Acta Cryst. (1972). B**28**, 326

The positions of the hydrogen atoms in datolite as determined by nuclear magnetic resonance.

By Y. Sugitani, M. Watanabe and K. Nagashima. *Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Ohtsuka, Tokyo, Japan*

(*Received* 29 *September* 1969 *and in revised form* 8 *September* 1971)

The positions of the hydrogen atoms and the oxygen–hydrogen distances in datolite, $CaBSiO_4(OH)$, were determined by proton magnetic resonance using a natural single crystal. The result was in reasonable agreement with the hydrogen positions suggested from X-ray analysis and a measurement of infrared pleochroism of the OH stretching-frequencies.

The crystal structure of datolite, $CaBSiO_4(OH)$, was determined by Ito & Mori (1953) and Pavlov & Belov (1960), and was refined by Pant & Cruickshank (1967). Sahl (1966) suggested the probable position of the hydrogen atoms on the basis of the infrared pleochroism of the OH stretching-frequencies in datolite. The present study has been made to determine the position of hydrogen atoms by proton magnetic resonance by referring to Pant & Cruickshank's result.

The space group of datolite is $P2_1/c$ with the cell dimensions $a = 4{\cdot}84 \pm 0{\cdot}005$, $b = 7{\cdot}60 \pm 0{\cdot}01$, $c = 9{\cdot}62 \pm 0{\cdot}01$ Å and $\beta = 90°9'$. There are four formula units in the cell. Hydrogen atoms are bound to the hydroxyl oxygen atoms O(1), O(2), O(3), and O(4) in Fig. 1 which shows the crystal structure projected along [100] according to Pant & Cruickshank's result.

A single crystal of natural datolite having the *bc*, *ca*, and *ab* faces was used for the measurements. The crystal was fixed to a Teflon rod of 15 cm in length which was set on a goniometer head. The crystal orientation was adjusted to the desired directions within ± 1°. The proton magnetic resonance spectra were recorded at room temperature at 15° intervals of rotation about the a^*, b^*, and c^* axes from 0 to 180°, using a JEOLCO JNM-W-30 spectrometer operated at 30 MHz. The absorption lines observed in a^* and c^* axis rotations are all single and nearly Gaussian in shape, while those in b^* axis rotation split into a broad doublet.

The theoretical values of the second moments were calculated on the basis of van Vleck's equation taking account of proton–proton and proton–boron interactions (Abragam, 1961). Boron has two isotopes ^{11}B and ^{10}B with natural abundance 80·4 and 19·6% respectively (Newton, Tyrrell & Sanders, 1959). The second moment for the proton–boron interactions was estimated by assuming a weighted average of the contributions from these isotopes.

The second moments were calculated for an arrangement of hydrogen atoms located on a sphere of radius 0·97 Å around the oxygen atom of the hydroxyl ion. If the space group is $P2_1/c$ including the hydrogen atoms, the latter occupy the fourfold general positions. The cut-off radius in the calculations was taken to be 4·7 Å. The contributions from spins beyond this radius were found to be negligible. Thus, the position of the hydrogen atoms was first determined such that the calculated angular dependence of the second moment fitted the observed value for rotation of the crystal about the c^* and a^* axes.

The same fitting was then repeated for rotations about the two axes, with the O–H distance as the new parameter. Fig. 2 shows the comparison between the calculated and observed angular dependences, where the calculated curves are those corresponding to the best fit which was obtained from more than forty possible arrangements. The fractional coordinates of the hydrogen atom and the O–H distance thus determined were given as $x = 0{\cdot}829 \pm 0{\cdot}003$, $y = 0{\cdot}552 \pm 0{\cdot}006$, $z = 0{\cdot}584 \pm 0{\cdot}015$ for H(1), and $0{\cdot}970 \pm 0{\cdot}001$ Å for O(1)–H(1). The starting value of O(1)–H(1) was 0·97 Å, which was assumed on the basis of X-ray results (Zachariasen, 1954: Zachariasen & Plettinger, 1963). However, the final value of this distance did not differ substantially from the initial one.

Sahl (1966) showed from the measurement of the infrared pleochroism of the OH stretching-frequency ($\lambda = 2{\cdot}85\mu$), that the O(2)–H(2) dipole makes an angle of about 30–35° with the *c* axis, with the angle B(2)–O(2)–H(2), about 106°. These angles agree with the corresponding values of 31·5 ± 1°, and 116 ± 4° obtained from our n.m.r. results.

The positions of hydrogen atoms shown in Fig. 1 are reasonable from an electrostatic point of view. H(1) interacts attractively with O(5) and O(6), while it interacts repulsively with Ca(1), Ca(2), B(1) and H(2). These positions are also reasonable in view of the law of electroneutrality.

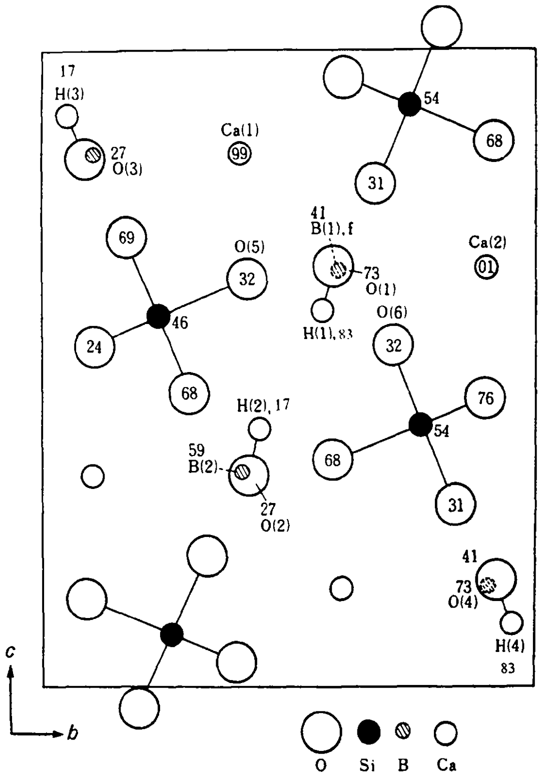

Fig. 1. Projection of the structure along [100] axis. The hydrogen positions determined here are drawn in the projection.

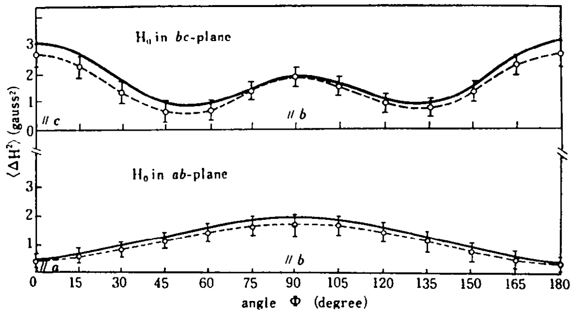

Fig. 2. The angular dependences of the second moment as a function of angle Φ between H_0 and the *a* axis (for H_0 in *ab* plane), and between H_0 and the *c* axis (for H_0 in *bc* plane). The solid and dotted curves correspond to theoretical and experimental results respectively.

The authors wish to thank Professor S. Fujiwara for his support in this work and Professor T. Sudo for his helpful information about the sample used.

References

Abragam, A. (1961). *The Principles of Nuclear Magnetism*, Chap. 4. Oxford: Clarendon Press.
Ito, T. & Mori, H. (1953). *Acta Cryst.* **6**, 24.
Newton, D. C., Tyrrell, A. C. & Sanders, J. (1959). *Nature, Lond.* **184**, 185.
Pant, A. K. & Cruickshank, D. W. J. (1967). *Z. Kristallogr.* **125**, 286.
Pavlov, P. V. & Belov, N. V. (1960). *Sov. Phys. Crystallogr.* **4**, 300.
Sahl, K. (1966). *Neues Jb. Miner. Mh.* p. 45.
Zachariasen, W. H. (1954). *Acta Cryst.* **7**, 305.
Zachariasen, W. H. & Plettinger, H. A. (1963). *Acta Cryst.* **16**, 376.

Acta Cryst. (1972). B**28**, 327.

Die Kristallstrukturen des $LiCu_2P_2$ und des $Li_{1.75}Cu_{1.25}P_2$.

Von H. Schlenger und H. Jacobs, *Institut für Anorganische Chemie der Universität, Kiel, Deutschland (BRD)*

(*Eingegangen am* 25. *Mai* 1971)

The lattice parameters, space groups and the atomic positions for the crystal structures of $LiCu_2P_2$ and $Li_{1.75}Cu_{1.25}P_2$ are given.

Das ternäre System Li–Cu–P ist von uns phasenanalytisch untersucht worden.

Über die Ergebnisse dieser Untersuchungen werden wir demnächst berichten (Schlenger, Jacobs & Juza, 1971). Hier sollen die Kristallstrukturdaten zweier mit Hilfe von Einkristallen bestimmter Strukturen mitgeteilt werden. Es sind dies die des $LiCu_2P_2$ und des $Li_{1.75}Cu_{1.25}P_2$.

$LiCu_2P_2$ kristallisiert tetragonal mit:

$$a=3{,}887,\ c=9{,}55\ \text{Å und } c/a=2{,}46$$

und zwei Formeleinheiten in der Elementarzelle ($d_4^{25}=4{,}52$ und $Z=2{,}03$). Die Strukturbestimmung führte zum $D1_3$-Typ. Die Raumgruppe ist $I4/mmm$–D_{4h}^{17}. Mit Hilfe der 53 symmetrieunabhängigen, aus integrierten Weissenberg-Aufnahmen (Mehrfilmtechnik) photometrierten Intensitäten (Drehung um [100]) ergab sich folgende Verteilung der Atome:

4 Cu	in 4(*d*)	0	$\frac{1}{2}$	$\frac{1}{4}$
4 P	in 4(*e*)	0	0	z, $z=0{,}388$
2 Li	in 2(*a*)	0	0	0

mit einem R_F-Wert von 13,4%. Die Struktur enthält P_2-Gruppen längs [001].

Das lithiumreichere $Li_{1.75}Cu_{1.25}P_2$ wurde ebenfalls mit Einkristallmethoden untersucht. Es kristallisiert orthorhombisch mit:

$$a=3{,}874,\ b=12{,}67 \text{ und } c=8{,}74\ \text{Å},$$

mit sechs Formeleinheiten in der Elementarzelle ($d_4^{25}=3{,}62$ und $Z=5{,}98$). Die Raumgruppe ist $Immm$–D_{2h}^{25}. Die Reflexintensitäten von 220 Reflexen ergaben sich ebenfalls aus photometrierten Weissenberg-Aufnahmen (Mehrfilmtechnik) um [100] und [001]. (In beiden Fällen wurde auf die Anwendung von Absorptions- und Temperaturfaktoren bei der Verfeinerung verzichtet.)

Die Anordnung der Atome in der Elementarzelle ist folgende:

7,5 Cu	in 8(*l*)	0	0,172	0,267
8 P(1)	in 8(*l*)	0	0,352	0,377
4 P(2)	in 4(*h*)	0	0,085	0,5
2 Li(1)	in 2(*a*)	0	0	0
4 Li(2)	in 4(*g*)	0	0,27	0
4 Li(3)	in 4(*j*)	0,5	0	0,33

Die Strukturrechnung konnte bis zu einem R_F-Wert von 11,5% angenähert werden. Auch in dem $Li_{1.75}Cu_{1.25}P_2$ liegen P_2-Gruppen vor, jedoch in zwei Richtungen [001] und [010].

Beide Verbindungen sind demnach als ternäre Polyphosphide anzusehen; sie weichen in dieser Hinsicht von den anderen im System Li–Cu–P untersuchten Phasen ab.

Der Deutschen Forschungsgemeinschaft danken wir für die Unterstützung dieser Arbeit.

Literatur

Schlenger, H., Jacobs, H. & Juza, R. (1971). *Z. anorg. allgem. Chem.* Im Druck.