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The NMR Analysis of the Water of Crystallization in Beryl

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The existence of two types of protons in beryl was proved by the proton magnetic resonance technique; one is as a molecular form of water in the channel of the crystal, while the other is as a hydroxyl-ion replacing O^{2-} ion of the crystal lattice. The proton-proton line of the water was found to be parallel to the c-axis of the crystal.

There are many minerals which contain an indefinite amount of the water of crystallization. Beryl, $Be_3Al_2Si_6O_{18}\cdot nH_2O$, is one of them; it usually contains about one to three weight per cent of water.

Some studies have been carried out concerning the water in beryl by thermogravimetric analysis (TGA), infrared spectroscopy, differential thermal analysis (DTA), and so on. According to Matsuda's finding,[1] two abrupt changes in the ignition loss of water were observed in TGA, and also two endothermic peaks in DTA.

Furthermore, after a detailed consideration using the ordinary methods mentioned above, Sugiura[2] proposed the presence of two types of water in cordierite and beryl - one, a molecular form in the tubular channel of the crystal, and the other, an OH^- ion form replacing the O^{2-} ion of the lattice point. In the present paper, the structure of water in beryl will be investigated by the broad-line NMR technique.

The crystal structure of beryl is shown in Fig. 1. Its crystal system is hexagonal, with a space group 6/m 2/m 2/m. A unit cell contains two molecules; the lattice parameters are $a=9.215$ Å and $c=9.17$ Å. As can be seen in the figure, there are holes about 4.5 Å in diameter, and they line up in a row along the c-axis, making tubular channels which serve to accomodate water molecules, occluded gases and alkali ions. The holes are 4.59 Å apart from each other. If a water molecule is placed in each of these holes, the n number in the chemical formula is equal to 1; if they are placed in every other hole, n is equal to 0.5.

Experimental

A single crystal of the prismatic form, which was obtained in Saga,* was cut into a size proper for being

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1) S. Matsuda, *J. Min. Soc. Japan* (*Kobutsugaku Zasshi*), **6**, 40, 53 (1963).

2) K. Sugiura, *Tokyo Kôgyô Daigaku Gakuho, Ser.-B*, **1**, 1 (1959).

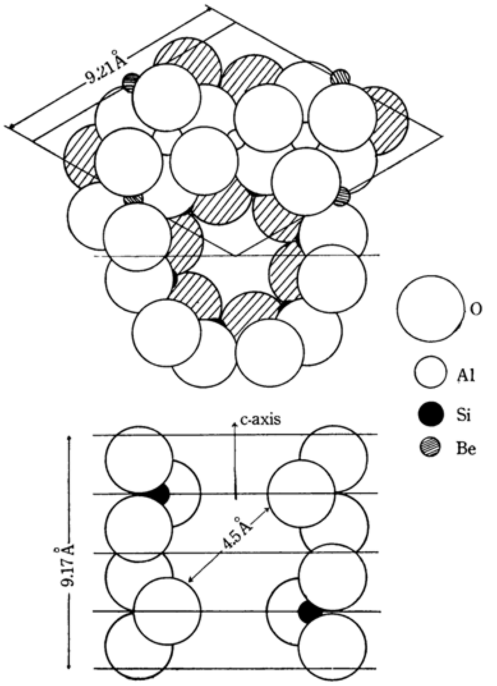

Fig. 1. The structure of beryl.

inserted into an rf coil. The water content of this sample is determined to be 3.05% by means of the ignition-loss method. A simple calculation shows that the *n* number in the chemical formula of this sample is nearly equal to 1.

The spectra were measured at 30 Mc and in the $-100\leftrightarrow+150$°C temperature range by using an NMR spectrometer, type JNM-W-30, manufactured by the Japan Electron Optics Laboratory Co., Ltd.

Results and Discussion**

First, the sample was placed in a probe with the c-axis perpendicular to the main magnetic field, H_0. The crystal was then rotated and measured at 15° intervals about the c-axis. The line shape of the spectrum did not change with this rotation. One of the spectra obtained is given in Fig. 3. Next, the crystal was placed with the c-axis parallel to H_0, and rotated about the g_1- or $[2\bar{1}\bar{1}0]$-axis, so as to change the angle, Φ, between the c-axis and the magnetic field H_0. The line shape varied with the angle Φ, as is shown in Fig. 5. Similar results within the range of experimental errors were obtained for rotations about five other axes, g_2, g_3, g_4, g_5, and g_6; these are shown in Fig. 6.

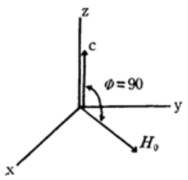

Fig. 2. The c-axis is fixed parallel to the z-axis, and the H_0 field rotates around the origin, O, with the Φ angle always kept 90°.

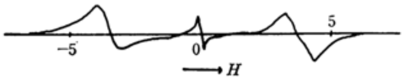

Fig. 3. One of the NMR spectra observed. The other spectra closely resemble this fugure.

As may be seen in Fig. 5, each observed spectrum is composed of three parts, one very narrow, and two broad. The two broad parts are always symmetrically shifted from the center of the narrow part.

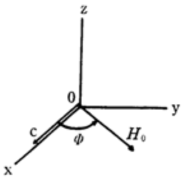

Fig. 4. The angle, Φ, between the c-axis and the H_0 field varies as H_0 rotates around the origin, O, in the xy plane.

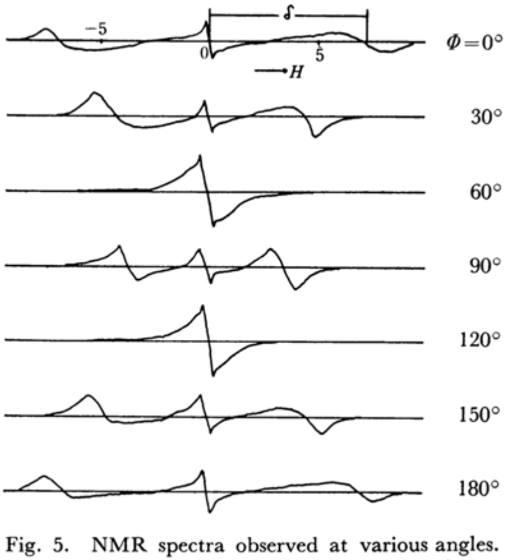

Fig. 5. NMR spectra observed at various angles. The spectra were measured at 15° intervals between 0° and 180°; however, only the spectra observed at 30° intervals are shown in this figure.

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* Sugiyama in Saga prefecture. The sample is hexagonal prismatic, about 1.5 cm. long, 0.7 cm. in diameter, and pale green in color.

** After we finished our work, the following paper has come to our attention: X. Parè and P. Ducros, Bull. Soc. Franç. Minér. Crist. (1964) LXXXVII, 429—433. While their results are in accordance with ours, they do not indicate the presence of two types of protons.

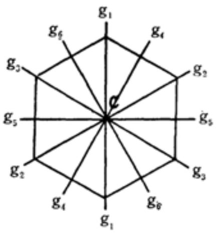

Fig. 6. The hexagon represents the (0001) plane of the single crystal of beryl, while the line perpendicular to this plane at point c is the six-fold axis of the crystal.

From the results obtained above, the protons which contribute to the observed NMR spectra may be classified into two types. The narrow component may be ascribed to either protons which are very easy to move, such as the water molecules in the liquid state, or to protons which are isolated from each other and which so have negligible dipolar interactions.

The former possibility can be eliminated for two reasons: i) The water molecule in beryl can not be removed easily by heating it up to several hundred degrees, and therefore, it cannot be in a liquid state; ii) we could not find any fluid inclusion in our sample under a microscope.

Therefore, we may assume that the narrow part of the spectrum is due to the protons of the OH$^-$ ions which occupy the position of the O^{2-} ions in the crystal. This conclusion coincides with the results obtained by the IR and other methods by Sugiura.

The remaining two broad parts may be interpreted in terms of the dipolar interactions between two protons belonging to the same water molecule. This means assuming a two-spins system. The magnetic field provided by one of the two water protons is given by[3]:

$$H = H_0 \pm \alpha(3\cos^2\theta - 1), \quad \alpha = \frac{3}{4}\frac{\gamma\hbar}{r^3}$$

where θ is the angle between the line connecting the two protons and the H_0 field; γ, the proton gyromagnetic ratio; $\hbar$, Planck's constant divided by 2π, and r, the distance between two interacting protons in a water molecule.

In Fig. 7, the open circles are the observed shifts, δ, of the broad part from the center of the narrow part, while the solid lines represent the plots of the function, $\pm\alpha(3\cos^2\theta - 1)$, fitted to the experimental value at $\Phi = 90°$. The agreement between the two plots is fairly good.

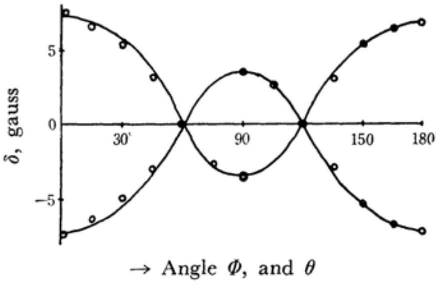

Fig. 7. The solid lines are the calculated lines of the functions, $\pm\alpha(3\cos^2\theta - 1)$, while the open circles are the observed values of δ.

From these results, it can be concluded that the angle, θ, between the proton-proton line and the H_0 field indicates the angle, Φ, between the c-axis and the H_0 field; that is, the proton-proton line of a water molecule is parallel to the c-axis of the crystal. (The position of the oxygen atom of the water molecule has not been determined by the present experiment).

Measurements of the temperature dependence of the line shapes were taken in the $-100 \leftrightarrow +150$°C range. In this experiment, the crystal was placed in the probe with the c-axis perpendicular to the H_0 field. The separation, 2δ, of the two broad parts varied slightly with the temperature, as is shown in Fig. 8. The explanation of this temperature dependence will be the subject of a future study.

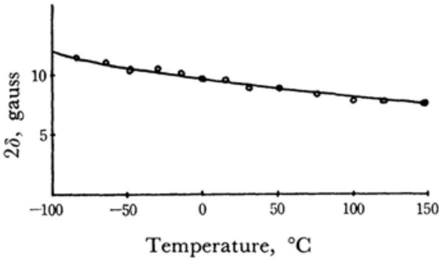

Fig. 8. Temperature dependence of the separation 2δ between the two broad parts.

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[3] G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).