NUCLEAR MAGNETIC RESONANCE SPECTRAL FUNCTION AND MOMENTS FOR PROTON PAIRS IN POWDERED PARAMAGNETIC SUBSTANCES MnSO$_4$·H$_2$O AND NiSO$_4$·H$_2$O

The NMR spectrum is determined by interaction of resonating nuclei between the particles of the substance. These interactions depend on the spatial arrangement of the particles and their motion. Parameters characterizing interactions between the paramagnetic ions Me^{2+} (Me = Mn and Ni) and the protons of crystalline water in powdered MnSO$_4$·1H$_2$O and NiSO$_4$·1H$_2$O were derived from the temperature dependences on the second moment of the NMR spectra. The parameters characterizing the local magnetic field acting on the proton pairs were calculated and compared with those obtaind from the analysis of the shape of the NMR spectrum.

Key words: nuclear magnetic resonance (NMR), magnetic substances, hydrates

Funkcija spektra magnetne rezonancije jezgre i momenata za parove u praškastim paramagnetnim tvarima MnSO$_4$·1H$_2$O i NiSO$_4$·1H$_2$O. MRJ spektar je određen interakcijom rezonantnih jezgri između čestica materije. Te interakcije ovise o prostornom rasporedu čestica i njihovog kretanja. Parametri koji karakteriziraju interakcije između paramagnetnih iona Me^{2+} (Me = Mn i Ni) i protona kristalne vode u praškastim MnSO$_4$·1H$_2$O i NiSO$_4$·1H$_2$O su izvedene iz ovisnosti tempreture o drugom momentu MRJ spektra. Parametri koji obilježavaju lokalno magnetno polje koje djeluje na parove protona su izračunati i uspoređeni s onima koji su dobiveni iz analize oblika MRJ spektra.

Ključne riječi: magnetna rezonancija jezgre (MRJ), magnetne tvari, hidrati

INTRODUCTION

The influence of paramagnetic ions on the shape and the second moment of the proton NMR line and some problems associated with the NMR study line shape and with the local magnetic field calculations in paramagnetic substances were studied in papers [1 - 6].

In this paper we analyse the dependences of the NMR second moment M_2 on temperature. Beside the second moment M_{20} which corresponds to the nuclear dipole-dipole interactions, the Curie-Weiss constant θ and the magnetic moment μ_i of paramagnetic ions may be determined from the temperature dependences. The two parameters θ and M_{20} may be determined directly from experimental data. However, some knowledge on crystralline structures for studied substances required for calculation of the magnetic moment μ_i. The parameters characterizing the local magnetic field acting on the resonating nuclei may

be calculated on the basis of the structural data. We have calculated these parameters according to a simplified structural model in which only two paramagnetic ions Me^{2+} (Me = Mn, Ni) are allowed to interact with the proton pair of crystalline water. The spectral function was calculated for MnSO$_4$·1H$_2$O and NiSO$_4$·1H$_2$O and the parameters characterizing the local magnetic field were evaluated from experimental spectrum.

THEORETICAL PART

In examining the NMR phenomenon the ^{1}H - ^{1}H nuclei are in a magnetic field with induction [1 - 4, 9]:

$$B = B_r + B_d^{(i)} + B_d^{(n)} \tag{1}$$

where:

B_r - the induction of the external magnetic field, $B_r = 2\pi f_r/\gamma$, f_r = 14,1 MHz or 30,0 Mz (in this case) is the resonance frequency, and γ is the gyromagnetic constant of the ^{1}H nuclei;

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$B_d^{(i)}$ - the induction of the magnetic field formed by the paramagnetic ions Me^{2+} ($Me = Mn$, Ni), including demagnetising effects which operate in these substances;

$B_d^{(n)}$ - the induction of the magnetic field in the area of a single nuclei formed by another nucleus of the quasi-isolated pair H-H.

The inductions $B_d^{(i)}$ and $B_d^{(n)}$ can be expressed according to papers [1, 3] in the form:

$$B_d^{(i)} = \frac{\mu_0 \cdot \mu_i^2 B_r}{4\pi \cdot 3k(T-\theta)}\Big(A_1 \cos^2\vartheta + A_2 \sin^2\vartheta \cos 2\varphi$$
$$+ B_1 \sin^2\vartheta \sin 2\varphi + B_2 \sin 2\vartheta \sin \varphi$$
$$+ \frac{3}{2}B_3 \sin 2\vartheta \cos \varphi + C\Big) \tag{2}$$

and

$$B_d^{(n)} = \pm \frac{3}{2}\frac{\mu_0}{4\pi}\frac{\mu_p}{r_p^3}\big(3\cos^2\vartheta - 1\big), \tag{3}$$

where:

μ_0 - the permeability of vacuum,
μ_i - the magnetic moment of paramagnetic ions,
k - Boltzmann's constant,
T - the temperature,
θ - Curie-Weiss constant,
μ_p - the proton's magnetic moment,
r_p - the proton - proton distance in the crystalline water.

The angles φ and ϑ characterize the orientation of external magnetic field $\vec{B}_r$ in the reference frame used. The parameters A_1, A_2, B_1, B_2, B_3 and C depend on the configuration of paramagnetic ions and resonating nuclei and are expressed as [1, 3]:

$$A_1 = 3\sum_l r_l^{-3} P_2 \cos \beta_l,$$

$$A_2 = \frac{1}{2}\sum_l r_l^{-3} P_2^2 \cos \beta_l \cos 2\alpha_l,$$

$$B_1 = \frac{1}{2}\sum_l r_l^{-3} P_2^2 \cos \beta_l \sin 2\alpha_l,$$

$$B_2 = \frac{1}{2}\sum_l r_l^{-3} P_2^l \cos \beta_l \sin \alpha_l,$$

$$B_3 = \frac{1}{2}\sum_l r_l^{-3} P_2^l \cos \beta_l \cos \alpha_l,$$

$$C = -\frac{1}{3}A_1, \tag{4}$$

where:

$\vec{r}_l$ - the vector joining the reference nucleus with the l - th paramagnetic ion,

α_l, β_l - the angles characterizing the orientation of $\vec{r}_l$ and P_2^m are Legendre polynomials.

According to equations (2) and (3) the local magnetic field $B_{loc} = B_d^{(i)} + B_d^{(n)}$ may be thought as a quadratic form relative to the components of the unit vector $\vec{e}_r (\sin\vartheta \cos\varphi, \sin\vartheta \sin\varphi, \cos\vartheta)$ parallel to $\vec{B}_r$. This quadratic form may be diagonalized and the roots of the secular equation determine the invariant parameters of the local magnetic field (denoted as B_x^+, B_y^+, B_z^+, B_x^-, B_y^-, B_z^-), through which the spatial function may be expressed [1].

According to [1, 3] the second moment of NMR spectrum may be expressed in the form:

$$M_2 = \frac{AB_r^2}{(T-\theta)^2}, \tag{5}$$

where

$$A = \left(\frac{\mu_0}{4\pi}\right)^2 \cdot \frac{\mu_i^4}{9k^2} \cdot \frac{4}{45}\Big[A_1^2 + 3\big(A_2^2 + B_1^2 + B_2^2 + B_3^2\big)\Big]. \tag{6}$$

The equation (5) expresses the temperature and the field dependence of the second moment in paramagnetic. For isolated proton pairs the second moment M_{20} may be expressed in the form [1, 4]:

$$M_{20} = \frac{9}{5}\left(\frac{\mu_0 \mu_p}{4\pi r_p^3}\right)^2. \tag{7}$$

For the spectral function $f_0(x)$ of the isolated pairs of the nuclei, we used the following form [1, 3, 7]:

$$F_0(x) = f_0^+(x) + f_0^-(x), \quad x = B - B_r \tag{8}$$

for $(\varepsilon) = +$ or $-$

$$f_0^{(\varepsilon)}(x) = \begin{cases} 0, & B_z^{(\varepsilon)} < x < B_x^{(\varepsilon)}, \\[2ex] \dfrac{K(k)}{\sqrt{\big(B_z^{(\varepsilon)} - x\big)\big(B_y^{(\varepsilon)} - B_x^{(\varepsilon)}\big)}}, & B_x^{(\varepsilon)} < x < B_y^{(\varepsilon)}, \\[3ex] \dfrac{K\left(\dfrac{1}{k}\right)}{\sqrt{\big(x - B_x^{(\varepsilon)}\big)\big(B_z^{(\varepsilon)} - B_y^{(\varepsilon)}\big)}}, & B_y^{(\varepsilon)} < x < B_z^{(\varepsilon)}, \end{cases} \tag{9}$$

where:

$$k = \frac{\left(x - B_x^{(\varepsilon)}\right)\left(B_z^{(\varepsilon)} - B_y^{(\varepsilon)}\right)}{\left(B_z^{(\varepsilon)} - x\right)\left(B_y^{(\varepsilon)} - B_x^{(\varepsilon)}\right)} \tag{10}$$

and

$$K(k) = \int \frac{d\alpha}{\sqrt{1 - k \sin^2 \alpha}}.$$

In the above equations B_x^+, B_y^+, B_z^+, B_x^-, B_y^-, B_z^- are the components of the local field fulfilling the relationship [1 - 6]:

$$\sum_k B_k^{(\varepsilon)} e_k^2 = 0.$$

The magnetic interaction between different pairs of the nuclei was taken into account by means of convolution of the spectral function for isolated pairs with the normalized Gaussian function. Taking into account the fact that the experimental NMR spectra was recorded in the form of derivation of the absorption spectra, the modelling function of the spectrum for crystalline water was selected in the derivation form [1 - 6]:

$$F'(x) = \int F_0(x) S'(\xi - x) d\xi, \quad x \in \mathbb{R}. \tag{11}$$

$S'(\xi - x)$ is the derivation form of the Gaussian function:

$$S(\xi - x) = \frac{1}{\sqrt{2\pi}\beta_G} \cdot e^{-\frac{(\xi - x)^2}{2\beta_G^2}}. \tag{12}$$

The spectral function $F'(x)$ may be calculated numerically [7]. The moments M_n of the spectral function $F'(x)$ by equation (11) may be expressed analytically in the form [3]:

$$M_1 = M_1^{(0)}, \quad M_2 = M_2^{(0)} + \beta_G^2, \quad M_3 = M_3^{(0)},$$
$$M_4 = M_4^{(0)} + 6 M_2^{(0)} \beta_G^2 + 3 \beta_G^4. \tag{13}$$

where:

$M_n^{(0)}$ - the corresponding moments for isolated pairs,
β_G - the parameter of the Gaussian function.

EXPERIMENTAL PART

Broad - line NMR measurements were performed on powdered samples of $MnSO_4 \cdot 1H_2O$ and $NiSO_4 \cdot 1H_2O$ press-

ed to a cylindrical form in diameter 8 mm and about 20 mm in height. The temperature dependences were measured at two frequencies: $f_{r_1} = 14,1$ MHz (0,331 T) and $f_{r_2} = 30,0$ MHz (0,705 T) in the temperature range from 123 K to 313 K. Measurements at frequency 30,0 MHz were done at the Institute of Physics, A. Mickiewicz University in Poznan. The experimental conditions and the method of calculation of moments of the NMR spectra were the same as those described in our previous papers [1 - 6].

RESULTS AND DISCUSSION

The proton NMR spectra of substances $MnSO_4 \cdot 1H_2O$ and $NiSO_4 \cdot 1H_2O$ have an asymmetric form caused by the anisotropy of he local magnetic field acting on resonating nuclei. The central part of the spectra is somewhat distorted by a narrow signal which corresponds to the free water present in the sample as moisture. The spectra measured at room temperature and at different frequencies are similar to each other, but they differ in their widths. The higher is the frequency, the greater is the width of the spectrum.

The temperature dependences of the second moment M_2 are shown in Figure 1. Besides the individual
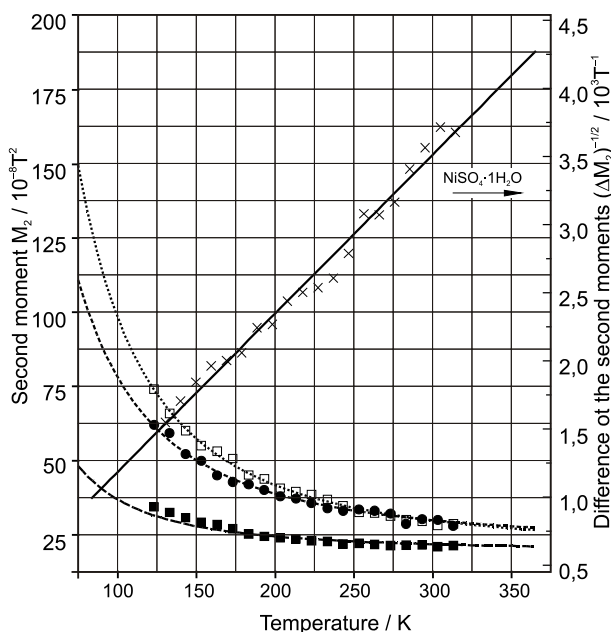

Figure 1. **The temperature dependences of NMR second moment M_2 and $[\Delta M_2]^{-1/2}$ for $MnSO_4 \cdot 1H_2O$ (●) and $NiSO_4 \cdot 1H_2O$ (□, ■) measured at $B_{r_1} = 0,331$ T (●, ■) and $B_{r_2} = 0,705$ T (□)**

Slika 1. **Ovisnost temperature o drugom momentu MRJ i $[\Delta M_2]^{-1/2}$ za $MnSO_4 \cdot 1H_2O$ (●) i $NiSO_4 \cdot 1H_2O$ (□, ■) izmjeren pri $B_{r_1} = 0,331$ T (●, ■) i $B_{r_2} = 0,705$ T (□)**

dependences $M_2(T)$ measured at f_{r_1} or f_{r_2} is convenient to analyse the temperature depenence of the difference $\Delta M_2 = M_2(B_{r_2}) - M_2(B_{r_1})$. The dependence of ΔM_2 on

T may be linearized and the parameters A and θ can be easily determined. According to equation (5) the following relation holds:

$$\left[\Delta M_2\right]^{-\frac{1}{2}} = \frac{T - \theta}{\sqrt{A\left(B_{r_2}^2 - B_{r_1}^2\right)}}.$$

(14)

The dependence of $\left[\Delta M_2\right]^{-\frac{1}{2}}$ on temperature is also shown in Figure 1.

As expected, this dependence is linear and the straight line drawn through the experimental points is expressed by equation (14) with the following values of Curie-Weiss parameters θ and A for $NiSO_4\cdot 1H_2O$: $\theta = -13$ K and $A = 2{,}026\times 10^{-2}K^2$. For $MnSO_4\cdot 1H_2O$ parameters determined by the least squares are: parameter $\theta = -9{,}9$ K and $A = 10{,}54\times 10^{-2}K^2$. As the parameters θ and A are known, the second moment M_{20} may be evaluated by means of equation (5). It was done by extraction of the term $A\cdot B_r^2\left(T - \theta\right)^2$ from the experimental values of M_2 at each measured temperature. By means of this procedure we have obtained the value of $M_{20} = (19{,}50 \pm 0{,}95)\times 10^{-8}T^2$ for $NiSO_4\cdot 1H_2O$ and for $MnSO_4\cdot 1H_2O$ is $M_{20} = (21{,}30 \pm 1{,}2)\times 10^{-8}T^2$.
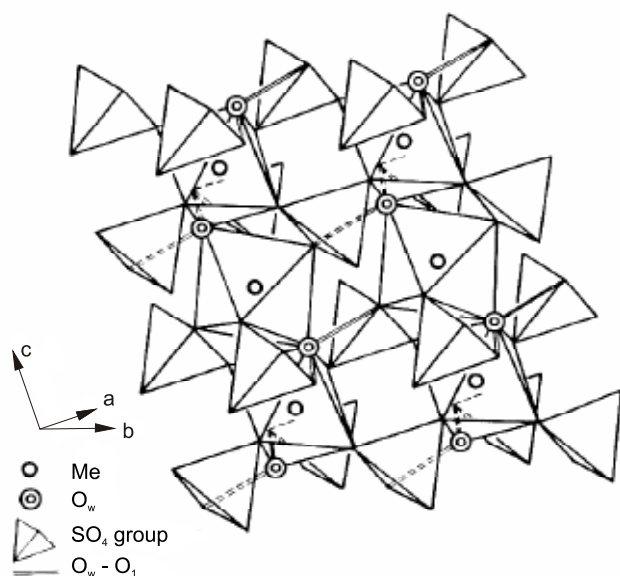
Figure 2. **Coordination surroundings of the Me²⁺ ion in monohydrates MeSO₄·1H₂O (Me²⁺ = Mn, Ni)**
Slika 2. **Koordinacija okoline iona Me²⁺ i monohidrata MeSO₄·1H₂O (Me²⁺ = Mn, Ni)**

A negative value of the temperature parameter θ shows that $NiSO_4\cdot 1H_2O$ and $MnSO_4\cdot 1H_2O$ should be antiferromagnetic at the temperatures $T < |\theta|$ [9]. Measurements of the temperature dependences of the molar magnetic susceptibility in the temperature range from 5 K up to 300 K (Charles University Prague, Dept. of Metal Physics) confirmed this conclusion.

By means of NMR measurements (according to equation (6)) it is possible to determine the magnitude of the magnetic moment μ_i of paramagnetic ions in a given substance, however, the structural parameters A_i and B_i have to be known. We have calculated them in the approximation in which the nearest enviroment of the crystalline water molecule is formed by two Me²⁺ (Me = Mn, Ni) ions. This configuration is shovn in Figure 2. and Figure 3.

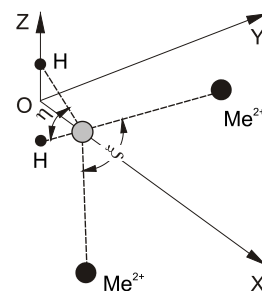Figure 3. **Local coordinate system**
Slika 3. **Lokalni koordinatni sustav**

The individual hydrates from $MeSO_4\cdot 1H_2O$ group were studied by X-ray method [7, 8]. All the hydrates of this group are isomorphous with the monoclinic unit cell. According to [7, 8] the Me²⁺ ions have octahedral surrounding formed by two atoms O_w and by four atoms of O_S which belong to the different ionic complexes SO_4^{-2}. Each molecule of crystal water has tetrahedral surrounding formed by two Me²⁺ ions and by two oxygen atoms O_S. Separation of the individual particles and bond angles taken from papers [7, 8] are: $r_{O_wNi} = 0{,}206$ nm, $r_{O_wMn} = 0{,}225$ nm, $r_{O_wH} = 0{,}1$ nm; ξ is the angle between $Me - O_w - Me = 123°$ and η is the angle $H_1 - O_w - H_2 = 109{,}5°$ for our hydrates.

The local coordinate system O_{xyz} was chosen in such a way that the origin O lies in the centre of joining the atoms H_1 and H_2, the x axis runs through the point where the oxygen atom O_w is placed and it lies in the plabe formed by O_w, Me_1 and Me_2 ions. The structural parameters A_i, B_i and C were calculated from relation (4) using the structural data stated above. The final form of these parameters for $MnSO_4\cdot 1H_2O$, are:

$$A_1 = -2{,}17624\cdot r^{-3}, A_2 = -0{,}48730\cdot r^{-3},$$
$$B_1 = B_2 = 0, B_3 = -1{,}10865\cdot r^{-3}$$

and, for $NiSO_4\cdot 1H_2O$, are:

$$A_1 = -2.05780\cdot r^{-3}, A_2 = -0{,}9601\cdot r^{-3},$$
$$B_1 = B_2 = 0, B_3 = -1{,}19930\cdot r^{-3},$$

(15)

where r is the distance between the Me-ions and H-atoms (expressed in the units of 10^{-10} m). All distances $Me_1 - H_1$, $Me_1 - H_2$, $Me_2 - H_1$ and $Me_2 - H_2$ are the same, $r = 0{,}265$ nm for Me = Mn and $r = 0{,}253$ nm for Me = Ni.

The structural parameters given by relation (15) are expressed for hydrogen nucleus H_1. The respective parameters for hydrogen nucleus H_2 are the same as those for H_1 but they differ from each other in the sign of the parameter B_3, i.e. $B_3(H_1) = -B_3(H_2)$. However, the quantity

$A_1^2 + 3\left(A_2^2 + B_1^2 + B_2^2 + B_3^2\right)$ standing in equation (6) has the same value for both protons H_1 and H_2. Using the experimental value for parameter A in equation (6) we have found that the magnetic moment μ_i of paramagnetic ion Mn^{2+} in $MnSO_4 \cdot 1H_2O$ is 5,74 μ_B and Ni^{2+} in $NiSO_4 \cdot 1H_2O$ is 3,49 μ_B, where $\mu_B = 0{,}9273 \times 10^{-23}$ J·K^{-1} is the Bohr's magneton.

Measurements of magnetic molar susceptibily for our hydrates in the temperature range $5 \approx 300$ K have shown that the NMR method gives valuable information about the magnetic properties of paramagnetic subsancies. From measurements of susceptibility we have found: magnetic moment μ_i of paramagnetic ion Mn^{2+} in $MnSO_4 \cdot 1H_2O$ is 5,72 μ_B and in $NiSO_4 \cdot 1H_2O$ is 3,31 μ_B, Curie-Weiss parameter θ: for $MnSO_4 \cdot 1H_2O$ is $\theta = -21$ K and for $NiSO_4 \cdot 1H_2O$ is $\theta = -18{,}5$ K.

According to equations (1-3) it is now possible to calculate the magnitude B_{loc} of the local magnetic field acting on proton pair. B_{loc} means in our case the component of the local magnetic field parallel to the external magnetic field B_r. By means of equation (2, 4) and (15) the magnitude of B_{loc} may be expressed as a quadratic form:

$$B_{loc}^{(\varepsilon)} = \left(A_2' + C_\varepsilon'\right)e_x^2 + \left(C_\varepsilon' - A_2'\right)e_x^2 + \left(A_{1\varepsilon}' + C_\varepsilon'\right)e_x^2 + 2B_3' e_x e_z \qquad (16)$$

where:

$$A_{1\varepsilon}' = \frac{\mu_0}{4\pi} \frac{\mu_i^2 B_r}{k(T-\theta)} A_1 + \varepsilon 3 \delta_n, \quad A_2' = \frac{\mu_0}{4\pi} \frac{\mu_i^2 B_r}{k(T-\theta)} A_2,$$

$$B_3' = \frac{\mu_0}{4\pi} \frac{\mu_i^2 B_r}{k(T-\theta)} B_3, \qquad C_\varepsilon' = \frac{\mu_0}{4\pi} \frac{\mu_i^2 B_r}{k(T-\theta)} C - \varepsilon \delta_n$$

and

$$\delta_n = \frac{3}{2} \frac{\mu_0}{4\pi} \frac{\mu_p}{r_p^3}. \qquad (17)$$

The symbol ε stands for the two signs ($\pm$) in $B_d^{(n)}$, which results from the quantum mechanical solution [1, 3, 4].

From the data stated above it is now possible to construct the theoretical maps of the local field $B_{loc}(\vartheta, \varphi)$, for given temperature T and the magnitude of the external magnetic field B_r. Another way for determining the local field is based on the analysis of the NMR line shape. The spectral function for isolated proton pairs in paramagnetics was derived in the works [3, 5]. To obtain this function the quadratic form (15) has to be transformed into the canonical form:

$$B_{loc}^{(\varepsilon)} = B_x^{(\varepsilon)}\left(e_x'\right)^2 + B_y^{(\varepsilon)}\left(e_y'\right)^2 + B_z^{(\varepsilon)}\left(e_z'\right)^2, \qquad (18)$$

where e_x', e_y', e_z' are the components of the unit vector $\vec{e}'$, characterizing the direction of the vector $\vec{B}_r$ in the new coordinate system, and the principal components $B_x^{(\varepsilon)}$, $B_y^{(\varepsilon)}$, $B_z^{(\varepsilon)}$ are the roots of the secular equation:

$$\begin{vmatrix} C_\varepsilon' + A_2' - \lambda & 0 & B_3' \\ 0 & C_\varepsilon' - A_2' - \lambda & 0 \\ B_3' & 0 & C_\varepsilon' + A_{1\varepsilon}' - \lambda \end{vmatrix} = 0. \qquad (19)$$

The spectral function $F_0(x) = f_+(x) + f_-(x)$ where $x = B - B_r$, is completely determined by the sets of values $B_x^{(\varepsilon)}$, $B_y^{(\varepsilon)}$, $B_z^{(\varepsilon)}$ [3, 5]. Using the structural data on $MeSO_4 \cdot 1H_2O$ stated previously, the equation (19) gives the following values for $B_i^{(\varepsilon)}$, for $NiSO_4 \cdot 1H_2O$:

$$B_x^+ = -7{,}62, \quad B_y^+ = 2{,}94, \quad B_z^+ = 4{,}68,$$

$$B_x^- = 6{,}70, \quad B_y^- = -5{,}57, \quad B_z^- = 12{,}27, \qquad (20)$$

and, for $MnSO_4 \cdot 1H_2O$:

$$B_x^+ = -5{,}94, \quad B_y^+ = 0{,}25, \quad B_z^+ = 5{,}69,$$

$$B_x^- = -9{,}36, \quad B_y^- = -6{,}52, \quad B_z^- = 15{,}92, \qquad (21)$$

calculated for $T = 293$ K and $B_r = 0{,}331 \cdot T$. All values of $B_i^{(\varepsilon)}$ are expressed in the units of $10^{-4} T$.

The spectral function $F_0(x)$ calculated for these values for $NiSO_4 \cdot 1H_2O$ together with the experimental spectrum recorded in the derivate form are shown in Figure 4.

As we can see, the theoretical spectrum reflects quite well the features of the experimental one. The points $B_{ie}^{(\varepsilon)}$ in the experimental spectrum (in Figure 4.) correspond to the respective values $B_i^{(\varepsilon)}$ of the calculated spectral function. The position of the points $B_{ie}^{(\varepsilon)}$ on the x axis relative to the origin O are as follows:

$$B_{xe}^+ = -8{,}4, \quad B_{ye}^+ = 4{,}0, \quad B_{ze}^+ = 5{,}8,$$

$$B_{xe}^- = -6{,}0, \quad B_{ye}^- = -4{,}0, \quad B_{ze}^- = 11{,}4.$$

They are different from the corresponding $B_i^{(\varepsilon)}$ stated above in (19). It can be shown that the sum of principal components of local field is always zero, i.e.:

$$\sum_{k,\varepsilon} B_k^{(\varepsilon)} = 0, \qquad (22)$$

if the components are related to the resonance field of the free protons, for which $x = B - B_r = 0$. The origin O' on the x - axis for the theoretical spectrum was chosen in such a way.
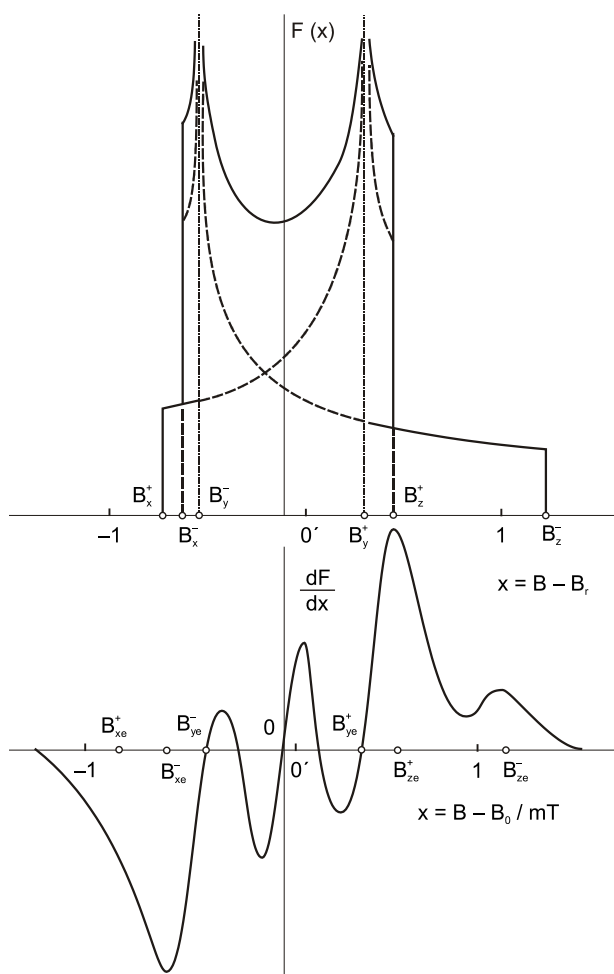
Figure 4. **Theoretical and experimental ^{1}H NMR spectra for NiSO$_4$· 1H$_2$O at T = 293 K and B_r = 0,331 T. The central part of the experimental spectrum is influenced by the moisture of the sample**

Slika 4.   **Teorijski i eksperimantalni ^{1}H MRJ spektar za NiSO$_4$·1H$_2$O pri T =293 K i B_r = 0,331 T. Centralni dio eksperimentalnog spektra je pod utjecajem vlage u uzorku**

The origin O on the x axis for the experimental spectrum may be chosen quite arbitrary if we have no possibility to measure external magnetic field during the experiment. Hence, the abscissa values x both spectra may be shifted relatively to each other as it is also in our case. To make these two axes equivalent, the centre of gravity for experimental spectra 0^* has to be found.

The position of the new origin 0^* relative to the old one 0 is defined as:

$$x_0^* = \frac{1}{6} \sum_k B_{k\varepsilon}^{(\varepsilon)}.$$

$$(23)$$

The quantity of x_0^* is identical with the first moment M_1 of the experimental spectrum related to the origin 0. In aur case x_0^* calculated from the quantities $B_{ie}^{(\varepsilon)}$ stated above

$0,467 \times 10^{-4}$ T and the new redefined quantities $(B_{ie}^{(\varepsilon)} - x_0^*)$ denoted again as $B_i^{(\varepsilon)}$ are:

$$B_x^+ = -8,86, \quad B_y^+ = 3,53, \quad B_z^+ = 5,33,$$

$$B_x^- = -6,47, \quad B_y^- = -4,47, \quad B_z^- = 10,94.$$

$$(24)$$

All values of $B_i^{(\varepsilon)}$ are expressed in the units of 10^{-4} T.

We may consider the set of values $B_i^{(\varepsilon)}$ in (23) as the experimental values of the principal components of local magnetic field as they are derived from the experimnental spectrum. The relative differences between the corresponding theoretical and experimental values of $B_i^{(\varepsilon)}$ are in the range from 3 % (for B_x^-) up to 24 % (for B_y^-). The differences between the theoretical and experimental values of $B_i^{(\varepsilon)}$ are not so significant as they seem to be at first sight if we take into account the used approximation.

In the [6] it was shown that the proportion of the free bonded water in monohydrate MnSO$_4$·1H$_2$O was approximately 9 % (as regards the number of H$_2$O molecules). This is less than in the NiSO$_4$·1H$_2$O. Monohydrate MnSO$_4$·1H$_2$O is not so sensitive than NiSO$_4$·1H$_2$O on the free water, that was recorded on the experimental NMR spectra. After the analysis of the components of the local magnetic field from experimental spectra, when $x_0^* = 0,221 \times 10^{-4}$ T, we have obtained these values of the components of the local fields:

$$B_x^+ = -5,71, \quad B_y^+ = 0,23, \quad B_z^+ = 5,70,$$

$$B_x^- = -9,51, \quad B_y^- = -6,42, \quad B_z^- = 15,69,$$

all in the units 10^{-4} T. The relative differences between the corresponding theoretical and experimental values of $B_i^{(\varepsilon)}$ are in the range from 1,1 % (for B_z^-) up to 15 % (for B_y^+).

In our study we are calculated the components of the local magnetic field also from the measurements of the molar magnetic susceptibility. Using the structural data on NiSO$_4$·1H$_2$O stated previously, the equations (16 - 19) gives the following values for $B_i^{(\varepsilon)}$ at temperature T = 293 K:

$$B_x^+ = -7,85, \quad B_y^+ = 3,2, \quad B_z^+ = 4,65,$$

$$B_x^- = -6,40, \quad B_y^- = -5,44, \quad B_z^- = 11,88,$$

and, for MnSO$_4$·1H$_2$O:

$$B_x^+ = -6,02, \quad B_y^+ = 0,46, \quad B_z^+ = 5,55,$$

$$B_x^- = -9,36, \quad B_y^- = -6,51, \quad B_z^- = 15,87.$$

All values of $B_i^{(\varepsilon)}$ are expressed in the units of 10^{-4} T.

The final modelling spectrum (by the equations (11,12)) of the monohydrate $NiSO_4 \cdot 1H_2O$ with the parameters obtained from NMR measurements and from measurements of the molar magnetic susceptibility is shown at the Figure 5.
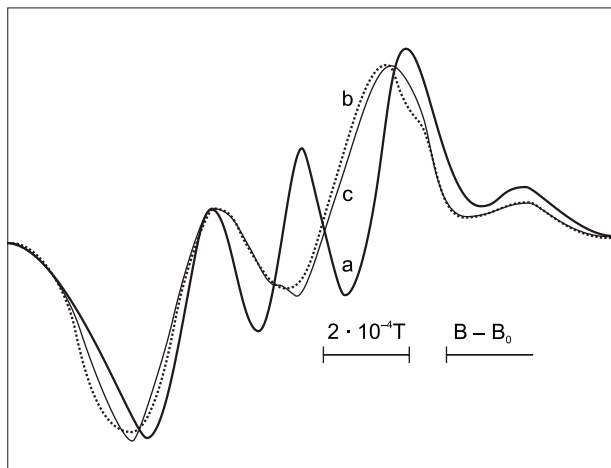

Figure 5. **NMR spectrum of $NiSO_4 \cdot 1H_2O$ at temperature $T = 293$ K: a) experimental; b) theoretical from Figure 4. modelling by equations (11, 12); c) theoretical from the susceptibility measurements**
Slika 5. **Spektar MRJ $NiSO_4 \cdot 1H_2O$ pri temperaturi $T = 293$ K: a) eksperimentalni; b) teorijski iz slike 4. modeliranjem jednadžbi (11, 12); c) teorijski iz mjerenja osjetljivosti**

The parameter β_G in the equation (11) was done by extraction of the term $M_{2exp} = M_2$ and $M_{2teor} = M_2^{(0)}$. In our case: $\beta_G = 1,6 \times 10^{-4} \cdot T$.

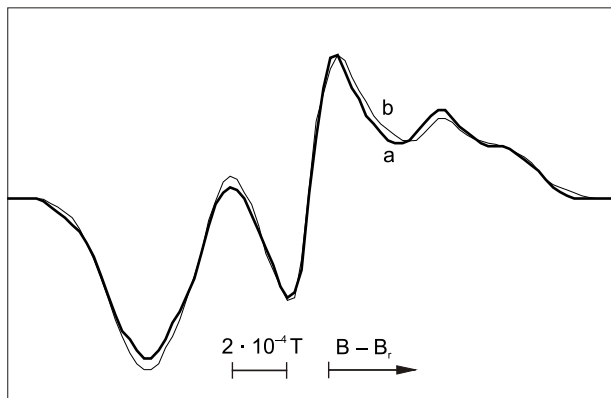Figure 6. **Experimental a) and best-fit b) NMR spectra of $MnSO_4 \cdot 1H_2O$ at 293 K**
Slika 6. **Eksperimentalno a) i najbolja podudarnost b) MRJ spektra za $MnSO_4 \cdot 1H_2O$ pri 293 K**

The comparison of the experimental spectra with the modelling spectra showed the shift of the central part of experimental NMR spectra distorted by a narrow signal corresponds to the free water present in the sample as moisture.

Figure 6. shows the experimental and modelling theoretical NMR spectrum for the substance $MnSO_4 \cdot 1H_2O$ which is obtained by optimalisation [6].

The best-fit parameter in equation (12) is $\beta_G = 1,81 \times 10^{-4} \cdot T$.

CONCLUSION

The analysis of the field and temperature dependence on the NMR second moment for proton of crystalline water in paramagnetic $MnSO_4 \cdot 1H_2O$ and $NiSO_4 \cdot 1H_2O$ give results which are in a good agreement with the theory. Several physically important parameters characterizing the studied paramagnetic substances may be derived from NMR spectra. Quasi isolated pairs of resonating nuclei should prove to be sensitive probes for detection of the local magnetic fields acting on them.

The NMR calculated spectral function, although in the scope of approximative model of the structure and interactions, can serve as a key for identification of the local field components in the experimental NMR spectra. More accurate determination of the parameters of the spectrum thus enables a more correct physical interpretation of the processes in the substance.

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