08.X-05 HIGH-TEMPERATURE STRUCTURAL STUDY OF OLIVINE-TYPE STRUCTURES AND SPINELS. By Y. Takéuchi, T. Yamanaka, N. Haga and M. Hirano, Faculty of Science, University of Tokyo, Tokyo, Japan.

The crystal structures of synthetic Mg_2SiO_4 (forsterite) and synthetic $MgAl_2O_4$ (spinel) have been studied at the temperatures from 25°C up to around 1600°C based on reflexion intensities collected on a four-circle diffractometer; a new gas-flame heater and technique (Yamanaka et al. Z. Krist. (1981) 154, 147) were used for the temperatures above 1000°C, while a miniature electric-resistance furnace was used for those below 1000°C. The structures at various temperatures were refined to R = 2.0 ∿ 5.8% for 1035 ∿ 286 reflexions (forsterite), and for 145 ∿ 85 reflexions (spinel). We further studied the olivine-type structures such as $LiScSiO_4$, Mg_2GeO_4, Ca_2GeO_4, Al_2BeO_4, $MgAlBO_4$, and silicate spinels, Fe_2SiO_4, Ni_2SiO_4 at temperatures up to 800°C ∿ 1400°C. The results include: (1) The bond lengths of the three non-equivalent Si-O bonds in forsterite vary as shown in Fig. 1. The different three bond lengths appear to converge to a single value at around the melting point.

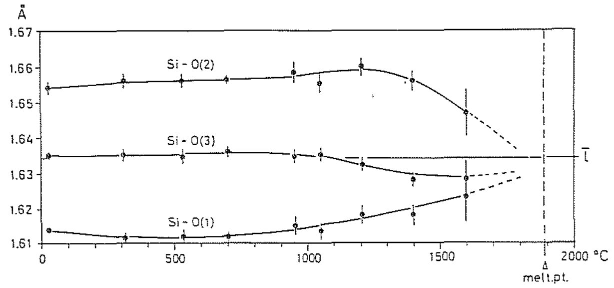

Fig. 1

(2) T - O(2) bonds of the olivine-type structures tend to show anomalous modes of variation which may be explainable in terms of the modes of thermal expansion of octahedra.

(3) The GeO_4 tetrahedra in Ca_2GeO_4 show unusually large thermal expansion; at around the transition temperature of 1450°C, to the hexagonal form, the volume is about 6% greater than the room-temperature volume. An abrupt shrinkage of the tetrahedra at the transition temperature would play a role in triggering the transition.

(4) The thermal expansions of tetrahedral (A - O) and octahedral (B - O) bonds of spinel are discontinuous at a temperature between 600°C and 700°C (Fig. 2) in accordance with the reported anomaly in thermal expansion of the cubic cell edge (Suzuki and Kumazawa, Phys. Chem. Minerals (1980) 5, 279). It is now very likely that spinel undergoes an order-disorder transition at around that temperature. By means of ψ - scan technique, the space group Fd3m was confirmed for spinel.

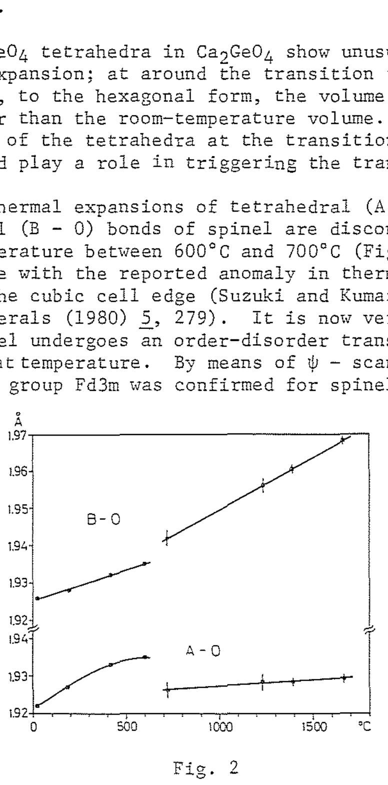

Fig. 2

08.X-06 ASYMMETRIC PEAKS IN POWDER DIFFRACTOMETRY: COMPUTER ANALYSIS OF A MECHANISM. By M. Rieder, Institute of Geological Sciences, Charles University, Albertov 6, 12843 Praha 2, Czechoslovakia.

When a perfectly flat sample is aligned in a divergent X-ray beam, as is commonly the case in instruments with a monochromator on the detector arm, peaks are broadened on their low-angle sides. This concerns primarily peaks at low Bragg angles. The effect has been ascribed to diffraction from particles in deeper parts of the sample.

Geometric analysis identifies three limits of the effect: (i) thickness of sample, (ii) divergence of primary beam, and (iii) width of sample. Depending on the instrumental arrangement, broadening in a single pattern may be dominated by any one of these, alone or in combination.

A computer program calculates peak profiles for a given geometric limit and appropriate mass absorption coefficients, reflecting thus the fact that intensity contributions from particles below the surface are weakened by absorption.

The present approach permits the effects of broadening to be made ineffective where they cannot be eliminated instrumentally. Corrections to theta measurements and/or intensities obtained by integrating the area under the peak can be put on a sounder basis. Awareness of the above approach should aid in cell-data refinement, in X-ray phase analysis, in treating data for poorly diffracting phases, or in interpretation of patterns obtained in high-temperature devices.

08.X-07 ANHARMONIC THERMAL VIBRATIONS IN PYROELECTRIC ZnO. By K. Kihara and Gabrielle Donnay, Geol. Sciences, McGill University, Montreal, P.Q., Canada H3A 2A7.

Intensities of wurtzite-type ZnO were measured on a spherical crystal of 0.39mm diameter with AgKα radiation at 20°, -200° and -400°C. Scale factors and isotropic extinction corrections were calculated by least squares for each temperature. The symmetry-related F values agree to 1.4% for the 20° data set; the number of independent observed reflections is 253 at 20°, 196 at 200° and 208 at 400°. The correction for single phonon thermal diffuse scattering has not yet been applied. In refinements based on *harmonic approximation* (First and Second cumulant calculations) the thermal vibrations appear isotropic for both atomic species at the three temperatures investigated. The only structural parameter, z of $O^=$, changes only insignificantly from 0.3815(3) at 20°C to 0.3821(6) at 400°C. Over the same temperature range, the thermal parameter B of Zn varies from 0.525(2) to 1.182(9)$Å^2$; that of O, from 0.524(8) to 1.057(21)$Å^2$. At elevated temperatures *anisotropic* refinement reveals larger mean-square displacements along c than perpendicular to it for Zn and O, showing that the potential-energy well becomes anisotropic at such temperatures. *Third cumulant calculations* (Johnson, 1969) lead to slight decreases in z at every temperature. At 20°, for instance, z refined to 0.3811(6), very close to 0.3800, the value derived from the Keffer-Portis equation of 1957. Further support for the anharmonic nature of such thermal vibrations comes from the intensities of two groups of reflections, 07.ℓ and 35.ℓ, which should be the same according to the harmonic approximation. Intensities are observed to differ slightly but significantly with 35.2n more intense than 07.2n, whereas 07.2n+1 are more intense than 35.2n+1, at both 20° and -200°C. These observations parallel those reported by Whiteley *et al.* on CdSe (1978).