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1967

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Abstract

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UDC 548.0:538+548.314

CRYSTALLOGRAPHY

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(Presented by Academician V. S. Sobolev on 25 IV 1966)

Edingtonite $BaAl_2Si_3O_{10} \cdot 4H_2O$ is one of the very rarely occurring fibrous zeolites of the natrolite group ¹. Its structure was investigated by X-ray methods by Taylor ². The unit cell of edingtonite contains two formula units; the space group is D_{2d}^3 . The channels in the aluminosilicate-oxygen framework of the zeolite, parallel to the c axis of the crystal, are filled with Ba^{2+} ions and water molecules. It is considered established ³ that the arrangement of the H_2O molecules in edingtonite, as in other fibrous zeolites, is determined by hydrogen bonds with the aluminosilicate framework. However, since the positions of the protons have not yet been determined, the role of the hydrogen bonds cannot be regarded as established. In order to clarify the position of the protons and the character of their motions, we undertook an investigation of edingtonite by the method of proton magnetic resonance (p.m.r.).

Fig. 1. Temperature dependence of the doublet splittings of the p.m.r. spectra of edingtonite (field $H_0 \parallel X$). Schematic representations are also given of derivative spectra characteristic of low (a) and room (b) temperatures at the same crystal orientation.

The proton magnetic resonance in edingtonite was studied at room temperature by Ducros et al. ^{4,5}. It was shown that near $+20^\circ$ the water molecules take part

in an intensive anisotropic motion (rotation), the axis of which is the c axis of the crystal unit cell.

The behavior of water molecules in edingtonite differs sharply from their behavior in other fibrous zeolites—natrolite⁶, thomsonite⁷, and scolecite⁴—in which the water molecules at room temperature are “rigidly” fixed (from the point of view of NMR). In connection with the high mobility of water in edingtonite at room temperature, in order to obtain information on the equilibrium or preferred positions of the protons it is necessary to lower the temperature of the sample so as to “freeze out” the mobility of the H₂O molecules observed at room temperature. For this purpose, using a JNM-3H-60, BL-2 spectrometer, the p.m.r. spectra of a single crystal of natural edingtonite from a wide temperature range were studied.

Böhlet, Västergötland (Sweden). The specimen studied had dimensions $4 \times 4 \times 6$ mm³ and was oriented as follows: the Z axis \perp (001), the X axis \perp (110), and the Y axis \perp ($\bar{1}10$).

When the temperature of the specimen is lowered, the doublet form of the edingtonite spectrum characteristic of room temperature (and the corresponding character of the mobility of the water molecules) is preserved down to a temperature of about -20° . It is interesting to note that over a wide temperature interval (from -20 to $+70^\circ$, the highest temperature of observation) the magnitude of the doublet splitting ΔH does not change and depends only on the orientation of the crystal relative to the external magnetic field:

$$\Delta H = 4.67(3 \cos^2 \theta - 1) \text{ oersted,}$$

where θ is the angle between the direction of the magnetic field and the Z axis of the crystal. The half-width of the doublet components changes from 1 oersted at -21° to 0.1 oersted at $+70^\circ$ (Fig. 1). This means that the intramolecular component of the local field, determined by the interaction between the protons of a given water molecule, does not change, whereas the intermolecular part, due to the interaction of protons belonging to different water molecules, changes very sharply. The result obtained can be explained if it is assumed⁽⁸⁾ that, along with anisotropic rotational motion of the H₂O molecules about the c axis, translational motions of the water molecules (diffusion) also take place.

Fig. 2. Arrangement of protons and direction of hydrogen bonds in edingtonite. Projection onto the (001) plane. Only the nearest environment of the water molecule is shown. $O_{IP}I$ —oxygen atoms and protons of H₂O_I molecules; $O_{II}P_{II}$ —oxygen atoms and protons of H₂O_{II} molecules; O_K —oxygen atoms of the (Al, Si) framework; dashed lines—hydrogen bonds. The figures indicate the heights of atoms above the drawing plane in Å.

The presence of intense diffusion or exchange of positions between different water molecules also explains the fact, strange at first sight, that the rotational

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motion of water molecules which are nonequivalent in structural respect is completely identical, so that at room temperature only one doublet is observed. The intensity (rate) of diffusion increases sharply with increasing temperature, whereas the angular probability-density distribution of the different orientations of the proton-proton (p-p) vectors of the water molecules remains unchanged within these temperature limits.

At temperatures below -22° the NMR spectrum of edingtonite broadens strongly, its intensity decreases, and at temperatures below -50° the signal intensity again increases. At temperatures below -60° the NMR spectrum of edingtonite splits into five components (see Fig. 1a). The magnitude of the doublet splittings depends appreciably on temperature and, when the temperature is changed from -60 to -130° , increases by $\sim 20\%$. Such large changes of the doublet splittings with temperature had not previously been observed for crystal hydrates. They can be explained by assuming the presence of large librational oscillations of the water molecules near equilibrium configurations. At -130° the spectra correspond to a practically rigid structure. The angular dependence of the doublet splittings upon rotation of the crystal about the Z axis is well described by Pake's formula⁽⁹⁾

$$\Delta H = \frac{3}{2} \mu r^{-3} [3 \cos^2(\varphi - \varphi_0) - 1] \text{ oersted},$$

where ΔH is the distance between the components of the doublet; μ is the magnetic moment of the proton; r is the proton-proton distance; φ_0 is the angle between the direc-

...between the p-p vector and the X axis of the crystal. The two doublets in the spectrum at -130° correspond to $r = 1.57 \pm 0.015$ Å and $\varphi_0 = 0$ and 90° .

Comparison with the structure of edingtonite shows that the experimentally obtained arrangement of the p-p vectors is in complete agreement with that expected on the assumption of the formation of hydrogen bonds by water molecules

Fig. 3. Hydrogen bonds in edingtonite. Arrangement of the protons in planes of three oxygen atoms: a $-\text{H}_2\text{O}_I$, b $-\text{H}_2\text{O}$. Letter designations are the same as in Fig. 2

Figure 3: Fig. 3. Hydrogen bonds in edingtonite. Arrangement of the protons in planes of three oxygen atoms: a $-\text{H}_2\text{O}_I$, b $-\text{H}_2\text{O}$. Letter designations are the same as in Fig. 2

with the nearest oxygen atoms of the framework. Fig. 2 shows a portion of the edingtonite structure that includes the positions of the protons localized on the basis of the data obtained on the directions of the p-p vectors and the inter-proton distances. Fig. 3 shows the hydrogen bonds of the water molecule with oxygen of the framework.

Fig. 3. Hydrogen bonds in edingtonite. Arrangement of the protons in planes of three oxygen atoms: **a** $-\text{H}_2\text{O}_I$, **b** $-\text{H}_2\text{O}_{II}$. Letter designations are the same as in Fig. 2.

Thus, neither in the length nor in the configuration of the hydrogen bonds is edingtonite in any way distinguished among fibrous zeolites. Therefore it seems surprising that there are large librational oscillations of the water molecules in it at temperatures below -60° , and the unusual behavior of the water molecules at temperatures above -20° , characteristic of zeolites of the type of chabazite, gmelinite, harmotome, etc. ⁽⁸⁾.

The causes of these phenomena may be understood to a certain extent if one notes that in the channels of the edingtonite structure the water molecules are not arranged in isolation, as in other fibrous zeolites, but in groups of 4 H_2O molecules. In such a group, along with interaction with the framework through hydrogen bonds, the water molecules will interact strongly with one another. In particular, one may expect that a substantial role will be played, for example, by the electrostatic interaction of the dipole moments of the water molecules; moreover, the equilibrium configuration of the water molecules for electrostatic interaction need not at all coincide with the equilibrium configuration of the water molecules bound by hydrogen bonds. It is possible that the large librational oscillations of water molecules in edingtonite at low temperature and the anisotropic rotation of H_2O molecules at room temperature correspond precisely to transitions between such equilibrium configurations.

The authors express their deep gratitude to Prof. A. M. Kuzmin for providing the edingtonite sample.

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Received

2 IV 1966

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