Busing, W. R., Smith, H. G., Peterson, S. W. & Levy, H. A. (1964). *J. Phys. (Paris) Colloq.* **25**, 495–496.
Chidambaram, R. (1962). *J. Chem. Phys.* **36**, 2361–2365.
Chidambaram, R., Sequeira, A. & Sikka, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.
Datt, I. D. & Ozerov, R. P. (1972). *Sov. Phys.-Crystallogr.* **17**, 383–401.
Hamilton, W. C. & Ibers, J. A. (1968). In *Hydrogen Bonding in Solids*. New York: Benjamin.
Jensen, A. T. (1940). *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **17**(9), 1–17.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
Kleinberg, R. (1969). *J. Chem. Phys.* **50**, 4690–4696.
Mizuno, J. (1960). *J. Phys. Soc. Jpn*, **15**, 1412–1420.
Mizuno, J. (1961). *J. Phys. Soc. Jpn*, **16**, 1574–1580.
Padmanabhan, V. M., Busing, W. R. & Levy, H. A. (1978). *Acta Cryst.* B**34**, 2290–2292.
Pauling, L. (1969). *The Nature of the Chemical Bond*, 3rd ed., pp. 514–518. Ithaca: Cornell Univ. Press.
Shchukarev, S. A., Stroganov, E. V., Andreev, S. N. & Purvinskii, O. F. (1963). *Zh. Strukt. Khim.* **4**, 56–58.
Shull, C. G. (1972). Personal communication. The values were measured by L. Koester.
Sorrell, C. A. & Ramey, R. R. (1974). *J. Chem. Eng. Data*, **19**(1), 31–32.
Wehe, D. J., Busing, W. R. & Levy, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1985). C**41**, 10–13

Electron-Density Distribution in Crystals of Lithium Nitrite Hydrate, $LiNO_2.H_2O$, at 120 K

By S. Ohba, T. Kikkawa and Y. Saito

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, *Kohoku-ku, Yokohama* 223, *Japan*

(*Received* 11 *May* 1984; *accepted* 25 *September* 1984)

Abstract. $M_r = 70{\cdot}96$, monoclinic, $P2_1/c$, $a = 3{\cdot}306\,(1)$, $b = 14{\cdot}242\,(1)$, $c = 6{\cdot}396\,(1)$ Å, $\beta = 106{\cdot}14\,(1)^\circ$, $V = 289{\cdot}3\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}63$ Mg m^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å, $\mu = 0{\cdot}157$ mm^{-1}, $F(000) = 144$, $T = 120\,(1)$ K, final $R = 0{\cdot}028$ for 1512 observed unique reflections. The lone-pair electron of the nitrite O atom was observed as separate peaks of 0·28 (4) e Å^{-3} on the difference synthesis at 110–115° to the N—O bond axis and 0·50–0·55 Å from the O nucleus, suggesting sp^2 hybridization. N—O bonding and N lone-pair electrons were also observed as peaks of 0·25 (4) and 0·47 (4) e Å^{-3}, respectively.

Introduction. Charge distribution in $[Co(NO_2)_6]^{3-}$ has been studied experimentally (Ohba, Toriumi, Sato & Saito, 1978) as well as theoretically by an *ab initio* MO method (Ohba, Kitaura, Morokuma & Saito, 1979). The theoretical deformation density showed sp^2 hybridization of the O atoms, whereas the experimental density suggested *sp* hybridization. To resolve the disagreement, the electron-density distribution of an NO_2^- ion not coordinated to a metal atom has been studied. An attempt with $AgNO_2$ was unsuccessful because of the large anisotropic thermal vibrations of NO_2^- (Ohba & Saito, 1981). Crystal structures of alkaline and alkaline-earth nitrites have not been reported except for $NaNO_2$ (Kay & Frazer, 1961), KNO_2 (Solbakk & Strømme, 1969) and $Ba(NO_2)_2.H_2O$ (Abrahams, Bernstein & Liminga, 1980). Charge distribution in ferroelectric crystals of $NaNO_2$ has been investigated by Iwata, Koyano & Shibuya (1979) and Ito (1984). However, $NaNO_2$ has a non-centrosymmetric structure and hence includes phase approximations (Ito & Shibuya, 1977). For its advantage in valence/core electron ratio (Stevens & Coppens, 1976), Li was selected as a counter ion. We determined the structure of $LiNO_2.H_2O$, which is centrosymmetric, and obtained the deformation density at 300 (1) K. Quite independently, almost the same results on $LiNO_2.H_2O$ at 295 K were reported by Hermansson & Thomas (1983). However, the resolution of the deformation density was not sufficient to discuss the hybridization of the nitrite O atoms; therefore a redetermination was carried out at 120 K.

Experimental. Crystals of $LiNO_2.H_2O$ grown from filtrate of mixture of LiCl and $AgNO_2$ aqueous solution by slow evaporation under sulfuric acid in a desiccator. Hygroscopic, nearly spherical crystal of 0·5 mm diameter sealed in glass capillary with dry N_2 gas. Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. There is a possibility that the crystal is twinned, where the twinned cells are related by a mirror plane perpendicular to **a** (Hermansson & Thomas, 1983) and they cannot be

0108-2701/85/010010-04$01.50

distinguished from single crystals because $a \simeq -2c\cos\beta$ at room temperature [$a = 3{\cdot}338$ (2), $b = 14{\cdot}295$ (1), $c = 6{\cdot}396$ (1) Å, $\beta = 105{\cdot}11$ (3)° at 300 (1) K]. Cell parameters are not changed by axis transformation, $a' = a$, $b' = -b$ and $\mathbf{c}' = -\mathbf{a}-\mathbf{c}$. Specimen confirmed to be a single crystal by observing systematic absences $h0l$, l odd (see Table 1). Crystal, cooled by blowing cold N_2 gas evaporated from liquid N_2, did not show phase transition. Collimator 1·0 mm ∅, detector aperture 1·55 × 1·55°, θ–2θ scan, scan speed 6° min^{-1} in θ, scan width $(1{\cdot}3 + 0{\cdot}5\tan\theta)°$, no repetition. Other details of intensity measurement have been reported previously (Ohba & Saito, 1984). Mean ratio of structure factors of five standard reflections $0{\cdot}977 < \sum(|F_o|/|F_o|_{\rm initial})/5 < 1{\cdot}002$. Cell parameters refined by least squares of 20 2θ values ($60 < 2\theta < 77°$). 3809 reflections measured ($2\theta \le 80°$, h 0–6, k −25–25, l −11–11; $80 < 2\theta \le 120°$, h 0–8, k 0–34, l −15–15), 48 unobserved [$|F_o| \le 3\sigma(|F_o|)$], 427 zero, 3334 observed reflections. Variation of $|F(110)|$ with azimuthal angles around scattering vector 4%. After averaging equivalent reflections 1512 unique hkl obtained with $R_{\rm int} = 0{\cdot}010$. Corrections for Lorentz–polarization but not for absorption, $\mu r = 0{\cdot}04$, absorption correction factor 1·037 for all reflections. Atomic parameters and a scale factor refined with full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). Atomic coordinates at 300 (1) K (determined previously) utilized as initial parameters. $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = [\sigma_F(\text{count})]^2 + (0{\cdot}020|F_o|)^2$. After conventional refinement, positional and thermal parameters of non-H atoms determined based on high-order reflections with $\sin\theta/\lambda \ge 0{\cdot}6$ Å^{-1}. Then H parameters and a scale factor refined based on all unique reflections. Isotropic secondary extinction correction parameter (Zachariasen, 1967) did not reduce R significantly so was not introduced. Final $R = 0{\cdot}028$, $wR = 0{\cdot}045$, $S = 1{\cdot}74$.* $R(F^2)$ and $wR(F^2)$ of 0·056 and 0·084 are a little larger than those of Hermansson & Thomas (1983) for 1375 room-temperature data. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). $\Delta/\sigma < 0{\cdot}3$. Parameter/reflection ratio 74/1512. Atomic parameters are given in Table 2. Thermal parameters of non-H atoms decreased to 45% on average by lowering temperature from 300 to 120 K. However, anisotropy in thermal vibrations did not change drastically (see Table 3).

Discussion. The difference synthesis on the NO_2 plane showed bilateral symmetry (see Fig. 1*a*). An averaged difference synthesis assuming mirror symmetry is also presented (Fig. 1*b*) (Toriumi & Saito, 1978). Around the O atom there are positive peaks of 0·28 (4) e Å^{-3} at 0·50–0·55 Å from the O nucleus making angles of 110–115° with the N—O bond axis. It suggests that the hybridization of the O atom is sp^2 in agreement with the theoretical expectation by the CNDO/2 method (see Fig. 3*b* of Ohba, Toriumi, Sato & Saito, 1978). The

Table 1. *Systematic absences for* $LiNO_2.H_2O$ *single and twinned crystals*

	Single crystal (*a,b,c* setting)	Single crystal (*a,−b,−a−c* setting)	Twinned crystal
$h0l$	l odd	$h + l$ odd	h odd and l odd
$00l$	l odd	l odd	l odd
$h00$	None	h odd	None
$0k0$	k odd	k odd	k odd

Table 2. *Positional parameters* (×10^5; *for* Li ×10^4; *for* H ×10^3) *and equivalent isotropic temperature factors* (*Hamilton,* 1959)

	x	y	z	$B/B_{\rm eq}$(Å^2 ×10)
Li	3644 (3)	8331 (1)	6322 (1)	11 (1)
N	76250 (9)	36015 (2)	27788 (4)	9 (1)
O(1)	63500 (9)	28263 (2)	18843 (4)	10 (1)
O(2)	80494 (9)	42271 (2)	14812 (4)	10 (1)
O*w*	7219 (8)	39172 (2)	73843 (4)	9 (1)
H(1)	77 (4)	451 (1)	760 (2)	25 (2)
H(2)	−17 (4)	384 (1)	601 (2)	16 (2)

Table 3. *Root-mean-square displacements* (Å)

$u_{\rm max}$ and $u_{\rm min}$ are maximum and minimum vibrational displacements.

	120 K			300 K		
	$u_{\rm max}$	$u_{\rm min}$	$u_{\rm max}/u_{\rm min}$	$u_{\rm max}$	$u_{\rm min}$	$u_{\rm max}/u_{\rm min}$
Li	0·128 (2)	0·108 (2)	1·19 (2)	0·191 (2)	0·149 (2)	1·28 (2)
N	0·115 (1)	0·095 (1)	1·21 (1)	0·177 (1)	0·142 (1)	1·25 (1)
O(1)	0·134 (1)	0·090 (1)	1·49 (1)	0·212 (1)	0·143 (1)	1·48 (1)
O(2)	0·137 (1)	0·093 (1)	1·47 (1)	0·208 (1)	0·139 (1)	1·50 (1)
O*w*	0·121 (1)	0·091 (1)	1·33 (1)	0·188 (1)	0·133 (1)	1·41 (1)

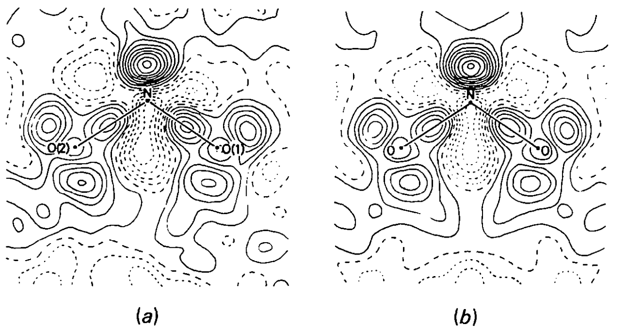

Fig. 1. Section of (*a*) the difference synthesis through the NO_2 plane and (*b*) the difference synthesis averaged assuming mirror symmetry. Contours are drawn at intervals of 0·05 e Å^{-3}. Negative contours are dotted, zero contours chain-dotted.

---

* List of structure factors, anisotropic thermal parameters and a difference synthesis on the plane containing the N—O(2) axis and perpendicular to the NO_2 plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39768 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Interatomic distances* (Å) *and angles* (°)

N—O(1)	1·2609 (4)	O(2)—N···H(2^{ii})	118·9 (3)
N—O(2)	1·2518 (4)	N···H(2^{ii})—O_w^{ii}	177·5 (12)
O(1)—N—O(2)	114·04 (3)	O(2)···H(1^{i})—O_w^{i}	168·1 (13)
O*w*—H(1)	0·855 (14)	O*w*···Li^{iv}	2·0320 (12)
O*w*—H(2)	0·853 (12)	O*w*···Li^{v}	1·9985 (11)
H(1)—O*w*—H(2)	106·2 (13)	H(1)—O*w*···Li^{iv}	108·9 (10)
N—O(1)···Li^{i}	120·82 (4)	H(1)—O*w*···Li^{v}	111·9 (10)
N—O(1)···Li^{iii}	92·90 (3)	H(2)—O*w*···Li^{iv}	106·6 (8)
N—O(2)···Li^{iii}	94·55 (3)	H(2)—O*w*···Li^{v}	112·8 (8)
N—O(2)···H(1^{i})	121·4 (4)	Li^{iv}···O*w*···Li^{v}	110·21 (4)
O(1)—N···H(2^{ii})	126·3 (3)		

Symmetry code:
(i) $1-x, 1-y, 1-z$
(ii) $1+x, y, z$
(iii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(iv) $-x, -\frac{1}{2}+y, \frac{3}{2}-z$
(v) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$

neighboring atoms within 2·5 Å of an NO_2^- ion approximately lie on the NO_2 plane, as shown in Fig. 2, and their arrangement is nearly symmetric. An *ab initio* study of the binding of H_2O to the nitrite ion in the gas phase showed a favorable electrostatic interaction with the coplanar arrangements of the two molecules (Pullman & Berthod, 1981). The preferred orientation of the metal cation to the nitrite ion is also expected to coincide with the direction of the lone-pair electrons. Interatomic distances and angles are listed in Table 4. The angle N—O(1)···Li^+ $(1-x,\ 1-y,\ 1-z)$ is 120·82 (4)°. In the crystals of $Sr(NO_2)_2.H_2O$, the angles N—O···Sr^{2+} are in the range 121·6 (4) to 136·8 (4)°, where the Sr^{2+} ion lies approximately on the NO_2 plane (Kikkawa, Ohba & Saito, 1984). These structural data also indicate sp^2 hydridization of the O atom. The bonding electron peak appears on the N—O axis at 0·7 Å from the N nucleus and not elongated perpendicularly to the NO_2 plane, as shown in Fig. 3, in contrast to the slightly elongated N—O bonding peak and a pair of positive peaks, which appeared above and below the N—O axis of $K_2Na[Co(NO_2)_6]$ (Ohba *et al.*, 1978). Further investigations on the transition-metal complexes should be made to conclude whether the difference is due to electron redistribution by coordination or by thermal smearing of the charge distribution. The lone-pair peak of the N atom is observed at 0·55 Å from the N nucleus, 0·47 (4) e $Å^{-3}$ in height. In Fig. 3 two negative peaks of −0·32 (4) e $Å^{-3}$ appear above and below the N atom, suggesting electron deficiency in the *p* orbital perpendicular to the molecular plane. The error in the deformation density at a general position estimated from $\sigma(|F_o|)$ and the e.s.d. of the scale factor was 0·04 e $Å^{-3}$. The error near the N and O nucleus within 0·15 Å is 0·05 e $Å^{-3}$.

A projection of the crystal structure is shown in Fig. 4. The Li atom is surrounded by two hydrate O atoms and three nitrite O atoms at distances 1·9985 (11) to 2·1736 (9) Å. The two O*w*···Li contacts are directed from the O*w* nucleus to the two unoccupied tetrahedral sites around it, the remaining two of which are occupied by the H atoms (see Table 4). Fig. 5 shows sections of

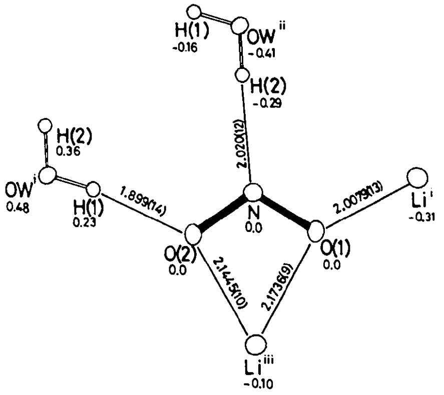

Fig. 2. Molecular arrangement around the NO_2^- ion. The number below the atom numbering indicates the deviation of the atom from the NO_2 plane (Å).

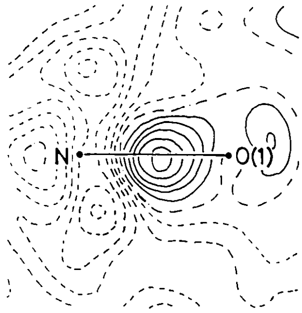

Fig. 3. Section of the difference synthesis through the N—O(1) bond axis and perpendicular to the NO_2 plane.

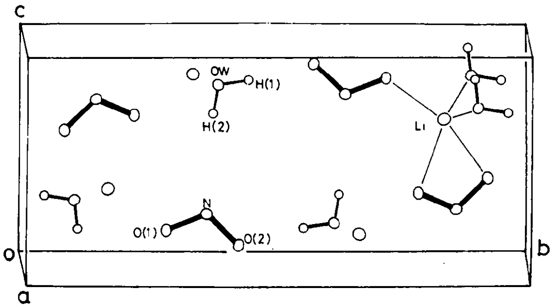

Fig. 4. A projection of the crystal structure.

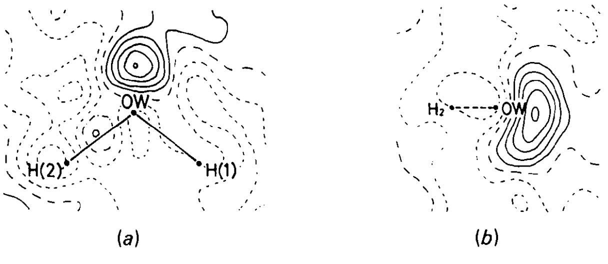

Fig. 5. Section of the difference synthesis (*a*) through the H_2O plane and (*b*) through the O*w* atom and perpendicular to the H_2O plane.

the difference synthesis in the H_2O plane and perpendicular to it. The lone pair of the H_2O oxygen atom is found as a peak of 0·25 (4) e $Å^{-3}$ at 0·4 Å from the O nucleus and almost on the bisector of the $Li^+\cdots Ow\cdots Li^+$ angle, in contrast to the room-temperature experiment (Fig. 3*b* of Hermansson & Thomas, 1983) where the lone-pair peak is significantly off the bisector.

The charge distribution of the nitrate ion has also been investigated: uronium nitrate (Harkema, 1971), $NaNO_3$ (Göttlicher & Knöchel, 1980), thiotrithiazyl nitrate (Moss, Guru Row & Coppens, 1980) and $LiNO_3.3H_2O$ (Hermansson, Thomas & Olovsson, 1984). Hermansson *et al.* (1984) showed the sp^2 hybridization of the nitrate O atom clearly. The formate ion has also been studied: $LiHCOO.H_2O$ (Thomas, Tellgren & Almlöf, 1975) and $KH(HCOO)_2$ (Hermansson & Tellgren, 1983). It seems that the terminal O atoms of these planar anions, NO_2^-, NO_3^- and HCO_2^-, take sp^2 hybridization.

References

Abrahams, S. C., Bernstein, J. L. & Liminga, R. (1980). *J. Chem. Phys.* **72**(11), 5837–5862.

Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.

Göttlicher, S. & Knöchel, C. D. (1980). *Acta Cryst.* B**36**, 1271–1277.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Harkema, S. (1971). Thesis. Twente Univ. of Technology, Enschede, The Netherlands.

Hermansson, K. & Tellgren, R. (1983). *Acta Cryst.* C**39**, 1507–1510.

Hermansson, K. & Thomas, J. O. (1983). *Acta Cryst.* C**39**, 930–936.

Hermansson, K., Thomas, J. O. & Olovsson, I. (1984). *Acta Cryst.* C**40**, 335–340.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Ito, T. (1984). Private communication.

Ito, T. & Shibuya, I. (1977). *Acta Cryst.* A**33**, 71–74.

Iwata, Y., Koyano, N. & Shibuya, I. (1979). *Annu. Rep. Res. React. Inst. Kyoto Univ.* **12**, 161–165.

Kay, M. I. & Frazer, B. C. (1961). *Acta Cryst.* **14**, 56–57.

Kikkawa, T., Ohba, S. & Saito, Y. (1984). In preparation.

Moss, G., Guru Row, T. N. & Coppens, P. (1980). *Inorg. Chem.* **19**, 2396–2403.

Ohba, S., Kitaura, K., Morokuma, K. & Saito, Y. (1979). *Annu. Rev. Inst. Mol. Sci. Okazaki*, pp. 21–22.

Ohba, S. & Saito, Y. (1981). *Acta Cryst.* B**37**, 1911–1913.

Ohba, S. & Saito, Y. (1984). *Acta Cryst.* C**40**, 1639–1641.

Ohba, S., Toriumi, K., Sato, S. & Saito, Y. (1978). *Acta Cryst.* B**34**, 3535–3542.

Pullman, A. & Berthod, H. (1981). *Chem. Phys. Lett.* **81**, 195–200.

Solbakk, J. K. & Strømme, K. O. (1969). *Acta Chem. Scand.* **23**, 300–313.

Stevens, E. D. & Coppens, P. (1976). *Acta Cryst.* A**32**, 915–917.

Thomas, J. O., Tellgren, R. & Almlöf, J. (1975). *Acta Cryst.* B**31**, 1946–1955.

Toriumi, K. & Saito, Y. (1978). *Acta Cryst.* B**34**, 3149–3156.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1985). C**41**, 13–15

Structure of Homilite, $Ca_{2.00}(Fe_{0.90}Mn_{0.03})B_{2.00}Si_{2.00}O_{9.86}(OH)_{0.14}$

By R. Miyawaki, I. Nakai and K. Nagashima

Department of Chemistry, The University of Tsukuba, Ibaraki 305, *Japan*

(*Received* 27 *July* 1984; *accepted* 24 *September* 1984)

Abstract. $M_r = 370{\cdot}0$, monoclinic, $P2_1/a$, $a = 9{\cdot}786\ (2)$, $b = 7{\cdot}621\ (2)$, $c = 4{\cdot}776\ (1)$ Å, $\beta = 90{\cdot}61\ (2)°$, $V = 356{\cdot}2\ (1)$ $Å^3$, $Z = 2$, $D_x = 3{\cdot}451$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 37{\cdot}7$ cm^{-1}, $F(000) = 364{\cdot}58$, room temperature, final $R = 0{\cdot}033$ for 1596 observed reflections. The crystal structure consists of sheets built up from alternating SiO_4 and BO_4 tetrahedra, parallel to (001). The calcium and iron atoms are located between the sheets and form a CaO_8 tetragonal antiprism and an FeO_6 octahedron respectively.

Introduction. Homilite was first described by Paikjull (1876), and later Tennyson (1978) determined the lattice parameters. It has been known that homilite has close structural relationships with gadolinite, $RE_2FeBe_2Si_2O_{10}$, (RE = rare earth), datolite, $CaBSiO_4(OH)$, *etc.* However, the structure analysis of homilite, which enables us to compare the structures of these minerals, has not yet been accomplished. The authors, therefore, have investigated its crystal structure. The homilite specimen used in the present study is from Stokö near Brevig, Langesundfjord, Norway.

Experimental. The electron microprobe analysis of the specimen gave SiO_2, 31·58; FeO, 17·03; MnO, 0·50; CaO, 29·43 wt %, and revealed the presence of trace amounts of rare-earth elements: Y, La, Ce, Pr, Nd and Dy. The ion microprobe mass analyzer indicated that boron is present in major amounts, while

0108-2701/85/010013-03$01.50