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 ~0.4% Cr and ~1% Fe were carried out at room temperature, 690°C, 830°C and, after quenching, again at room temperature. Additional measurements were made at thermal equilibrium at 880°C, 830°C, 805°C, 780°C and, after slow cooling to 680°C, again at room temperature.

Above phase transition, which sets in at about 750°C, and after cooling from these temperatures, $MgAl_2O_4$ belongs to the space group Fd3m. Only for the low temperature spinel do ψ-scan measurements at λ_n = 2.418 Å (strong reduction of Umweganregung) show clear reflexions of the type 0 k 1: k+1 = 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~0, the result obtained for all spinels measured at high temperatures and cooled subsequently was i>0 (e.g. 830°C: i~0.2; room temperature (quenched): i~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_F-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 F$d3m$. 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 (F$d3m$; F$d3$, F$4_1$32) or (4a+4c) (F$\bar{4}3m$; F23). The morphological arguments remain to-day as convincing as ever; they follow. Diamond single crystals show tetrahedral habit, the tetrahedron being alone or in combination; the "octahedron" is a sham, resulting from a 90°-twin of 2 crystals each of which has the larger tetrahedron truncated by the smaller. These observations, together with five confirmed tritetrahedra {$hh\ell$}, rule out all cubic point groups other than $\bar{4}3m$ and 23. Four tetrahexahedra {$0k\ell$} 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 F$d3m$, 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 θ/λ = 1.22Å^{-1} with MoKα 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 Fd3m 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 Fd3m 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 Zak (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°C, reversibly. Although gases are lost above c. 400°C, the silica framework is maintained up to at least 1175°C. An endothermal DTA peak at ca. 1475°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°C. The crystal structure of the cubic form at 200°C has been refined: a_0 = 13.436(3)Å, Pm3n, 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 $\rho_{obs} - \rho_{calc}$ (Si,O) it is