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# Alternating current calorimetry under hydrostatic pressure on pure and Zn-doped $\text{CuGeO}_3$

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## Abstract

We have studied the evolution of the spin–Peierls temperature  $T_{SP}$  in pure and 2% Zn-doped  $\text{CuGeO}_3$  as a function of hydrostatic pressure  $P$  up to 9 GPa. The transition temperature has been determined by ac-calorimetry measurements inside anvil cells under high-quality hydrostatic conditions achieved by using helium or argon as the transmitting medium. The pressure was tuned in a continuous way at low temperature, which enables us to explore the diagram  $T_{SP} = f(P)$  very precisely. We have shown that, in the two compounds,  $T_{SP}$  increases with  $P$  up to the highest pressure we reached. Moreover, two different linear stages are clearly evidenced. Both features could be consequences of the existing frustration due to the second-neighbour magnetic interaction.

## 1. Introduction

Since the discovery of a spin–Peierls transition in the inorganic compound  $\text{CuGeO}_3$  by Hase *et al* [1], the physics of low-dimensional magnetic systems has received a great deal of interest and many results have been obtained on this compound (for a review, see [2]). The spin–Peierls transition occurs in spin-1/2 antiferromagnetic chain systems, where spin–lattice coupling leads to a structural and magnetic phase transition, between a uniform (U) phase above the spin–Peierls temperature  $T_{SP}$  and a dimerized (D) phase below  $T_{SP}$ . In this D phase, distances and magnetic exchanges between nearest-neighbour spins along the chains alternate, and a gap  $\Delta_{SP}$  appears between the singlet ground state and the first excited state in the magnetic excitation spectrum. In  $\text{CuGeO}_3$ , substitution of Cu by a small amount of Zn (or Ge by Si) leads to a strong decrease of  $T_{SP}$  with doping and to the appearance of a three-dimensional antiferromagnetic order at low temperature [3].

In such systems, where structural, magnetic and elastic properties are strongly correlated, hydrostatic pressure  $P$  is a pertinent parameter to induce changes in the coupling, and therefore in the properties of the system. In pure  $\text{CuGeO}_3$ , Raman [4] and neutron-scattering [5]

experiments, as well as ultrasonic velocity measurements [6], have evidenced an increase of  $T_{SP}$  with  $P$  ( $+4.5 \text{ K GPa}^{-1}$ ) for pressures up to 2 GPa. This increase of  $T_{SP}$  is enhanced in Zn-doped  $\text{CuGeO}_3$  ( $+8 \text{ K GPa}^{-1}$ ) in the same pressure range, as reported by Fischer *et al* [7] from Raman and magnetic susceptibility measurements. At present, no results have been reported about the behaviour of  $T_{SP}$  at higher pressures (due to the insulating nature of these compounds, resistivity measurements cannot be performed). Recent instrumental developments in our laboratory allowed us to perform ac-calorimetry measurements under pressure up to 10 GPa with very homogeneous hydrostatic conditions [8].

## 2. Experiments

Single crystals of  $\text{CuGeO}_3$  and  $\text{Cu}_{0.98}\text{Zn}_{0.02}\text{GeO}_3$  were synthesized by a floating zone method. Pieces of  $150 \times 150 \times 50 \mu\text{m}^3$  were cut from small cleaved  $50 \mu\text{m}$  thick slices.

Measurements were carried out in two different pressure cells. The first one was a conventional ‘piston–cylinder’ assembly with 0.7 mm diameter diamond anvils and a stainless steel gasket. The second one was a *Merrill–Bassett* cell with 1.5 mm diameter sapphire anvils and a copper–beryllium gasket. In order to insure good hydrostatic conditions up to 10 GPa,  $^4\text{He}$  as well as argon were used as the pressure transmitting medium. The precise pressure value was determined at low temperature by using the ruby fluorescence technique. Experiments were performed in a  $^4\text{He}$  cryostat and we used a mechanical device to tune the pressure at low temperature in a continuous way [9]: a bellows operated by  $^4\text{He}$  gas under pressure generates a force which is amplified by levers up to a maximum of 25 000 N and is directly transmitted to the mobile part of the cell. The complete experimental set-up (figure 1) allows us to sweep the pressure in steps smaller than 0.2 GPa and to determine the resultant value with a sensitivity better than 0.1 GPa.

Ac-calorimetry measurements are based on the detection of temperature oscillations induced when an alternating heating power is provided to the sample [10, 11]. In our experimental device (figure 1), the power is supplied by the beam of an argon ion laser, mechanically chopped at frequency  $f$ , and transmitted to the pressure chamber via an optic fibre. Inside the pressure chamber, a gold–iron/gold thermocouple is introduced to detect the temperature oscillations inside the sample. The thermocouple is attached to the sample with GE varnish. As  $\text{CuGeO}_3$  is a transparent material, the sample has been blackened with ink in order to absorb heating power. Gold and gold–iron flattened wires are used to insure electrical continuity between the thermocouple and the outside of the chamber and are insulated from the gasket by means of a fine layer of epoxy. The thermocouple signal, which is related to the temperature oscillation via its thermoelectric power  $S$ , is detected at frequency  $f$  with a lock-in amplifier. In ac-calorimetry, the frequency must be low enough that internal thermal equilibrium can be achieved, but high enough to insure a suitable thermal decoupling between the sample and the transmitting medium, via a conductance  $K$  ( $f \sim 4 \text{ kHz}$  in our experiments). In this configuration, the thermocouple voltage follows the temperature oscillation of the sample. Using complex notation, the temperature oscillation can be roughly related to the heating power  $p = P_0 \cos \omega t$  by the formula

$$T_{ac} = P_0 / (K + iC\omega), \quad (1)$$

where  $C$  is the heat capacity of the sample. Expression (1) is only valid when the thermal link between the sample and the heat sink can be approximated by a pure conductance  $K$  with no heat capacity. This is not the case for helium but our tests in frequency showed that (1) remains a good approximation, at least in an argon filled shell. Thus, the measured signal  $V_{ac} = ST_{ac}$  contains information about the specific heat and anomalies in  $C$  can be precisely detected.

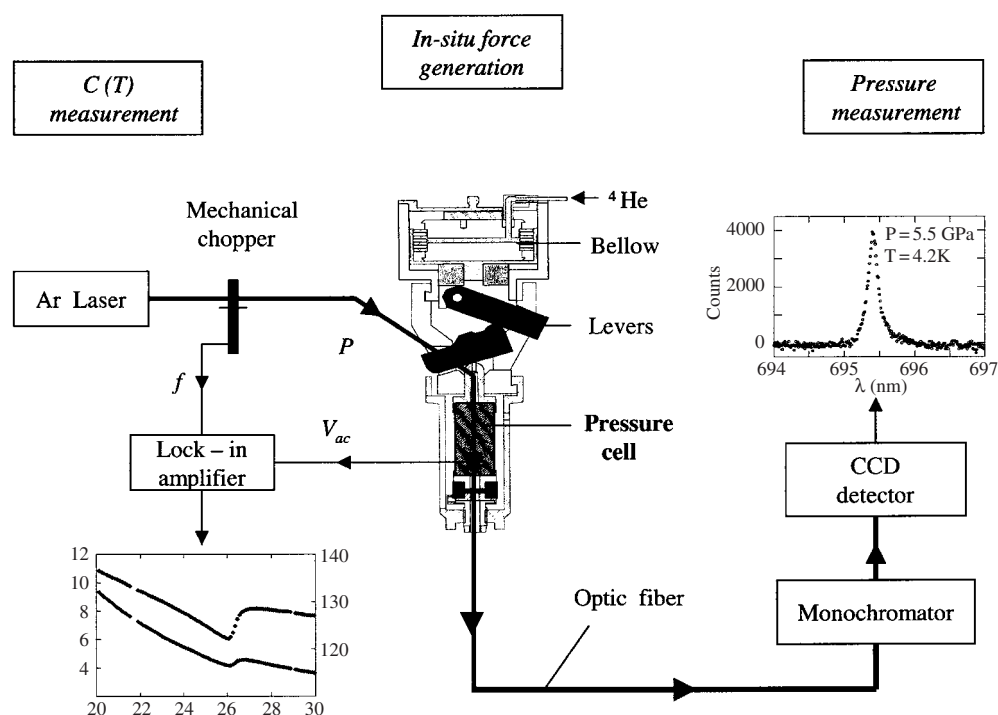
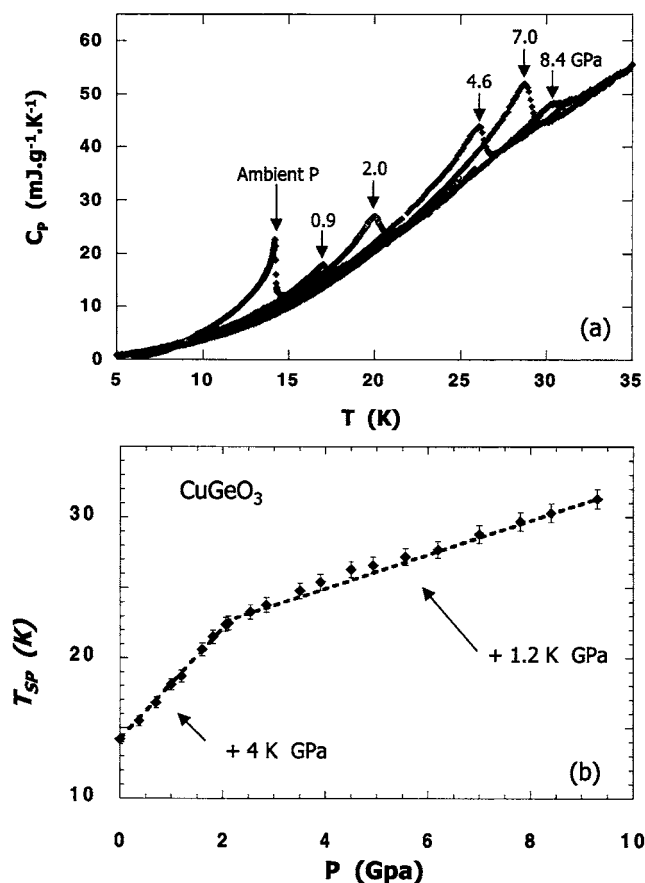


Figure 1. Schematic view showing the three main parts of the experimental set-up.

However, it is difficult to extract quantitative values of  $C$  for several reasons. First of all, the effective heating power reaching the sample is not known. Secondly, the contribution of the environment (mainly the transmitting medium) to the measured heat capacity cannot be evaluated. Moreover, this external contribution depends on the thermal contact between the sample and the thermocouple, which can change with the pressure. Nevertheless, it is possible to extract estimated values for  $C$  and  $K$  by performing two measurements at low ( $f \sim 300$  Hz) and high ( $f \sim 4$  kHz) frequency at the same pressure. More details concerning this experimental part can be found in [8].

### 3. Results

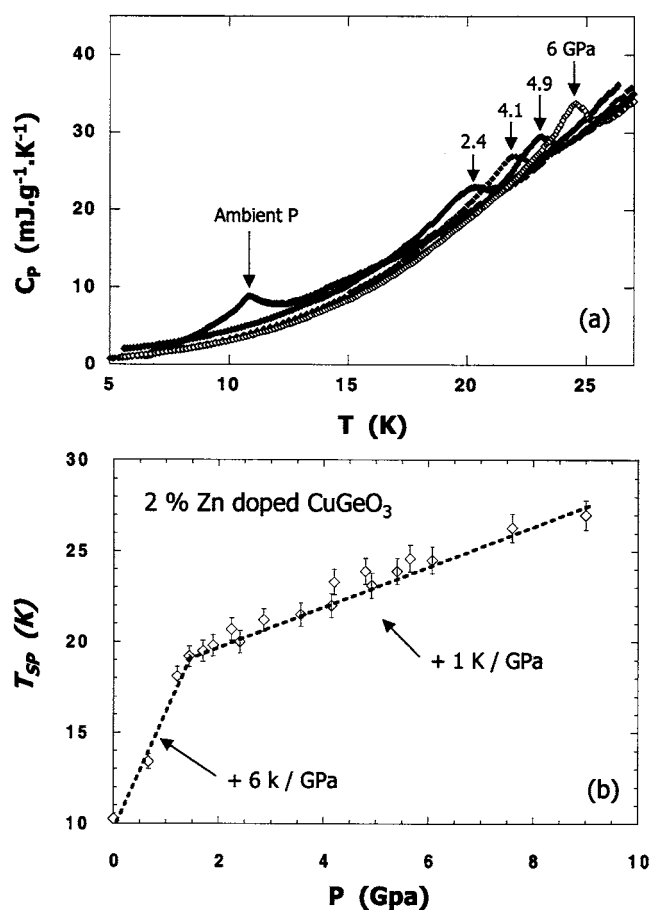
In figure 2(a) we have reported the temperature dependence of the heat-capacity component of the ac-calorimetry signal for pure  $\text{CuGeO}_3$  at different pressures. The presented curves have been extracted from measurements carried out in a cell with argon as the pressure transmitting medium. Liquid helium was used inside a different cell in order to compare the external contributions to the recorded signal. In the case of helium, we managed to extract the anomaly temperature from the phase component, but not from the real part of the signal. The  $C(T)$  curves in figure 2(a) have been renormalized with regard to a  $P = 0$  measurement carried out on the same sample by using an adiabatic method, which allows us to obtain the absolute value of the specific heat. The plotted data at  $P \neq 0$  are closed to the real specific heat but still contain a heat capacity contribution due to the environment: thus the observed change in the anomaly shape above 7 GPa cannot be unambiguously attributed to a true decrease of the sample's specific heat. Nevertheless, our measurements allow us to determine the evolution



**Figure 2.** Results of ac-calorimetry measurements under pressure on  $\text{CuGeO}_3$ . (a) Temperature dependence of the renormalized heat capacity component of the signal for different pressures. The ambient-pressure curve has been obtained from an adiabatic method experiment and represents the absolute value of the specific heat of the sample. (b) Evolution of the transition temperature with pressure.

of the anomaly temperature in a very precise way. The change in the spin–Peierls transition temperature  $T_{SP}$  (defined as the maximum of the anomaly) as a function of pressure is reported in figure 2(b). Two distinct stages can clearly be observed. For pressures ranging from 0 to 2 GPa,  $T_{SP}$  increases linearly with  $P$  at a rate of  $\sim +4 \text{ K GPa}^{-1}$ , which is consistent with previously reported results [4–6]. Above 2 GPa,  $T_{SP}$  still increases in a linear and positive way with  $P$  but the slope decreases to  $+1 \text{ K GPa}^{-1}$ . This is the first time that such a behaviour has been clearly exhibited, due to the previously explained advantages resulting from the *in situ* pressure tuning.

Similar results recorded for  $\text{Cu}_{0.98}\text{Zn}_{0.02}\text{GeO}_3$  are shown in figure 3. This doped material exhibits two phase transitions at ambient pressure: the spin–Peierls transition at  $T_{SP} = 10 \text{ K}$  and a 3D antiferromagnetic transition at  $T_N = 1.8 \text{ K}$ . We have followed the shift of  $T_{SP}$  with pressure up to 9 GPa, but we failed to observe the antiferromagnetic anomaly as the pressure was increased. This behaviour could be due to a rapid decrease of  $T_N$  with  $P$ , leading to a shift below 1.5 K (the lowest limit of our cryostat) at the smallest pressure at which we performed the measurements (0.6 GPa). This expectation must be confirmed by studying samples with higher  $T_N$  (Mn-doped compounds). As seen in figure 3(b), the transition temperature exhibits

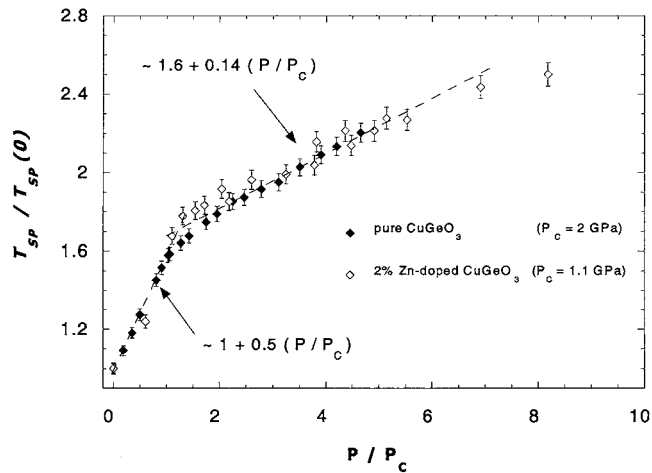


**Figure 3.** Results of ac-calorimetry measurements under pressure on  $\text{Cu}_{0.98}\text{Zn}_{0.02}\text{GeO}_3$ . (a) Temperature dependence of the renormalized heat capacity component of the signal for different pressures. (b) Evolution of the transition temperature with pressure.

a behaviour close to that observed in the pure compound. For pressures up to 1.1 GPa, the  $P$  dependence of  $T_{SP}$  is linear and strongly positive,  $+6 \text{ K GPa}^{-1}$ , a rate higher than in the pure sample. At higher pressures, the increase remains linear but at a lower rate,  $+1 \text{ K GPa}^{-1}$ . In figure 4, we have plotted the evolution of  $T_{SP}$  with  $P$  for both compounds with reduced coordinates  $T_{SP}/T_{SP}(0)$  and  $P/P_c$ ,  $T_{SP}(0)$  being the transition temperature value at ambient pressure. The critical pressure  $P_c$  is defined as the pressure of the break in the evolution of  $T_{SP}$ . In pure  $\text{CuGeO}_3$   $P_c \sim 2 \text{ GPa}$ , and for the doped compound  $P_c \sim 1.1 \text{ GPa}$ . As can be seen in figure 4, the behaviour of  $T_{SP}/T_{SP}(0)$  is quite similar up to  $P/P_c = 5$  for both compounds.

#### 4. Discussion

The recorded data exhibit two main features: the continuous rise in  $T_{SP}$  with pressure up to 9 GPa, which is in good agreement with previous results in the low-pressure range [4–7], and the existence of two different rates below and above the critical pressure  $P_c$ . From the theoretical predictions of Bray [12], it is expected that in a spin–Peierls compound the transition temperature should decrease with  $P$  following the relationship  $T_{SP} = T_{SP}(P = 0)[1 - \gamma P]^4$ ,



**Figure 4.** Comparison of the evolution of the normalized spin–Peierls temperatures in the two compounds.

where  $\gamma$  is related to the elastic constants. This is in total contradiction with the experimental observations. One explanation can be found in the unusual nature of  $\text{CuGeO}_3$ , which is known as a non-classical spin–Peierls system, because additional magnetic interaction  $\alpha J$  occurs from a second-neighbour interaction leading to the appearance of frustration in the spin chains.  $\alpha$  ranges from 0.2 to 0.35 depending onto the model used to describe the magnetic exchange. This exchange is governed by the angle  $\eta = \text{O}(2)\text{–Cu–O}(2)$ , where  $\text{O}(2)$  are the oxygens closer to Cu along the  $a$  axis. Braden *et al* [13] have studied the evolution of the  $\text{CuGeO}_3$  structure with pressure at room temperature, up to 6.2 GPa. They observed a decrease in  $\eta$  and calculated that such a decrease results in an increase of the frustration. In this case  $\alpha$  becomes larger than the critical value  $\alpha_c = 0.24$ , which is the limit beyond which a spontaneous gap  $\Delta_f$  appears in the magnetic excitation spectra in an antiferromagnetic frustrated chain of spin-1/2. Following calculations from Chitra *et al* [14], the gap  $\Delta_f$  increases with  $\alpha$ . Thereby, the total gap  $\Delta = \Delta_{SP} + \Delta_f$  in  $\text{CuGeO}_3$  increases with pressure and, from the BCS relation  $\Delta = 1.765 k_B T_{SP}$ , it follows that the spin–Peierls temperature can increase with pressure.

Concerning the break occurring in the variation of  $T_{SP}$  at  $P_c$ , we can tentatively suggest two hypotheses. The first one concerns the existence of a structural phase transition around 2 GPa. Such a transition around 180 K has been reported by van Loosdrecht *et al* [4], and recent work performed at room temperature by Jayaraman *et al* [15] shows a complex crystallographic structure in the range 8–36 GPa. Such changes in structure could influence the frustration via the angles between atoms. In this case, we can expect a different behaviour as we go through  $P_c$ . In our measurements, we failed to observe any signature of a transition around 200 K by ac calorimetry. However, we cannot definitively rule out this possibility as the lack of a detectable signal could be due to the low sensitivity of the thermocouple in the high-temperature range. Another possible origin could be a change in the behaviour of  $\Delta$  occurring at a critical value  $\alpha_0$ , corresponding to  $P_c$ , of the frustration parameter [13]. Above this value, the gap  $\Delta_f$  remains nearly constant, leading to a slowing down in the increase of the total gap  $\Delta$ . This means that, above  $P_c$ ,  $T_{SP}$  should be mainly driven by the frustration, in contrast to the low-pressure range, where the spin–Peierls distortion should be the dominant factor.

Further studies are needed to improve the model interpretation. We plan to check the existence of a new structural phase transition by performing neutron diffraction experiments

at low temperature up to 3 GPa. Moreover, it should be useful to determine the behaviour of CuGeO<sub>3</sub> under magnetic field on both sides of  $P_c$  (by using the ac-calorimetry technique) in order to determine the main contributions to the total gap  $\Delta$ .

## 5. Conclusion

We have shown that the spin–Peierls temperature  $T_{SP}$  in CuGeO<sub>3</sub> compounds increases in a monotonic way under the effect of hydrostatic pressure up to 9 GPa. This increase can be separated into two ranges, both with linear variations but different slopes. The general behaviour of  $T_{SP}$  can be understood by taking into account the existence of frustration in the linear magnetic chains, but the role of a structural phase transition around 2 GPa cannot be definitively ruled out.

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