Double nuclear magnetic resonance in a two-spin system in a solid

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We consider the problem of the spectrum of electron-nuclear double magnetic resonance in a two-spin system in a solid; the system consists of nuclei with different gyromagnetic ratios. Expressions are obtained for the position and intensities of the lines of the electron-nuclear double magnetic resonance spectrum, as functions of the frequency and the intensity of the additional radiofrequency field. The theoretical relations are compared with experimental data on a two-spin system consisting of hydrogen and fluorine nuclei in single-crystal fluorapatite $Ca_5(F, OH)(PO_4)_3$.

1. INTRODUCTION

The general theory of double nuclear magnetic resonance (DNMR) in solids was developed by F. Bloch[1]. Sarles and Cotts[2] were the first to observe experimentally the narrowing of the spectrum in DNMR in polycrystalline NaF continuously irradiated by a radiofrequency (RF) field. Narrowing of a single resonance line was also observed in the few other known experiments on double resonance in solids[3,4].

Investigations of double resonance in single crystals can yield in principle additional information concerning the theoretical aspects of DNMR, and also concerning the properties of the investigated crystals. In the NMR spectra of the single crystals one can observe a fine structure that arises, for example, as a result of the internuclear dipole-dipole interaction. In the simplest case, when the interacting nuclei in the crystal constitute relatively isolated pairs (two-spin system), the resonance spectrum of one of the nuclei of the pair will yield a doublet if the other nucleus has a relatively large magnetic moment (H^1, F^{19}) and is located at a distance 1–2 Å from the first. In DNMR, the dipole-dipole interaction is altered and this should lead to a change in the spectra. We have therefore carried out a theoretical analysis of DNMR in a two-spin system in a solid, and compared the results with an experiment performed on single-crystal apatite $Ca_5(F, OH)(PO_4)_3$.

2. THEORY

We consider a system consisting of two nuclei with spins I_1 and I_2 and with different gyromagnetic ratios γ_1 and γ_2. In addition to the constant field H_0 directed along the z axis and the weak RF field H_1 of frequency $\omega_1 = \gamma_1 H_0$, which is needed to record the spectrum, in the case of double resonance one applies to the system an additional RF field with rotating component H_2 and frequency ω_2 close to $\gamma_2 H_0$.

If no account is taken of the relaxation and the perturbation produced by the field H_1, and if the quadrupole interaction of the nuclei with the gradient of the electric field of the crystal is disregarded, then the Hamiltonian of the system in question can be represented in the form (in frequency units)

$$\begin{aligned}\mathscr{H}=\gamma_1H_0I_{1z}+\gamma_2H_0I_{2z}+AI_{1z}I_{2z}+\gamma_2H_2(I_{2x}\cos\omega_2t\\+I_{2y}\sin\omega_2t)+\gamma_1H_2(I_{1x}\cos\omega_2t+I_{1y}\sin\omega_2t),\end{aligned}\qquad(1)$$

where $A = \hbar\gamma_1\gamma_2 r_{12}^{-3}(3\cos^2\theta - 1)$, ħ is Planck's constant, r_{12} is the distance between the nuclei, and θ is the angle between the vector $\mathbf{r}_{12}$ and the direction of the magnetic field H_0. In the Hamiltonian (1), the term characterizing the dipole-dipole interaction is written in the form $AI_{1z}I_{2z}$, inasmuch as for nuclei with different gyromagnetic ratios ($\gamma_1 \neq \gamma_2$) one can neglect the "flip-flop" interaction that leads to a mutual flipping of the nuclear spins[5].

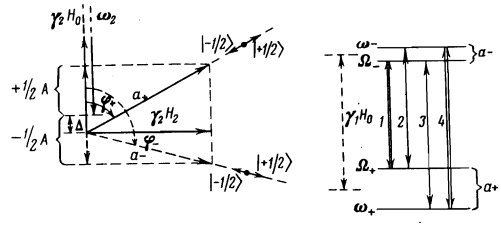

FIG. 1. a) Effective magnetic field (in rotating coordinate system) acting on the spins I_2 at different orientations of the spin I_1 ($\Delta > 0$, $I_1 = I_2 = 1/2$). b) Transitions between energy levels of two-spin system in DNMR (2, 3—allowed, 1, 4—forbidden transitions).

If one changes to a rotating coordinate system with the aid of the unitary transformation $U = \exp(i\omega_2 I_{2z}t)$, the Hamiltonian $\mathscr{H}' = U\mathscr{H}U^{-1}$ contains only stationary terms[5] and can be written in the form

$$\mathscr{H}'=\gamma_1H_0I_{1z}+(\Delta+AI_{1z})I_{2z}+\gamma_2H_2I_{2x},\qquad(2)$$

where $\Delta = \gamma_2 H_0 - \omega_2$.

We note that a Hamiltonian of similar form was obtained by Bloom and Shoolery[6], who solved the double-resonance problem for a two-spin system in a liquid in the presence of indirect spin-spin interaction.

The quantization axis for the first spin coincides with the z axis (m_1 is a good quantum number), and the second spin is quantized in the direction of its effective field in the rotating coordinate system—a vector with components (Fig. 1)

$$\Delta+m_1A,\quad \gamma_2H_2.\qquad(3)$$

In our case of a two-spin system (H—F), the spins are $I_1 = I_2 = \frac{1}{2}$. Taking all the foregoing into account, we can easily obtain the four eigenvalues of the Hamiltonian (2) in the form

$$\omega_+=(\omega_1+a_+)/2,\quad \omega_-=-(\omega_1+a_-)/2,\qquad(4)$$

$$\begin{aligned}\Omega_+=(\omega_1-a_+)/2,\quad \Omega_-=-(\omega_1-a_-)/2;\\ a_\pm=[(\Delta\pm{}^1/_2A)^2+(\gamma_2H_2)^2]^{1/2}.\end{aligned}\qquad(5)$$

The vectors $a_\pm$ make angles $\varphi_\pm$ with the z axis, where

$$\operatorname{tg}\varphi_\pm=\frac{\gamma_2H_2}{\Delta\pm{}^1/_2A}.\qquad(6)$$

If resonance is observed at the nuclei I_1, then in the absence of the field H_2 only two transitions, $\omega_+ \longleftrightarrow \Omega_-$ and $\Omega_+ \longleftrightarrow \omega_{-1}$, are possible between the levels (4) and correspond to the selection rules $\Delta m_1 = \pm 1$ and $\Delta m_2 = 0$. In the presence of the RF field, all four transitions become possible: $\Delta m_1 = \pm 1$, $\Delta m_2 = 0, \pm 1$[6].

Thus, in the general case four lines should be observed in the DNMR spectrum, at the frequencies

$$\begin{gathered}\omega_1+(a_+-a_-)/2, \quad \omega_1-(a_+-a_-)/2, \\ \omega_1+(a_++a_-)/2, \quad \omega_1-(a_++a_-)/2,\end{gathered} \tag{7}$$

which are symmetrical about the frequency $\omega_1 = \gamma_1 H_0$ and form an internal doublet with spacing $(a_1 - a_-)$ between components, and an external doublet with spacing $(a_+ + a_-)$.

The relative intensities of the lines (7), calculated under the assumption that the probability of each transition is proportional to the square of the matrix element corresponding to the initial and final states of the spin I_1, are[5]

$$\begin{gathered}\sin^2\frac{1}{2}(\varphi_+-\varphi_-), \quad \sin^2\frac{1}{2}(\varphi_+-\varphi_-), \quad \cos^2\frac{1}{2}(\varphi_+-\varphi_-), \\ \cos^2\frac{1}{2}(\varphi_+-\varphi_-).\end{gathered} \tag{8}$$

In a solid, each of the lines (7) has an appreciable width, since the initial components in the spectrum of the two-spin system are broadened at $H_2 = 0$ by a dipole-dipole interaction with the more remote nuclei. In this connection, the spectral line intensity should be taken to mean, as usual, the area under the line.

As seen from (7) and (8), the positions of the components and their intensities, for a crystal with a given A, depend on the pump field H_2 and on the detuning Δ. In the particular case of exact resonance, i.e., $\Delta = 0$, we have $\varphi_+ = -\varphi_- = \varphi$,

$$a_+=a_-=a=[(\tfrac{1}{2}A)^2+(\gamma_2 H_2)^2]^{1/2}. \tag{9}$$

It follows from (7) that in this case the spectrum consists of three lines with frequencies

$$\gamma_1 H_0 - a, \quad \gamma_1 H_0, \quad \gamma_1 H_0 + a \tag{10}$$

and relative intensities, according to (8),

$$\cos^2\varphi, \quad 2\sin^2\varphi, \quad \cos^2\varphi. \tag{11}$$

We note, however, that the second moment of the entire spectrum, in accord with the general theory[1], should remain invariant under all changes of the RF field H_2 and of the detuning Δ.

3. SAMPLE AND APPARATUS

The foregoing approximate theory and some of its consequences were tested with a single crystal of natural fluorapatite. This crystal belongs to a hexagonal syngony with space group $P6_3m$. We chose for the investigation a sample cut in the form of a cylinder of 10 mm diameter and 15 mm length, with axis perpendicular to the c axis of the single crystal. From the IR and NMR spectra[7] it is known that in this crystal approximately 15% of the fluorine atoms are replaced by OH hydroxyl groups, as a result of which hydrogen bonds O—H···F are formed in the apatite. The fluorine, hydrogen, and oxygen atoms lie on a hexagonal crystal axis with an F—F distance equal to 3.44 Å. The H—F distance is equal to 2.01 Å, which is less than half the distance from the proton to the other nearest fluorine nuclei, so that the proton magnetic resonance spectrum of the apatite is a doublet due to the dipole-dipole interaction of the hydrogen and fluorine nuclei[7].

To perform the double-resonance experiments, we developed and constructed a special spectrometer. The proton magnetic resonance spectra of the apatite were registered with a Pound-Knight type of autodyne detector with frequency sweep, using 6S51NV nuvistors. The autodyne coil was placed in a high-frequency head containing an additional coil that produced in the sample a high-power RF field at the frequency ω_2. The axes of both coils were in a plane perpendicular to the direction of the constant magnetic field H_0, and the angle between them was 90°. The coil that produced the field of frequency ω_2 in the sample was the resonant element of a series circuit connected through a coupling transformer to a high-frequency oscillator of approximately 200 W power. By varying the coupling it was possible to obtain in the sample volume a rotating component of an RF magnetic field at 16 MHz frequency ranging from 0 to 15 Oe. To prevent overheating of the sample and the elements of the DNMR spectrometer head, a jet of cold nitrogen was blown through the pickup. The experiment was performed in a constant field of approximately 4 kOe, produced by an electromagnet, with a resolving power of approximately 10^{-6} in the interior of the sample.

The main difficulty in the experiment was the problem of cancelling out the noise induced in the autodyne coil. Since the resonant frequencies for the proton and for the fluorine are close to each other (approximately 17 and 16 MHz in a field of 4 kOe), the use of tuned filters between the tank circuit and the first tube of the autodyne was not very effective. We therefore used a "flux compensation" system[8], which made it possible to reduce the induced noise to a level that kept the autodyne from pulling and prevented overloading the RF amplifier. The spectra were recorded at a modulation frequency 85 Hz, with $H_{\text{mod}} = 0.4$ Oe and with a synchronous-detector time constant 4 sec. The intensity H_2 was determined from the emf induced in a 10-turn coil of 3 mm diameter, which was placed inside the autodyne coil.

4. EXPERIMENTAL RESULTS

The proton magnetic resonance spectrum of the apatite single crystal, recorded at room temperature and with the magnetic field H_0 oriented parallel to the c axis of the crystal, is shown in Fig. 2a. The small signal at the doublet center is due apparently to an insignificant proton content in the sample (not more than 20% of the total H^1 content), which are not located on the O—H···F hydrogen bonds. The doublet splitting ΔH, as a function of the orientation of the crystal relative to H_0, corresponded to the well known Pake formula[9]

$$\Delta H=\mu_F r_{12}^{-3}(3\cos^2\theta-1), \tag{12}$$

where $\mu_F = \gamma_2\hbar/2$ is the magnetic moment of the F^{19} nucleus, and the remaining symbols have the same meaning as in (1). With H_0 parallel to the c axis, the doublet splitting is maximal and equal to 6.1 Oe. Almost all the DNMR spectra were recorded at this orientation, since the investigated regularities are most strongly pronounced in this case.

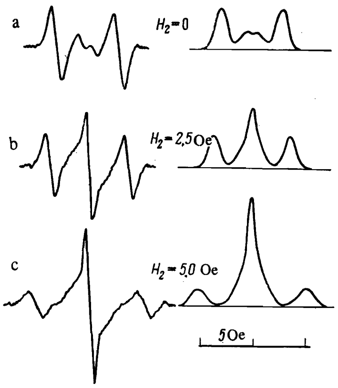

FIG. 2

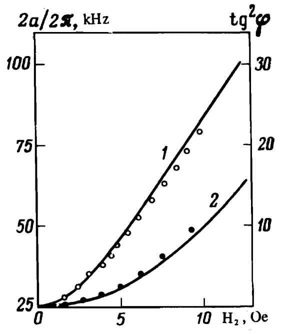

FIG. 3

FIG. 2. DNMR spectra of apatite (left–derivative, right–integral absorption curves) at various intensities of the RF field H_2 in the case of exact resonance ($\Delta = 0$).

FIG. 3. Dependence of the splitting (1) and of the relative intensity (2) of the lines in the DNMR spectrum on the level of the HF field H_2 at $\Delta = 0$. Solid curves–theoretical, points–experiment.

At exact resonance for fluorine, i.e., at $\Delta = 0$ and $\omega_2 = \gamma_2 H_0$, the spectrum is described by expressions (9)–(11). When $H_2 = 0$, we have $\varphi_\pm = 0$ and $a = \pm A/2$, and the allowed transitions yield an initial doublet with frequencies

$$\gamma_1 H_0 + m_2 A = \gamma_1 H_0 \pm {}^1/_2 \gamma_1 \Delta H,$$

where ΔH is determined by (12). With increasing field H_2, a line appears at the center of the doublet and its intensity increases, while the side components move apart, in accord with (10) and (11), and their intensity decreases. The distance between the components varies like

$$2a = [(\gamma_1 \Delta H)^2 + 4(\gamma_2 H_2)^2]^{1/2}, \qquad (13)$$

and the ratio of the intensity of the spectral component to the intensity of the side components varies like

$$2\,\mathrm{tg}^2\,\varphi. \qquad (14)$$

Figure 2 shows certain spectra recorded at different values of the field H_2, while Fig. 3 shows the plots of Eqs. (13) and (14) as well as the corresponding experimental points. As seen from Fig. 3, there is good agreement between the experimental and theoretical values. We note that at sufficiently high values of the field, $H_2 \gg \Delta H$, all that remains in the spectrum is in fact the central line with intensity equal to the sum of the intensities of the components of the initial doublet, corresponding to a complete suppression of the dipole-dipole interaction between the spins I_1 and I_2.

In the presence of a frequency deviation ($\Delta \neq 0$), the DNMR spectra consist of four lines (Fig. 4). If a definite level of H_2 is set, and the frequency of this field is varied within the range $\pm\Delta$, then one can see how a quartet is obtained from the triplet as the absolute value of the deviation is gradually increased. The central line splits into two components, which move apart with increasing $|\Delta|$, and in the limit, at large deviation, assume the positions and the intensities of the components of the unperturbed doublet. At the same time, the side components move apart in accordance with (7) and (8), their intensity decreases gradually to zero. Figures 5 and 6 make it possible to compare the theoretical and experimental values of the splittings of the internal and external doublets for different H_2 and Δ.

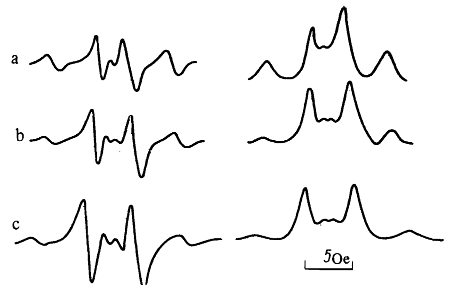

FIG. 4. DNMR spectra of apatite at $\Delta \neq 0$, $H_2 = 5$ Oe (left–derivative, right–integral absorption curves): a) $\Delta/2\pi = 10$ kHz, b) $\Delta/2\pi = 18$ kHz, c) $\Delta/2\pi = 25$ kHz.

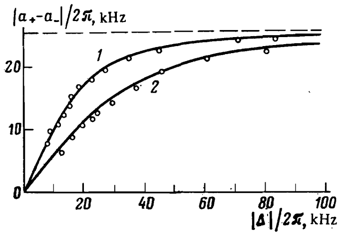

FIG. 5

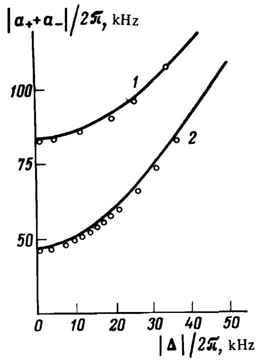

FIG. 6

FIG. 5. Dependence of the splitting of the internal doublet in the DNMR spectrum on Δ: 1) $H_2 = 5$ Oe, 2) $H_2 = 10$ Oe. Solid curves–theoretical, circles–experimental.

FIG. 6. Dependence of the splitting of the external doublet in the DNMR spectrum on Δ. 1) $H_2 = 10$ Oe, 2) $H_2 = 5$ Oe, solid curves–theoretical, circles–experiment.

As seen from Fig. 4, in the presence of deviation the spectra exhibit a noticeable asymmetry in the line intensities. Experiment shows that the character of the asymmetry varies with the sign of the detuning: at $\Delta > 0$ the high-frequency transitions (relative to $\gamma_1 H_0$) are more intense, while the low-frequency transitions are stronger at $\Delta < 0$. We note that at $\Delta = 0$ there is no asymmetry and the relative intensities of the lines of the triplet correspond to (11).

The asymmetry observed in the spectrum can be explained by recognizing that if $-A/2 < \Delta < A/2$ the following relations should hold between the populations of the levels (4) (see Fig. 1)

$$N_{\omega+} > N_{\Omega+}, \quad N_{\omega-} > N_{\Omega-}, \qquad (15)$$

$$N_{\omega+} - N_{\Omega+} = N_{\omega-} - N_{\Omega-} \quad \text{if } \Delta = 0, \qquad (16)$$

$$N_{\omega+} - N_{\Omega+} > N_{\omega-} - N_{\Omega-} \quad \text{if } \Delta > 0, \qquad (17)$$

$$N_{\omega+} - N_{\Omega+} < N_{\omega-} - N_{\Omega-} \quad \text{if } \Delta < 0. \qquad (18)$$

As seen from Fig. 1, the relation $N_{\omega_-} > N_{\Omega-}$ is the consequence of the fact that at $I_1 = -{}^1/_2$ the spins I_2 have a positive z-projection at $m_2 = -{}^1/_2$, and consequently have a lower energy in the field H_0 (a larger population) than in the case $m_2 = +{}^1/_2$. Since the levels 4 are due to the action exerted on the spins I_1 of the local fields by the spins I_2, the distribution of the latter with respect to energy becomes transformed directly into populations of the levels of the spins I_1, the spectrum of which is observed in DNMR. The remaining relations (10)—(18) are obvious. It follows from (16) that at $\Delta = 0$ the population differences of the levels between which the forbidden transitions take place are identical, so that the intensities of the outer lines of the triplet (10) are equal. At $\Delta \neq 0$ the values of the indicated differences are such that in the case of positive detuning the high-frequency transition in the outer doublet is more intense than the low-frequency transition, and at negative detuning the situation is reversed. If $|\Delta| > A/2$, the relation (15) is not satisfied, but this does not lead to violation of inequalities (17) and (18), nor therefore of the character of the asymmetry of the line intensities of the outer doublet.

For the allowed transitions we have $N_{\omega+} - N_{\Omega-} > N_{\Omega+} - N_{\omega-}$ for all Δ, so that the transition $\omega_+ \rightarrow \Omega_-$ is more intense than the transition $\Omega_+ \rightarrow \omega_-$, but the lines corresponding to these transitions change position relative to the center of the multiplet when the deviation sign is reversed.

We note in conclusion that, in contrast to the earlier studies[2,3,4], we have also observed, for the first time for double resonance in a solid, side components besides the central line; this has made it possible to measure experimentally the second moment of the entire spectrum at different values of H_2. The results of these measurements confirm Pake's theorem[1] of the conservation of the second moment in DNMR, regardless of the value of the field H_2 and the detuning Δ.

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