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NUCLEAR MAGNETIC RESONANCE IN SOME CALCIUM HYDROSILICATES AND CALCIUM HYDROXIDE

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The structure of the crystal lattice of most calcium hydrosilicates is at present either unknown or has been determined with insufficient reliability. The method of nuclear magnetic resonance, which makes it possible to estimate the distance between hydrogen nuclei in a crystal lattice, may prove useful for refining and checking the correctness of proposed structures of calcium hydrosilicates. Until now these phases have not been investigated individually by the method of nuclear magnetic resonance. Earlier exploratory experiments on studying the hardening process of Portland cement by the method of nuclear magnetic resonance[1–3] merely showed that it is impossible to identify the calcium hydrosilicates formed during hydration of Portland cement.

In the structure of calcium hydrosilicates, the structural motif of the mineral portlandite (calcium hydroxide) apparently plays an important role. However, the data on the positions of hydrogens in the structure of this rather well-studied hydroxide are contradictory. Thus, in [4] a value of 0.99 Å is given for the internuclear distance in the OH group, in [5] 0.93 Å, and in [6] 0.79 Å.

In the present work the objects of investigation were artificially prepared calcium hydrosilicates, whose synthesis conditions and properties are described in detail in [7]. Calcium hydroxide was prepared by hydration of chemically pure calcium oxide. Crystals of $Ca(OH)_2$ of size of the order of $3\,\mu$ were dried in vacuum at a pressure of about 1 mm Hg and 250° for 4 hours, and then sealed in glass ampoules. To observe the nuclear magnetic resonance signals of hydrogen, a broad-line spectrometer was used, constructed at the Department of General and Chemical Physics of Moscow State University. A magnetic field of intensity 2950 gauss is produced by a permanent magnet. The inhomogeneity of the field within the sample volume is less than 0.03 gauss. The signal sensor was a Hopkins oscillator. The frequency stability of the oscillator was better than $1 \cdot 10^{-3}\%$. The time constant of the phase detector was from 6 to 14 sec. The

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curves obtained are shown in Fig. 1 (because of their symmetry, everywhere one half of the experimentally observed curve is given).

Study of the shape of the curves showed that almost each of them can be described as a sum of several Gaussian curves $g = Ae^{-h^2/b^2}$, where $g = g(h)$ is the shape function of the absorption line; $h = H_0 - H$, where H is the magnetic-field intensity, H_0 is the resonance value of the intensity; A and b are constants.

The analysis was carried out as follows. Transforming the expression written above to the form

$$\lg \frac{h}{B} = \lg \frac{b^2}{2A} + \frac{0.434}{b^2} h^2,$$

where $B = \frac{dg}{dh}$ is the derivative of the shape function of the nuclear magnetic resonance absorption line, directly recorded in the experiment, we obtain the equation of a straight line in the coordinates $(h^2, \lg h/B)$. Using this equation and processing the experimental curves, beginning with the largest values of h of each curve, all constants were successively found. These data are presented in Table 1; the calculated position of the maximum is also given there,

$$(h_m = b/\sqrt{2}),$$

the value of the second moment

$$S_2 = \int_0^\infty h^2 g(h)\, dh \Big/ \int_0^\infty g(h)\, dh := \frac{b^2}{2}.$$

and the magnitude of the area under each elementary curve as a percentage of the total area $(S = (A_i b_i / \sum A_i b_i) \cdot 100)$.

The curves calculated from these parameters are indicated in Fig. 1 by solid lines. The upper solid line is the total curve. The dashed line shows portions of the experimental curve where it diverges from the total calculated curve. Divergence from experiment is observed, as a rule,

Fig. 1. Derivative signals of proton nuclear magnetic resonance absorption in hydrosilicates and calcium hydroxide at room temperature.
1–gyrolite; 2–CSH (B); 3–tobermorite; 4–xonotlite; 5–C_2SH_2; 6–C_2SH (A); 7–C_2SH (B); 8–C_2SH (C); 9–C_3SH_2; 10–Ca$(OH)_2$

at the ends of the curves, where the experimental data are least reliable. In two cases (C_3SH_2 and Ca$(OH)_2$) it was not possible to find an analytical expression for the shape of the absorption curve. Table 1 also gives the values of the total second moment for all elementary curves, calculated by the formula $S_2 = \frac{1}{2}\left(\sum A_i b_i^3 / \sum A_i b_i\right)$, and the second moments of the experimental curve, computed by numerical integration. The difference in these data is explained by the inaccuracy of the experimental data for the ends of the curves.

The data presented show that most experimental curves can be represented as the sum of broad, medium, and narrow elementary curves of Gaussian form. This indicates the presence in the substance of three types of hydrogen nuclei. Without knowing the effect of temperature on the shape of the absorption line, it is rather difficult to relate the width of the absorption line with sufficient certainty to one or another type of water in the structure. However, it is evident that the narrow line corresponds to adsorbed water. The presence of adsorbed water in the specimens, despite drying, can be explained by the high dispersion of the specimens. Judging from the width of the other two lines,

it may be assumed that they correspond to protons that are comparatively weakly and strongly bound in the hydrosilicate lattice. The content of each of these types of water can be characterized by the area under the corresponding curve (Table 1).

Table 1

Characteristics of nuclear magnetic resonance absorption curves

Hydrosilicates	I: A	I: b, gauss*	I: h_m, gauss	I: S_2, gauss^2	I: S, %	II: A	II: b, gauss	II: h_m, gauss	II: S_2, gauss^2	II: S, %	III: A	III: b, gauss	III: h_m, gauss	III: S_2, gauss^2	III: S, %	S_2, calc., gauss^2	S_2, exp., gauss^2
Gyrolite Ca$_4$(Si$_6$O$_{15}$)(OH)$_2$·3H$_2$O	158	5.25	3.7	13.8	69	150	2.11	1.5	2.2	26	50.5	1.10	0.8	0.6	5	10.1	8.4
CSH (B) poorly crystallized tobermorite	199	4.31	3.0	9.3	74	141	1.58	1.1	1.2	19	104	0.79	0.6	0.3	7	7.1	5.0
Tobermorite Ca$_4$(Si$_6$O$_{18}$H$_2$)Ca·4H$_2$O or Ca$_{10}$(Si$_{12}$O$_{31}$)(OH)$_6$·nH$_2$O	162	4.54	3.2	10.3	72	117	1.75	1.2	1.6	20	104	0.85	0.6	0.4	8	7.7	6.9
Xonotlite Ca$_6$(Si$_6$O$_{17}$)(OH)$_2$	147	4.28	3.0	9.2	67	72.5	1.41	1.0	1.0	11	302	0.68	0.5	0.3	22	6.3	5.7
C$_2$SH$_2$ close to CSH (B)	185	6.20	4.4	19.3	76	195	2.31	1.6	2.7	14	227	[illegible]	[illegible]	[illegible]	[illegible]	15.1	10.6
C$_2$SH(A) Ca$_2$(SiO$_3$OH)OH	226	4.60	3.3	10.6	54	110	2.14	1.5	2.3	45	34.6	0.82	0.6	0.4	1	6.7	5.4
C$_2$SH(B) Ca$_2$(Si$_6$O$_{17}$)$_2$(OH)$_4$·12Ca(OH)$_2$	245	5.52	3.9	15.2	88	49	2.26	1.6	2.6	7	95.4	0.82	0.6	0.4	5	13.5	3.7

Hydrosilicate*	I: A	I: b, gauss	I: h_m, gauss	I: S_2, gauss^2	I: S, %	II: A	II: b, gauss	II: h_m, gauss	II: S_2, gauss^2	II: S, %	III: A	III: b, gauss	III: h_m, gauss	III: S_2, gauss^2	III: S, %	S_2, calc., gauss^2	S_2, exp., gauss^2
$C_2SH(C)$	164	5.44	3.8	14.8	78	136	1.47	1.0	1.1	18	84.2	0.54	0.4	0.2	4	11.8	9.5
C_3SH_2 $Ca_4(Si_2O_7)(OH)_2 \cdot 2Ca(OH)_2$	–	–	4.0	–	–	–	–	–	–	–	–	–	0.4	–	–	–	7.6
$Ca(OH)_2$	–	–	4.2	–	–	–	–	–	–	–	–	–	0.4	–	–	–	9.0

* The following designations are adopted: C–CaO, S–SiO_2, H–H_2O. The names of hydrosilicate (of the type CSH(B)) do not precisely reflect its composition, being conventional. Likewise, $C_2SH(A)$, $C_2SH(B)$, and $C_2SH(C)$ are not different modifications of one compound; they are different phases.
** The figures refer to the fourth, narrowest curve.

Structural calculations were carried out by us for $Ca(OH)_2$. The hypothesis concerning the position of hydrogen in the structure of this hydroxide (Fig. 2) was put forward as early as 1935 (^{8}) and was subsequently confirmed. As is seen from Fig. 2, the OH groups are arranged parallel to the *c*-axis of the cell. The numerical characteristics of the structure of calcium hydroxide according to the data of (^{5,6}) are given in Table 2.

For the calculation we used the Van Vleck formula for the second moment of the absorption line in polycrystalline substances (^{9}):

$$S_2 = \frac{6}{5}\left(\frac{I+1}{I}\right) M^2 N^{-1} \sum_{j>k} r_{j,k}^{-6},$$

Table 2

Parameters of the unit cell of calcium hydroxide at 25° in angstroms

Parameter	According to (^{5})	According to (^{6})	Our data
a	3.5918	3.5853	–
c	4.9063	4.895	–
Ca–O*	1.1486	1.1405	–
O–H	0.936 ± 0.003	0.79 ± 0.04	1.02 ± 0.03 (^{5}); 0.99 ± 0.03 (^{6})
H–H*	0.737	1.03	0.577 (^{5}); 0.592 (^{6})
H–H**	2.202	2.31	2.153 (^{5}); 2.152 (^{6})

* Distance between layers.
** Distance between nearest hydrogens.

where I is the nuclear spin; M is the nuclear magnetic moment; $r_{j,k}$ is the distance between nucleus k and nuclei j (in Å); N is the number of nuclei.

Fig. 2. Structure of $Ca(OH)_2$

Figure 2: Fig. 2. Structure of $Ca(OH)_2$

Fig. 3. Derivative of the nuclear magnetic resonance absorption signal of protons in calcium hydroxide at 25° (1) and −196° (2)

Figure 3: Fig. 3. Derivative of the nuclear magnetic resonance absorption signal of protons in calcium hydroxide at 25° (1) and −196° (2)

For hydrogen nuclei we obtain

$$S_2 = 3.58 \cdot 10^2 \, N^{-1} \sum_{j \neq k} r_{j,k}^{-6}.$$

The experimentally determined value of the second moment at room temperature in calcium hydroxide was 8.95 gauss^2 (with an accuracy of ±5%), and at liquid-nitrogen temperature 12.54 gauss^2 (accuracy of determination of the order of ±15%). This value of the second moment was taken for the calculations. The increase in the width of the absorption curve ($h_m = 4.98$ gauss as against 4.20 gauss at room temperature) is apparently explained by the presence of self-diffusion of hydrogen nuclei in the $Ca(OH)_2$ lattice, which decreases when the temperature is lowered.

On the basis of data(5,6) on the values of the parameters a and c, and the distance between the Ca and O layers, and also using data(10) on the coefficient of thermal expansion of $Ca(OH)_2$ (along the c axis $\alpha = 3.34 \cdot 10^{-5}$, along the a axis $\alpha = 0.98 \cdot 10^{-5}$), we calculated the quantity appearing on the right-hand side of the Van Vleck formula; as the unknown parameter the shortest distance between proton layers was taken. The summation was carried out over hydrogen nuclei located nearer than approximately 5 Å. For the remaining nuclei the sum was replaced by an integral. The value of the unknown parameter was determined with an accuracy of 3%. The results of the calculations, recalculated for room temperature, are given in Table 2.

Fig. 2. Structure of $Ca(OH)_2$

Fig. 3. Derivative of the nuclear magnetic resonance absorption signal of protons in calcium hydroxide at 25° (1) and −196° (2)

Comparison of the data obtained with the data(4,5,6) shows that the parameters determined by us coincide with the results of(4).

Since the coordinates of the atoms in the structure of most of the calcium hydrosilicates investigated by us are unknown, full use of the data obtained is at present difficult.

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

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