

08.4-3 AN ATTEMPT OF STRUCTURE REFINEMENT OF QUARTZ. By K. Kihara, Dept. of Earth Sciences, Faculty of Science, Kanazawa University, Kanazawa, 920 Japan

Integrated intensities of Bragg reflections from a clear natural quartz ( $\text{SiO}_2$ ) were measured at five temperatures below and above the  $\alpha$ - $\beta$  transition ( $T_c^*$ ), using  $\text{Mo K}\alpha$  radiation. All symmetrically independent reflections up to  $2\theta = 80^\circ$  were used in least-squares refinements, which were based on the Gram-Charlier expansion. The atomic positions for  $\beta$  quartz were constrained on the sites with symmetry 222 for Si and with 2 for O. The R<sub>w</sub> values in the refinements of the model including terms up to the fourth-order were improved as shown below with those of the second-order refinements in parentheses: 0.0377 (0.0520) at  $T_c+14$  K, 0.0366 (0.0531) at  $T_c+4$  K, 0.0413 (0.0528) at  $T_c-10$  K, 0.0374 (0.0478) at  $T_c-60$  K and 0.0302 (0.0356) at room temperature. Of the 38 third- and fourth-order coefficients, 13 were nearly zero for the room temperature data, while only a few were zero for the high temperature data. Atomic probability density functions (pdf) obtained from the high-order calculations were all unimodal at the five temperatures. A split-atom model for  $\beta$  quartz, where O and Si respectively split into two sets of positions corresponding to  $\alpha$  quartz, related each other by the Dauphine twin law, was also fitted to the ( $T_c+4$  K) data. This calculation converged at  $R_w=0.0439$  for the positional parameters in good agreement with those obtained by neutron diffraction data at  $T_c+60$  K (Wright & Lehmann, 1981, J. Solid State Chem., 36, 371). The pdf's obtained from the high-order refinements and the split-atom refinement will be discussed.

\* Although Gouhara et al. (1983) (J. Phys. Soc. Japan, 52, 3697) have found an incommensurate phase in the range of 1.8 K between  $\alpha$  and  $\beta$ , we will continue our discussion, for the present, on the basis of the transition scheme traditionally adopted.

08.4-4 COMPUTATIONAL MODEL OF THE STRUCTURAL AND ELASTIC PROPERTIES OF THE HIGH-PRESSURE PHASES OF  $\text{MgSiO}_3$  (GARNET, ILMENITE AND PEROVSKITE). By M. Matsui, Chemical Laboratory, Kanazawa Medical University, Japan; M. Akaogi and T. Matsumoto, Department of Earth Sciences, Faculty of Science, Kanazawa University, Japan.

The three high-pressure phases of  $\text{MgSiO}_3$ , garnet (majorite), ilmenite and perovskite, are considered to be the major constituents of the deep mantle. The purpose of this investigation is to develop a realistic potential energy model, which is applicable to characterizing and predicting the structural and elastic properties of these three high-pressure phases, as a function of pressure. The computational techniques are based on energy minimization with respect to the structural variables. The potential energy of the crystal is approximated to be the sum of Coulomb interaction, van der Waals attraction and short-range repulsive interaction between atoms. The energy parameters required to model the three phases are determined from a best fitting of the parameters to the observed zero-pressure structures of the ilmenite and perovskite phases as well as to the measured single-crystal elastic constants of the ilmenite phase. The resulting potential model is applied to simulating (1) the zero-pressure structure and elasticity of the garnet phase, (2) the zero-pressure elasticity of the perovskite phase, and (3) the high-pressure behaviors of the structures and elastic constants of the three phases.

08.4-5 THE CRYSTAL STRUCTURE OF SYNTHETIC LIPSCOMBITE: A REDETERMINATION: By I. Vençato, Depto. Física, UFSC, Florianópolis, SC, Brazil, E. Mattievich, Inst. Fís., UFRJ, Rio de Janeiro, RJ, Brazil and Y.P. Mascarenhas, Inst. Fís. Quím., São Carlos, USP, São Carlos, SP, Brazil.

The synthetic compound  $\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})_2$  is tetragonal, space group  $P4_32_12$ ,  $a = 7.310(3)$ ,  $c = 13.212(7)$  Å,  $Z = 4$ ,  $D = 3.68(1)$  g.cm<sup>-3</sup>,  $\mu = 63.1$  cm<sup>-1</sup>. The structure was solved by the heavy atom technique and refined by the least-squares method to an R value of 0.108 for 347 observed reflections. The structure consists of two disordered  $\text{Fe}^{2+}$  ions in special positions and one  $\text{Fe}^{3+}$  ion in general position, octahedrally coordinated by  $(\text{PO}_4)^{3-}$  ligands and  $(\text{OH})^-$  groups. The octahedra form infinite face sharing chains alternatively in the  $[110]$  and  $[1\bar{1}0]$  directions. Unusual features of the structure include a  $\text{Fe}^{3+}$ -OH distance of 2.26 Å and a mean-value of O-O' edges of 2.74 Å of octahedral shared faces.

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08.4-6 OH=F SUBSTITUTION IN THE AMBLYGONITE-MONTEBRASITE SERIES: A CRYSTAL STRUCTURE AND SPECTROSCOPIC STUDY. By L.A. Groat, M. Raudsepp, F.C. Hawthorne, Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, R3T 2N2; B.L. Sherriff, Department of Geology, McMaster University, Hamilton, Ontario, L8S 4M1; J.S. Hartman, Department of Chemistry, Brock University, St. Catharines, Ontario, L2S 3A1.

We have used single-crystal structure refinement, IR and MAS NMR spectroscopies to investigate OH=F substitution in the amblygonite-montebbrasite series ( $\text{LiAlPO}_4(\text{OH},\text{F})$ ). The structures of compositions with  $F/(F+\text{OH}) = 0.04, 0.15, 0.30, 0.44, 0.54, 0.70$  and  $0.80$  were refined from  $\text{MoK}\alpha$  X-ray data. R indices were approximately 2-3% except for the 0.70 composition, for which four different refinements gave R indices of 5-8%. The  $\langle\text{P-O}\rangle$  distance was constant across the series, and the  $\langle\text{Al-O},\text{OH},\text{F}\rangle$  distances were a linear function of the  $F/(F+\text{OH})$  ratio. The Li position had an unusually high anisotropic temperature factor that increased with increasing F content; a split atom model was used and the splitting was a maximum at the  $\sim 0.70$  composition. The infrared spectrum of the near OH end-member showed a sharp peak at  $\sim 3390$  cm<sup>-1</sup>, corresponding to the principal (O-H) stretching band. With progressive F=OH substitution, this peak rapidly broadened and shifted to lower wave-numbers, reaching  $\sim 3355$  cm<sup>-1</sup> for  $F/(F+\text{OH})$  of  $\sim 0.70$ . All samples had a reasonably smooth envelope in this region, except for the 0.70  $F/(F+\text{OH})$  sample, which had a distinct shoulder on the high energy side of this band. The  $^3\text{P}$  MAS NMR spectra gave a broad  $^3\text{P}$  peak at  $-15.75$  ppm that was insensitive to  $F/(F+\text{OH})$  ratio. The  $^{27}\text{Al}$  spectrum gave a broad peak that decreased in width and shifted to slightly lower field with increasing F content. A TEM study is in progress to investigate the possibility of a variable domain structure across the series.