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Abstract

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ON THE BEHAVIOR OF WATER OF CRYSTALLIZATION IN THE FERROELECTRIC $K_4Fe(CN)_6 \cdot 3H_2O$

(Presented by Academician V. N. Kondrat' ev, 21 VII 1960)

The ferroelectric properties of yellow prussiate of potash (YPS) below −22° were discovered by Waku et al. (^{1}). Monoclinic crystals of YPS contain 4 molecules of $K_4Fe(CN)_6 \cdot 3H_2O$ in a cell with dimensions $a = 9.32$ Å, $b = 16.84$ Å, $c = 9.32$ Å (^{2}). In a study of YPS by the method of proton magnetic resonance, a considerable change was noted (^{3}) in the second moment of the proton absorption line upon passage through the Curie point.

The second moment of the absorption line

$$S = \int_{-\infty}^{+\infty} f(H)(H - H_0)^2 \, dH \tag{1}$$

(where $f(H)$ is a normalized function describing the line shape, and $(H - H_0)$ is the difference between the current value of the magnetic field and its resonance value) characterizes the interaction of protons in the substance, and its change indicates a change in the positions or mobility of the protons (^{4}).

In view of the discovered temperature correlation between the change in the second moment of the absorption line and the appearance of spontaneous polarization in YPS, we carried out a more detailed study of the behavior of the molecules of crystallization water in YPS by the method of proton magnetic resonance.

The apparatus used is described in (^{5}). In order to increase the signal-to-noise ratio in studying polycrystalline specimens, the YPS powder was pressed under a pressure of up to 150 kg/cm^2 into a cylinder 13 mm in diameter and 20 mm long. Single crystals of YPS with dimensions $12 \times 6 \times 20$ mm^3 and $12 \times 8 \times 20$ mm^{3*} were also investigated. The study of temperature effects was carried out in the temperature interval from 77 to 400° K in a special Dewar vessel analogous to that described in (^{6}).

The absorption spectra were recorded with a time constant of 3.5 sec in a magnetic field $H_0 = 3000$ oersted, with field-sweep rates of 0.0194 and 0.0097 oersted/sec. The modulation depth during recording did not exceed 0.8 oersted.

Figure 1 gives the dependence of the second moment on temperature for polycrystalline YPS, and Fig. 2 shows the form of the derivatives of the absorption spectra at various temperatures.

The expression for the second moment may be written in the form

$$S = S_0 + S_1, \tag{2}$$

where S_0 is the intramolecular part, caused by the pair interaction of protons in water molecules, and S_1 is the intermolecular part, due to

by the interaction of the protons of the "pair" with other nuclei possessing a magnetic moment. The components of the second moment, written for the case of a polycrystal containing water molecules, have the form (^{7})

$$S_0 = 358.1 \cdot 10^{-48} r^{-6},$$

$$S_1 = 358.1 \cdot 10^{-48} \sum_j r_j^{-6} + \frac{4}{15} \sum_k I_k(I_k+1) g_k^2 \beta^2 r_k^{-6}, \tag{3}$$

where r is the interproton distance in the water molecule (in cm); r_j is the distance to the protons of other water molecules; r_k is the distance to other nuclei with spin I_k and hydromagnetic ratio g_k; β is the nuclear magneton.

To separate the experimentally observed value of the second moment at oxygen temperatures into S_0 and S_1, measurements were carried out with a single crystal. Figure 3 shows the proton-resonance spectrum of a single crystal of PFC at a temperature of $-183°$, with a maximum splitting $\Delta H_{\max} = 21.6$ oersted between the components (peaks) of one of the doublets.

The magnitude of the intermolecular part can be determined from the width of the resolved peak, since its broadening is caused mainly by intermolecular interaction. This gives the value $S_1 = 0.6 \pm 0.06$ oersted^2, and from (2), with $S_0 = 24.6 \pm 1.2$ oersted^2, we have $S_0 = 24.0 \pm 1.2$ oersted^2.

Fig. 1. Temperature dependence of the second moment of the proton magnetic-resonance line for polycrystalline $K_4Fe(CN)_6 \cdot 3H_2O$

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* The single crystals were cut in the form of parallelepipeds with edges denoted by x, y, z. The y axis was chosen as the axis b of the unit cell; the x and z axes coincided with the directions [101] and [10$\bar{1}$], respectively.

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The value of S_0 can also be determined (^{4}) from the splitting ΔH_{max} between the peaks (Fig. 3) by the formula $\Delta H_{\text{max}} = 3\mu r^{-3}$ (μ is the magnetic moment of the proton); whence $r = 1.575 \pm 0.015$ Å, and from (3) $S_0 = 23.5 \pm 1.2$ oersted^2, which agrees well with the value obtained above.

It should be noted that distances between protons in water molecules of about 1.58 Å and, correspondingly, values of the second moment of 23.5 oersted^2 are characteristic of rigid water molecules in crystal hydrates (^{8}).

The decrease in the magnitude of the second moment, beginning at a temperature of $\sim -150°$, may in general be caused by two reasons—the removal of protons from one another or the appearance of rotational or translational degrees of freedom in the water molecules (^{4}). The presence of hindered rotation (reorientation) of a large polar molecule of asymmetric form at such low temperatures seems at first glance unlikely. It should be noted, however, that reorientation of water molecules in some crystal hydrates at comparable temperatures was recently reported in (^{9}). Moreover, if one assumes that the decrease of the second moment is caused by the removal of protons along the hydrogen bonds $O-H\cdots N$, then, first, the presence of a strong temperature dependence contradicts the usual behavior of hydrogen bonds and, second, calculations of the expected moments, performed on the basis of the structural data given in (^{2}), make this supposition improbable.

Thus, it should be considered that the decrease of the second moment above $-150°$ is associated with reorientation of the water molecules of PFC. From theoretical consideration for proton-proton (p—p) vectors isotropically distributed in the polycrystal and reorienting about fixed axes, it follows that the magnitude of the second moment should decrease by a factor of 4 in

compared with the value for fixed (p—p)-vectors ( ). This relation, in our case, for the temperature $-35°$, where the decrease of the moment ceases, is not satisfied.

To clarify this circumstance, additional experiments were carried out with a single crystal. By rotating the crystal about three mutually perpendicular axes at a temperature of $-183°$, the directions of the (p—p)-vectors of all 12 water molecules entering the unit cell were found. It turned out that in each of the three mutually perpendicular planes coinciding with the faces of the crystals there lie four (p—p)-vectors, pairwise perpendicular to one another and situated at an angle of 45° to the edges (in fact, the planes in which the (p—p)-vectors are located are inclined at an angle of about 10° to the corresponding faces).

Fig. 2. Derivatives of proton-resonance spectra in a polycrystal of ZHKS

Figure 2: Fig. 2. Derivatives of proton-resonance spectra in a polycrystal of ZHKS

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In the positions corresponding to the maximum splittings of the doublets, the temperature dependences of the intensities of these doublets were measured for all three planes. The doublets from the (p—p)-vectors lying in the X and Z planes disappear at a temperature of about −35°. They apparently correspond to two water molecules whose oxygens were localized in work (^{2}), where it was shown that these molecules have identical surroundings. The disappearance of the peaks from these protons at a temperature of −35° indicates that at this temperature all the corresponding molecules participate in reorientation.

For the "third" water, entering the molecule $K_4Fe(CN)_6 \cdot 3H_2O$, whose position was not established in (^{2}) and to which, probably, the (p—p)-vectors lying in the Y plane correspond, the doublet disappears only at −20°. Therefore the potential barrier for reorientation of this molecule differs from the barriers for the first two molecules; as a consequence, the moment at −35° does not decrease by a factor of 4.

A considerable change in the second moment of the absorption line of ZHKS in the region of the Curie point is noteworthy. This indicates a further lowering of the potential barriers for the reorientation of water molecules at the Curie point, probably associated with a change in the symmetry of the crystal; as a result, the axes of reorientation do not have a fixed position in space.

space, as is indicated, in particular, by the smallness of the value of the second moment above the transition point.

Subsequently, the value of the second moment and the form of the absorption line change little up to a temperature of about +60°, where a narrow central peak appears, caused, apparently, by self-diffusion of the water molecules, which leads to a further decrease in the second moment.

At 130° the "wings" of the curve (see Fig. 2) disappear, and only the narrow peak remains.

It should be noted that in all spectra, from a temperature of −138° up to temperatures of about +100°, a central peak is observed whose intensity changes only slightly with temperature; the appearance of this peak is unusual for spectra of crystalline hydrates. It may be assumed that it is caused by the presence of a small number of hydrogen bonds of the type $O \cdots H - N$. The presence of such bonds leads to the appearance of protons remote from one another, which explains the appearance of the central peak.

Fig. 3. Absorption line of a ZHKS single crystal at a temperature of −183°.

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The magnetic field makes an angle of $\sim 45°$ with the [111] direction.
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Figure 3: Fig. 3. Absorption line of a ZHKS single crystal at a temperature of −183°. The magnetic field makes an angle of $\sim 45°$ with the [111] direction. $\Delta H_{\text{max}} = 21.6$ oersted.

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