

Crystal structure of CuGeO_3 under pressure

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We have investigated the crystal structure of orthorhombic CuGeO_3 under hydrostatic pressure ($P < 6.5$ GPa, $T = 298$ K) using high-resolution angle-dispersive x-ray powder diffraction. A nonlinear compression behavior is observed for all three crystallographic axes. Full profile refinements of the diffraction patterns provide the internal structural parameters in the stability range of the ambient pressure phase. The main structural changes induced by pressure consist of tilting of the CuO_4 ribbons around the c axis and a large decrease of the Cu1–O1 bond distance. Possible implications of these results for the explanation of the strong pressure dependence of the spin-Peierls transition temperature are discussed. [S0163-1829(97)52242-9]

I. INTRODUCTION

The recent discovery of a spin-Peierls transition (SPT) in CuGeO_3 (Ref. 1) has stimulated several detailed investigations of the structural properties.^{2–6} CuGeO_3 crystallizes in an orthorhombic structure⁷ (space group $Pbmm$, $Pmma$ in standard setting) which contains ribbons of edge-linked planar CuO_4 units and corner-sharing chains of GeO_4 tetrahedra running parallel to the c axis. The chains are interconnected, forming rippled layers stacked in the a direction and separated by long Cu–O1 bonds (see Fig. 1). Below the SPT temperature the structure remains orthorhombic, but the unit cell doubles along the a and c directions.

In view of the strong correlation between structural, elastic, and magnetic properties in SPT systems, the study of CuGeO_3 at moderate pressures and low temperatures has become an issue of great interest.^{8–12} Energy-dispersive x-ray powder diffraction at 300 K (Ref. 13) has shown that the stability field of the ambient pressure phase extends up to about 6.5 GPa, where a first-order structural phase transition occurs. The new phase was tentatively identified as monoclinic.¹³ The occurrence of a phase transition near 6.5 GPa was recently confirmed by Raman scattering and optical microscopy.^{10,11,14,15} However, the behavior between 6.5 and 12 GPa is rather complex, with three phases being identified by optical methods.^{11,15}

We report here a high-resolution x-ray powder-diffraction study of CuGeO_3 at pressures up to 6.5 GPa. The primary motivation was to accurately determine the nonlinear pressure dependence of the unit-cell parameters and, in particular, to follow the changes in atom positional parameters. The x-ray scattering factors of the different atom species of CuGeO_3 are distributed quite inhomogeneously. This introduces larger errors in the determination of oxygen positions as compared to neutron-diffraction (ND) experiments. Thus, as a crosscheck we also performed ND measurements on the

same powder sample at ambient conditions and at 1 GPa pressure.

II. EXPERIMENTAL

The pressure-induced structural changes of CuGeO_3 were investigated by powder x-ray diffraction (XRD) at the European Synchrotron Radiation Facility (Grenoble) using monochromatic x rays (wavelength 45.49 pm) and image plate detection. The two-dimensional diffraction patterns were converted to intensity versus 2θ data employing the program *Fit2D*.¹⁶ High-resolution powder ND was performed on the instrument D2B ($\lambda = 1.5938$ Å) at the Institut Laue-Langevin (Grenoble). Refinements of the lattice constants and positional parameters from the powder patterns were performed using the program system *CSD*.¹⁷ The polycrystalline sample of CuGeO_3 was prepared by reacting CuO powder and GeO_2 powder (both 99.999%, Johnson Matthey) at 1000°C in a platinum crucible in air. This powder sample was used in all diffraction experiments without any further grinding.¹⁸ For the XRD experiments, pressure was generated in a diamond

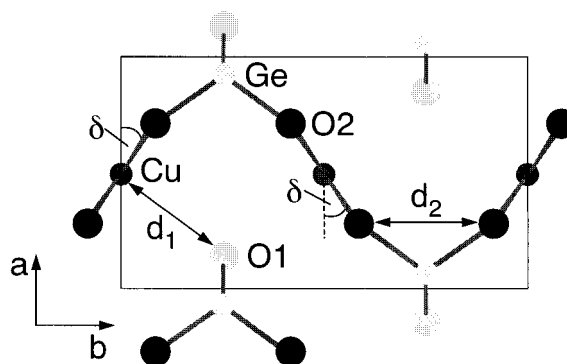


FIG. 1. View of the crystal structure of CuGeO_3 along the c direction (axes labeling according to space group $Pbmm$).

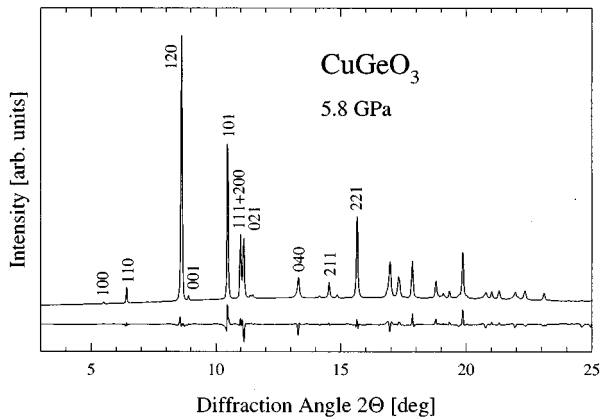


FIG. 2. X-ray powder-diffraction diagram of CuGeO_3 at 5.8 GPa. The lower curve represents the difference between experimental and refined profile.

anvil cell (DAC) using nitrogen or a 4:1 mixture of methanol/ethanol as pressure media. Pressure was determined by the ruby luminescence method. Visual inspection of samples immersed in the alcohol mixture showed burned spots after exposure to the x-ray beam when the pressure was below about 3 GPa. The corresponding diffraction patterns contained additional reflections of a second unidentified phase. Thus, XRD measurements with alcohol as pressure medium were done after applying an initial pressure of at least 3 GPa. In the ND experiment at $P=1$ GPa pressure was generated in a stainless steel clamp-type cell with Fluorinert as pressure medium.

III. RESULTS AND DISCUSSION

A typical XRD pattern of CuGeO_3 measured at 5.8 GPa is displayed in Fig. 2. The lower curve in Fig. 2 represents the difference between the experimental pattern and the profile calculated with refined structural parameters. In general, the quality of the high-pressure XRD diagrams was sufficient for full profile refinements of the lattice constants and positional parameters of Cu, Ge, and O. On the average, the residuals for intensities and profiles amounted to $R_1=0.08$ and $R_p=0.13$. Here, R_1 refers to intensities in peak regions only. Due to the needlelike shape of the crystallites, the XRD diagrams are affected by a nonstatistical distribution of powder particle orientations. In DAC experiments crystallites were found to be preferentially oriented with the [001] direction (needle axis) parallel to the diamond tips. A correction for preferred orientation was taken into account in the refinements. Refined parameters for the diagram in Fig. 2 are listed in Table I together with corresponding zero pressure data.

Figure 3 displays the pressure dependence of the lattice parameters and the volume. The compression is highly anisotropic, the soft direction being the b axis which up to 6 GPa decreases by 8%. The corresponding changes in the c axis (a axis) are only -0.5% (-1.2%). The solid line drawn through the volume data points corresponds to the result of a least squares fit of a Murnaghan relation¹⁹

$$V/V_0 = [1 + (B'/B_0)P]^{-1/B'}, \quad (1)$$

TABLE I. Refined structural parameters of CuGeO_3 at zero pressure and at 5.8 GPa, as obtained from XRD data of powder samples. The quantities given are cell volume V , lattice parameters a , b , and c , and those positional parameters which are not fixed by the space group symmetry ($Pbmm$). The temperature factors were assumed to be isotropic. For comparison, the ND results at 0 GPa are listed also.

Quantity	ND, 0 GPa	XRD, 0 GPa	XRD, 5.8 GPa
V (pm^3)	119.78(10)	119.71(10)	109.22(50)
a (pm)	479.88(20)	479.88(20)	474.91(60)
b (pm)	848.25(30)	847.95(40)	784.95(80)
c (pm)	294.25(8)	294.19(10)	292.99(60)
x/a (Ge1)	0.0738(5)	0.0767(5)	0.0527(8)
x/a (O1)	0.8619(7)	0.856(2)	0.837(4)
x/a (O2)	0.2848(6)	0.284(2)	0.268(2)
y/b (O2)	0.0834(3)	0.0827(9)	0.0693(14)

where V_0 , B_0 , and B' are volume, bulk modulus, and its pressure derivative at $P=0$ GPa. A nonlinear pressure dependence is evident for all three lattice parameters. We have fitted the normalized lattice parameter values by a similar relation, where we denote the corresponding modulus (the inverse of the linear compressibility) and its pressure derivative by β_0 and β' , respectively.²⁰ The fitted parameters are summarized in Table II.

The value of $B'=8.5$ is significantly larger compared to values around 4 to 6 which are typical for many isotropic materials. It compares well with data for graphite,²¹ which is the archetype material with strongly anisotropic compression behavior. The values for the linear moduli β_0 differ from the results of Adams *et al.*¹³ (see Table II) partly because they averaged over the pressure range 0–7 GPa. The compression of the c axis is weakly nonlinear in pressure; a linear behavior would fall outside the correlated 95% probability limits of the parameter values (c.f. Table II). The compression of the a axis is anomalous, indicating an unusually strong decrease of the compressibility with increasing pressure. Such

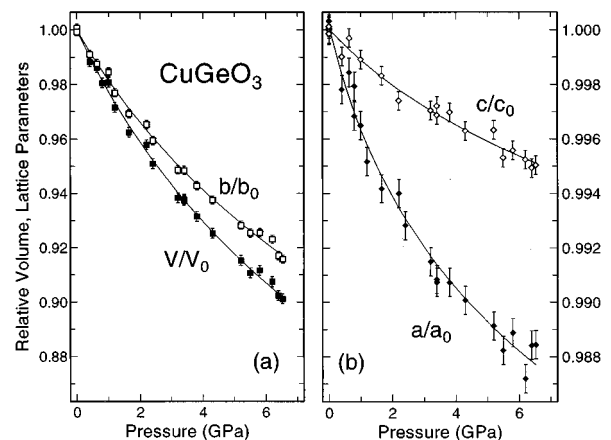


FIG. 3. Relative volume and lattice parameters of CuGeO_3 as a function of pressure. Solid lines correspond to least-squares fits of Murnaghan-type relations. Note the expansion of the vertical scale in (b) by a factor of 10 as compared to (a).

TABLE II. Parameters obtained from fits of Eq. (1) to the experimental data for volume V and lattice parameters a , b , and c of CuGeO_3 under pressure. The bulk modulus and its pressure derivative at zero pressure are denoted as B_0 and B' , respectively, and β_0 and β' are the corresponding parameters describing the compression of crystal axes. See Table I (XRD column) for the zero pressure values of volume and lattice constants.

Data	B_0, β_0 (GPa)	B', β'	$\bar{\beta}^a$ (GPa)
V	39.5(30)	8.5(15)	
a	201(40)	135(30)	91
b	49.2(45)	9.3(20)	56
c	845(240)	170(120)	310

^aRef. 13, averaged over a pressure range of 0–7 GPa.

a behavior appears plausible in view of the large compression along the b axis and the strong reduction of the Cu–O1 bond length (see below).

Figure 4 shows selected interatomic distances and bond angles as a function of pressure. The ND results obtained for the same sample material are also shown in Fig. 4. At ambient pressure our ND data agree, within mutual experimental errors, with corresponding results for single crystal samples.⁶ Here, the ND data serve in part as a reference for the reliability of the analysis of the powder XRD data. We find good agreement between our zero pressure XRD and ND results (see Table I).

The main results regarding changes in interatomic distances and bond angles under pressure can be summarized as follows: (1) The distances within the basic building blocks of the structure (the CuO_4 rectangles and GeO_4 tetrahedra) remain almost constant within the average scatter of the x-ray data points. The weak effect of pressure on the Cu–O2 distance is consistent with the small change in the c axis (see Fig. 3). (2) The Cu–O2–Cu bond angle, which partly determines the character and strength of the exchange interaction between neighboring Cu atoms (see, e.g., Ref. 6), is essentially constant to within 1° . (3) A major effect, directly related to the shortening of the b axis, consists of a tilting of the Cu–O2 planes towards the c axis ($\Delta\delta/\Delta P = -1.27(20)$ deg/GPa). (4) The interlayer Cu–O1 distance d_1 undergoes a large change [$\Delta d_1/\Delta P = -3.7(4)$ pm/GPa], at 6 GPa it is reduced by 9%. Consequently, if one considers the coordination of Cu as a distorted octahedral one, the distortion is reduced significantly. Nevertheless, even at 6 GPa a distance of $d_1 = 250$ pm is relatively large and does not readily fit the notion of an octahedral coordination of Cu. We note, that d_1 becomes very similar to a Cu–O distance reported for the compound Cu_2GeO_4 , a decomposition product of CuGeO_3 at high pressures and elevated temperatures.²²

The structural changes as a function of decreasing temperature reported by Braden *et al.* are qualitatively similar,⁶ i.e., the most pronounced effects between 298 and 20 K are a decrease of δ by 0.8° and a relatively large reduction of the Cu–O1 distance by 1%.

The SPT temperature T_{SP} is strongly pressure dependent,^{9,11} it increases from about 14 K at zero pressure to 25 K at 3 GPa. This leads to the question whether the structural changes reported here have some relevance for the

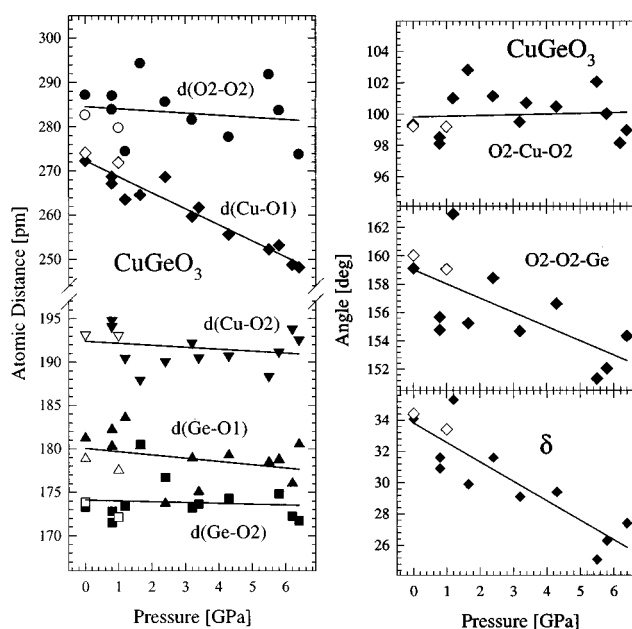


FIG. 4. Selected interatomic distances and bond angles in CuGeO_3 as a function of pressure. Closed and open symbols refer to x-ray and neutron-diffraction results, respectively. Solid lines correspond to results of linear regressions.

explanation of the positive pressure dependence of T_{SP} on a microscopic scale. Assuming that magnetic interactions contribute to driving the SPT, one would look for a structural feature which, by applying pressure, increases the superexchange interactions between neighboring Cu ions given the fairly rigid CuO_4 units. One possibility would be the sensitivity of the superexchange to side groups coupled to the O2 atoms, i.e., the Ge–O2 bonds. The angle between these bonds and the Cu–O2 planes may significantly modify the Cu–Cu exchange interaction by changing the relative stability of the oxygen $p_{x,y}$ orbitals.²³ However, this angle (denoted O2–O2–Ge in Fig. 4) changes from 159 to 156° at 3 GPa. It is difficult to imagine that such a small change could cause an increase of T_{SP} by almost a factor of 2. Alternatively, one would consider a scenario where the minimization of elastic energies is the main driving force for the structural changes below T_{SP} . In this case, in addition to the change of the O2–O2–Ge bond angle, one also has to take into account the increase of interlayer coupling, as evidenced by the strong pressure dependence of d_1 .

The present paper is limited to the stability field of the orthorhombic low-pressure phase of CuGeO_3 . Using single crystals, the phase transitions occurring above 6.5 GPa are easily detected by visual observation. The actual phase transition sequence under pressure and its reversibility depends strongly on the degree of hydrostaticity of the pressure medium.^{11,15} We have experienced some difficulties in XRD studies of these phase transitions when *polycrystalline* starting material is used. In this case the structure determination of the high-pressure phases is complicated by a sluggish transition behavior and the presence of phase mixtures with varying relative amounts in different runs. At this point we only like to mention, that above 6.5 GPa we could not reproduce a diffraction pattern consistent with the proposed

monoclinic phase.¹³ Furthermore, Raman spectra taken at pressures above 14 GPa were interpreted in terms of a gradual transition to a highly disordered phase.^{10,14} The compound has, however, not become completely amorphous in our XRD studies. Thus, the indication for amorphization seen in Raman scattering may eventually turn out to be another crystal-crystal transition of CuGeO₃.

In conclusion, the compression of the orthorhombic low-pressure phase of CuGeO₃ is highly directional along the *b* axis. The overall axial compression at 6 GPa is a factor of 15 (6) smaller along the *c*–(*a*–) direction. Structural parameters describing the planar and tetrahedral oxygen coordination of Cu and Ge atoms, respectively, exhibit only a weak pressure dependence. A major rearrangement of the stiff building blocks (Cu–O₄ units and GeO₄ tetrahedra) on applying pres-

sure consists of a tilting of the CuO₂ chains around the *c* axis (direction of the Cu–O₂ ribbons), resulting in a reduction of the tilt angle δ by about 6 deg at 6 GPa. Furthermore, the Cu–O1 distance decreases by about 24 pm at 6 GPa. This behavior mimics the structural changes which occur on cooling down CuGeO₃ at ambient pressure.

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