ISSN 1512-1461

UDC 538.9 Condensed matter physics. Solid state physics

THE LOW-FREQUENCY METHOD TO MEASURE THE LONGITUDINAL RELAXATION RATES OF THE SEPARATE TRANSITIONS OF THE SPIN-TRIPLET STATES

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Abstract

The compounds with the spin-triplet states (STS) find wide application in science and technology. Therefore, the investigation of the STS interaction with the lattice is of the great importance. This interaction is characterized by the spin-lattice relaxation rates – in other words, by the rates of the longitudinal (with respect to the acting magnetic field) relaxation. The special attention of the experimenters is directed to the rates of the longitudinal relaxation at the separate transitions of STS, the measurement of which was realized earlier only by the high-frequency method (electron paramagnetic resonance). In the given paper, the low-frequency method is suggested, enabling the measurement of the longitudinal relaxation rates at the STS separate transitions in the Gorter type experiment where the STS levels crossing is provided by the appropriate choice of the constant magnetic field value.

***Keywords**:* spin-triplet state, longitudinal relaxation rate, Gorter type experiment, relaxational resonance

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The compounds with the spin-triplet state (STS) find the wide application at the realization of the nuclear dynamic polarization [1-3], in the molecular electronics [4-5] and in such optoelectronic devices, as light-emitting diodes, transistors and solar cells [6]. They play important role in photosynthesis [7] and at the creation of the "entangled" spin states, which are of interest at the elaboration of the quantum processors [8].

In the given paper, we suggest the method, enabling the measurement of the longitudinal relaxation rates at the STS separate transitions by the Gorter method, i.e. by the observation of the spin-system (SS) susceptibility to the low-frequency (LF) magnetic field. The relaxational spin dynamics in paramagnetic salts was investigated by the Gorter method before the electron paramagnetic resonance discovery [9]. However, could be, the method of the relaxational resonance will also be of interest for the studying of the spin relaxation in the molecular crystals with STS. It should be mentioned that this method needs only a low-frequency equipment and does not need an EPR spectrometer.

Let us consider the SS of a sample with the STS, subjected to the constant magnetic field $\mathbf{B}\|\mathbf{Z}$ and the LF varying magnetic field $\mathbf{B}_1\|\mathbf{X}$. Here **X,Y,Z** are the main axes of the quadrupolar interaction

ISSN 1512-1461

tensor $\mathcal{H}_Q = D\left[S_Z^2 - (1/3)S(S+1)\right] + E\left(S_X^2 - S_Y^2\right)$, which, along with the Zeeman interaction $g_Z\mu_B BS^Z$, forms the principal Hamiltonian of the problem $\mathcal{H}_{Ze+Q}^Z = g_Z\mu_B BS^Z + \mathcal{H}_Q$. S_X, S_Y, S_Z are the projections of the STS electron spin S=1 on the **X,Y,Z** axes. The SS interaction with the LF field $\left(g_X\mu_B/\hbar\right)S_X 2B_{1X}\cos\omega t$ and the lattice are the perturbations of the principal Hamiltonian.

For example, we would like to describe the suggested method of the measurement of the longitudinal relaxation rate $\left(T_1^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}^{-1}$ at the STS transition 2-3, which is characterized by its resonance quantum $\hbar\omega_{23}^Z = -D + \sqrt{\left(g_Z\mu_B B\right)^2 + E^2}$. This measurement should occur with the help of the observation of the dynamic susceptibility $\chi_{XX}(\omega)$ to the LF field with the frequency $\omega \sim \left(T_1^{2-3}\right)^{-1}$, which is essentially smaller than all the three resonance frequencies of STS. The exact equations of the regular (non-relaxational) motion of the magnetization components $M_{X,Y,Z}^{2-3}$ of the 2-3 transition have the form:

$$\dot{M}_X^{2-3} = -\omega_{23}^Z (g_X/g_Y) M_Y^{2-3} - \sqrt{2}C_Z (g_X/g_Y) M_Y^{1-3}\left(g_X\mu_B/\hbar\right)B_{1X}\cos\omega t$$

$$\begin{aligned}\dot{M}_Y^{2-3} &= \omega_{23}^Z (g_Y/g_X) M_X^{2-3} - \\ &-\sqrt{2}\left(2A_Z (g_Y/g_Z) M_Z^{2-3} - C_Z (g_Y/g_X) M_X^{1-3}\right)\left(g_X\mu_B/\hbar\right)B_{1X}\cos\omega t\end{aligned} \qquad (1)$$

$$\dot{M}_Z^{2-3} = -\sqrt{2}(g_Z/g_Y)\left(C_Z M_Y^{1-2} - 2A_Z M_Y^{2-3}\right)\left(g_X\mu_B/\hbar\right)B_{1X}\cos\omega t$$

where $g_{X,Y,Z}$ are the diagonal components of the g-factor tensor, μ_B is the Bohr magneton, the values A_Z and C_Z are determined at the end of this paper. The derivation of these equations will be described in our another paper.

It is supposed at the further description of the experiment scheme that the inequality $D > |E|$ takes place. Then for the realization of the method the constant field should be fitted to the value $B = \sqrt{D^2 - E^2}/g_Z\mu_B$. At that the 2-3 transition quantum 2-3 $\hbar\omega_{23}^Z$ becomes zero, and the three-level SS turns effectively to the two-level one. The two other resonance quanta $\hbar\omega_{12}^Z = \hbar\omega_{13}^Z = 2D$ significantly exceed the LF field quantum, therefore the frequency resonances of the 1-2, 1-3 transitions will not be excited. This means that the precession of the magnetizations of these transitions around the Z axis does not takes place, i.e. the corresponding transverse to the Z axis magnetization components are zero: $M_{X,Y}^{\substack{1-2\\1-3}} = 0$.

As to the 2-3 transition magnetization, it is effectively subjected to the zero constant field and according to the experiment conditions feels only the LF filed $\mathbf{B}_1\|\mathbf{X}$ with the frequency $\omega \sim \left(T_1^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}^{-1}$ and the value $2H_1\mu_0\cos\omega t$. Therefore, according to [10], its only X-component relaxes to its instantaneous equilibrium value in this field. It follows from the above-mentioned facts that the equations (1) under the proposed experimental conditions come to the following equations:

ISSN 1512-1461

$$\dot{M}_X^{2-3} = -\frac{M_X^{2-3} - \chi_0^{2-3} 2H_1 \cos\omega t}{\left(T_1^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}}$$

$$\dot{M}_Y^{2-3} = -\frac{M_Y^{2-3}}{\left(T_2^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}} - \sqrt{2} A_Z \left(g_Y / g_Z\right) M_Z^{2-3} \left(g_X \mu_B / \hbar\right) 2B_{1X} \cos\omega t \qquad (2)$$

$$\dot{M}_Z^{2-3} = -\frac{M_Z^{2-3}}{\left(T_2^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}} + \sqrt{2} A_Z \left(g_Z / g_Y\right) M_Y^{2-3} \left(g_X \mu_B / \hbar\right) 2B_{1X} \cos\omega t$$

Here we suppose already the presence of the relaxation: of the longitudinal one (with the rate $\left(T_1^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}$) along the **X** axis in the equation for $\dot{M}_X^{2-3}$ and of the transverse one (with the rate $\left(T_2^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}$) in the equations for the transverse to the acting LF field components $\dot{M}_Y^{2-3}$ и $\dot{M}_Z^{2-3}$. It should be noted that under these conditions the first equation of the (2) system appears to be disentangled from the two others. The system of the two latter equations in the stationary case has only the trivial stationary solution $M_Y^{2-3} = 0$; $M_Z^{2-3} = 0$. The calculation of the full X-component of the magnetization $M_X = \sqrt{2} A_Z M_X^{2-3}$ leads to the expression of the type of (III.39a) in [10], and, consequently, to the analogous values of the LF dynamic susceptibility

$$\chi'_{XX}(\omega) = \frac{\chi_0^{2-3}\Big|_X^Z}{1 + \omega^2 \left(T_1^{2-3}\right)^2_{\mathbf{B}\|\mathbf{X}}}; \qquad \chi''_{XX}(\omega) = \frac{\chi_0^{2-3}\Big|_X^Z \omega \left(T_1^{2-3}\right)_{\mathbf{B}\|\mathbf{X}}}{1 + \omega^2 \left(T_1^{2-3}\right)^2_{\mathbf{B}\|\mathbf{X}}}, \qquad (3)$$

where $\chi_0^{2-3}\Big|_X^Z = \dfrac{\left(g_X \mu_B\right)^2 n \mu_0}{3 k_B T_L} A_Z^2$.

The expression of the imaginary part $\chi''_{XX}(\omega)$ of the complex dynamic susceptibility (3) shows that as a result of such experiment the sample absorbs the energy of the LF field. Finding the varying field frequency $\omega\big|_{\max}$, providing the maximal absorption – the maximal value of $\chi''_{XX}(\omega)$, it is possible to extract the required value $\left(T_1^{2-3}\right)^{-1}_{\mathbf{B}\|\mathbf{X}} = \omega\big|_{\max}$ (i.e. the so called relaxational resonance takes place) [11]).

In the general form, the tensor of the LF complex susceptibility has only the diagonal elements; it is convenient to write them in the form of the Table:

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LF susceptibilities in the constant fields	$\chi_{XX}(\omega)=\frac{g_X^2\mu_B^2\mu_0 n}{3k_BT}\times$	$\chi_{YY}(\omega)=\frac{g_Y^2\mu_B^2\mu_0 n}{3k_BT}\times$	$\chi_{ZZ}(\omega)=\frac{g_Z^2\mu_B^2\mu_0 n}{3k_BT}\times$
B ‖ Z	$A_Z^2F\left(T_1^{2-3}\right)_{\mathbf{B}\parallel\mathbf{X}}$	$C_Z^2F\left(T_1^{2-3}\right)_{\mathbf{B}\parallel\mathbf{Y}}$	$3\left(1-th^2\frac{g_Z\mu_BB}{k_BT}\right)\times$ $\times F\left(T_1^{1-3}\right)_{\mathbf{B}\parallel\mathbf{Z}}$; $E=0$
B ‖ Y	$A_Y^2F\left(T_1^{1-2}\right)_{\mathbf{B}\parallel\mathbf{X}}$; $E>0$	$3\left(1-th^2\frac{g_Y\mu_BB}{k_BT}\right)\times$ $\times F\left(T_1^{1-3}\right)_{\mathbf{B}\parallel\mathbf{Y}}$; $E=0$	$C_Y^2F\left(T_1^{1-2}\right)_{\mathbf{B}\parallel\mathbf{Z}}$; $E>0$
B ‖ X	$3\left(1-th^2\frac{g_X\mu_BB}{k_BT}\right)\times$ $\times F\left(T_1^{1-3}\right)_{\mathbf{B}\parallel\mathbf{X}}$; $E=0$	$C_X^2F\left(T_1^{1-2}\right)_{\mathbf{B}\parallel\mathbf{Y}}$; $E<0$	$A_X^2F\left(T_1^{1-2}\right)_{\mathbf{B}\parallel\mathbf{Z}}$; $E<0$

where $\chi_{\alpha\alpha}(\omega)$ describes the response of the α -component of the magnetization to the LF field directed along the α axis, in the items with $F\left(T_1^{2-3}\right)$ the constant field has the value $B=\sqrt{D^2-E^2}/g_Z\mu_B$; in the items with $F\left(T_1^{1-2}\right)$ the constant field has the value $B=\sqrt{2|E|(D+|E|)}/g_{X,Y}\mu_B$; subscript at $g_{X,Y}$ should be choosed according to the direstion of $\mathbf{B}$; in the items with $F\left(T_1^{1-3}\right)$ the constant field has the arbitrary value $B>>D$, also it is taken $E=0$ in these latter items for the simplification of the result. Everywhere $A_{X,Y,Z}^2=1+\sin\Theta_{X,Y,Z}$; $C_{X,Y,Z}^2=1-\sin\Theta_{X,Y,Z}$;

$$\sin\Theta_Z=-\left[\left(D_X-D_Y\right)/2\right]/\sqrt{\left(g_Z\mu_BB\right)^2+\left[\left(D_X-D_Y\right)/2\right]^2}=-E/\sqrt{\left(g_Z\mu_BB\right)^2+E^2};$$

the values of $\sin\Theta_{X,Y}$ are obtained by the cyclic repositioning of the indices in the values D_X, D_Y, D_Z and by the using of the table from the monography [12]; $F\left(T_1^{i-j}\right)\equiv\frac{1-i\omega T_1^{i-j}}{1+\omega^2\left(T_1^{i-j}\right)^2}$.

In conclusion we would like to note the following: if the spin-lattice relaxation is of the one-phonon type and realizes according to the van Fleck mechnism, then the values of the relaxation rates obtained with the help of the suggested method can be compared with the expressions obtained by us for the relaxation rates on the STS separate transitions, which will be published in our another paper.

Acknowledgements:

This work was supported by Shota Rustaveli National Science Foundation (SRNSF) [grant number № FR/299/6-110/14]

ISSN 1512-1461

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Article received 2017-12-01