*Acta Cryst.* (1977). **B33**, 2287–2288

# Refinement of the Crystal Structure of $Mg_2GeO_4$ Spinel

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(*Received* 28 *January* 1977; *accepted* 3 *March* 1977)

**Abstract.** $Mg_2GeO_4$, *Fd3m*, $a = 8{\cdot}2496 \pm 0{\cdot}0006$ Å, $x = 0{\cdot}3758 \pm 0{\cdot}0005$, from a refinement of 15 integrated intensities to a residual of $R = 0{\cdot}021$. The structure of synthetic $Mg_2GeO_4$ spinel, as obtained from a refinement of neutron powder diffraction data, is normal with $0{\cdot}00 \pm 0{\cdot}01$ fractional occupancy of the octahedral site by germanium.

**Introduction.** The $Mg_2GeO_4$ 'olivine' was prepared from a stoichiometric mixture of reagent-grade MgO (Baker) and $GeO_2$ (quartz form, Sylvania) by heating in air for five days at 1100 °C in a platinum crucible in a temperature-controlled furnace. The 'olivine' was transformed to the spinel hydrothermally in an internally heated pressure vessel (Holloway, 1971). The sample and 5 wt% water were sealed in a gold tube and reacted for two days at 850°C and 5 kbar. The product was a well crystallized and sintered spinel phase containing less than one per cent unreacted 'olivine', as determined from an X-ray powder diffraction pattern.

Neutron powder diffraction data were obtained at the Los Alamos Omega West Reactor, scanning from $2\theta = 4$ to $68{\cdot}8°$ at an interval of $0{\cdot}10°$, and a wavelength of 1·3365 Å. The neutron flux at the sample was $\sim 10^9$ $m^{-2}$ $s^{-1}$. The 14 g sample was contained in a parallel-sided holder made from Ti–Zr null-matrix alloy, and was placed in the symmetrical transmission position. An absorption parameter of $\mu t = 0{\cdot}50$ was assumed. The pattern contained only the spinel peaks and one extremely weak peak at $d = 3{\cdot}13$ from the 'olivine' impurity.

The observed peak intensities were determined by least-squares analysis of the diffraction data (Bowman, Wallace, Yarnell, Wenzel & Storms, 1965), and were fitted to the normal spinel structure by least-squares solution of the equation (Bacon, 1962)

$$I = K\,\frac{\exp(-\mu t \sec\theta)}{\sin^2 2\theta}\exp\left(-2B\,\frac{\sin^2\theta}{\lambda^2}\right)jF^2,$$

to give $K = 0{\cdot}000182$ (3), $B = 0{\cdot}32$ (8), $u = 0{\cdot}3758$ (5) and $R = 0{\cdot}021$, where $R = \Sigma w|I_o - I_c|/\Sigma wI_o$. Neutron scattering lengths of 5·16 fm for Mg, 8·4 fm for Ge, and 5·77 fm for O were used. A lattice parameter of $a_o = 8{\cdot}2496$ (6) was determined, in good agreement with previous work (Dachille & Roy, 1960; Navrotsky, 1973). Several occupancy models were refined by varying the effective scattering lengths for the tetrahedral and octahedral metal positions. The resulting variances $[\Sigma w(I_o - I_c)^2/13]$ and residuals are shown in Table 1. The reflection positions and intensities from the final refinement are in Table 2.

Table 1. *Refinement of occupancy models for* $Mg_2GeO_4$

| Tetrahedral site occupancy | Variance | Residual |
|---|---|---|
| All Ge | 3·22 | 0·021 |
| 0·99 Ge + 0·01 Mg | 3·02 | 0·021 |
| 0·95 Ge + 0·05 Mg | 3·93 | 0·026 |
| 0·90 Ge + 0·10 Mg | 8·91 | 0·044 |
| All Mg | 736·00 | 0·427 |

Table 2. *Reflection positions and intensities for* $Mg_2GeO_4$ *from the final refinement*

| *HKL* | $Q_{obs}$ | $Q_{calc}$ | $I_{obs}$ | $I_{calc}$ | $d_{calc}$ |
|---|---|---|---|---|---|
| 111 | – | 0·441 | 1·24 ± 0·60 | 0·66 | 4·763 |
| 220 | 0·1174 | 0·1175 | 29·11 ± 0·45 | 29·17 | 2·917 |
| 311 | 0·1616 | 0·1616 | 74·06 ± 0·74 | 75·38 | 2·488 |
| 222 | 0·1762 | 0·1763 | 29·90 ± 0·51 | 30·21 | 2·382 |
| 400 | 0·2351 | 0·2351 | 66·91 ± 0·69 | 65·99 | 2·063 |
| 331 | – | 0·2791 | 0·05 ± 0·66 | 0·09 | 1·893 |
| 422 | 0·3527 | 0·3526 | 19·64 ± 0·31 | 20·37 | 1·684 |
| 511/333 | 0·3967 | 0·3967 | 41·15 ± 0·46 | 41·35 | 1·588 |
| 440 | 0·4703 | 0·4703 | 198·13 ± 1·12 | 194·45 | 1·458 |
| 531 | – | 0·5142 | 0·35 ± 0·63 | 0·37 | 1·395 |
| 600/442 | – | 0·5289 | 0·25 ± 0·63 | 0·00 | 1·375 |
| 620 | 0·5876 | 0·5877 | 13·18 ± 0·27 | 12·94 | 1·304 |
| 533 | – | 0·6318 | 21·43 ± 0·66 | 21·52 | 1·258 |
| 622 | – | 0·6464 | 24·98 ± 0·69 | 27·57 | 1·244 |
| 444 | 0·7052 | 0·7052 | 32·11 ± 0·40 | 32·91 | 1·191 |

**Discussion.** The spinel polymorph of $Mg_2GeO_4$ is stable below 810 °C at atmospheric pressure, and is also

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stable at high pressure (Dachille & Roy, 1960). Because of its relatively easy preparation, it has been used as a model compound for studying the olivine–spinel transition which probably occurs in Fe–Mg silicates in the upper mantle of the earth at depths of ~400 km (Ringwood, 1975). However, there has been some unresolved controversy about the cation distribution in $Mg_2GeO_4$: Dachille & Roy (1960) show evidence for an inverse distribution, while Tarte (1963), Reinen (1968), and Durif-Verambon, Bertaut & Pauthenet (1956) propose a normal distribution analogous to that in other germanate spinels (Navrotsky, 1973). The cation distribution in silicate and germanate spinels is of interest to geophysics because the configurational entropy arising from a somewhat disordered distribution could have a significant effect on the pressure–temperature slopes of phase transitions in the mantle (Jackson, Liebermann & Ringwood, 1974; Navrotsky & Kasper, 1976) and on the thermodynamics of solid-solution formation in multicomponent silicate and germanate systems (Navrotsky, 1973).

Because of this interest, we have refined the structure of $Mg_2GeO_4$ using powder neutron diffraction to obtain accurate values of lattice parameters, oxygen position and metal site occupancy.

From the results of this refinement, it is evident that $Mg_2GeO_4$ spinel is completely normal with an occupancy of germanium ($0{\cdot}00 \pm 0{\cdot}01$) on the octahedral sites. The value of the oxygen positional parameter, $x = 0{\cdot}3758 \pm 0{\cdot}0005$, indicates that the oxygen anion array is nearly perfectly closest-packed with little or no distortion, and is similar to that found, $x = 0{\cdot}375$, for the other normal germanate spinels, $Fe_2GeO_4$, $Co_2GeO_4$, and $Ni_2GeO_4$ (Blasse, 1964).

This work was supported in part by the United States Energy Research and Development Administration (ERDA) and by the National Science Foundation.

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*Acta Cryst.* (1977). B33, 2288–2291

# Urocanic Acid Dihydrate (4-Imidazoleacrylic Acid Dihydrate)

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(*Received* 4 *August* 1976; *accepted* 2 *March* 1977)

**Abstract.** $C_6H_6N_2O_2.2H_2O$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}624$ (1), $b = 12{\cdot}881$ (1), $c = 6{\cdot}714$ (1) Å, $Z = 4$, $D_c = 1{\cdot}389$, $D_m = 1{\cdot}391$ (2) g cm$^{-3}$ (at 22 ± 2°C), FW 174·16, $F(000) = 368$. Intensity data were collected on an automated diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement yielded an $R$ of 0·038 for 825 observed data. The nearly planar molecules are in the zwitterion form and are organized into stacks in the crystal (the imidazolium ring of one molecule being placed over the carboxylate group of the next). These stacks are held together *via* hydrogen bonding, principally through water molecules, involving all available H atoms.

**Introduction.** Urocanic acid is a naturally occurring metabolite derived from histidine, and is a major absorber of ultraviolet radiation in epidermal tissues where it undergoes several interesting photochemical reactions (Anglin & Everett, 1964). The compound is found to isomerize and form photodimers in aqueous solution; however, crystals of the dihydrate do not