

Pressure-Temperature Phase Diagram of the Spin-Peierls Compound CuGeO_3

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Using Raman scattering we have mapped out the phase diagram of CuGeO_3 at temperatures from 3 to 300 K and pressures up to 11 GPa. At 300 K and above 6 GPa we identify three high-pressure phases. Details of the phase transition behavior including reversibility depend on the shear strength of the pressure medium. The present results do not support the recent claim that the structural behavior is affected by intercalation. Low temperature (LT) Raman spectra show that the spin-Peierls transition temperature (14.3 K at $P = 0$) increases to 25 K at 3 GPa. Above this pressure a new LT phase is observed. The phase stable above 6.6 GPa (hydrostatic conditions) exhibits, upon cooling, an additional Raman feature near 46 cm^{-1} , which we tentatively assign to a singlet-triplet spin excitation. [S0031-9007(96)00784-3]

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The recent discovery of a spin-Peierls (SP) phase of CuGeO_3 occurring below 14 K [1] has triggered a large number of investigations concerned with the characterization of its structural [2], thermodynamic [3,4], and magnetic properties [5] at ambient pressure. The unique orthorhombic crystal structure of CuGeO_3 [6] is characterized by chains of planar CuO_4 units and corner-sharing chains of GeO_4 tetrahedra running parallel to the c axis (see Fig. 1). The chains are interconnected forming rippled layers stacked in the a direction and separated by long Cu-O(1) bonds. For an open structure like CuGeO_3 the application of high pressure provides a means of inducing major structural changes involving a higher effective coordination of the metal ions. X-ray powder diffraction [7] has revealed a first order structural phase transition occurring at 6.6–7.3 GPa ($T = 300 \text{ K}$). This new phase was tentatively identified as monoclinic. The occurrence of a phase transition near 6.5 GPa was confirmed more recently by Raman scattering and by optical microscopy [8,9]. Furthermore, between 14 and 20 GPa CuGeO_3 undergoes a sluggish transition towards an amorphous phase, as is indicated by the disappearance of Raman activity [8,9].

In view of the strong relationship between structural, magnetic, and elastic properties in spin-Peierls compounds the study of the high pressure behavior of CuGeO_3 at low temperatures has become an issue of great interest. For example, magnetic susceptibility measurements below 1 GPa indicate an *increase* of the SP-transition temperature T_{SP} with pressure, and evidence for the existence of a ferromagnetic phase at 10 K and above 4.5 GPa was also obtained [10]. The associated structural changes still need to be clarified.

This Letter reports a detailed characterization of the different crystalline phases of CuGeO_3 for pressures up to 11 GPa and temperatures between 3 and 300 K using Raman spectroscopy. At room temperature CuGeO_3 transforms reversibly at 6.6 GPa to a phase characterized by a $\sim 20\%$ reduction of the b axis (denoted in the following as phase II). This transition is observed only in fluid

pressure-transmitting media like alcohol mixtures as well as condensed He [9]. Our observations do not support the recently proposed hypothesis [9] that a pressure-induced intercalation is involved in the transition to phase II near 6.6 GPa. This transition, however, is suppressed in solid pressure media such as Xe or CsI. Instead, two successive transformations to phases denoted IIa and IIb occur at 7.5 and 9.5 GPa, respectively, with no noticeable change in sample dimension but pronounced color changes.

From the changes of the low temperature (LT) Raman spectra we have determined the pressure dependence of the SP-transition temperature up to 2.8 GPa. Above this pressure we have found a new LT phase (Ib) characterized by the appearance of new Raman lines. Finally, we have obtained indications for magnetic spin-flip excitations in phase II.

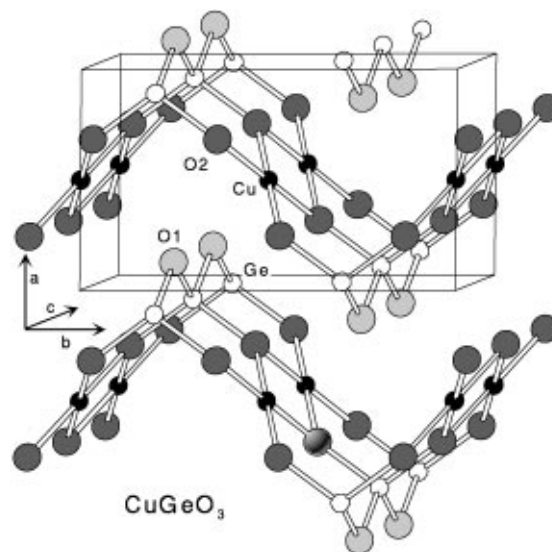


FIG. 1. View of the crystal structure of CuGeO_3 at ambient conditions. The orthorhombic unit cell is indicated. In this figure and throughout the paper axes are denoted according to space group $Pbmm$.

Needle-shaped single crystals of CuGeO_3 were grown from a 1:1.2 mixture of GeO_2 and CuO as described elsewhere [11]. Samples were cleaved to a thickness of about $30 \mu\text{m}$, cut into pieces about $100 \times 100 \mu\text{m}^2$ in size, and then loaded into a diamond-anvil cell (DAC). Room temperature experiments were performed in different pressure media providing either fully hydrostatic (He, alcohol mixtures) or quasihydrostatic (Xe, CsI) conditions. For LT experiments only He was used as a pressure medium in order to ensure the best possible hydrostatic sample environment. Pressure was measured *in situ* using the ruby luminescence method with appropriate temperature correction of the ruby calibration [12]. Raman spectra in backscattering geometry were excited with the 5145 \AA line of an Ar^+ ion laser and recorded employing a triple spectrograph coupled to a multichannel detector.

We first present results obtained for the phase stability at room temperature. Figure 2 shows unpolarized Raman spectra of a CuGeO_3 single crystal measured at 296 K for different pressures and using different pressure-transmitting media. At zero pressure we observe almost all the Raman-allowed modes expected for the orthorhombic phase I [13]. All mode frequencies increase with increasing pressure [14]. When a liquid or fluid pressure medium like an alcohol mixture or condensed He is used, CuGeO_3 undergoes a phase transition at 6.6(2) GPa. A typical Raman spectrum of phase II for 8.8 GPa is shown in Fig. 2. In the new phase the number of Raman modes is almost doubled, suggesting a doubling of the unit cell in at least one direction. The I-II transition is characterized by a 20% reduction of sample dimension in the b direction, which can be easily followed under the microscope [9]. This macroscopic change is most likely related to an

enhanced corrugation of the layers in the b - c planes (see Fig. 1). At the phase transition, the color changes from blueish to greenish. Optical absorption experiments [8,15] show that this weak color change is due to the shift of a near-UV absorption edge to lower energies as well as a blueshift by about 0.1 eV of overlapping Cu^{2+} crystal field (CF) transitions centered near 1.7 eV [16,17]. Although the phase transition is of first order, it is fully reversible with very little hysteresis.

We emphasize that the pressure value for the I-II transition as well as the Raman and absorption spectra of phase II are not affected by the chemical nature of the pressure medium. In particular, the phase transition is also observed in chemically inert helium. Therefore, we rule out the possibility that intercalation of the pressure medium (involving a chemical reaction) plays a role in the phase transition behavior. Also, the mode frequency vs pressure behavior of phase I shows no evidence for diffusion of helium into the lattice.

The pressure-induced transition from phase I to II is suppressed in *solid* pressure media. Raman scattering as well as optical microscopy studies indicate a different pressure behavior of CuGeO_3 when Xe or CsI is used. By raising the pressure in the first run to about 7.5–8 GPa the sample starts to turn deep blue (azuritelike) in transmitted light. With further increase of pressure it becomes dark green (malachitelike) above 9.5 GPa. For both new high-pressure phases, labeled hereafter as IIa and IIb, no change in sample dimension is observed. Representative Raman spectra of these phases obtained with a Xe medium are shown in the upper half of Fig. 2. Optical absorption measurements show that the change to blue color in phase IIa is related to the shift from 1.7 to 2.1 eV of an absorption band arising from CF excitations of the Cu^{2+} ions. In phase IIb the highest energy CF transition shifts back to about 1.7 eV, but a near-UV absorption edge moves into the blue spectral range. This explains the darker green color of phase IIb compared to phase II. Upon releasing the pressure, the sample transforms back from phase IIb to IIa at pressures around 5 GPa. The blue phase IIa persists and is recovered in metastable form at $P = 0$.

The structural behavior of CuGeO_3 under pressure thus depends critically on the degree of hydrostaticity. The large change in sample shape associated with the I-II phase transition requires the pressure medium to flow. In a solid medium this transition is apparently inhibited due to the finite shear strength of the medium. This, for instance, also explains why the I-II transition was not observed neither when only CuGeO_3 powder was loaded into the DAC nor for solid Ar or H_2O as pressure medium [9]. Obviously, in a solid pressure medium a different route of structural changes is imposed, which for the blue phase IIa results in an oxygen coordination of Cu giving rise to a significant modification of CF splittings.

We now turn to the discussion of the LT results. At ambient pressure five new modes have been observed in the Raman spectrum of CuGeO_3 below T_{SP} , which are

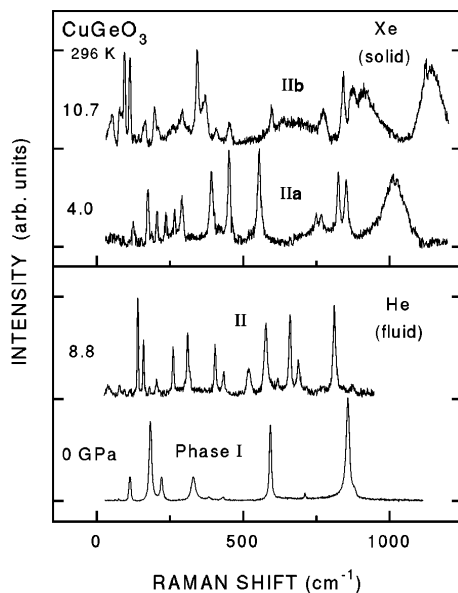


FIG. 2. Room temperature Raman spectra of four different phases of CuGeO_3 . For clarity the spectra are displaced vertically. The 4.0 GPa spectrum of phase IIa was taken when releasing the pressure in a run which went up to 11 GPa.

characteristic for the spin-Peierls phase [18]. The new modes most probably correspond to vibrations involving Cu and O(2) atoms, which become Raman allowed due to a lowering of a crystal symmetry. Figure 3 shows two Raman spectra at 0 GPa for temperatures above and below T_{SP} . In the SP phase three additional peaks, indicated by arrows, are clearly seen for this particular sample orientation in the 5 K spectrum.

We have used the appearance of the new modes below T_{SP} to determine the pressure dependence of the spin-Peierls transition temperature T_{SP} by Raman spectroscopy. In order to ensure the best possible hydrostatic conditions, pressure changes were always made near 300 K. The results for T_{SP} versus pressure are displayed in the inset to Fig. 3. We find that T_{SP} increases sublinearly with pressure P . A quadratic fit yields $T_{SP}[\text{K}] = 13.8(5) + 5.5(8)P - 0.6(5)P^2$, where pressure P is in GPa. The large positive pressure coefficient, which is in good agreement with results of magnetic susceptibility measurements up to 1 GPa [10] and estimates based on ambient pressure thermal expansion and specific heat experiments [4], cannot be accounted for by only considering a possible enhancement of magnetic interactions. The increase under pressure both of T_{SP} and of the spin-Peierls gap [19] speak for a decrease of the cost in elastic energy related to the three-dimensional lattice distortion, favoring dimerization at higher temperatures.

The additional Raman lines of the spin-Peierls phase decrease in intensity with increasing pressure and are no longer observed above 3 GPa. Instead, for pressures $3 < P < 6$ GPa and temperatures $T < 180$ K the Raman spectra indicate the existence of a new crystalline phase of CuGeO_3 (denoted as Ib). Two additional peaks at 150 and

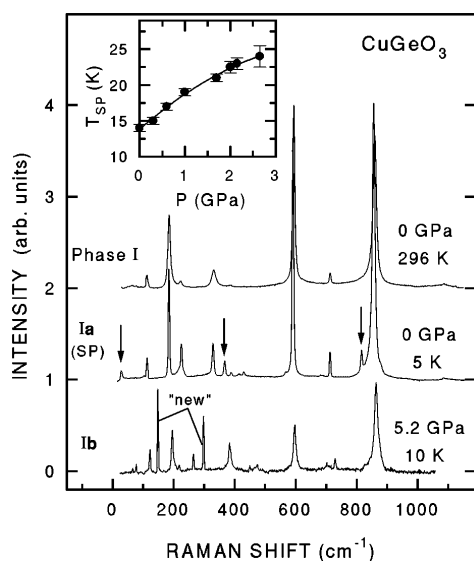


FIG. 3. Raman spectra of the spin-Peierls phase (Ia) and the second low-temperature phase (Ib) of CuGeO_3 . For comparison, a spectrum taken at ambient conditions is also shown. Arrows point to additional Raman lines appearing in the spin-Peierls (SP) phase. The inset shows the SP transition temperature versus pressure.

300 cm^{-1} are prominent, as shown in Fig. 3 for a spectrum at 5.2 GPa. The observation of just a few new Raman modes in addition to those of phase I is indicative of a slightly distorted crystal structure in the LT phase Ib. The transition between phase I and Ib is reversible.

Our results obtained by Raman scattering concerning the different phases of CuGeO_3 under hydrostatic conditions are summarized in the pressure-temperature phase diagram displayed in Fig. 4. The solid lines represent phase boundaries and are drawn as a guide to the eye. At pressures above 4 GPa the I-Ib phase boundary runs nearly parallel to the liquid-solid line of He [20]. Thus, we cannot rule out the possibility that at these pressures the course of the I-Ib phase boundary is affected by the presence of a weak shear stress component in solid He.

Recently, Takahashi *et al.* [10] reported evidence of ferromagnetic behavior in CuGeO_3 near 4.5 GPa and below 10 K. It is not clear at this point if ferromagnetism is characteristic for the phase Ib identified in this work, because the magnetic susceptibility measurements were carried out in a nonhydrostatic medium. In view of the sensitivity of the structural behavior to nonhydrostatic stresses and the close relation between copper coordination and magnetic interactions [21], the experimental observations may depend very much on the pressure medium used in the particular study.

Evidence for magnetic excitations in the phase II of CuGeO_3 is obtained from LT Raman measurements. Figure 5 shows spectra taken at 8.2 GPa for different temperatures. An additional, relatively broad feature at 46 cm^{-1} is apparent from the spectra. In contrast to the phonon

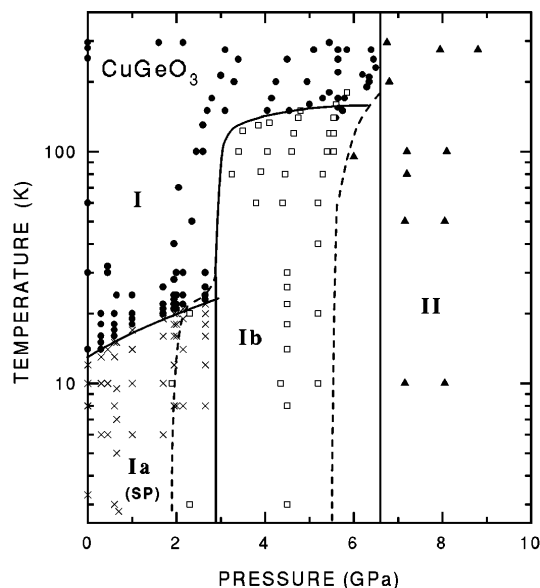


FIG. 4. Temperature-pressure phase diagram of CuGeO_3 as determined from Raman scattering under hydrostatic conditions. Solid lines are a guide to the eye and represent phase boundaries obtained upon increasing pressure. The dotted lines indicate the approximate width of hysteresis ranges. Each data point corresponds to a measurement of the characteristic Raman spectrum of each phase.

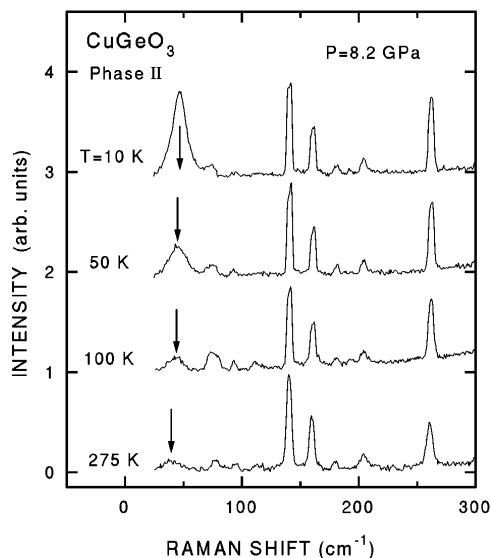


FIG. 5. Raman spectra of phase II of CuGeO_3 recorded at 8.2 GPa for different temperatures. The feature at about 46 cm^{-1} is tentatively attributed to a magnetic excitation.

peaks, the intensity of this peak decreases with increasing temperature but is still observable at 275 K. The logarithm of the integrated intensity (area under the peak) versus the inverse temperature exhibits a thermally activated behavior with an activation energy of $5(2) \text{ meV}$, in good agreement with the excitation energy of $5.7(1) \text{ meV}$ at 10 K.

We tentatively assign the low-energy peak at $5.7(1) \text{ meV}$ to a magnetic excitation at the energy of a spin-flip gap. Without a detailed knowledge of the crystal structure of phase II, we can just speculate about the origin of such a singlet-triplet spin gap. It is likely that the enhanced layer corrugation along b (characteristic for phase II) leads to a distortion of the Cu chains and to the formation of Cu dimers. As a mechanism for this pressure-induced distortion we may consider an alternating tilting of rigid corner-sharing GeO_4 tetrahedra along the c axis. This would result in a doubling of the unit cell in the c direction consistent with the observed changes in the Raman spectra. Further interpretation requires a crystal structure determination of the high-pressure phase II.

In summary, using Raman scattering we have investigated the pressure-temperature phase diagram of CuGeO_3 under hydrostatic as well as quasihydrostatic pressure conditions. We have clarified the issue concerning the observation of different phase transitions at 300 K when different pressure-transmitting media are used. The controlling factor is not the previously proposed intercalation of alcohol, but the shear strength of the pressure medium. From LT Raman experiments under hydrostatic conditions we have determined the pressure dependence of the spin-Peierls transition temperature up to 3 GPa, and we have discovered a new LT phase for $3 < P < 6 \text{ GPa}$. We have also observed Raman scattering by magnetic excitations in phase II, which we attribute to the opening of a spin-flip gap.

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