



**Experiment title:** CuGeO<sub>3</sub>: Structure determination of high pressure phase

**Experiment number:**

HC465

**Beamline:**

ID9

**Date of Experiment:**

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**Shifts:**

6

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**Report:**

At ID 9 we have performed high pressure monochromatic powder diffraction experiments of the insulating cuprate CuGeO<sub>3</sub> using gasketed diamond anvil cells and an image plate system. The compound CuGeO<sub>3</sub> crystallizes in a unique orthorhombic structure where edge-sharing chains of planar CuO<sub>2</sub> groups and tetrahedral Ge-O groups run along the c-axis. The primary aim of the study was to solve and refine the crystal structure of CuGeO<sub>3</sub> at pressures above the first-order structural phase transition which occurs near 6 GPa. This phase change had been detected earlier by Raman spectroscopy of single-crystal samples using hydrostatic pressure media.

The results from a 6-shifts experiment are as follows:

- 1) High precision lattice constants were obtained for the orthorhombic phase up to 6 GPa (see Fig. 1). In this low pressure range, we noticed a reaction of the sample with alcohol pressure media under monochromatic synchrotron irradiation. Switching to a chemically inert pressure medium (nitrogen) solved this the problem.
- 2) Phase transitions were reproducibly observed between 6 and 7 GPa. However, for the polycrystalline sample obtained by grinding single crystalline starting material, the transition was not to a single phase regime. In fact, diffraction patterns indicate the presence of at least 2 phases, independent of the pressure medium. This was unexpected and is in clear contrast to the behaviour of single crystal samples under fully hydrostatic pressure. By now it is known [1], that also in the case of single crystals the material shows transition to two other phases in the pressure range of 7 to 8 GPa, if the pressure conditions are not fully hydrostatic. Even though the powder diffraction experiments were performed with a essentially hydrostatic media, it appears that the intrinsic (surface) strain in the polycrystals

results in a pressure-induced transition to a mixture of phases. Analysis of the presently available data does not allow us to propose reliable crystal structures for all the different high pressure phases present in the transformed samples. One component can be indexed in the orthorhombic system (Pbmm,  $a=475.6$  pm,  $b=713.4$  pm,  $c=286.3$  pm at 11.3 GPa).

A further attempt will be made to produce a single phase high pressure modification of polycrystalline  $\text{CuGeO}_3$ . For such studies we have prepared as-grown polycrystalline material, and we plan to use helium as a pressure medium in order to avoid any mechanical effects from the pressure environment.

3) Based on Raman studies [1,2],  $\text{CuGeO}_3$  was believed to become amorphous at pressures above 14 GPa. In contrast, the present x-ray diffraction experiments clearly indicate the crystalline nature of  $\text{CuGeO}_3$  up to 22 GPa, the highest pressure investigated in the present experiment.

[1] A.R. Goñi, T. Zhou, U. Schwarz, R.K. Kremer, K. Syassen, *Phys. Rev. Lett.* **77**, 1079 (1996) *Pressure-temperature phase diagram of the spin-Peierls compound  $\text{CuGeO}_3$ .*

[2] T. Zhou, A.R. Goñi, S. Ves, R.K. Kremer, K. Syassen, *High Pressure Science and Technology*, edited by W. Trzeciakowski (World Scientific, Singapore 1996) p. 423 *Phase transitions of  $\text{CuGeO}_3$  at high pressures.*

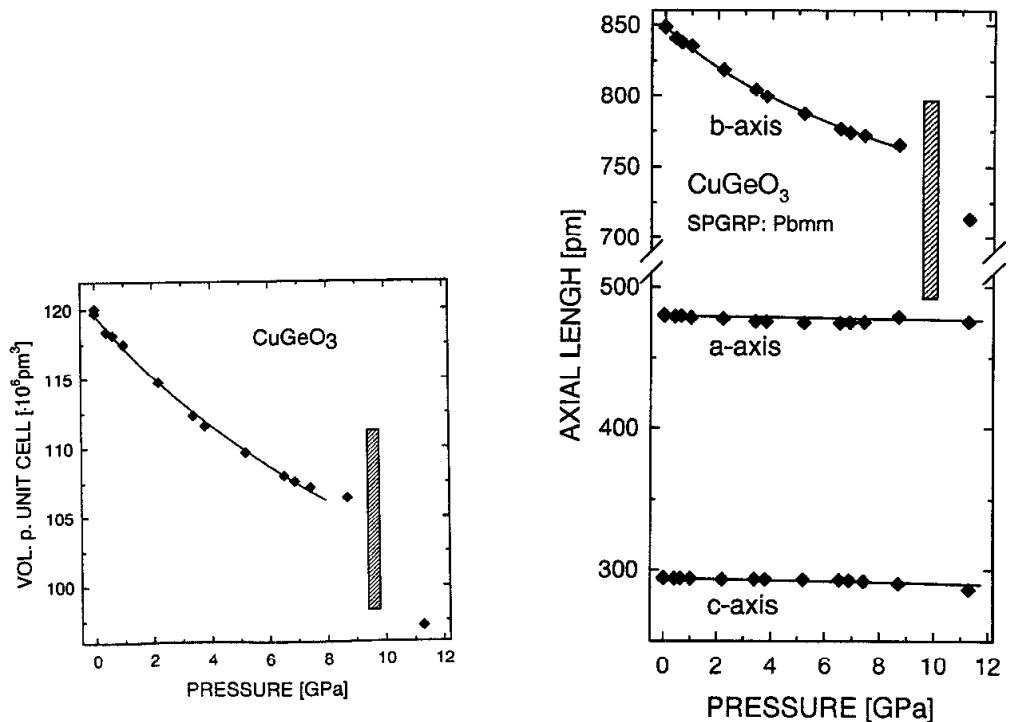


Fig. 1: Lattice parameters and volume of  $\text{CuGeO}_3$  as a function of pressure.