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Abstract

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BEHAVIOR OF ZEOLITIC WATER AND THE SYMMETRY OF HARMOTOME

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The structure of harmotome—$Ba_2Al_4Si_{12}O_{32} \cdot 12H_2O$—has recently been determined by a group of Japanese authors (^{1}). It was shown that harmotome belongs to the space group $P2_1$ and has the unit-cell parameters:

$$a = 9.87\ \text{Å}, \quad b = 14.14\ \text{Å}, \quad c = 8.78\ \text{Å}, \quad \beta = 124°50'.$$

Harmotome is a representative of the family of zeolites with a three-dimensional aluminosilicate framework, in the cavities of which Ba ions and molecules of crystallization water are located. The elementary cell of the crystal contains two cavities, related by a symmetry axis 2_1, and in each cavity there is one Ba atom and 6 water molecules. The authors of (^{1}) did not find appreciable deviations from the center of symmetry in the positions of all atoms, except for the oxygens of two water molecules, whereas the presence of piezoelectric properties in this crystal (^{2}) indicates the absence of a center of symmetry. Since the positions of the hydrogen atoms were not determined in (^{1}), it could be assumed that the deviations from the centrosymmetric structure are to a considerable extent associated with the positions of the protons of the zeolitic water. The investigations were carried out by the method of nuclear magnetic resonance (NMR), which is sensitive to the position and character of the mobility of protons in the structure (^{3,4}).

A single crystal of harmotome (Scotland) with dimensions $4 \times 4 \times 6$ mm^3 was obtained from the Mineralogical Museum of the Academy of Sciences of the USSR (No. 51815). Goniometric measurements and the discovery of two cleavage planes of different perfection, {010} and {001} (^{5}), made it possible to determine unambiguously the orientation of the crystal. We note that harmotome may be regarded as pseudorhombic if one passes to new cell axes: $a' = a_0$, $b' = b_0$, and $c' = 2c_0 + a_0$. Then the c' axis deviates from the {001} plane by only 28′. On the apparatus described in (^{3}), at room temperature, the orientational dependence of the NMR spectra was investigated upon rotation of the sample about three nonequivalent directions in the crystal. The spectra are quadruplets, which at certain orientations degenerate into triplets, doublets, and singlets. Figure 1 gives the dependence of the doublet splittings of the NMR spectra upon rotation of the crystal about the b axis. The small value of

$\Delta H_{\max}$ in comparison with $\Delta H_{\max} = 20$ Oe in ordinary crystal hydrates with fixed proton positions indicates the mobility of the protons in the structure of harmotome (6).

The results of the experiments could be explained only on the assumption that the water molecules possess two rotational degrees of freedom (precession). In this case, as Yano showed (7), the dependence of the doublet splittings on orientation has the form

$$\Delta H = \frac{3}{4}\mu r^{-3}(3\cos^2\alpha - 1)(3\cos^2\beta - 1)(3\cos^2\gamma - 1), \qquad (1)$$

where μ is the magnetic moment of the proton, r is the H—H distance in the water molecule, equal to 1.60 Å, α is the reorientation angle, β is the precession angle, and γ is the angle

between the precession axis and the direction of the external magnetic field. The experimental dependence shown in Fig. 1 corresponds to the presence of two precession axes oriented at angles of $\pm 10^\circ$ to the c' axis in the $a'c'$ plane. In this case $\alpha = 90^\circ$ and $\beta = 40^\circ$.

Thus, in the structure of harmotome there are two groups of water molecules precessing about two different axes directed at an angle of 20° to one another.

Since the intensities of all the lines of the quadruplet are identical, it is necessary to conclude that both groups contain an equal number of water molecules.

For a more detailed elucidation of the nature of the mobility of zeolitic water, NMR spectra of harmotome were recorded in the temperature interval -196° to $+165^\circ$. The crystal was oriented so that the direction of the magnetic field coincided with the diagonal between the a' and c' axes. Some of the spectra obtained at this orientation are shown in Fig. 2. At -196° the spectrum is broad, characteristic of hydrates with a fixed arrangement of protons. Fine structure is not manifested, which proves to be a consequence of the presence in the structure of a large number of proton–proton directions oriented in different ways. As the temperature is raised, beginning at approximately -100°, the spectrum begins to narrow, becoming at -60° a doublet with rather broad components. This means that mobility of the water molecules has appeared in the structure, similar to the mobility at room temperature (precession). However, the width of the doublet components indicates that either the precession axes of the individual water molecules do not coincide with one another but are close to the c' direction, or the precession angles of different molecules may deviate slightly from the value $\beta = 40^\circ$. At -20° both components of the doublet in turn begin to split into two narrow lines, so that at -4° the spectrum has the form of a quadruplet characteristic of this crystal orientation at room temperature.

Fig. 1. Dependence of the doublet splittings of the proton magnetic-resonance spectra in harmotome upon rotation of the crystal about the b axis. Angles are measured from the c' direction.

Figure 1: Dependence of the doublet splittings of proton magnetic-resonance spectra in harmotome on rotation of the crystal about the b axis. Angles are measured from the c' direction.

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Fig. 2

Figure 2: Fig. 2

Thus, already at -4° two directions of the precession axes have become distinguished in the structure, and the precession angle β is the same for all water molecules. It may be expected that with increasing temperature the precession angle will increase.

and, according to (1), the splitting of the quadruplet decreases. Such an effect was indeed observed, and at $+165^{\circ}$ the quadruplet degenerated into a singlet of width 1.2 oersted, which corresponds to an increase of β to $54^{\circ}40'$.

As follows from structure (1), each of the water molecules in harmotome has a different environment. What is unusual in the behavior of zeolitic water is the fact that, despite the different environment, all the water molecules behave identically. One has to assume that this is due to the collective interaction of the water molecules.

Fig. 2. Magnetic-resonance spectra of water protons in harmotome at different temperatures

In this case, the change in the state of mobility from low temperatures, when each water molecule is oriented in accordance with its environment, to higher temperatures, at which the collective motion of water begins to appear, must be accompanied by a phase transition.

The question remains unclear as to around which axes the water molecules occupying the given cavity in the structure precess. It would be most natural to suppose that all six water molecules in the cavity precess about one and the same axis, inclined to the c' axis at an angle of $+10^{\circ}$ or -10°. In this case, from the condition that there be no residual electric moment in the crystal, it is necessary to have at least four cavities in the unit cell, i.e., it is necessary to double the period along c' or a'. It may also be supposed that in each cavity there are two groups of water molecules which precess about different axes. In both cases the arrangement of the precession axes of the water molecules is consistent with the presence of a twofold screw axis and, with respect to the arrangement of the protons of the structure, is apparently centrosymmetric.

Thus, it may be asserted that the probabilities of the distribution of protons in the harmotome structure are approximately centrosymmetric. The acentricity of the structure should then be attributed entirely to the deviations of the two water molecules noted in (1), as well as to the presence in the structure of a small amount of alkali elements not taken into account in the structure determination.

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