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Double Nuclear Magnetic Resonance and Crystal Chemistry at the Lattice Positions of Diamagnetic Atoms, Both Structural, and Foreign

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Abstract. Double nuclear magnetic resonance (DNMR) with Jeener's pulsed sequence on proton and fluorine frequencies was used to investigate the electric quadrupole interactions of (i) ^{23}Na in $Na_2Cd(SO_4)_2 \cdot 2H_2O$, $B_2^0 = \pm 218.5 \pm 1$ kHz, $B_2^2 = \pm 98 \pm 5$ kHz, (ii) of ^{23}Na, which enter the crystal, CaF_2: Na^+ (0.07 wt. %) $B_2^0 = \pm 85.7 \pm 0.5$ kHz, trigonal position, and (iii) ^{23}Na which are near the foreign atom in $NaF:Ca^{2+}$ (0.02 wt.%) $B_2^0 = \pm 86.7 \pm 0.5$ kHz, tetragonal position. Some details of DNMR experiments are analyzed. The conditions for maximum transfer of a Zeeman energy to a dipole-dipole reservoir are described for multispin systems and some crystal hydrates. The angular dependence of the Hamiltonian containing the spherical tensor operators of second rank was obtained for all possible orientations of a local coordinate system relative to a laboratory system.

Introduction

Frequently, necessary information about crystal structure or crystal defect cannot be obtained by applying *nuclear magnetic resonance* (NMR) since the NMR signal is below the sensitivity limit of the spectrometer. This typically occurs if the nuclei in question have a low concentration, a small magnitude of the nuclear magnetic moment, a long spin-lattice relaxation time, etc.

NMR sensitivity can be enhanced directly by strong magnetic fields or low temperatures. Another approach is based on the application of double resonance techniques that, especially in combination with direct methods, permit a considerable increase in sensitivity. This paper treats some aspects of pulsed *double nuclear magnetic resonance* (DNMR) in crystals (Anderson and Hartman 1962; Hartman and Hahn 1962; Lurie and Slichter 1964).

The enhanced sensitivity in this experiment results from the interaction between two systems of nuclei, one of which (the primary one) exhibits a strong NMR signal. The primary nuclear spin system is usually cooled, i.e., the population of some of its energy levels, which exist either in the presence of a *high-*

frequency (HF) field or without it, is changed accordingly. The necessary contact between the *primary*, *I*, and *secondary*, *S*, nuclear systems is achieved by applying a second HF field. The effective contact (cross-relaxation) is obtained by choosing equal quanta in both subsystems that participate in DNMR. The rate of cross-relaxation with equal quanta is defined by the value of dipole-dipole interaction of *I* and *S* spins (Hartman and Hahn 1962).

After a contact is established in DNMR either a direct signal from rare *S* nuclei (a direct method of DNMR registration) or a change of signal from the primary spins (an indirect method of registration) can be measured. The first method is widely used and is one of the alternatives for obtaining NMR spectra of high resolution in solids. Here we shall consider the second alternative, which yields a high sensitivity and is more convenient for the study of a wide selection of atoms having a magnetic moment not equal to zero. In this case, the one registers a change of spin temperature, i.e., a change in population of energy levels of the primary spins, which results from the HF saturation of the secondary nuclear systems. There are a number of DNMR schemes which differ in the way the main stages are carried out: cooling of the primary spin system and saturation of the secondary spins, i.e., in the way contact is established between them (Goldman 1970). From the possible ways of cooling the primary system, (i) change of the applied magnetic field H_0, (ii) spin locking, (iii) adiabatic diamagnetization in the rotating reference frame, (iv) pulse off-resonance saturation of the NMR line and application of a pair of phase-shifted pulses, we selected the latter (Jeener and Broekaert 1967; Jeener 1968). This method is realized rather simply, and is sufficiently effective in cooling the *dipole-dipole reservoir* (DDR). It also permits application of DNMR in samples with short spin-lattice relaxation times.

The experiment is carried out as follows (Fig. 1). By means of a pulsed sequence consisting of two phase-shifted high-frequency pulses $(90° - \tau_{12} - \theta^0_{90°})$
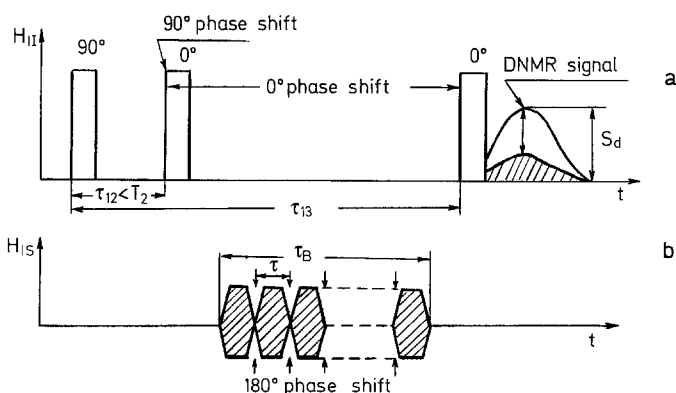
Fig. 1a and b. DNMR pulse sequence. **a** Phase-shifted pulsed pair of HF magnetic field applied to *I* spins is cooling the system of dipole-dipole interactions; third HF pulse is monitoring resulting spin temperature. T_2: spin-spin relaxation time; S_d: dipolar signal; θ, duration of the second pulse. **b** Pulse sequence applied to *S* spins with periodic 180° phase shift in $\tau \gg T_{IS}$, where T_{IS} is the characteristic time of cross-relaxation between the *I* and *S* spin system. A change of dipolar signal corresponds to application of this sequence on resonance frequency of *S* spins

and operating on the Larmor frequency of the primary nuclei, the DDR of the sample is cooled (τ_{12} is the interval between the pulses). Then the second HF field is switched on, which saturates the Zeeman system of the rare nuclei in the rotating reference frame and connects it to the dipole-dipole system as a whole. To obtain a continual saturation process, it is necessary to carry out either a periodic phase rotation of the HF field at 180° or sine-wave modulation of the amplitude of the HF field (Goldman 1970). The sequence of double resonance ends with the third HF pulse on the primary spins. The desired dipolar signal is determined with this pulse by adjusting the phase detector in exact quadrature with the Zeeman component of *free induction signal* (FIS). The magnitude of dipolar signal is proportional to the resulting inverse temperature of the DDR. A change in this signal after the influence of the second HF field on the sample is detected as a DNMR signal.

The above experiment was performed with a spectrometer that excites and monitors the primary nuclei at a Larmor frequency $v_L = 21.2$ MHz and a unit that creates the second HF field with an output power of about 150 watt in the frequency range 0.5–17 MHz.

Maximum Cooling of the Dipole-Dipole Interaction Reservoir

We shall now briefly consider the first stage of double resonance: decrease of the temperature of the dipole-dipole system by means of the pair of phase-shifted pulses which operate at the frequency of the primary spins. In the investigation of multispin systems such as NaF and LiF, a question arises regarding the role of the nonresonant spins S, particularly when their contribution to the unified DDR cannot be ignored. In other words, we want to know the maximum inverse temperature and optimum conditions for cooling the system of dipole-dipole interactions by the pair of phase-shifted pulses. The inverse DDR temperature obtained in this case can be expressed in the Gauss approximation for a form of NMR line with the following formula (Anderson and Hartman 1962; Goldman 1970; Shchepkin et al. 1976):

$$\frac{\beta}{\beta_L} = \frac{\partial G}{\partial t} \left[\frac{M_{2II} \cdot \text{Cos}\,\theta + M_{2IS}}{M_{2II} + M_{2IS}} \right] \cdot \frac{H_0 \cdot \text{Sin}\,\theta}{\gamma_I \cdot {}^I H_L^2}. \tag{1}$$

Here β_L and β are the initial and final inverse temperatures of DDR respectively, G is a standardized function of the FIS (Abragam 1961), M_{2II} and M_{2IS} are the respective second moments of homonuclear and heteronuclear dipole-dipole interactions, ${}^I H_L$ is the local magnetic field of the I nuclei, γ_I is the corresponding gyromagnetic ratio and θ is the duration of the second HF pulse. It follows from (1) that maximum cooling is attained at the interval between the pulses

$$\tau = M_2^{-\frac{1}{2}} = (M_{2II} + M_{2IS})^{-\frac{1}{2}} \tag{2}$$

and at the duration of the second HF pulse

$$\theta = \arccos\left[(a^2 + \tfrac{1}{2})^{\frac{1}{2}} - a\right], \tag{3}$$

where $a = \dfrac{M_{2IS}}{4M_{2II}}$.

Thus, the inverse DDR temperature is proportional to $\partial G/\partial t$ in multispin systems not only for small angles θ (Jeener 1968; Goldman 1970), but also within the limits when the Gaussian approximation of the line shape is valid. Maximum cooling is reached at durations of the second HF pulse of $\theta > 45°$.

Application to Crystalline Hydrates

We shall also consider here some aspects of the application of this pulsed sequence to crystalline hydrates, which can be objects of DNMR. Some NMR data on $Na_2Cd(SO_4)_2 \cdot 2H_2O$ crystals will serve as examples.

Since FIS has an oscillating character in crystalline hydrates, the optimal conditions for most effective cooling of the spin-spin reservoir and for use in double resonance are not apparent. It is known that in the first approximation of the perturbation theory one can distinguish two quasi-invariants of motion in the dipole-dipole proton system of crystalline hydrate: the energy of intrapair and the energy of interpair dipole-dipole interactions (Jeener 1968; Eisendrath et al. 1978).

Application of the pair of phase-shifted pulses to the hydrate crystal oriented so that all proton-proton vectors are magnetically equivalent yields the following reciprocal temperatures of intrapair β_B and interpair β_M subsystems of dipole-dipole interaction:

$$\frac{\beta_B}{\beta_L} = -\omega_0 \frac{\mathrm{Sin}\,\theta \cdot \mathrm{Cos}\,\theta}{\mathrm{Sp}(B)^2} \cdot \mathrm{Sp}(I_y)^2 \left[\phi \cdot \mathrm{Sin}\,(\phi\tau) \cdot G_M(\tau)\right]_{\tau = \tau_{12}} \tag{4}$$

and

$$\frac{\beta_M}{\beta_L} = \omega_0 \cdot \frac{\mathrm{Sin}\,\theta \cdot \mathrm{Cos}\,\theta}{\mathrm{Sp}(B'')^2} \cdot \mathrm{Sp}(I_y)^2 \left[\mathrm{Cos}\,(\phi\tau) \cdot \frac{\partial G_M}{\partial \tau}\right]_{\tau = \tau_{12}}. \tag{5}$$

Here, Sp means trace and $B = \sum_{j>k} B_{jk} \cdot I_{zj} \cdot I_{zk}$. B'' is the reduced secular part of the Hamiltonian of interpair dipole-dipole interaction B'; B'' is equal to $2/3\ B'$ (Boden 1975). Moreover,

$$B' = \sum_{j,k} B'_{jk} \cdot I_{zj} \cdot I_{zk},$$

$$B'_{jk} = \frac{3}{2}\frac{\gamma^2\hbar}{r_{jk}^3}(1 - 3\,\mathrm{Cos}^2\,q_{jk}), \quad \text{and} \quad B_{jk} = \frac{3}{2}\frac{\gamma^2\hbar}{r^3}(1 - 3\,\mathrm{Cos}^2\,\xi).$$

The prime on B indicates that the summation is carried out over interpair distances; B_{rjk} and ξ are the respective angles of the interpair r_{jk} and intrapair
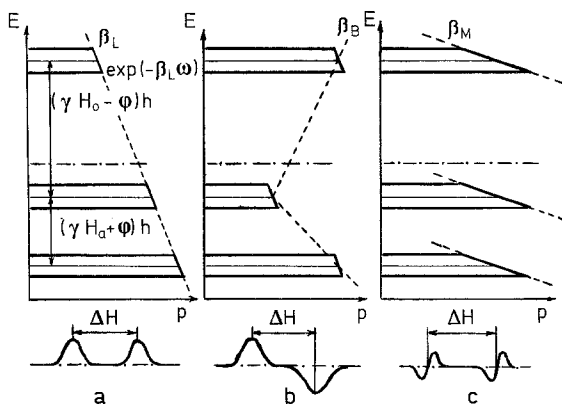
Fig. 2. Schematic representation of the transfer process of the Zeeman energy into the intrapair and interpair DDR subsystem in a hydrate crystal for the NMR doublet line. *Ordinate*, energy E; *abscissa*, population of the levels. *a* Initial equilibrium state; *b* Zeeman energy is transferred into the intrapair DDR subsystem; *c* Zeeman energy is transferred into the interpair DDR subsystem. For clarity the absorption signals of continual NMR are drawn *below* for the populations of the energy levels as shown *above*

r vectors formed with the direction of the magnetic field H_0; ϕ is equal to $B_{jk}/2$, G_M is the standardized function of magnetic moment for the interpair dipole-dipole interactions and γ is the gyromagnetic ratio.

From (4) and (5) both inverse temperatures are seen to be oscillating functions from the interval τ_{12} between the pulses. Moreover, the phase of the oscillating functions are shifted relative to each other by 90°. In this case the inverse temperature of an intrapair subsystem is proportional so the FIS G_M, which is determined by interpair dipole-dipole interactions. The inverse temperature of the interpair subsystem is proportional to the derivative of G_M. The transfer of the Zeeman energy to each DDR subsystem of the hydrate crystal is shown schematically in Fig. 2.

The agreement of the theory (formulas 4 and 5) with experiment is shown by the application of Jeener's sequence to a crystal of cadmium kröhnkite $Na_2Cd(SO_4)_2 \cdot 2H_2O$ (Fig. 3).

Orientational Dependence of Quadrupolar Spectrum

The angular dependence of double resonance spectra is usually studied in the *laboratory reference frame* (LRF).

To obtain the formulas for the Hamiltonian of the quadrupole interaction, the resulting turn between the applied magnetic field, H_0, and the local *crystalline field reference frame* (CRF) is represented by two successive rotations: firstly by β which is the angle between H_0 and an arbitrary direction of the crystal, and secondly by the Eulerian angles, α_i, β_i, γ_i, which determine the orientational position of the main crystalline field axes.
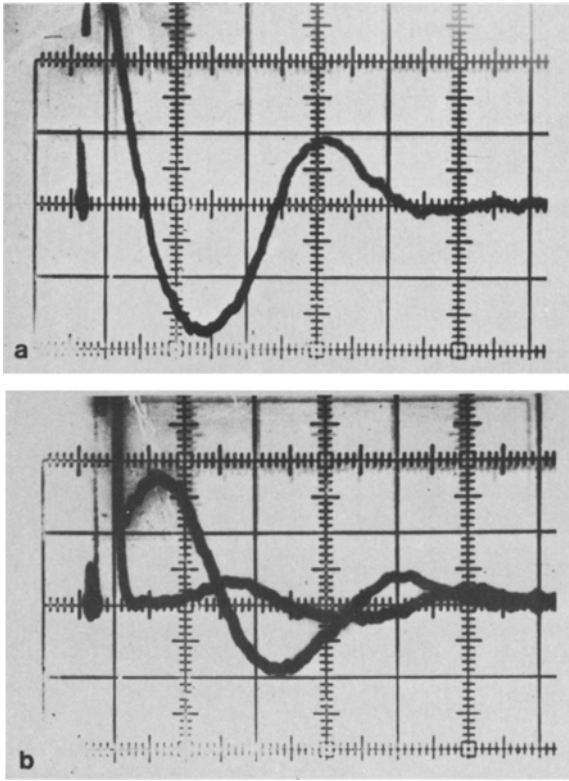
Fig. 3a and b. Oscillograms showing transfer of the proton Zeeman energy into the *dipole-dipole reservoir* (DDR) of the $Na_2Cd(SO_4)_2 \cdot 2H_2O$ crystal. **a** *Free induction signal* (FIS) of ^1H after the 90° pulse; **b** superposition of ^1H dipolar signals after the 45° high-frequency pulse for $\tau_{13}=1.5$ ms following cooling of DDR by the pulse sequence $90° - \tau_{12} - 45°_{90°}$. A large amplitude is obtained at $\tau_{12}=18$ μs (zero of Zeeman FIS), which corresponds to the condition of maximum energy transfer into intrapair DDR subsystem. A smaller amplitude ($\tau_{12}=35$ μs) corresponds to the condition of maximum energy transfer into the interpair DDR subsystem. The oscillograph scanning is 20 μs/division. The applied magnetic H_0 field was parallel to the a,c plane of the crystal and formed an angle of 173° form $+c$ towards $+a$

The quadrupole Hamiltonian in CRF has the general form of

$$\mathcal{H} = B_2^0 O_2^0 + B_2^2 O_2^2, \tag{6}$$

where

$$B_2^0 = \frac{e^2 Q q_{zz}}{4I(2I-1)} = \frac{v_Q}{6}\,\hbar = A \cdot q_{zz},$$

$$B_2^2 = A(q_{xx} - q_{yy}),$$

and $q_{ii} = \frac{1}{e}\frac{\partial^2 V}{(\partial i)^2}$, where V is the electrostatic potential at the nuclear site. Q in (6) is the nuclear quadrupole moment. Further,

$$O_2^m = \frac{1}{2}(Q_2^m + Q_2^{-m}), \quad \tilde{O}_2^m = \frac{1}{2i}(Q_2^m - Q_2^{-m}).$$

Q_2^m and Q_2^{-m} are spin operators (Al'tshuler and Kozyrev 1972).
In the LRF, (6) may be written in the form

$$\mathscr{H} = B_2^0 O_2'^0 + B_2^2 O_2'^2. \tag{7}$$

The operators marked with and without prime are connected to each other as shown in Table 1, where for the sake of brevity the following designations are introduced:

$$
\begin{aligned}
c &= \cos\beta, & c_i &= \cos\beta_i, & c_{mm'} &= \cos(m\gamma_i + m'\alpha_i) \\
s &= \sin\beta, & s_i &= \sin\beta_i, & s_{mm'} &= \sin(m\gamma_i + m'\alpha_i) \\
a_1 &= s_i^2 c_{02}, & a_2 &= c_i s_i c_{01}, & a_3 &= 3c_i^2 - 1 \\
a_4 &= s_i^2 \cdot s_{02}, & a_5 &= c_i s_i s_{01} &&
\end{aligned}
$$

$$a_6 = -s_i(1+c_i)c_{12} + s_i(1-c_i)c_{1-2}$$
$$a_7 = (2c_i^2 + c_i - 1)c_{11} + (2c_i^2 - c_i - 1)c_{1-1}$$
$$a_8 = c_i \cdot s_i \cdot c_{10}$$
$$a_9 = s_i(1+c_i) \cdot s_{12} + s_i(1-c_i) \cdot s_{1-2}$$
$$a_{10} = (2c_i^2 + c_i - 1)s_{11} - (2c_i^2 - c_i - 1)s_{1-1}$$
$$a_{11} = (1+c_i)^2 \cdot c_{22} + (1-c_i)^2 \cdot c_{2-2}$$
$$a_{12} = s_i(1+c_i)c_{21} - s_i(1-c_i)c_{2-1}$$
$$a_{13} = s_i^2 \cdot c_{20}, \quad a_{14} = (1+c_i)^2 \cdot s_{22} - (1-c_i)^2 \cdot s_{2-2}$$
$$a_{15} = s_i(1+c_i)s_{21} + s_i(1-c_i)s_{2-1}$$
$$a_{16} = -s_i(1+c_i)s_{12} + s_i(1-c_i)s_{1-2}$$
$$a_{17} = (2c_i^2 + c_i - 1)s_{11} + (2c_i^2 - c_i - 1)s_{1-1}$$
$$a_{18} = c_i \cdot s_i \cdot s_{10}$$
$$a_{19} = s_i(1+c_i)c_{12} + s_i(1-c_i)c_{1-2}$$
$$a_{20} = (2c_i^2 + c_i - 1)c_{11} - (2c_i^2 - c_i - 1)c_{1-1}$$
$$a_{21} = (1+c_i)^2 \cdot s_{22} + (1-c_i)^2 \cdot s_{2-2}$$
$$a_{22} = s_i(1+c_i)s_{21} - s_i(1-c_i) \cdot s_{2-1}$$
$$a_{23} = s_i^2 \cdot s_{20}$$
$$a_{24} = (1+c_i)^2 c_{22} - (1-c_i)^2 c_{2-2}$$
$$a_{25} = s_i(1+c_i)c_{21} + s_i(1-c_i)c_{2-1}.$$

These transformations enable us to write the resulting Hamiltonian as

$$\mathscr{H} = -\gamma\hbar I_z H_0 + f_0 O_2^0 + f_1 O_2^1 + \hat{f}_1 \hat{O}_2^1 + f_2 O_2^2 + \hat{f}_2 \hat{O}_2^2. \tag{7}$$

Here the values f_m and $\hat{f}_m$ are obtained by summing up the coefficients of O_2^m and $\hat{O}_2^m$, respectively. Analysis of a great number of experiments can be carried out with the perturbation theory according to the formula:

$$v_{m,m-1} = v_L + f_0(3-6m) + \frac{(f_1^2 - \tilde{f}_1^2)}{8v_L} \cdot \{24m(m-1) - 4I(I+1) + 9\}$$

$$+ \frac{(f_2^2 - \tilde{f}_2^2)}{4v_L} \{-12m(m-1) + 4I(I+1) - 6\}, \tag{9}$$

where $v_L = \gamma H_0 / 2\pi$.

Table 1. Matrix of transformation of the operators O_2^m and $\tilde{O}_2^m$. Operators with prime are operators transformed reference frame

	O_2^0	O_2^1	O_2^2	$\tilde{O}_2^1$	$\tilde{O}_2^2$
$O_2'^0$	$\frac{3}{4}s^2 a_1 - 3csa_2$ $+\frac{1}{4}(3c^2-1)a_3$	$-3csa_1 + 6(2c^2-1)a_2$ $+3csa_3$	$\frac{3}{4}(1+c^2)a_1 + 3csa_2$ $+\frac{3}{4}s^2 a_3$	$-3sa_4$ $+6ca_5$	$\frac{3}{2}ca_4$ $+3sa_5$
$O_2'^1$	$-\frac{1}{8}s^2 a_6 - \frac{1}{4}csa_7$ $-\frac{1}{4}(3c^2-1)a_8$	$\frac{1}{2}csa_6 + \frac{1}{2}(2c^2-1)a_7$ $-3csa_8$	$-\frac{1}{8}(1+c^2)a_6 + \frac{1}{4}csa_7$ $-\frac{3}{4}s^2 a_8$	$-\frac{1}{2}sa_9$ $+\frac{1}{2}ca_{10}$	$\frac{1}{4}ca_9$ $+\frac{1}{4}sa_{10}$
$O_2'^2$	$\frac{1}{8}s^2 a_{11} + \frac{1}{2}csa_{12}$ $+\frac{1}{4}(3c^2-1)a_{13}$	$-\frac{1}{2}csa_{11} - (2c^2-1)a_{12}$ $+3csa_{13}$	$\frac{1}{8}(1+c^2)a_{11} - \frac{1}{2}csa_{12}$ $+\frac{3}{4}s^2 a_{13}$	$-\frac{1}{2}sa_{14}$ $-ca_{15}$	$\frac{1}{4}ca_{14}$ $-\frac{1}{2}sa_{15}$
$\tilde{O}_2'^1$	$\frac{1}{8}s^2 a_{16} + \frac{1}{4}csa_{17}$ $+\frac{1}{4}(3c^2-1)a_{18}$	$-\frac{1}{2}csa_{16} - \frac{1}{2}(2c^2-1)a_{17}$ $-3csa_{18}$	$\frac{1}{8}(1+c^2)a_{16} - \frac{1}{4}csa_{17}$ $+\frac{3}{4}s^2 a_{18}$	$-\frac{1}{2}sa_{19}$ $+\frac{1}{2}ca_{20}$	$\frac{1}{4}ca_{19}$ $+\frac{1}{4}sa_{20}$
$\tilde{O}_2'^2$	$-\frac{1}{8}s^2 a_{21} - \frac{1}{2}csa_{22}$ $-\frac{1}{4}(3c^2-1)a_{23}$	$\frac{1}{2}csa_{21} + (2c^2-1)a_{22}$ $-3csa_{23}$	$-\frac{1}{8}(1+c^2)a_{21} + \frac{1}{2}csa_{22}$ $+\frac{3}{4}s^2 a_{23}$	$-\frac{1}{2}sa_{24}$ $-ca_{25}$	$\frac{1}{4}ca_{24}$ $-\frac{1}{2}sa_{25}$

Application of DNMR to $Na_2Cd(SO_4)_2 \cdot 2H_2O$

Let us now consider double resonance in a hydrate crystal using as an example $Na_2Cd(SO_4)_2 \cdot 2H_2O$, which is isostructural to the mineral kröhnkite $Na_2Cu(SO_4)_2 \cdot 2H_2O$ and has space group $p2_1/c$ (Rao 1961). The unit cell has two different magnetic directions of proton-proton vectors and two magnetically nonequivalent positions of ^{23}Na nuclei. If H_0 is parallel to the plane (010), the spectra merge so that just one spectrum of ^{23}Na and one doublet spectrum of protons are observed.

The experiment was carried out with a crystal having less than 0.1 wt.% Mn. The spin-lattice relaxation time of protons, T_{1Z}, depends to some extent on orientation and is about 1 second.

A DNMR spectrum of Cd-kröhnkite is shown in Fig. 4. In the course of the experiment significant dependence of the DNMR signal on the amplitude of the saturating field was observed for sodium as well as for cadmium frequency transitions (Fig. 5). It should be noted that a wide minimum in similar dependence (McArthur et al. 1969; Lang and Moran 1970) occurs in systems with regular nuclear distribution such as CaF_2 and LiF. This fact must be taken into account if the search for DNMR signals in hydrate crystals is to be successful. What is more, DNMR signals in $Na_2Cd(SO_4)_2 \cdot 2H_2O$ could be registered when Zeeman energy was transferred into the intrapair as well as interpair DDR
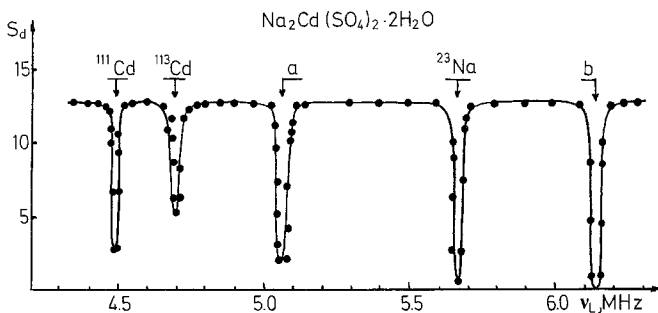
Fig. 4. DNMR spectrum of a $Na_2Cd(SO_4)_2 \cdot 2H_2O$ crystal. $H_0 \| [010]$; $H_{1S} \simeq 5$ Gauss; $\tau_B = 140$ ms; a, b are satellite transitions of ^{23}Na
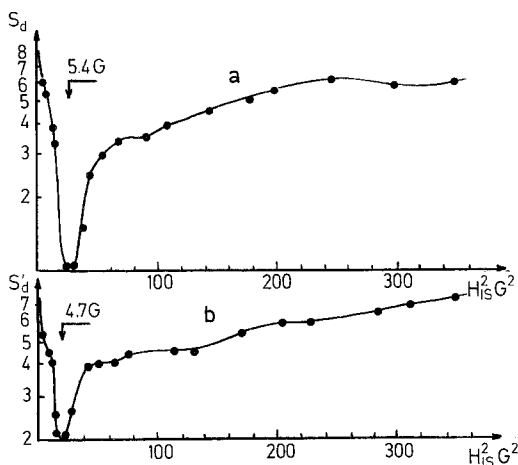
Fig. 5. Dependence of the dipolar signal S_d (measurement by protons) on the amplitude of saturating field H_{1S} in $Na_2Cd(SO_4)_2 \cdot 2H_2O$ for different ^{23}Na transitions. a Transition $1/2 \leftrightarrow -1/2$, $f = 5.584$ kHz; b transition $1/2 \leftrightarrow 3/2$, $f = 6.582$ kHz. The direction of H_0 is the same as in Fig. 3; $\tau_B = 60$ ms; frequency of the phase alternation is 500 Hz; $\tau_{12} = 18$ μs, i.e., the Zeeman energy is transferred to the intrapair reservoir; $H \simeq 6.7$ Gauss

subsystems. The latter is explained by the fact that subsystems can be considered isolated only in the first order of the perturbation theory and in general, a balance between them can be established during the interval $T_2 < t < T_{1Z}$.

Study of the spectrum of ^{23}Na nuclei in the crystal $Na_2Cd(SO_4)_2 \cdot 2H_2O$ yields the following values: $B_2^0 = \pm 218.5 \pm 1$ kHz and $B_2^2 = \mp 98 \pm 5$ kHz. The **Z** axis of the local crystalline field is parallel to the **a, c** plane of the crystal and forms an angle of 16° with the $+\mathbf{c}$ axis towards the $+\mathbf{a}$ axis. The **y** axis is perpendicular to the **z** axis and forms an angle of 33.5° with the **a, c** plane towards $+\mathbf{a}$. One of the most effective applications of the double resonance method is the investigation of crystals with atomic substitutions. Of special interest in this connection are crystals containing heterovalent impurities.

DNMR to CaF$_2$ and NaF

It is known that nuclei with spins $I > 1/2$ do not experience any static quadrupole interaction at cubic lattice positions. When some atom is substituted by a foreign atom, the local symmetry of the nuclear position is reduced, either in the closest proximity of that position or in the position of the foreign atom itself. This may result, of course, in a nonzero *electric field gradient* (EFG). Such nuclei that experience quadrupole interaction reveal unique information about the local structure of the defect in question and may be investigated with the DNMR method.

We now consider the results of a study of two substitutional crystals: CaF$_2$: Na$^+$ and NaF : Ca^{2+}. A spectrum of calcium difluoride doped with about 0.07 wt. % Na according to chemical analysis is given in Fig. 6. The angular dependence of the DNMR spectrum of substitutional ^{23}Na shows that the charge compensation occurs as a result of a vacancy at one of the nearest fluorine positions. This is obvious from the fact that the observed static EFG at the sodium nuclei exhibits trigonal symmetry along the [111] direction in the crystal. The quadrupole constant of the Hamiltonian for ^{23}Na nuclei in these positions is equal to $B_2^0 = \pm 85.7 \pm 0.5$ kHz (Shchepkin et al. 1977).

The concentration of the nuclei observed in the experiment was determined by DNMR. The dependence of the intensity of the dipole signal s_d on the number of phase rotations n in the saturating HF pulse was used, which is expressed (Lurie and Slichter 1964) as:

$$s_d/s_{d(0)} = \exp(-2n\varepsilon) = \exp\left(-2\frac{\tau_B}{T}t\right). \tag{10}$$

ε-ratio of respective heat capacities. Here T and then ε are determined experimentally from the diagram shown in Fig. 7. For the definition of τ_B, see Fig. 1 b. The relative concentration N_S/N_I is obtained from the formula

$$\frac{N_S}{N_I} = \frac{\gamma_I^2 I(I+1) H_L^2}{\gamma_S^2 S(S+1) H_{1S}^2} \cdot \frac{\varepsilon}{1-\varepsilon}. \tag{11}$$

It should be noted that (10) is valid only when $\tau \gg \tau_{IS}$, where T_{IS} is the cross-relaxation time between the I and S spin systems.
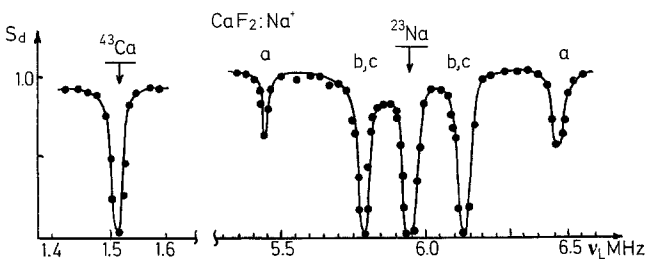
Fig. 6. DNMR spectrum in a CaF$_2$: Na$^+$ crystal. $\mathbf{H}_0 \| [111]$; $\tau_B \simeq 1$ s; $H_{1s} \simeq 4.5$ Gauss; the periodic phase alternation frequency is 4 kHz; $T_{1z} \simeq 11.5$ s, $T_{1d} \simeq 0.85$ s. *a*, *b*, *c* correspond to different orientations of impurity-vacancy dipoles
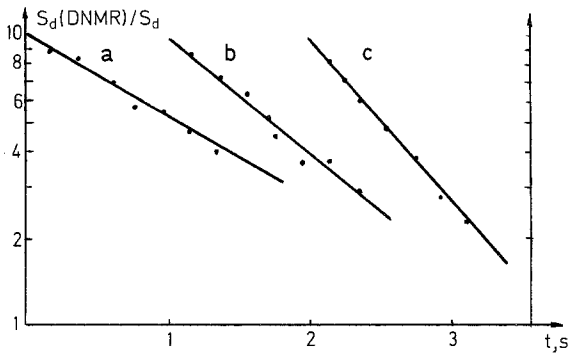
Fig. 7. Dependence of the DNMR signal of ^{43}Ca in $CaF_2:Na^+$ on the number ($n=\tau_B/\tau$) of phase alternations in the saturating impulse. a $H_{1s}=12.8$ Gauss; $\tau=25.5$ ms; $\varepsilon/H_{1s}^2=100\cdot10^{-6}$ G^{-2}. b $H_{1s}=12.8$ Gauss; $\tau=17.1$ ms; $\varepsilon/H_{1s}^2=96\cdot10^{-6}$ G^{-2}. c $H_{1s}=15.5$ Gauss; $\tau=17.1$ ms; $\varepsilon/H_{1s}^2=89\cdot10^{-6}$ G^{-2}

The realization of this condition is controlled by estimating ε/H_{IS}^2, which in this case depends neither on H_{IS} or τ. For example, the experimental data for ^{43}Ca in CaF_2 (Fig. 7) give the following ratio:

$$N_{^{43}Ca}/2N_F=N_{^{43}Ca}/N_{Ca}=(1.36\pm0.07)\cdot10^{-3}.$$

The measurement of ^{23}Na concentration was performed analogously by using both central and satellite transitions. In this way the total number of ^{23}Na nuclei entering the structure can be ascertained. With the satellite transition the number of ^{23}Na nuclei in trigonal positions, i.e., the number of isolated impurity-vacancy dipoles, is determined.

The measurement of concentration with the satellite transition yields the number of ^{23}Na nuclei in trigonal positions: $N_{Na}/N_F=0.51\;10^{-3}$ ($f=6.140$ kHz, $H/[111]$. Taking this result into account, and also that for the central transitions, we can obtain the total number of ^{23}Na nuclei in the crystal $N_{Na}/N_F=0.75\;10^{-3}$, i.e., the number of ^{23}Na in other possible positions is half that in trigonal positions. From the above data the amount of ^{23}Na entering the crystal structure is 0.044 wt. % which is somewhat less than that obtained from chemical analysis.

In our crystal $NaF:Ca^{2+}$ a rough chemical analysis of Ca impurity atoms yields 0.02 ± 0.01 wt. % Ca. In the crystal a tetragonal quadrupole-split spectrum of ^{23}Na with the constant $B_2^0=\pm86.7\pm0.5$ kHz was found, the main direction of the tensor being parallel [111] (Shcheptin et al. 1979). The presence of tetragonal symmetry and the absence of any other noncubic spectra provide evidence for charge compensation in the second coordination sphere of ligands. The estimate of Ca^{2+} concentration using the satellite transition of ^{23}Na nuclei yields a calcium content of about 0.006 wt. %. However, this result should be considered as a lower limit since some of the impurity-vacancy dipoles are aggregated in complexes. Heat treatment of the sample qualitatively confirms this. A considerable signal increase (~2.5 times) of the tetragonal ^{23}Na spectrum is observed after annealing the crystal at $\sim500\,°C$ for 30 min and subsequent rapid cooling.

Conclusion

DNMR spectra of ^{23}Na nuclei in $Na_2Cd(SO_4)_2 \cdot 2H_2O$ confirm that the crystal belongs to space group $p2_1/c$, in agreement with which there are two magnetically nonequivalent positions of ^{23}Na in the crystal. One of the most effective applications of DNMR is the study of diamagnetic substitutions in the crystal. By this method impurities can be identified at their positions and information can be obtained on the structure of defects, as was illustrated by DNMR experiments with $CaF_2 : Na^+$ (0.07 wt. %) and $NaF : Ca^{2+}$ (0.02 wt. %).

Phase-shifted pulse sequence may be used successfully in DNMR experiments. Depending on the object under investigation, it is necessary to take into account that maximum cooling of DDR in multispin systems is achieved when the duration of the second HF pulse in this sequence is more than or equal to 45°. In the Gaussian approximation for the NMR line, the reciprocal temperature of DDR for a multispin system, as well as in a single spin system, is proportional to a derivative from FIS.

Of importance for crystal hydrates is the facts that in their DDR two subsystems can be distinguished in the first approximation: the subsystem of interpair and the subsystem of intrapair dipole-dipole interactions. According to this, e.g., in systems having an NMR doublet, the reciprocal temperatures of both subsystems are simple periodic functions of the interval τ_{12} between pulses in phase-shifted pulse sequence. The signal of DNMR in $Na_2Cd(SO_4)_2 \cdot 2H_2O$ was observed upon cooling of any one of the subsystems, since an equilibrium state between the subsystems may arise more quickly than the spin-lattice relaxation (T_{1z}, T_{1d}) may occur.

If, for example, the orientation of the local crystal field is known from the structure of the crystal, then the angular dependence of the Hamiltonian may be found. For interactions described by a tensor not exceeding second rank, the frequency of transitions was determined on the basis of second-order perturbation theory.

The examples of DNMR applied to crystallographic problems as presented in this paper show new possibilities for investigations in the physics and chemistry of crystals. Moreover, we are of the opinion that DNMR has potential for broad applications in studying properties of different mineral groups.

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