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Abstract

Full Text

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PHYSICS

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COMPLEX SPLITTING OF THE NUCLEAR MAGNETIC RESONANCE SPECTRUM OF A TWO-SPIN SYSTEM

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The NMR spectrum of an isolated two-spin system ([1]), under certain conditions, undergoes a noticeable change as a result of the interaction of the resonating pair with the nuclear magnetic moments of the rigid lattice. Such an effect can be observed in some zeolites: $(Na_2, Ca)(AlSi_3O_8) \cdot 5H_2O$, $(Na_2, Ca)(Al_2Si_6O_{16}) \cdot 6H_2O$.

The spectra of polycrystals of these substances are a doublet, each peak of which is split into four incompletely resolved lines. Spectra with a similar structure have not been observed previously. Figure 1 presents the derivative of the absorption line. The maxima most distant from the center were observed only at small modulation values ($0.2 \div 0.1$ G), in the absence of saturation and with a small time constant of the phase detector (0.1 sec). The complex splitting begins to appear in the region from -60° and above. The central peak observed in the proton spectrum in these aluminosilicates is due to H^+, which substitutes for Na^+ and Ca^{++} ions in the crystal lattice.

Analysis of the experimental data showed that the complex splitting of the doublet in the powder must be due to the interaction of the Na^{23} nucleus, with which the H_2O molecule is associated, and its two protons.

The spin Hamiltonian of the system $2H^+$—Na^{23} has the form

$$\hat{H} = -\gamma\hbar H_0 \left(\hat{I}_{z_1} + \hat{I}_{z_2} + \frac{\gamma_{\mathrm{Na}}}{\gamma} I_{z\mathrm{Na}}\right) + \frac{\gamma^2\hbar^2}{r_{12}^3}(1 - 3\cos^2\theta_{12}) +$$

Fig. 2. Model of two-axis reorientation of a molecule. I, II—axes of reorientation; p_1, p_2—protons; φ—angle of reorientation of $p_1 - p_2$ about the axis I

Figure 2: Fig. 2. Model of two-axis reorientation of a molecule. I, II—axes of reorientation; p_1, p_2—protons; φ—angle of reorientation of $p_1 - p_2$ about the axis I

$$+\frac{\gamma\gamma_{\mathrm{Na}}\hbar^2}{r_{13}^3}(1-3\cos^2\theta_{13})\hat{I}_{z_1}\hat{I}_{z\mathrm{Na}}+\frac{\gamma\gamma_{\mathrm{Na}}\hbar^2}{r_{23}^3}(1-3\cos^2\theta_{23})\hat{I}_{z_2}\hat{I}_{z\mathrm{Na}}, \qquad (1)$$

where r_{12} is the proton-proton distance; θ_{12} is the angle between H_0 and r_{12}; r_{13}, r_{23} are the distances between the first and second proton and the sodium nucleus, respectively; θ_{13}, θ_{23} are the angles of r_{13} and r_{23} with H_0.

The temperature dependence of the proton-proton splitting and of the second moment of the spectra indicates that the two protons under normal conditions are in a state of two-axis reorientation. This agrees with earlier investigations ([2]). Therefore, in order to obtain

of the spin Hamiltonian of the system for the temperature at which splitting is observed, it is necessary in (1) to average the factors that depend on angles and distances.

From crystallochemical considerations, as a model of the motion (Fig. 2) one should assume a reorientation of the water molecule about the axis I, coinciding with the direction of the proton-proton vector in the absence of rotation, with simultaneous precession of the axis I about the axis II, which connects the midpoint of the vector r_{12} with the Na nucleus. The coefficients of the Hamiltonian are averaged successively over the azimuthal angles of rotation and precession φ_1 and φ_2.

Fig. 2. Model of two-axis reorientation of a molecule. I, II—axes of reorientation; p_1, p_2—protons; φ—angle of reorientation of $p_1 - p_2$ about the axis I.

As a result, the spin Hamiltonian for two-axis reorientation of the water molecule takes the form

$$\hat{H}=-\gamma\hbar H_0\left(\hat{I}_{z_1}+\hat{I}_{z_2}+\frac{\gamma_{\mathrm{Na}}}{\gamma}\hat{I}_{z\mathrm{Na}}\right)-\frac{\gamma^2\hbar^2}{4r_{12}^3}(1-3\cos^2\Delta)\left(\frac{3}{2}\hat{I}_{z_1}\hat{I}_{z_2}-\frac{1}{2}\hat{I}_1\hat{I}_2\right)+\frac{b\gamma\gamma_{\mathrm{Na}}\hbar^2}{R_0^3}(1-3\cos^2\Delta)\hat{I}_{z_1}\hat{I}_{z\mathrm{Na}}+\frac{b\gamma\gamma}{}$$

where Δ is the angle between the field and the axis II, and b is determined by the expression

$$b = \frac{1 - 3\cos^2 \delta_0}{1 + 0.35(1 - 3\sin^2 \delta_0) R_0^{-2}}.$$

Considering the proton-proton and proton-sodium interactions as a perturbation, we obtain, in the first approximation, the line shape in a single crystal

$$H_0 = H^* \pm \alpha(3\cos^2 \Delta - 1) - \beta(3\cos^2 \Delta - 1),$$

where H^* is the resonance value of the field of an isolated proton,

$$\alpha = \frac{3}{16} \frac{\gamma\hbar}{r_{12}^3}, \qquad \beta = \frac{b\gamma_{\mathrm{Na}}\hbar I_{z\mathrm{Na}}}{R_0^3}.$$

Expressing the spectrum in a powder by means of a δ-function:

$$g(h) = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \delta(h' - h) \sin \Delta \, d\Delta \, d\varphi$$

(where $h' = (\varepsilon\alpha - \beta)(3\cos^2 \Delta - 1)$; $\varepsilon = \pm 1$, depending on the type of transition), as a result of integration we obtain

$$g(h) \simeq \frac{1}{6\sqrt{\frac{1}{3}\left(\frac{h}{\varepsilon\alpha - \beta} + 1\right)}}. \tag{2}$$

Upon summing the contributions over all $I_{z\mathrm{Na}}$, the resulting powder curve will have a symmetric shape with 8 maxima. The distance between neighboring peaks of the fine splitting is determined by the formula

$$\Delta h = b\gamma_{\mathrm{Na}}\hbar / R_0^3. \tag{3}$$

From the observed splitting of 0.66 Oe, the proton-sodium distances were determined to be $R_0 = 2.2$ Å, which is in agreement with X-ray structu-

literature data ([3]). For the calculation, the mean experimental values of the sodium splitting between peaks corresponding to $I_{z\,\mathrm{Na}} = \pm 1/2$ were used, in order to avoid correction of the maxima when the spectrum is incompletely resolved. The mechanism considered for the occurrence of the complex structure, as follows from formula (3), should lead to equal spacings Δh. This equality is confirmed experimentally to an accuracy of 3%.

The reason that the complex splitting is not observed at low temperatures is the broadening of the spectrum and the associated decrease in the signal amplitude.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.