

08.4-05 LOW AND HIGH TEMPERATURE SPINEL ($MgAl_2O_4$): STUDIES ON NATURAL SINGLE CRYSTALS BY NEUTRON DIFFRACTION. By O. Baumgartner, A. Preisinger, Inst.f.Mineralogie, Kristallographie und Strukturchemie, Techn. Univ. Wien, Austria, and G. Heger, H. Guth, Kernforschungszentrum Karlsruhe, Inst.f.Angewandte Kernphysik I, FRG.

Studies on natural single crystals of $MgAl_2O_4$ (China) with $\sim 0.4\%$ Cr and $\sim 1\%$ Fe were carried out at room temperature, $690^\circ C$, $830^\circ C$ and, after quenching, again at room temperature. Additional measurements were made at thermal equilibrium at $880^\circ C$, $830^\circ C$, $805^\circ C$, $780^\circ C$ and, after slow cooling to $680^\circ C$, again at room temperature.

Above phase transition, which sets in at about $750^\circ C$, and after cooling from these temperatures, $MgAl_2O_4$ belongs to the space group $Fd\bar{3}m$. Only for the low temperature spinel do ψ -scan measurements at $\lambda_n = 2.418 \text{ \AA}$ (strong reduction of Umweganregung) show clear reflexions of the type $0\ k\ l$: $k+l = 2n$, and thus clearly indicate space group $F\bar{4}3m$. This decrease in the space-group symmetry may be primarily caused by a distortion of the oxygen lattice due to replacement of Mg by Fe.

Whereas for the low- $MgAl_2O_4$ the degree of inversion was determined to be $i \sim 0$, the result obtained for all spinels measured at high temperatures and cooled subsequently was $i > 0$ (e.g. $830^\circ C$: $i \sim 0.2$; room temperature (quenched): $i \sim 0.2$). The distortions of the Mg-O- and Al-O-polyhedra resulting from the inversion were taken into consideration in the refinement, which showed R_p -values of about 0.02.

08.4-06 THE SYMMETRY OF DIAMOND. By Gabrielle Donnay and J.D.H. Donnay, Geological Sciences, McGill University, 3450 University St., Montreal, PQ, Canada H3A 2A7.

Diamond had been assigned to point group $\bar{4}3m$ by the morphological crystallographers until Bragg and Bragg (1913) determined its crystal structure, by X-ray diffraction, and described it in $Fd\bar{3}m$. To this day this space group has remained the accepted one, even to eminent morphologists. Palache, Berman, and Frondel (Dana System, 1944), e.g., explain that point group $m\bar{3}m$ "is indicated by the arrangement of the atoms in the well-established structure." But that arrangement can be accommodated in five space groups: in either $8a$ ($Fd\bar{3}m$; $Fd\bar{3}$, $F4_132$) or ($4a+4c$) ($F\bar{4}3m$; $F23$). The morphological arguments remain to-day as convincing as ever; they follow. Diamond single crystals show tetrahedral habit, the tetrahedron being alone or in combination; the "octahedron" is a sham, resulting from a 90° -twin of 2 crystals each of which has the larger tetrahedron truncated by the smaller. These observations, together with five confirmed tritrahedra $\{hkl\}$, rule out all cubic point groups other than $\bar{4}3m$ and 23. Four tetrahedra $\{OKL\}$ are reported (C. Hintze, Hdb., 1904); some figure in Goldschmidt's Atlas -- they eliminate 23. The antihemihedry $\bar{4}3m$ is thus the only point group compatible with morphological facts. K. Lonsdale and H.J. Milledge (in *Phys. Prop. of Diamond*, R. Berman ed. 1965) wrote, "Diamonds do occasionally show hemihedral morphology, however, and no satisfactory explanation on the atomic scale has been found." One experimental approach now available to tell whether the eight carbon atoms are equivalent or not is to refine thermal parameters for Wyckoff positions $4a$ and $4c$, preferably without ellipsoidal constraint. Even if the structure should turn out to have been correctly assigned to $Fd\bar{3}m$, morphology would have to be recognized as the least symmetrical of all the properties of diamond, the one which lowers the crystal symmetry from $m\bar{3}m$ to $\bar{4}3m$.

08.4-07 SPACE-GROUP SYMMETRY AND STRUCTURE-PARAMETER REFINEMENT FOR MAGNESIUM ALUMINATE SPINEL. By N.W. Grimes and

P. Thompson, Physics Department, University of Aston in Birmingham, England and H.F. Kay, H.H. Wills Physics Laboratory, University of Bristol, Bristol, England.

X-ray-diffraction intensities have been collected from a small spherical single crystal of magnesium aluminate spinel over half a hemisphere of reciprocal space out to $\sin \theta/\lambda = 1.22 \text{ \AA}^{-1}$ with MoK α radiation and a CAD-3 diffractometer. Almost 4000 reflections have been measured including up to 24 equivalents for general hkl and used for a structure-parameter refinement under $F\bar{4}3m$ symmetry, following the suggestion by Grimes (Phil. Mag. (1972) 26 1217), and subsequently for refinement according to the conventionally assumed $Fd\bar{3}m$ symmetry. The former, having an R value of less than 0.02, is found to give a significantly superior fit to the experimental data, especially at high angles and with reflections having structure factors less than 5.0. New and very precise atom positions and bond lengths have been calculated, which demonstrate small but significant differences from those previously published.

The new results may lend credence to the electron-diffraction observations by Hwang, Heuer and Mitchell (Phil. Mag. (1973) 28 241) and Mishra and Thomas (Acta Cryst. (1978) A33 678) of the $Fd\bar{3}m$ forbidden reflections $hk0$ with $h+k = 4n+2$, which have been discounted as arising from double diffraction in recent work by Smith (Phil. Mag. (1978) 38 99) and by Tokonami and Horiuchi (Acta Cryst. (1980) A36 122).

08.4-08 MELANOPHLOGITE: COMPOSITION, THERMAL BEHAVIOR AND STRUCTURE REFINEMENT. By H. Gies and F. Liebau, Mineralogisches Institut der Universität, D 2300 Kiel, Germany.

Melanophlogite (M) is known as a very rare natural polymorph of silica which contains, in addition, up to 8 percent C, H, O, N, and/or S. According to Appleman and Kamb (Science (1965) 148, 232), M is isostructural with the cubic gas hydrates I, while Žak (N. Jb. Miner. Mh. (1975) 509) reported a tetragonal superstructure.

At room-temperature mass spectroscopic analyses of samples from four localities, we found that M contains CH_4 , CO_2 and N_2 in varying amounts. Under the microscope the birefringent crystals become isotropic above c. $40^\circ C$, reversibly. Although gases are lost above c. $400^\circ C$, the silica framework is maintained up to at least $1175^\circ C$. An endothermal DTA peak at ca. $1475^\circ C$ indicates transformation to cristobalite.

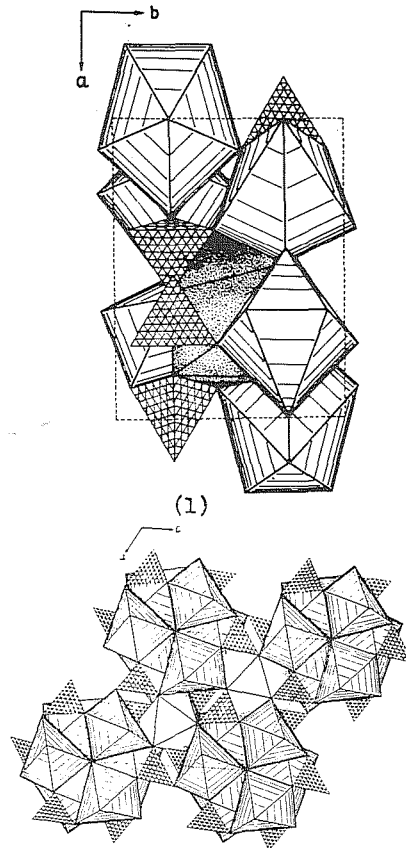
X-ray diagrams show that crystals of M are twinned at room temperature with a tetragonal superstructure and transform to cubic single crystals at c. $40^\circ C$. The crystal structure of the cubic form at $200^\circ C$ has been refined: $a_0 = 13.436(3) \text{ \AA}$, $Pm\bar{3}n$, 667 independent reflexions, $R = 0.061$, $R_w = 0.040$. In analogy with the gas hydrates I^w $[SiO_4]$ tetrahedra are linked to form two types of cages: two pentagondodecahedra $[5^{12}]$ and six tetrakaidecahedra $[5^{12}6^2]$ per unit cell. From $\{obs\} - \{calc\} (Si, O)$ it is

concluded that the $[5^{12}]$ cages contain CH_4 molecules while the $[5^{12}6^2]$ cages contain CO_2 and N_2 .

Bond lengths (\AA) and valence angles ($^\circ$) are given in the following table.

	range	mean value of $[5^{12}]$	mean value of $[5^{12}6^2]$	grand mean value
Si-O	1.569-1.596	1.579	1.572	1.576
O-Si-O	107.9-110.4	109.3	109.5	109.5
Si-O-Si	148.2-180	162.9	170.3	168.8

Si-O distances show only little variation, the grand mean value of 1.576 \AA being considerably lower than the value 1.608 \AA deduced by Brown & Gibbs (Amer. Miner. (1969) 54, 1528) for silica frameworks. Si-O-Si angles in M have values up to 180 $^\circ$ with a very high grand mean value of 168.8 $^\circ$. The structure of M is a good example of the negative correlation between Si-O distances and Si-O-Si angles reported by Hill & Gibbs (Acta Cryst. (1979) B 35, 25). - Melanophlogite is the first silicate known to contain pentagondodecahedra formed from $[\text{SiO}_4]$ tetrahedra.



08.4-09 THE CRYSTAL STRUCTURE OF LESSINGITE, RICH IN LIGHT RARE EARTH, CERIUM. By Li De-yu, Wang Pei-ling & Liu Jian-chen, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

The change of symmetry group of apatite from $P6_3/m$ to that of lessingite, $P2_1$, results from the shift of the Si and O atoms from the equivalent positions (6h) and (12i) as produced by distortion of polyhedra with 7- and 9-corners. The substitution of Ca in apatite for TR (to some extent) and the disorder distribution of atoms TR and Ca on the equivalent positions (6h) and (4f) may have contributed to the distortion of the 7- and 9-cornered polyhedra. This is significant for understanding both the characteristics of constituent and structure, and the relationship between the distribution of rare earth elements and the crystal chemistry of compounds with the apatite structure type which are important for laser application.

Unit cell determination was furnished on PW 1100 diffractometer by least-squares refinement: $a = 9.6283$, $b = 9.6305$, $c = 7.0495 \text{ \AA}$; $\gamma = 120.02^\circ$; $Z = 2(\text{TR}_{3.42}\text{Ca}_{1.415}\text{M}_{0.165}\text{Si}_3\text{O}_{12}\text{F})$; $d_{\text{obs}} = 4.877 \text{ g/cm}^3$; $d_{\text{calc}} = 4.918 \text{ g/cm}^3$.

The atomic coordinates, isotropic and anisotropic thermal parameters were refined to $R = 0.093$ and $R_w = 0.083$ for 808 independent reflections by means of least-squares calculations.



The projections of structure of lessingite (XZ) (Fig.1) and (XY) (Fig. 2).