and R. von Hodenberg (Hannover, Germany). The authors are grateful for the use of these crystals. We are indebted to G. Hoppmann and U. Bismayer for technical assistance. The DFG has supported the Raman work. The infrared spectra were made with the instruments of the Chemical Institutes in Hannover.

References

Baran, E. J., Botto, I. L. & Aymonino, P. J. (1976). *Z. anorg. allgem. Chem.* **423**, 280–288.

Born, M. & Huang, K. (1954). *Dynamical Theory of Crystal Lattices*. Oxford: Clarendon Press.

Brixner, L. H., Bierstedt, P. E., Jaep, W. F. & Barkley, J. R. (1973). *Mater. Res. Bull.* **8**, 497–504.

Cao-Xuan, M. M., Hauret, G. & Chapelle, J. P. (1975). *C. R. Acad. Sci. Paris, sér. B*, **280**, 543–546.

Ewald, P. P. (1921). *Ann. Phys.* **64**, 253–287.

Gene, V. V., Dudnik, E. F. & Sinyakov, E. V. (1974). *Fiz. Tverd. Tela*, **16**, 3530–3532.

Hodenberg, R. von, Salje, E., Recker, K., Walraffen, F. & Eckstein, J. (1977). To be published.

Isupov, V. A., Krainik, N. N. & Kosenko, E. L. (1973). *Isv. Akad. Nauk. SSSR, Neorg. Mater.* **9**, 154–155.

Keppler, U. (1970). *Z. Kristallogr.* **132**, 228–235.

Ng, H. N. & Calvo, C. (1975). *Canad. J. Phys.* **53**, 42–51.

Salje, E. (1974). *Z. Kristallogr.* **139**, 317–334.

Salje, E. & Hoppmann, G. (1976). *Mat. Res. Bull.* **11**, 1545–1550.

Salje, E. & Viswanathan, K. (1975). *Acta Cryst.* A**31**, 356–359.

Shiro, Y. & Miyazawa, T. (1971). *Bull. Chem. Soc. Japan*, **44**, 2371–2378.

Tørres, J. (1975). *Phys. Stat. Sol.* **b71**, 141–150.

Tørres, J., Aubree, J. & Brandon, J. (1974). *Opt. Commun.* **12**, 416–417.

Acta Cryst. (1977). A**33**, 408–411

Long-Period Superstructure in Sodium–Lithium Metasilicates

By A. R. West

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Aberdeen AB9 2UE, Scotland

(*Received* 14 *October* 1976; *accepted* 26 *November* 1976)

The solid-solution series, high-$(Na_{2-x},Li_x)SiO_3$, $0{\cdot}86 \lesssim x \lesssim 1{\cdot}02$, has an orthorhombic subcell similar to the unit cells of Na_2SiO_3 and Li_2SiO_3 but with a one-dimensional long-period superstructure. The ratio $\kappa = a_{\text{supercell}} : a_{\text{subcell}}$ varies linearly with composition and integral κ values occur at simple Na:Li ratios: $\kappa = 6$ for 1Na:1Li ($x = 1{\cdot}00$) and $\kappa = 5$ for 5Na:4Li ($x = 0{\cdot}89$). Possible origins of the superstructure are discussed.

1. Introduction

During a study of the phase equilibria in the system Na_2SiO_3–Li_2SiO_3, a phase named high-$(Na,Li)_2SiO_3$ was encountered which apparently has a one-dimensional, long superstructure (West, 1976). This phase has a subcell similar to the unit cells of Na_2SiO_3 and Li_2SiO_3 (orthorhombic, space group $Ccm2_1$) but with extra X-ray reflexions on a^* such that $a_{\text{supercell}} = 6a_{\text{subcell}}$. Since simple Na/Li ordering would not normally be expected to give such a long-period superstructure, further study of this phase was felt to be worthwhile.

The phase diagram of the Na_2SiO_3–Li_2SiO_3 system is known (West, 1976). Both Li_2SiO_3 and Na_2SiO_3 form a range of equilibrium solid solutions (s.s.), and the Na_2SiO_3 solid solutions are particularly extensive at solidus temperatures, covering just over half of the diagram at about 850 °C. Although the equilibrium phase diagram is simple, complexities arise during cooling of the Na_2SiO_3 solid solutions; they are associated with the occurrence of metastable phases and reactions. In the region of interest to this paper, around the 1:1 composition $(Na,Li)_2SiO_3$, the Na_2SiO_3 s.s. phase is stable only above about 810 °C; at all temperatures below this, two phases coexist at equilibrium. However, single-phase products may be retained metastably to room temperature by quenching from above 810 °C. With rapid quenching ($\sim$1 s; samples dropped into Hg), the high-$(Na,Li)_2SiO_3$ phase forms; this phase is apparently similar to the high-temperature Na_2SiO_3 s.s., but in addition has an X-ray superstructure. With somewhat slower cooling rates ($\sim$20 s; samples cooled in air), low-$(Na,Li)_2SiO_3$ forms: this phase is a monoclinic distortion of the orthorhombic high-temperature solid solution and does not have a superstructure. High-$(Na,Li)_2SiO_3$ may be converted to low-$(Na,Li)_2SiO_3$ by annealing at 400–500 °C and low-$(Na,Li)_2SiO_3$ may be decomposed into the equilibrium, low-temperature assemblage, (Na_2SiO_3 s.s. + Li_2SiO_3 s.s.), by heating at 600–700 °C.

2. Experimental

Bulk preparations (about 10 g) of metasilicate compositions were prepared by reaction in Pt crucibles in electric muffle furnaces of appropriate quantities of Na_2CO_3, Li_2CO_3 (both reagent grade) and SiO_2 (crushed natural quartz crystal), initially at about

600 °C for 24 h to drive off CO_2 and finally at 800–850 °C for 1–2 d. Completeness of reaction was checked by X-ray powder diffraction (Guinier method). The desired phase, high-$(Na_{2-x},Li_x)SiO_3$ solid solution, could only be prepared in small quantities. Small samples ($\sim$50 mg), wrapped in Pt foil, were suspended in conventional, vertical-tube quench furnaces at temperatures (820–840 °C) such that the samples were within the single phase Na_2SiO_3 s.s. field for 1–5 days. This length of time was necessary to obtain single crystals of sufficient size for X-ray work. The samples were then cooled rapidly to room temperature by dropping them into a dish of Hg.

Single-crystal X-ray photographs were taken with a Stoe 'Reciprocal Lattice Explorer'. Generally, the crystals were mounted about **c** (*i.e.* rotation axis parallel to lath axis) and *hk*0 and *hk*1 layer De Jong Bouman photographs taken. Distances on the photograph (in reciprocal space) could be converted to real-space distances with the formula $x = M\lambda/d$, where x is the real distance (Å), d the reciprocal distance (mm), M the camera constant (60) and λ the X-ray wavelength (Cu $K\alpha = 1{\cdot}5418$ Å). In order to determine accurately the relative values of $a_{\text{supercell}}$ and a_{subcell}, a travelling microscope was used to measure the separations of pairs of satellites and pairs of main reflexions on the same photograph.

3. Results

3.1. *Formation of high-*$(Na,Li)_2SiO_3$ *solid solution*

This phase was readily detected on Guinier photographs since some of the superstructure reflexions are sufficiently strong to appear as powder lines. By rapidly quenching Na_2SiO_3 solid solutions from 820–840 °C, high-$(Na,Li)_2SiO_3$ solid solution was the only product over the composition range 43–51 mol % Li_2SiO_3. Outside this range, either (*a*) cooling rates were too slow to prevent the formation of low-$(Na,Li)_2SiO_3$ s.s. (51–54% Li_2SiO_3) or (*b*) a mixture of Na_2SiO_3 s.s. derivative phases formed during cooling ($\lesssim$43% Li_2SiO_3).

3.2. *Single-crystal studies: supercell periodicities*

Single crystals of high-$(Na_{2-x},Li_x)SiO_3$ were studied for $x = 0{\cdot}90$, $0{\cdot}96$ and $1{\cdot}00$. Satellite reflexions were observed for all three compositions and the general distribution of satellite intensity was the same for each. However, the positions of the satellites relative to the main (subcell) reflexions varied with composition. For $x = 1{\cdot}0$, the satellites can be regarded as forming a simple supercell with $a = 6a_{\text{subcell}}$, and it was possible to index the powder data with this supercell (West, 1976). For other compositions, the separations of satellites and main reflexions are not rationally related, and it is necessary to introduce a fourth parameter, m, in order to index the satellites. The satellites lie on rows which pass through the main reflexions parallel to **a*** (Fig. 1*a*). They are indexed: *hkl,m*, where *hkl* are the subcell indices of the nearest main reflexion and m is the order of the satellites and can have values $\pm 1, \pm 2 \cdots$. The periodicity of the supercell is determined from the separation of adjacent reflexions $hkl, m \pm 1$.

Although absolute values of subcell and supercell periodicities can be measured, a more useful parameter for present purposes is the ratio of the periodicities $\kappa = a_{\text{supercell}}/a_{\text{subcell}}$. This is because unit-cell parameters will usually change with composition if the substituent atoms are of different size to those being replaced. Such size effects will be eliminated in determining κ values since the percentage change in subcell and supercell lattice parameters should be the same. Also, the dependence (or independence) of κ on temperature should be free from changes due to normal thermal expansion.

Results are given in Fig. 1(*b*) for the variation of κ with composition for high-$(Na,Li)_2SiO_3$ s.s. Within experimental error, the points fall on a straight line. For integral values of κ, the composition corresponds to a simple Na:Li ratio, *i.e.* 1:1 for $\kappa = 6$ and 5:4 for $\kappa = 5$ (extrapolated).

The variation in the d spacing of some high-$(Na,Li)_2SiO_3$ s.s. reflexions with changing composition is shown in Fig. 2. The straight-line plots, and also those for reflexions not shown, such as 002 and 020, are further evidence [less accurate, but more data points than in Fig. 1(*b*)] that κ is linearly composition dependent. With precession photographs, a simple and accurate method of determining κ values existed which avoided the determination of absolute lattice

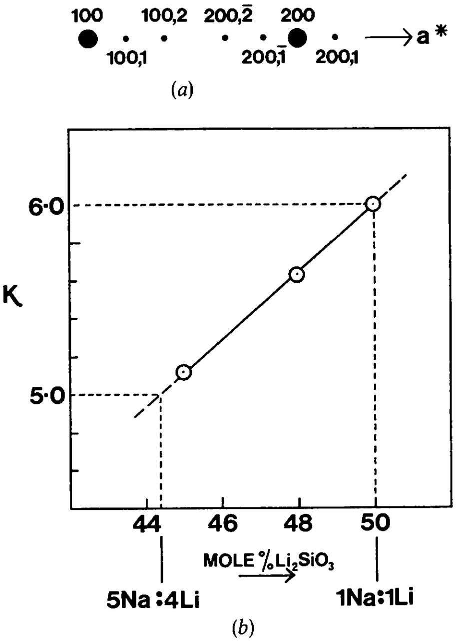

Fig. 1. (*a*) Method of indexing of satellite reflexions. (*b*) Variation of supercell periodicity (as a multiple of a_{subcell}), κ, with composition.

constants. No such simple method could be used on the powder patterns, mainly because of the absence of suitably indexed lines (only a few superstructure reflexions were sufficiently strong to appear on the powder pattern).

3.3. *Satellite intensities*

The general pattern of intensity distribution for both subcell and supercell reflexions was the same for all compositions studied. Composition $x = 1{\cdot}0$ was most studied and the satellites for this will be described (Fig. 3).

(i) For a given *hkl*, satellite intensities usually decrease rapidly with increasing *m*. Notable exceptions are 040,3 and 040,$\bar{3}$ which are fairly strong and much stronger than 040,2 and 040,$\bar{2}$; second and third order satellites are usually present but are normally observed only on grossly over-exposed photographs. From the rotation photograph about **a** (Fig. 3*a*), it is estimated that the satellites comprise $30 \pm 10\%$ of the total spot intensity; approximately 1% of the satellite intensity is in the higher order ($m = 2,3$) reflexions. (ii) There is no systematic relation between the intensity of the main spots and that of the satellites. The satellites are usually much weaker, but several exceptions occur, *e.g.* 040 is very weak but 040,1 and 040, $\bar{1}$ are quite strong. (iii) There is no systematic dependence of satellite intensity on angle 2θ. (iv) For a given *hkl*, the intensities of corresponding $+m$ and $-m$ pairs are usually different. Exceptions are satellites about 0*k*0 and probably 0*k*1, which are equal because of the orthorhombic symmetry. (v) For several crystals, the main reflexions are accompanied by streaks parallel to **a***. The origin of the streaks is thought to be different from that of the satellites and their occurrence appears to be specifically associated with the thermal history of the sample: rapidly quenched samples are relatively free from streaks whereas samples which have been cooled more slowly show considerable streaking (see also below). However, satellite intensities are dependent only on the amount of the high-$(Na,Li)_2SiO_3$ phase and, in this sense, are independent of the cooling rate. (vi) The subcell of high-$(Na,Li)_2SiO_3$, as well as the unit cells of Li_2SiO_3 and Na_2SiO_3, has space group *Ccm*2$_1$. However, the presence of satellites destroys much of the symmetry. The space group of high-$(Na,Li)_2SiO_3$ with $x = 1$ and $\kappa = 6$ is uncertain. Determination of systematic absences requires grossly over-exposed photographs. It seems fairly certain that both the *C* centring and the **c** glide are destroyed, leaving an **a** glide ($h0l$: $h = 2n$) and possibly a 2_1 screw axis ($00l$: $l = 2n$), although insufficient reciprocal space was seen on precession photographs with Cu $K\alpha$ radiation to be sure of the latter. None of the conventional orthorhombic space groups possesses both these sets of absences. Possible space groups, excluding the screw axis, are *Pmam*, *Pma*2 or *P*2$_1$*am*.†

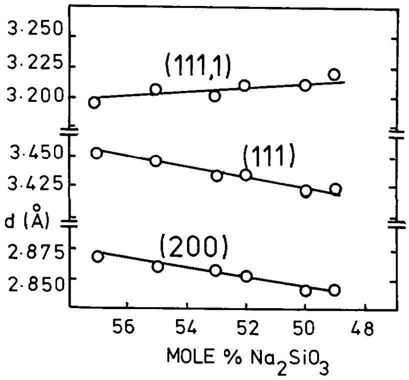

Fig. 2. Variation of *d* spacing with composition of subcell 111, 200 and supercell 111,1 reflexions. For the special composition 50% Na_2SiO_3 ($x = 1$), where $\kappa = 6$, all reflexions can be indexed on the supercell with $a_{\text{supercell}} = 6a_{\text{subcell}}$. The three reflexions above then become 611, 12,0,0 and 711, respectively.

3.4. *Temperature and time dependence of* κ

It is concluded that, for a given composition, κ is independent of both temperature and annealing time. (i) No precession photographs were taken at high temperatures, but several crystals of composition $x = 1$, which had been cooled at somewhat different rates, were studied and for all of them $\kappa = 6$. (Some of these crystals showed considerable streaking and others were almost free from streaks.) (ii) If κ were temperature dependent, it would be a remarkable coincidence that, for $x = 1$, κ should be integral at room temperature.

4. Discussion

Origin of the satellite reflexions

The origin of the satellites and the cause of the superstructure is at present unknown but some general observations can be made and certain possible causes can be eliminated.

(1) The satellites are not caused by phase separation within the single crystal, *i.e.* they are not the 'Bragg side-bands' characteristic of spinodal decomposition and which are caused by a periodic distribution in lattice parameter and/or scattering factor through the crystals (Daniel & Lipson, 1943, 1944; Hargreaves, 1951.) This is shown by (1) the independence of κ of temperature and annealing time and (ii) the formation of single-phase, low-$(Na,Li)_2SiO_3$ on continued annealing of high-$(Na,Li)_2SiO_3$ at ~400–500°C: spinodal decomposition would not yield a single-phase product of the same composition as the starting material.

(2) The satellites are probably not caused by incipient inversion phenomena associated with the orthorhombic, high-$(Na,Li)_2SiO_3$ → monoclinic, low-$(Na,Li)_2SiO_3$ transition such as observed in the feldspar adularia, $KAlSi_3O_8$ (McConnell, 1965, 1971).

---

† In the original report (West, 1976), the presence of the **a** glide was overlooked and the space group given erroneously as *P*222$_1$.

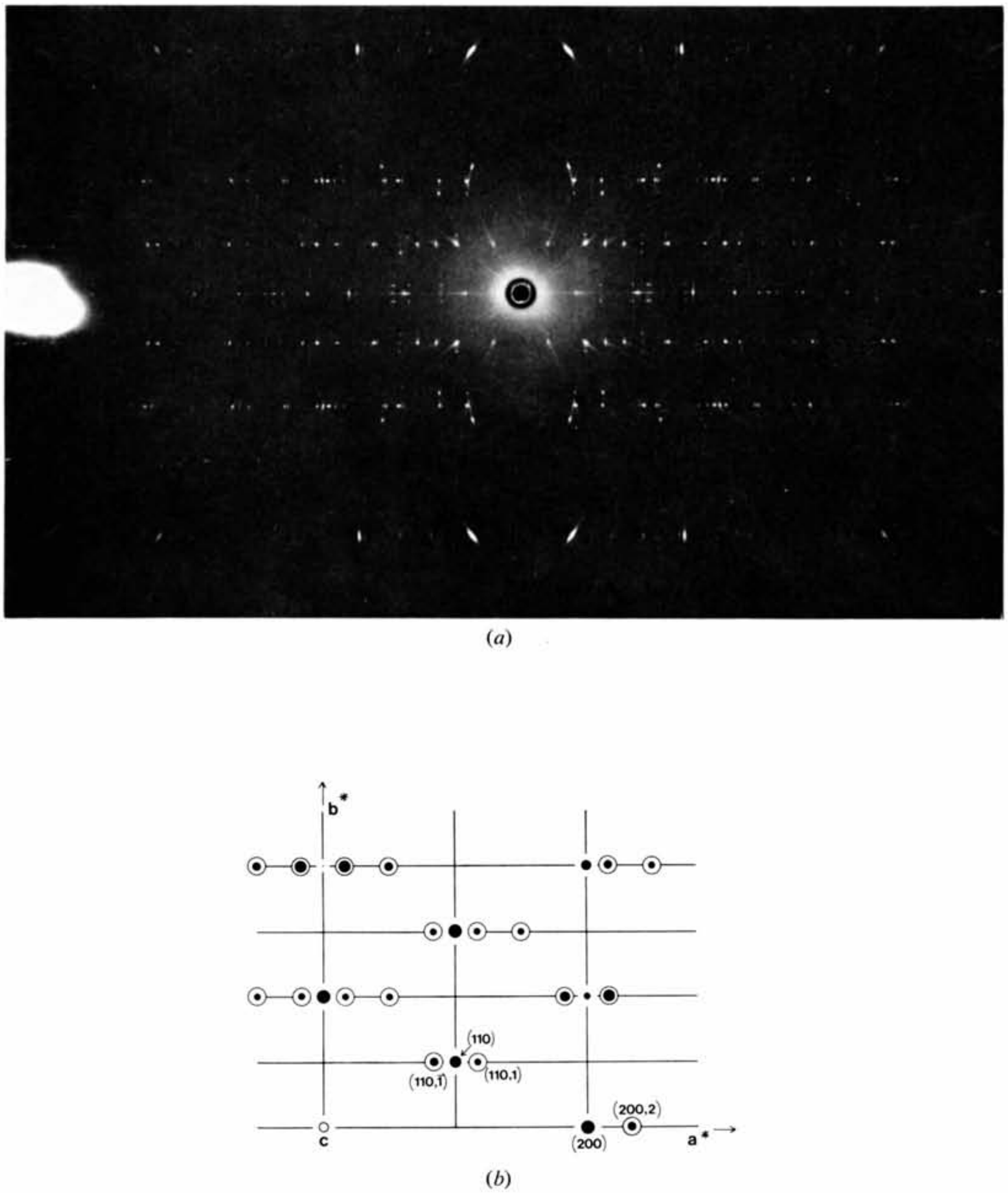

Fig. 3. (*a*) X-ray rotation photograph about **a**, showing the net distribution of subcell and satellite intensity. Five subcell layer lines are shown: $\bar{2}kl$ to $2kl$. About each, first-order satellite lines can be seen ($m = \pm 1$). Higher-order satellites are present but are generally very weak. (*b*) One quadrant of a *hk*0 precession photograph. The rectangular net forms the subcell lattice. Note that only subcell reflexions with $h+k=2n$ are observed because of the *C*-centring. Satellite spots are circled; spot sizes are very rough estimates of the intensity and are intended mainly to show the variation of intensity with *m* for a given *hkl*. The general intensity of satellites is thus somewhat exaggerated. *C* is the centre of the film.

The occurrence of higher-order satellites, although very weak, and the systematic dependence of κ on composition are more in keeping with a true superstructure than with a periodic lattice distortion. However, it is possible that the streaks, observed through the main reflexions in some specimens, are caused by symmetry constraints acting to prevent completion of the orthorhombic → monoclinic transition (McConnell, 1971). Crystals which have been annealed to yield low-$(Na,Li)_2SiO_3$ are invariably twinned with the *bc* plane as the twinning plane† (West, 1976). The twinning shows up on precession photographs as the doubling of spots along $\mathbf{a}^*$ and so the streaks, which are also observed along $\mathbf{a}^*$ in high-$(Na,Li)_2SiO_3$, could be interpreted as due to very fine scale, partial-inversion phenomena which have been constrained by the orthorhombic symmetry of the original crystal.

(3) The satellites are not solely due to the presence of anti phase domains. In systems which exhibit antiphase phenomena, *e.g.* CuAu (Johannson & Linde, 1936; Ogawa & Watanabe, 1954; Glossop & Pashley, 1959) and plagioclase feldspar (McConnell & Fleet, 1963), satellites are observed *around* the superlattice positions. In the present case, the satellites *are* the superlattice – there is no further splitting of the superlattice spots. It is still, of course, possible that the structure of high-$(Na,Li)_2SiO_3$ may be describable as a domain structure, but if so, the satellites are caused by the nature of the ordering and not by the domain texture.

(4) The satellites are probably caused by long-range ordering of Li and Na. This is supported particularly by the composition dependence of κ and the occurrence of integral κ values at simple Na:Li ratios. The nature of the ordering can only be guessed at present. It could be similar to the Fe atom/vacancy ordering found in the intermediate pyrrhotites in which filled Fe layers alternate with partly filled Fe layers (Tokonami, Nishiguchi & Morimoto, 1972). In the present case, alkali ion layers may exist perpendicular to $\mathbf{a}^*$ with perhaps Na layers, Li layers and mixed Na/Li layers. Satellites were observed about the *h*00 subcell reflexions and so, in addition to the ordering of Na and Li, some atomic displacements along $\mathbf{a}^*$ must also occur.

(5) From the temperature independence of κ, the Na/Li ordering is more likely to be of square-wave character than sinusoidal. Materials with temperature-dependent periodicities usually have sinusoidal types of superstructure, *e.g.* Na_2CO_3 (van Aalst, den Hollander, Peterse & de Wolff, 1976), K_2MoO_4 (van den Berg, Tuinstra & Warczewski, 1973) and $NaNO_2$ (Hoshino & Motegi, 1967).

Further insight into the superstructure of high-$(Na,Li)_2SiO_3$ must await the results of a full crystal structure determination, which it is hoped to carry out soon.

---

† The correct unit cell of low-$(Na,Li)_2SiO_3$ is primitive monoclinic, space group either $P2_1$ or $P2_1/m$ (West, 1976). However, a larger *C*-centred cell (with *c* unique) exists which is a slight distortion ($\gamma = 91{\cdot}5^\circ$) of the orthorhombic subcell of high-$(Na,Li)_2SiO_3$. Systematic absences for this cell are hkl: $h+k=2n+1$; $00l$: $l=2n+1$.

References

AALST, W. VAN, DEN HOLLANDER, J., PETERSE, W. J. A. M. & DE WOLFF, P. M. (1976). *Acta Cryst.* B**32**, 47–58.

BERG, A. J. VAN DEN, TUINSTRA, F. & WARCZEWSKI, J. (1973). *Acta Cryst.* B**29**, 586–589.

DANIEL, V. & LIPSON, H. (1943). *Proc. Roy. Soc.* A**181**, 368–378.

DANIEL, V. & LIPSON, H. (1944). *Proc. Roy. Soc.* A**182**, 378–387.

GLOSSOP, A. B. & PASHLEY, D. W. (1959). *Proc. Roy. Soc.* A**250**, 132–146.

HARGREAVES, M. E. (1951). *Acta Cryst.* **4**, 301–309.

HOSHINO, S. & MOTEGI, H. (1967). *Jap. J. Appl. Phys.* **6**, 708–718.

JOHANNSON, C. H. & LINDE, J. O. (1936). *Ann. Phys. (Leipzig)*, **25**, 1–48.

MCCONNELL, J. D. C. (1965). *Phil. Mag.* **11**, 1289–1301.

MCCONNELL, J. D. C. (1971). *Miner. Mag.* **38**, 1–20.

MCCONNELL, J. D. C. & FLEET, S. G. (1963). *Nature, Lond.* **199**, 586.

OGAWA, S. & WATANABE, D. (1954). *J. Phys. Soc. Japan*, **9**, 475–488.

TOKONAMI, M., NISHIGUCHI, K. & MORIMOTO, N. (1972). *Amer. Min.* **57**, 1066–1080.

WEST, A. R. (1976). *J. Amer. Ceram. Soc.* **59**, 118–121.