08.4−28   THE MYTH OF LOEWENSTEIN'S RULE. By Wulf
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Geneva, Switzerland.

Loewenstein's rule (W.Loewenstein, Amer. Miner.39,
92; 1954) essentially states that AlO_4 tetrahedra
should not share corners in tetrahedral framework
structures, if this can be avoided. This rule is some-
times misunderstood as an absolute prohibition. This
is valid especially in zeolite chemistry where it is
frequently argued that a lower limit of the ratio Si:Al
must be 1, "because of Loewenstein's rule". Further-
more, using the same argument, any excess of Al in the
total composition, if present, is explained by the
postulation of Al-rich occlusions within the cages.
However, there are several examples known where Loe-
wenstein's rule is not obeyed. The sodalite family
seems to exhibit a variable framework composition with
a Si:Al ratio between almost ∞ and 0 (Depmeier, Acta
Cryst.40B, in   press,1984) and stuffed tridymite-
like structures are known with pure AlO_4 frameworks
(e.g., Hörkner & Müller-Buschbaum, J.inorg.nucl.Chem.
38,983,1976). Another example is found in the series
gehlenite - pentacalcium trialuminate (Louisnathan, Can.
Miner.10,822,1970; Vincent & Jeffery,Acta Cryst.B34,
1422,1978) where one AlO_4 tetrahedron having framework
character is connected with other AlO_4 tetrahedra.
These examples suggest that a Si:Al ratio < 1.0 in the
framework should not be excluded a priori. Similarly,
the answer to the question whether Al-rich zeolites
exist must not necessarily be in the negative. It seems
that the violations of Loewenstein's rule are often
connected with severe distortions of the tetrahedra
(Depmeier,Acta Cryst.B40, in   press, 1984).

pattern to include the structural disorder and small
particle size. Terms describing the background intensity
(which appears to be of the form expected from amorphous
material) and the effects of the preferred orientation
of the clay particles on the Lorentz factor must also be
included. Applications of the program to complex inter-
stratifications in a calcium-montmorillonite at different
relative humidities (Ormerod, E.C. and Newman, A.C.D.
(1983). Clay Minerals 18, 289-99) and to illite-smectite
interstratifications in weathered Oxford Clay (Weir,
A.H. and Rayner, J.H. (1974). Clay Minerals 10, 173-187)
will be presented. Atomic coordinates are determined to
within approximately ±0.02Å, site occupancies to ±0.2
atoms and interlayer separations to ±0.01Å.

Although designed primarily for use in the study of soil
clays, the method is applicable to any material randomly
disordered in one dimension.

08.4−29   WHOLE PATTERN REFINEMENT OF RANDOMLY
           INTERSTRATIFIED CLAY MINERALS
By I.G. Wood and G. Brown, Soils and Plant Nutrition
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The information necessary to characterise interstratified
clay minerals is the number, type and distribution of
interlayer species and the average number of alumino-
silicate layers in each coherently diffracting unit. In
principle, all of these parameters may be determined from
the intensity distribution along the line in reciprocal
space normal to the plane of the alumino-silicate layers.
Provided that suitably oriented samples can be prepared,
the use of these basal reflections simplifies the problem
considerably as then only the calculation of a one-
dimensional diffraction pattern is required. If the
different interlayer species are also assumed to occur
in a random sequence further simplification results. The
auto-correlation function may then be determined simply
from the concentrations and spacings of the different
interlayers and the thicknesses of the coherently
diffracting domains, leading to an analytical solution
of the problem (Wright, A.C. (1975). Clays and Clay
Minerals 23, 278-88).

Previous analyses of interstratified minerals have
usually involved manual adjustment of the parameters to
obtain a calculated intensity distribution that resembles
the one observed. This is unsatisfactory as it gives no
indication of the probable error of the values obtained
or of correlations between variables. A program has,
therefore been developed which allows least-squares
refinement of the structural parameters to obtain the
best fit over the entire pattern. The procedure is
similar to that used in Rietveld refinement (Rietveld,
H.M. (1969). J. Appl. Cryst. 2, 65-71). It requires,
however, a much more exact calculation of the diffraction

08.4−30   CRYSTAL STRUCTURE AND LOCAL DEFOR-
MATION IN $K_2M_2^{++}(SO_4)_3$ - COMPOUNDS OF THE
LANGBEINITE - TYPE. By D. Speer and E. Salje,
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Republic of Germany.

The high temperature modifications of potassium -lang-
beinites $K_2M_2^{++}(SO_4)_3$ (M^{++} = Zn, Ni, Co and Mg) show
cubic symmetry with S.G. = $P2_13$ (Z=4). The structure
is described as a network of SO_4 - tetrahedra which
share common corners with distorted oxygen octahedra
around the divalent metal positions.
The potassium atoms fill the larger holes of the structure.
The local deformation of the $(M^{++}O_6)$ - octahedra changes
significantly with chemical composition and is closely
related to the structural polymorphism $P2_13$ - $P2_12_12_1$.
Two types of deformations were found:
a) a tilt around the trigonal axis of two triangular faces
   of the octahedra and
b) an offcentering of M^{++} along the trigonal axis.

The two symmetry - inequivalent octahedra show domi-
nantly either the deformation of type a) or b). The tilt
angle and the magnitude of the offcentering increase
with increasing ion - radius of M^{++}. Only $K_2Zn_2(SO_4)_3$
shows a slightly different behaviour. The known struc-

tures of $K_2Cd_2(SO_4)_3$ (Abrahams et al., J. Chem. Phys., (1978), 68, 1926) and $K_2Mn_2(SO_4)_3$ (Yamada et al., J. Phys. Soc. Japan, (1981), 50, 909) also exhibit the same tendency.

Diffuse scattering in all these compounds indicates the appearance of transversal elastic deformation waves parallel to the cubic axes. It has only a slight temperature dependence and reveals no abrupt changes near the structural phase transition $P2_13 - P2_12_12_1$ in $K_2Cd_2(SO_4)_3$.

08.4—31   COMPUTER SIMULATIONS OF THE STRUCTURAL AND PHYSICAL PROPERTIES OF THE POLYMORPHS OF Mg_2SiO_4. By G.D.Price, Department of Geology, University College London, Great Britain, and S.C Parker, Department of Physical Chemistry, Cambridge University, Great Britain.

The aim of the work presented is to develop a computer simulation technique which will predict the structural and physical properties of forsterite, and ringwoodite, the major Earth-forming polymorphs of Mg_2SiO_4. The technique is based upon energy minimization, in which all structural parameters are varied until the configuration with the lowest energy is achieved. The lattice energy and physical properties (e.g. elasticity and dielectric constants) are calculated from interatomic potentials, which include electrostatic and short-range terms. We investigate several types of traditional potential models, and present a new type of model which includes partial ionic charges and a Morse potential to describe the effect of covalency on the Si-O bond. This new form·of. potential model is highly successful, and not only reproduces the zero-pressure structural, elastic and dielectric properties of forsterite and ringwoodite, but also accurately describes their pressure dependence. In addition, the structure and energetics of the beta-phase polymorph, wadsleyite, and other spinelloid polytypic modifications of Mg_2SiO_4 have been investigated, and interpreted in terms of the relative magnitudes of the interaction energies between first, second and third neighbour structural modules. The results of this investigation shed light upon the possible mechanisms of deformation of ringwoodite and wadsleyite, and the rheology of the transition zone of the Earth's mantle.

08.4—32   CORRELATIONS BETWEEN Si-O BOND LENGTH, Si-O-Si ANGLE AND STATIC AND DYNAMIC DISORDER IN SILICA – AN EMPIRICAL METHOD TO CORRECT Si-O BOND LENGTHS. By F. Liebau, Mineralogisches Institut der Universität, 2300 Kiel, Germany.

Silicon-oxygen distances in silicates obtained from X-ray diffraction measurements, $d^X(Si-O)$, have been correlated with the coordination number of oxygen, electrostatic bond strength and Si-O-Si angle (e.g. Baur & Ohta, Acta Cryst. (1982) B 38, 390). However, only 9 percent of the variation of $d^X(Si-O)$ in SiO_2 polymorphs were explained by these authors indicating that one or more parameters·have been ignored.

These $d^X(Si-O)$ values are only apparent bond lengths. The real bond lengths, d^{real} (Si-O), are affected by various factors. The most important of these factors is the temperature factor obtained in the structure refinements, which accounts for both the influence of thermal motions and of static disorder.

Based on 25 structure determinations (performed at various temperatures) with 85 individual Si-O bonds of SiO_2 frameworks in clathrasils (Gies et al., Angew. Chem Int. Ed. Engl. (1982) 21, 206; Gies, Z. Krist. (1983) 164, 247) and in silica polymorphs the following regression equations have been derived:

$$\left[d^X(Si-O)\right]_{ind} = 1.6157 - 0.0070(6)\left[B(O)\right]_{ind}\ and$$

$$\left[d^X(Si-O)\right]_{ave} = 1.6220 - 0.0075(11)\left[B(O)\right]_{ave}\ (Fig.),$$

where ind and ave represent the individual and the average over all oxygen atoms of the structure respectively. These equations explain 63 and 67 percent of the total variation of the $d^X(Si-O)$ values respectively. With the aid of the equation

$$\left[d^{real}(Si-O)\right]_{ind} = \left[d^X(Si-O)\right]_{ind} + 0.007\left[B(O)\right]_{ind}$$

experimental Si-O distances can be corrected for dynamic and/or static disorder into real bond lengths.

For the present, the latter equation should be applied only to SiO_2 frameworks until it has been proved that the slope of 0.007 holds for bridging Si-O bonds in other silicates as well. It might be expected that a substantially different correction factor has to be used for terminal Si-O bonds. In any case, experimental Si-O distances should be corrected for disorder before reliable crystal chemical conclusions are drawn.

Corresponding correlations between the Si-O-Si angles and B(O) have also been obtained.