UDC 544.228:543.429.23

SINGLE-CRYSTAL ^{1}H NMR DATA AND HYDROGEN ATOM DISORDER IN LAWSONITE, CaAl$_2$[Si$_2$O$_7$](OH)$_2$·H$_2$O

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The dynamic structure of hydrogen sublattice in lawsonite, CaAl$_2$[Si$_2$O$_7$](OH)$_2$·H$_2$O is studied by the solid-state proton magnetic resonance (^{1}H NMR) spectroscopy of single crystal at room temperature. It is shown that both encapsulated water molecules, and hydroxyl OH-groups undergoes the rocking librations of the amplitudes of ~20° for H$_2$O, and ~40° for hydroxyls.

K e y w o r d s: ^{1}H NMR, hydrogen atom, disorder, lawsonite.

INTRODUCTION

Lawsonite CaAl$_2$[Si$_2$O$_7$](OH)$_2$·H$_2$O, a hydrated mineral which usually occurs in high pressure metamorphism, is regarded as a candidate for carrying water down to mantle depth of more then 200 km. The structure of lawsonite (Fig. 1) was refined from X-ray single-crystal data [1]. Two reversible phase transitions were found to occur: (l) Below 273(5) K the space group changes from *Cmcm* to *Pmcn*, accompanied by the loss of the --m mirror plane because of rotation of both H$_2$O and OH groups; (2) Below 155(5) K, where the space group symmetry is further reduced to *P*2$_1$*cn*,
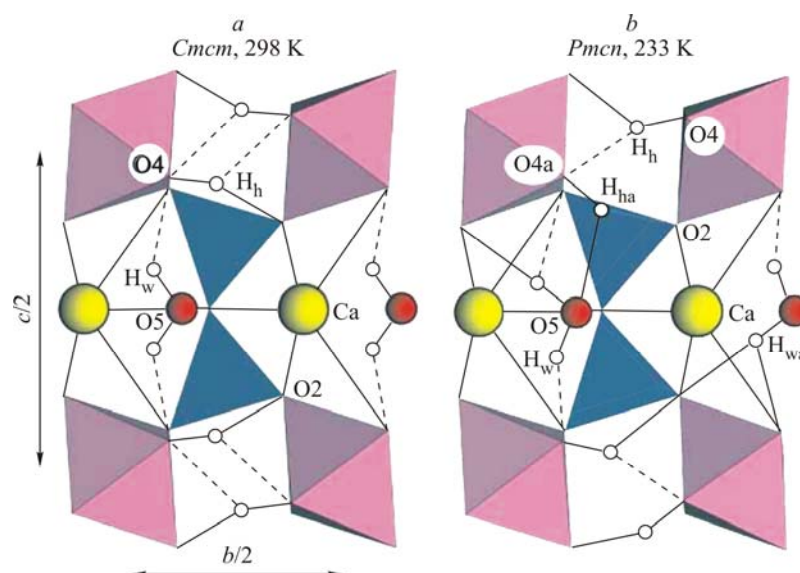

Fig. 1. The [100] projections of crystal structure of lawsonite at 295 K (*Cmcm*, *a*) and at 233 K (*Pmcn, b*). Small circles — hydrogen atoms of H$_2$O and OH-groups
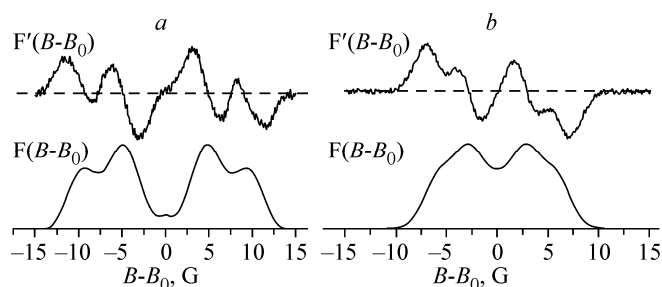
Fig. 2. ^{1}H NMR spectra of lawsonite recorded at orientations [001] (*a*) and [010] (*b*) of external magnetic field B_0 (~1 T). F(B—B_0) — absorption (in arbitrary units), F'(B—B_0) — first derivative

accompanied by the loss of the m-- mirror plane because of unidirectional shifts of the *x* coordinates of the H atoms of the H_2O and OH groups, thus resulting in a polar structure with interesting optical, elastic, and dielectric properties [2—5].

Structurally, the 273 K transformation may be displacive or of order-disorder type. In the latter case the *Cmcm* phase, stable above 273 K, must be orientationally disordered, either dynamically or statically. Here, the solid-state proton magnetic resonance (^{1}H NMR) spectroscopy was applied for refinement of the state of hydrogen sublattice in lawsonite *Cmcm* structure, first reported in [6].

EXPERIMENTAL

A colourless, gem-quality, cube-shaped crystal of lawsonite from Reed Ranch, Tiburon peninsula, California, 2×2×4 mm in size, was kindly provided by Professor Armbruster [1]. The sample was oriented with respect to its morphology as well as by optical and X-ray methods, and then was mounted on a NMR sample-holder.

The ^{1}H NMR study was conducted using the specialized wide-band spectrometer (of working magnetic field $B_0 \approx 10^4$ G) adopted for crystallographic measurements and precise recording of the form F(B—B_0) of magnetic resonance absorption lines. The room temperature ^{1}H NMR spectra revealed a multicomponent structure (Fig. 2), showing the complicated combination of intramolecular ^1H_w—^1H_w and of intermolecular ^1H_w—^1H_h and ^1H_h—^1H_h interactions of the proton spins in the infinite one-dimensional chains of hydroxyl and H_2O molecules: …OH…H_2O…OH…OH…H_2O… (Fig. 1).

For the further structural analysis were calculated the mean square widths of the recorded spectra, or the second moments M_2:

$$M_2 = \int F(B - B_0)(B - B_0)^2 dB. \qquad (1)$$

In Figure 3 are represented the data of M_2 determinations for 35 different orientations of lawsonite single crystal relatively to the external magnetic field obtained at
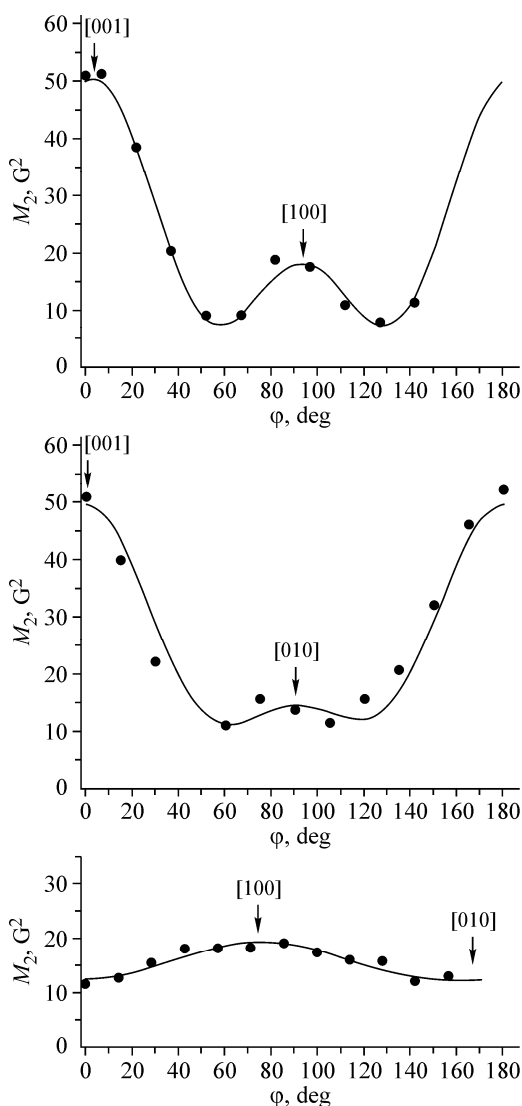

Fig. 3. Points: M_2 angular dependences at rotation the lawsonite single crystal around the axis [100], [010] and [001]; standard error: 5 %. Continuous line: calculated according to Van Vleck formula (2)

rotation the sample around the axis [100], [010] and [001]. For B_0 orientations parallel to the crystallographic axes, the M_2 values are as follows:

$$M_2[100] = (19.6 \pm 1.0)\ G^2,$$
$$M_2[010] = (11.7 \pm 0.6)\ G^2,$$
$$M_2[001] = (50.3 \pm 2.5)\ G^2.$$

DATA ANALYSIS AND DISCUSSION

i) Second moments of ^1H NMR spectra. The M_2 values allow the hydrogen atom structure of the studied system to be determined according to the classical Van Vleck′s formula [7]:

$$M_2 = 3/4\gamma^4\hbar^2 I(I+1)\ \Sigma_k\ (1 - 3\cos^2\theta_{ik})^2\ r_{ik}^{-6}, \tag{2}$$

where γ and I are the proton gyromagnetic ratio and spin; $\hbar$ is the Planck′s constant; r_{ik} is distance between given atom i and other hydrogen atoms k; and θ_{ik} is the angle between vector r_{ik} and the orientation of the external magnetic field B_0.

In general, for the resolution of the orthorhombic structure M_2 values are necessary for at least 6 different orientations [8—10]. However, due to r_{ik}^{-6} dependence, in the lawsonite structure only following three parameters are important: (1) the intramolecular H—H distance r in H_2O; (2) the intermolecular H—H distance R between an OH proton and the nearest H_2O proton; (3) the angle θ between the vectors R and r. These parameters can be calculated according to the following equation derived from (2):

$$M_2[100] = k\ (r^{-6} + 2R^{-6})\ + M_2', \tag{3}$$
$$M_2[010] = k\ [r^{-6} + 2R^{-6}(3\sin^2\theta - 1)^2] + M_2', \tag{4}$$
$$M_2[001] = k\ [4r^{-6} + 2R^{-6}\ (3\cos^2\theta - 1)^2] + M_2', \tag{5}$$

where $k = 221.33 \cdot 10^{-48}\ cm^6 G^2$ and M_2' is a relatively small contribution to M_2 from more distant hydrogen atoms surrounding the calculated group of (OH-H_2O-OH) spins. Using the X-ray structure data [1] we evaluated the value of $M_2' = 1.4\ G^2$.

Having solved this system of equations, we have calculated the experimental values for intramolecular and intermolecular H—H distances r and R, and the angle θ between the vectors R and r:

$$r = (1.68 \pm 0.02)\ \text{Å},$$
$$R = (1.96 \pm 0.06)\ \text{Å},$$
$$\theta = (31 \pm 1)°.$$

ii) H_2O thermal libration data. The calculated experimental parameters should be corrected in order to account for the influence of thermal librations of both H_2O molecules and of OH-groups derived from the vibration spectroscopy data [11, 12]. The libration mobility of H_2O molecules distorts slightly the NMR spectra, and as a result the derived interatomic distances r and R, calculated according to the Equations (2)—(5) will differ from the real equilibrium interatomic distances r_0 and R_0. For the H_2O molecules the correct intramolecular H—H distance r_0 is related to the ″measured″, or uncorrected distance $r = <r>$ according to the Formula [11]:

$$<r>^{-3} = r_0^{-3}(1 - 2.52 < \phi^2 >). \tag{6}$$

Here $<\phi^2>$ is the mean-square amplitude of the H—H vector oscillations, which is supposed to be derived from vibration spectroscopy data [11, 12]. On the other hand, the Formula [6] can be used for independent determination of $<\phi^2>$ if the correct intramolecular H—H distance r_0 is known *a priori*. In particular, the measured intramolecular H—H distances in H_2O molecules in different hydrates are close to the values of $r_0 \approx (1.52 \dots 1.54)\ \text{Å}$ [13]. It should be mentioned that the stability of intramolecular H_2O parameter $r_0 \approx (1.52 \dots 1.54)\ \text{Å}$ can be related to the high frequencies of stretching and valence vibrations (~ 1400 and $\sim 3100 \dots 3600\ cm^{-1}$) of the water molecules in different systems [14].
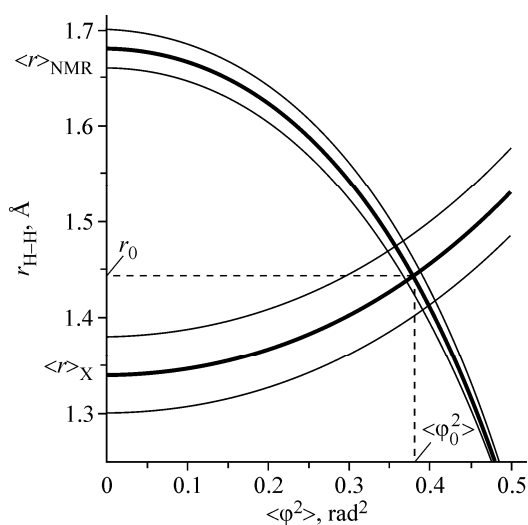
Fig. 4. The convergence of X-ray and NMR data for $r_{(H-H)}$ distance in lawsonite under the account of H_2O librations [according to Eq. (6) and (7)]

Using the above values $r = (1.68\pm0.02)$ Å and $r_0 = 1.54$ Å, $<\phi^2>$ amounts to $0.10\,rad^2$ (or $\sim18°$). It is interesting to note that the calculated $<\phi^2>$ value is close to the rotational angle $22°$ of the H_2O molecules in the low-temperature *Pmcn* (233 K) phase of lawsonite structure (Figure 1).

The found H_2O librations will distort the visible by X-ray distances r_X [1] in accordance to formula [15]:

$$<r>_X = r_0 <\cos \phi)> \approx r_0 (1 - <\phi^2>/2). \qquad (7)$$

Using the above mentioned r_0 and $<\phi^2>$ values, the expected value of the distorted intramolecular distance is $r_X \approx 1.44$ Å which is relatively close to the refined X-ray value [1.34(4) Å]. Obviously, the same considerations can be applied to the X-ray determined O—H bond lengths in both H_2O molecules and OH groups in lawsonite and in other hydrated crystals [16].

The above consideration may be regarded as a justification for determination of correct H—H-distances r_0 in H_2O molecules by solving the pair of Equations (6) and (7) using the visible (i.e. uncorrected) X-ray and ${}^1H$ NMR H—H-distances as experimental parameters. Figure 4 shows the expected r_{H-H} dependences for visible X-ray and NMR data plotted as function of $<\phi^2>$. The point of the best fit of two dependences is $r_0 = (1.44\pm0.04)$ Å, and $<\phi_0^2> = (0.38\pm0.10)$ rad^2.

iii) Influence of lattice oscillations on H_2O dynamics. The structural interpretation of H_2O dynamics and hydrogen atom ordering in the lawsonite *Cmcm* structure may be related to the interaction between the fast vibrations of the crystal lattice of frequency $\nu \sim 1000$ cm^{-1}, the typical stretching vibrations of the SiO_4 units [16], and localized libration motion of H_2O molecules of frequency $\nu_{loc} \approx 200-300$ cm^{-1}. In this case, the H_2O molecular dynamics can be regarded within the theory of oscillatory movements under the influence of a fast-alternating field [17]. In particular, if the direction of high-frequency oscillations coincides with the orientation of electric dipole of H_2O, the dipoles are influenced by the effective potential:

$$U_{eff} = U_0[-\cos\theta + (d^2\nu^2/(8D^2\nu^2_{loc}))\sin^2\theta], \qquad (8)$$

where U_0 is the maximum value of the initial unperturbed potential, ν is the frequency of the perturbing high-frequency mode, d is the amplitude of the perturbing oscillation, and D is the distance between the centers of negative and positive charges in H_2O molecules.

The first term in square brackets corresponds to the dependency of non-perturbed potential on the dipole orientation with respect to the direction of the molecular field. The second term shows the perturbing impact of high-frequency translational vibrations on the effective potential. If the amplitude d of such oscillations are high enough to make $d^2\nu^2 > 4D^2\nu^2_{loc}$, the potential (8) has two equilibrium states: $\theta = 0$, and $\theta = \pi$.

If the direction of high-frequency oscillations is orthogonal to the orientation of electric dipole of H_2O, the dipoles are influenced by the effective potential [17]:

$$U_{eff} = U_0[-\cos\theta + (d^2\nu^2/(8D^2\nu^2_{loc})) \cos^2\theta] \qquad (9)$$

similar to Equation (8). If the amplitude d and frequency ν of perturbing oscillations satisfy $d^2\nu^2 > 4D^2\nu^2_{loc}$, the potential (9) also represents to two stable states: normal, or initial state, if $\cos\theta = 1$, and the perturbed state, if

$$\cos^2 \theta > 4D^2\nu^2_{loc}/(d^2\nu^2) \qquad (10)$$

The latter state corresponds to the dipole orientation close to the direction of high-frequency oscillations normal to Ca—OH_2 bond. It means that the transversal vibrations of crystal lattice can be

regarded as the main source for activation of the high-amplitude librations of H_2O dipolar moments and for the distortion of observed O—Hw, O—Hh, and Hw—Hw′ distances in lawsonite.

CONCLUSION

The PMR data provide strong evidence that the hydrogen sublattice of the 295 K *Cmcm* lawsonite structure is substantially disordered. In a structural sense this disorder can be interpreted as a time averaged dynamic disorder, H_2O and OH groups oscillating between two equivalent sites similar to the ordered H positions of the *Pmcn* lawsonite structure.

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