25 to 300 K, the EPR spectrum of copper ions consists of one Lorentzian-shaped line with $g \sim 2$. The angular dependences of the EPR linewidth of CuTe$_2$O$_5$ calculated theoretically and measured at frequencies of 9.4 and 160 GHz at $T = 200$ K are presented in Fig. 2. The detailed calculation and values of $g$-tensor and exchange interaction parameters can be found in [8].

Figure 2. Angular dependences of the EPR linewidth in CuTe$_2$O$_5$ at frequencies of 9.4 GHz (circles) and 160 GHz (triangles) in three crystallographic planes measured at $T = 200$ K. The dotted lines show the contribution to the EPR linewidth from the spin-spin interactions between copper ions in a dimer and between copper ions belonging to neighboring dimers. The dashed line corresponds to the contribution from the anisotropic Zeeman effect at 160 GHz. The solid lines show the sum of all the contributions (for each frequency).

3. Anisotropic Zeeman interaction

If the EPR linewidth along one axis at a different frequency is greater than its value in the $X$-band, i.e. it depends on the field as $H^2$, it is logical to assume that this effect originates from the difference between the individual $g$-factors of interacting spins (anisotropic Zeeman effect). As a rule it is can be seen from the analysis of the structural data, where one finds that the unit cell contains two magnetically nonequivalent ligands surrounding the paramagnetic ions producing an EPR signal. Since the EPR spectrum exhibits only one line, its effective $g$-factor is the average of the $g$-factors of two magnetic centers located at the nonequivalent positions. The frequency-dependent contribution to the EPR linewidth due to the difference between the $g$-factors is given by [9]

$$\Delta H_{AZ} = \left( \frac{A g}{g} \right)^2 \frac{g \mu_B H_{\text{ms}}^2}{J_{\text{inter}}},$$  (17)
where $\Delta g$ is the difference between the $g$-factors of the nonequivalent paramagnetic centers. The resonance frequency is related to the resonance magnetic field by the relation $g\mu BH_{\text{res}} = \hbar \nu_{\text{res}}$. Using values of $\Delta g$ and $\Delta H_{\text{g}}$ as determined from the experimental data, we can find exchange integral $J_{\text{inter}}$ between magnetic nonequivalent paramagnetic ions. As noted in Fig. 2, the EPR linewidth along the $b$-axis at a frequency of 160 GHz is greater than its value in the $X$-band in CuTe$_2$O$_5$. Indeed, from analyzing the structural data [8], it follows that the unit cell contains two magnetically nonequivalent octahedra of oxygen ions that surround the paramagnetic copper ions producing an EPR signal. The frequency-dependent contribution to the EPR linewidth due to the difference between the $g$-factors is given by (16). The angular dependence of the EPR linewidth measured at 160 GHz shows that the difference between the $g$-factors of the two nonequivalent octahedra is maximal along the $b$-axis of the crystal and is minimal along the other directions. Since the geometric sizes of the two magnetically nonequivalent octahedra are equal, the principal values of the $g$-tensors in a local coordinate system of the octahedra also have to be equal. When fitting the experimental values of the EPR linewidth obtained at 160 GHz, we took into account that the contribution from the anisotropic symmetric interactions is the same as that in the $X$-band. The isotropic exchange interaction between the spins of the copper ions belonging to neighboring magnetically nonequivalent octahedra as estimated is $J_{\text{inter}} = 0.5$ K.

### 4. Anisotropic antisymmetric Dzyaloshinsky-Moriya interaction

The expressions for $M_2$ and $M_4$ in case of antisymmetric Dzyaloshinsky-Moriya (DM) interaction were obtained previously in Ref. [10].

The spin Hamiltonian of DM interaction of the spin system is written as

$$H_g = JS_S + \sum_{\alpha=x,y,z} D_\alpha \left[ S_\alpha \times S_j \right]_\alpha,$$

where $J$ is the parameter of the isotropic exchange interaction, $D_\alpha$ ($\alpha = x, y, z$) are parameters of antisymmetric DM interaction in the coordinate system with the $z$-axis parallel to the applied magnetic field. The interaction of spins with an external magnetic field is described by (4). The transformation between the crystallographic system ($a$, $b$, $c$) and the coordinate system ($x$, $y$, $z$) is determined by expressions:

$$D_x = D_x \cos \beta \cos \alpha + D_y \cos \beta \sin \alpha - D_z \sin \beta,$$

$$D_y = D_x \cos \alpha - D_y \sin \alpha,$$

$$D_z = D_x \sin \beta \cos \alpha + D_y \sin \beta \sin \alpha + D_z \cos \beta,$$

where $\cos \alpha$ and $\cos \beta$ are determined by (13). The expressions for second and fourth moments are expressed:

$$M_2 = \frac{2N}{3} \left[ D_x^2 + D_y^2 + 2D_z^2 \right],$$

$$M_4 = \frac{4N(2N-1)}{3} J^2 \left[ D_x^2 + D_y^2 + 2D_z^2 \right],$$

where $N = S(S + 1)$. Note that in Ref. [10] a three-dimensional compound of LaMnO$_3$ was considered. The components $D_x$, $D_y$, and $D_z$ of DM vector $\mathbf{d}_z$ refer to the pair Mn-Mn within the $ac$-plane, whereas components $D_x'$ and $D_y'$ of DM vector $\mathbf{d}_1$ refer to the Mn ions along $b$-axis (see Fig. 3). $J_{ac}$ and $J_b$ are the parameters of the isotropic exchange interaction between the spins of magnetic ions in the $ac$-plane and along the $b$-axis, respectively. Example of the contributions to the angular dependencies of EPR linewidth from DM interaction between spins of manganese ions in the plane ($d_2$) and between the planes ($d_1$) is shown in Fig. 4.
Figure 3. Next neighbor bond of the Mn ions and components of the DM vector in $ac$-plane ($d_5$) and along $b$-axis ($d_1$) in LaMnO$_3$.

5. Crystal field

In the local coordinate system, where the axes are directed along the bonds of the paramagnetic ion-ligand, the spin Hamiltonian of the crystal field is usually written in the following form

$$H_{cf} = DS_z^2 + E \left( S_z^2 - S_y^2 \right),$$

(21)

where $D$ and $E$ are crystal field parameters. Very often the axes of symmetry of the spin Hamiltonian (21) are not coincided to the crystallographic axes. The transformation from the local coordinate system to the crystallographic coordinate system under the rotation of the axes is described by the Euler angles. To calculate second and fourth moments of lines it is necessary to rotate the spin Hamiltonian into the coordinate system where the $z$-axis is directed along the external magnetic field. This procedure was described in [11].

In the coordinate system with the $z$-axis directed along the external magnetic field, the Hamiltonian (21) takes the form

$$H_{cf} = \lambda_{xx} S_x^2 + \lambda_{yy} S_y^2 + \lambda_{zz} S_z^2 + \lambda_{xy} (S_x S_y + S_y S_x) + \lambda_{xz} (S_x S_+ + S_+ S_x) + \lambda_{yz} (S_y S_+ + S_+ S_y).$$

(22)

Then, the expression for the second moment of the linewidth is written as [11]

$$M_2 = \frac{1}{20h^2} \left( 4N - 3 \right) \left( \lambda_{xx} - \lambda_{yy} \right)^2 + 4 \lambda_{yy}^2 + \left( \lambda_{xx} + \lambda_{yy} - 2 \lambda_{zz} \right)^2 + 10 \left( \lambda_{xx} + \lambda_{yy} \right),$$

(23)

where $N = S(S + 1)$, $h$ is Planck’s constant, the relevant combinations of quantities $\lambda_{\xi\eta} (\xi, \eta = x, y, z)$ via its values in crystallographic coordinate system ($a$, $b$, $c$) are similar to (8) - (12). The expression for the fourth moment taking into account the isotropic exchange interaction and crystal field is [11]

$$M_4 = \frac{4J_{ac}^2 + 2J_b^2}{10h^2} \left( \frac{4N - 3}{10h^2} \right) \left( \lambda_{xx} - \lambda_{yy} \right)^2 + 4 \lambda_{yy}^2 + \left( \lambda_{xx} + \lambda_{yy} - 2 \lambda_{zz} \right)^2 + 10 \left( \lambda_{xx} + \lambda_{yy} \right),$$

(24)

where $J_{ac}$ and $J_b$ are the parameters of the isotropic exchange interaction between the spins of magnetic ions in the $ac$-plane and along the $b$-axis, respectively.

The crystal field and antisymmetric Dzyaloshinsky-Moriya (DM) interaction are important for description angular dependencies of EPR linewidth in La$_{0.95}$Sr$_{0.05}$MnO$_3$ [10]. In three orthogonal planes in La$_{0.95}$Sr$_{0.05}$MnO$_3$, one observes a broad, exchange-narrowed resonance line.
The contributions of crystal field and DM interaction consist of the superposition of the four nonequivalent Mn ions in the orthorhombic unit cell. The crystal-field parameters for all Mn positions and the DM interaction for nearest-neighbor Mn ions along the $b$-axis as well as in the $ac$-plane were successfully extracted [10] from angular dependencies of EPR linewidth. Angular dependencies of EPR linewidth in $\text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$ are presented in Fig. 4.

![Figure 4](image)

**Figure 4.** Angular dependence of the EPR linewidth in $\text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$ for the magnetic field applied within the three crystallographic planes at 300 K. The solid lines represent the fit. The lines below illustrate the contributions of crystal field (CF) and Dzyaloshinsky-Moriya (DM) interaction, respectively.

### 6. Summary

In this short review we have outlined expressions for the second and the fourth moments of EPR linewidth in high-temperature limit obtained by various authors and described how they were used for the interpretation of angular dependencies of the EPR linewidth. Additional information about the anisotropic interaction parameters may be obtained via analyses of temperature dependences of EPR linewidth. Example of such study was recently presented in [12]. Combining analyses of angular and temperature dependencies of the EPR linewidth, authors were able to extract DM components for one more low-dimensional compound ($\text{Cs}_2\text{CuCl}_4$). Interesting example how crystal field can influence on the temperature dependence of EPR linewidth is described in [13].

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