

Ultrasonic Study of the Spin-Peierls System CuGeO_3 Under Pressure

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We present the temperature dependence of the acoustic sound velocity for a CuGeO_3 single crystal measured under pressure up to 10 kbar. Anomalous elastic behavior along the c axis, observed around 100 K, is accounted for by the existence of a magnetoelastic coupling. We show that this coupling is weakly affected by pressure. Moreover, the temperature dependence of the sound velocity below the Spin-Peierls phase transition is analyzed using a Landau-type model from which we obtain the temperature and pressure dependences of the order parameter. We find that the magnetic spin-Peierls energy gap increases with pressure at a rate of $d\Delta/dP = 0.11 \pm 0.01$ meV/kbar.

62.20.Dc, 75.30.Kz, 75.40.Cx, 75.40.Gb

The application of pressure has proven to be very useful in elucidating the fundamental properties of low-dimensional systems that normally reveal a wide variety of new and exotic phenomena. Unfortunately, for the most part high pressure techniques have been used in conjunction with resistivity measurements which limit this kind of study to non-insulating materials. It is true that attempts have been undertaken in the past to extend these studies to magnetic insulators. For example, Takahashi et al.¹ recently performed a series of AC susceptibility measurements, as well as magnetic balance measurements under high pressure on the spin-Peierls system CuGeO_3 . They however concluded that no reliable absolute value could be obtained from the AC susceptibility technique and thus they obtained only the pressure dependence of the spin-Peierls transition temperature T_{SP} . As we will show the ultrasonic technique is highly suited for studies under pressure and it certainly doesn't present the problems inherent in the AC susceptibility technique. Moreover, one of the greatest advantages of this technique compared to resistivity measurements is that it is not restricted to any particular materials; it can be used equally well for conductors and insulating materials.

In order to demonstrate the potential of the ultrasonic technique for studies under pressure, we present the temperature dependence of the ultrasonic velocity of CuGeO_3 measured under pressure up to 10 kbar. The growing interest for this compound as well as the fact

that large single crystals of CuGeO_3 can be synthesized have dictated our choice. CuGeO_3 is the first known inorganic magnetic insulator which shows the main characteristics of a spin-Peierls (SP) phase transition², the formation of a singlet ground state and a triplet excited state at an energy Δ_{sp} (the Spin-Peierls energy gap)³ as a result of a lattice dimerization⁴ driven by magnetic interactions. Since the first report of Hase et al.², the structural and magnetic properties of CuGeO_3 have been studied more extensively than the equivalent organic SP systems. The magnetic phase diagram deduced from AC magnetic susceptibility measurements⁵ as well as ultrasonic studies⁶ is consistent with the universal magnetic phase diagram of other SP systems^{7,8}. Recently, Poirier et al.⁹ have clearly shown that ultrasonic sound velocity measurements can be used to probe the order parameter in CuGeO_3 near the phase transition. Their results indicate that despite the expected reduction of the SP transition temperature under the application of a magnetic field, the amplitude of the gap at $T = 0$ K remained unaffected up to a field of 12 Tesla. In contrast, the application of pressure is known to increase the transition temperature of CuGeO_3 and results obtained by Nishi et al.¹⁰ seem to indicate that the energy gap is also increasing. However, their measurements seem to indicate that the BCS relation ($2\Delta_{SP} = 3.52 k_B T_{SP}$) is not observed at 1.9 GPa. Therefore, in order to verify this result and to investigate further the influence of pressure on the magnetoelastic behavior of CuGeO_3 , we have performed high-pressure sound velocity measurements along the chain axis. We have particularly focussed attention on the anomalous elastic behavior observed around 100 K^{9,11} and on the SP phase characteristics.

The CuGeO_3 single crystals used in this study were grown from the melt by a floating zone method in an image furnace¹². The results presented here have been obtained on a single crystal with a length of 6.1 mm along the c direction and dimensions in the a and b directions of 4.65 mm and 3.88 mm, respectively. Since the crystals cleave readily perpendicular to the a axis and the orthorhombic axes are the major (c axis) and minor (b axis) axes of the elliptical cleaved section, the principal axes are easily identified. Prior to the measure-

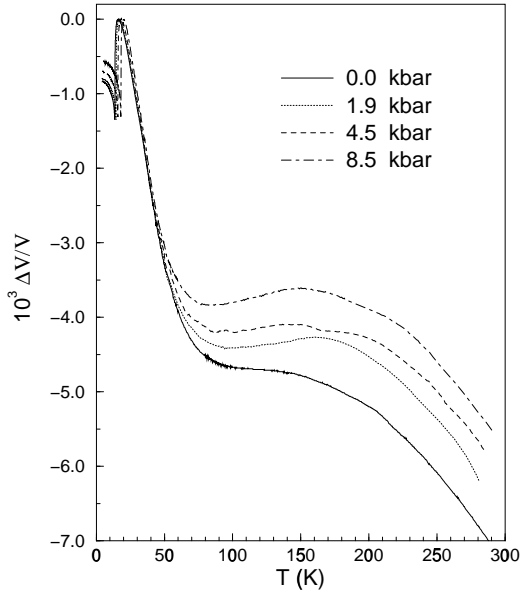


FIG. 1. Relative variation of the longitudinal sound velocity along the *c*-axis as a function of temperature for different pressures: $P = 0, 1.9, 4.5$ and 8.5 kbar.

ment, both faces perpendicular to the *c*-axis were carefully polished with diamond paste, and then a longitudinal LiNbO₃ piezoelectric transducer was bonded with GE silicon Sealant onto one of the faces. This configuration was chosen because it gives rise to the largest anomalies in the sound velocity at the spin-Peierls phase transition⁹. The crystal was then mounted in a Cu-Be clamp pressure cell where a 1:1 mixture of 3-Methyl-1-butanol and 2-Methylbutane was used as a pressure-transmitting medium. The pressure inside the cell was monitored at room temperature by measuring the resistivity change of a Lead wire mounted next to the sample. During the cooling process, a pressure loss of about 2 kbar occurs, which must be accounted for in the data analysis. The ultrasonic sound velocity was measured with a pulsed acoustic interferometer yielding a sensitivity in velocity variation of about 2 ppm. All results presented here have been obtained at the fundamental frequency of the transducer (30 MHz) or at the first overtone (90 MHz). We did not observe any significant difference between results obtained at 30 MHz and 90 MHz. Using this setup, we have measured the acoustic sound velocity of CuGeO₃ between 4.2 K and 300 K at pressures up to about 10 kbar. Measurements have also been performed on other samples and they indicate that results presented here are highly reliable.

The ultrasonic velocity value as deduced from our time-of-flight observations at room temperature is $7.6(4) \times 10^5$ cm/sec for the longitudinal mode along the *c*-axis. This value agrees with those reported previously^{9,13} and is a good indication that the proper mode has been

generated. In figure 1 we show the temperature dependence of the longitudinal velocity variation measured along the *c*-axis at different pressures. The data in figure 1 have not been corrected to take into account thermal expansion since the reported variation of the lattice constant along the *c*-axis¹⁴ is in general much smaller (even less below 30 K) than the acoustic velocity variation reported here. In order to appreciate the influence of pressure on the various features, all curves are normalized (zero velocity variation) at their maximum just above the spin-Peierls phase transition. Therefore, this figure does not yield the true pressure dependence at a given temperature. In fact, the pressure dependence measured at room temperature gives that the relative sound velocity increases at a rate of $\frac{\Delta V}{V_0} = 6.1 \times 10^{-4}$ /kbar. However, figure 1 does illustrate that all curves show a pronounced anomaly at the SP phase transition as well as an anomalous elastic behavior around 100 K. In addition, the anomaly observed at temperatures below 20 K is directly related to the SP order and, therefore as we will show, allows one to obtain some information about the SP order parameter. As the temperature increases above 30 K the velocity rapidly decreases, leveling off around 100 K, and then decreasing again. This anomalous behavior is not seen along other directions, where the sound velocity decreases gradually, and nothing particular is noticed around 100 K⁹. This extra softening along the *c*-axis has been analyzed by Dumoulin et al.¹¹ and attributed to a magnetoelastic coupling contribution. Moreover, it is claimed¹⁵ that it is unrelated to the occurrence of the SP phase transition. Their interpretation is based on the fact that this anomalous behavior is unchanged in Zn and Si doped CuGeO₃ crystals for which the SP phase transition is suppressed. As we will now show, our results under pressure seem to give further support to this interpretation. In order to determine the contribution of the magnetoelastic coupling along the *c*-axis, we need to subtract from our results the contribution due to the usual anharmonic interactions. Unfortunately, the exact temperature profile of that contribution is unknown, however we believe that it should be very similar to what we observe along other directions. Our estimate is also influenced by the expectation that the magnetoelastic coupling vanish at low and high temperatures.¹¹ The subtraction of the anharmonic contribution has thus been done according to the procedure presented in Ref. 11. The *c*-axis magnetoelastic contribution obtained in this way is presented in figure 2. We also show in the inset the extrapolation of the so-called normal elastic behavior that we used to get the magnetoelastic contribution. Surprisingly, the pressure seems to reduce mainly the anharmonic interaction contribution while the *c*-axis magnetoelastic contribution is only weakly reduced (only the curve at 8.5 kbar is significantly different), or even, unaffected by the increase of pressure. It is clear that the results presented in figure 2 depend somewhat on the estimate for the temperature profile of the anharmonic contribution. Thus, from this analysis,

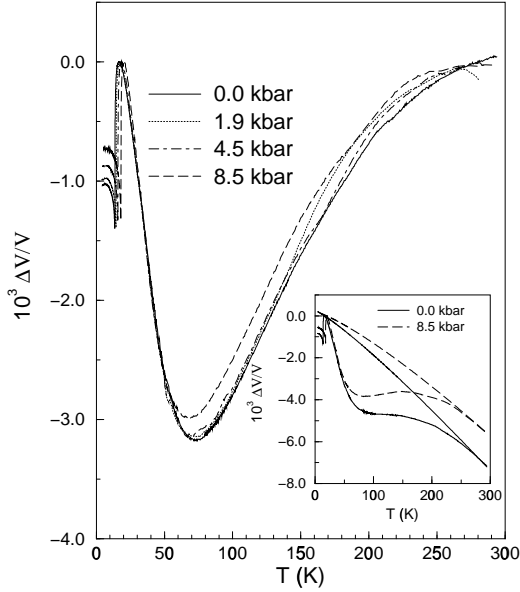


FIG. 2. Temperature dependence of the c-axis magnetoelastic coupling obtained from the sound velocity measurements for $P = 0, 1.9, 4.5$ and 8.5 kbar. Inset: Shows the sound velocity as well as the extrapolation of the normal elastic behavior for $P = 0$ kbar (full line) and 8.5 kbar (dash line).

we conclude that the pressure at most slightly reduces the magnetoelastic coupling along the c-axis while at the same time, since T_{SP} increases, it reinforces the stability of the SP phase. Our results thus support the interpretation that the anomaly observed at 100 K in the sound velocity along the c-axis is not a precursor effect of the SP phase transition.

In general, the properties of spin Peierls compounds are well described by the theory of Cross and Fisher (CF)⁸. According to the CF theory, where only nearest neighbour magnetic interaction J along the chain is considered, the transition temperature is determined by $T_{sp} \approx Jg_{\lambda}$, where g_{λ} is the dimensionless coupling constant: $g_{\lambda} \propto \lambda^2/2\pi v\omega_{2k_F}^2$. Here λ is the coupling constant, v is the spin velocity and ω_{2k_F} is the frequency of the phonon mode participating in the SP instability. Since the spin velocity is also proportional to J , it turns out that the dependence on J drops out. In this case, in order to explain the increase of T_{sp} as a function of pressure, one must look for a possible increase of the coupling constant λ or a decrease of the frequency of the phonon ω_{2k_F} . On the one hand, we expect pressure to increase the phonon frequencies by a small amount, which will result in a diminution of T_{sp} . On the other hand, since we don't observe a significant decrease in the c-axis magnetoelastic coupling with pressure, we can assume that the coupling constant λ for longitudinal modes along the c-axis is not strongly pressure dependent. This is not very surprising as it is known now that the c-axis is really the

hard axis in CuGeO_3 .^{14,16,17} However, it might be possible that the b-axis, which is the soft axis, plays a crucial role in the SP transition. Unfortunately, the sound velocity measurements along the b-axis⁹ don't reveal any anomaly that can be associated to a magnetoelastic coupling. Therefore, it is impossible to show whether or not the coupling constant λ changes significantly for any modes along the b-axis. Therefore, it is unclear how the large increase of T_{SP} with pressure can be accounted for by the conventional CF theory, especially as long as the phonon mode that participates to the SP instability is not identified.

So far, the need of a more complex theory for CuGeO_3 has been raised by the unusual temperature dependence of the magnetic susceptibility that deviates significantly from the Bonner-Fisher theory.¹⁸ For the moment, the most successful models take into consideration the nearest-neighbour interaction J along the chain, as well as the next-nearest-neighbour interaction J' . In that scenario, many authors¹⁹⁻²¹ have shown that it is possible to get good agreement between the theoretical prediction and the temperature dependence of the susceptibility. Even if the magnitude of J' has not yet been determined unambiguously, it has been shown that as long as the ratio J'/J is lower than the critical value $J'_c = 0.24$,²¹ most of the theoretical prediction retains the form obtained with the CF theory. This puts some limit on the possible value of J' since most of the experimental results on CuGeO_3 are consistent with the CF description. At the same time, Zang et al.²² have shown that even if $J'/J < J'_c$, the lattice dimerization magnitude increases as J' increases. If we consider the relation between the gap amplitude and the dimerization below T_{SP} , this would result in an augmentation of the gap as well as T_{SP} . Thus, as proposed by many authors¹⁹⁻²¹, the presence of a finite J' in CuGeO_3 , and its possible increase as a function of pressure proposed here, might be responsible for many peculiar properties of this compound. For the moment, the exact pressure dependence of the ratio J'/J is still unknown, therefore it is impossible to say whether this is the only mechanism driving the large increase of T_{SP} with pressure. Finally, we would like to point out that some authors²⁰ suggested a value that was larger than the critical value $J'_c/J = 0.2411$ leading in turn to a stabilization of the SP phase without any active participation of the phonons. However, as discussed recently by a few authors²³⁻²⁵, it is clear that phonons are involved in the SP instability of CuGeO_3 and, whether the instability is of the CF type or not, has yet to be determined. Here, the interpretation of the results involves both effects, although the theoretical verifications implied values of $J' < J'_c$.

The effect of pressure on the SP state can also be elucidated from the data. The results are presented in figure 3. All curves, which are again normalized at their maxima, present the same temperature dependence; as the temperature is lowered the velocity reaches a maximum and then decreases rapidly, followed by another

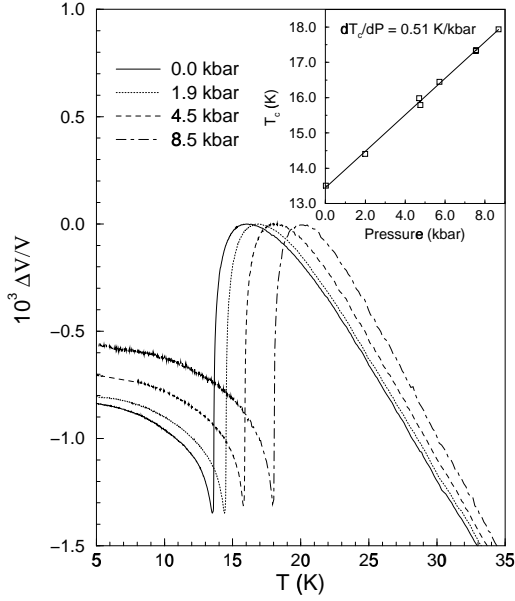


FIG. 3. Low temperature dependence of the relative variation of the longitudinal sound velocity along the c -axis as a function of temperature for $P = 0, 1.9, 4.5$ and 8.5 kbar. Inset: Shows the pressure dependence of the spin-Peierls temperature phase transition T_{SP} .

increase at the phase transition. From the temperature of the sharp minimum we accurately obtain the pressure dependence of T_{SP} . The result, presented in the inset of figure 3, shows that T_{SP} increases at a rate of 0.51 ± 0.02 K/kbar which agrees well with results from previous work^{1,26,27}. The temperature dependence of the sound velocity below the phase transition has already been analyzed by a few authors^{9,11}. In their approach, the elastic behavior below the Spin-Peierls transition can be accounted for by a Ginzburg-Landau free energy model. This particular temperature dependence along the c -axis is then the result of the competition between the uniform elastic deformation and the opening of the Peierls gap Δ_q . According to the model⁹, the elastic constant C_{33} along the c -axis is given, to a first approximation, by

$$C_{33} = C_o - \frac{2h^2}{2b + 3f|\Delta_q|^2} \quad (1)$$

where C_o is the value of the elastic constant at a temperature just above the opening of the SP gap, Δ_q , and b, f and h are the coefficients of the Landau expansion of the free energy. Using the fact that the sound velocity is related to the elastic constant via the expression $V = \sqrt{C/\rho}$ where ρ is the density, we can write $\frac{\Delta V}{V_o} = \frac{1}{2} \frac{\Delta C}{C_o}$ for small sound velocity variation. With equation 1 one obtains:

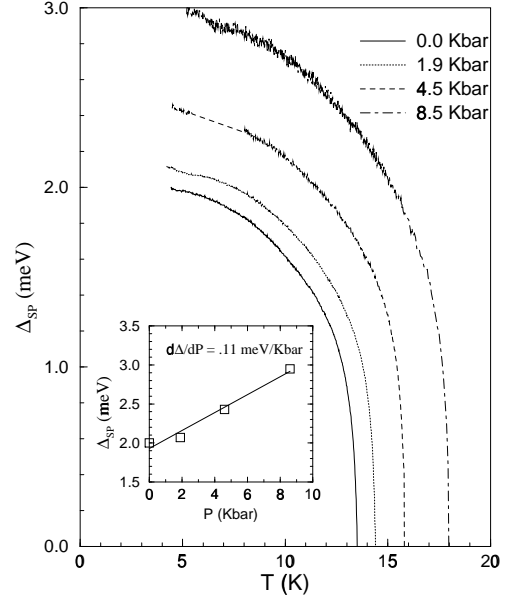


FIG. 4. Temperature dependence of Spin-gap for $P = 0, 1.9, 4.5$ and 8.5 kbar. The inset shows the pressure dependence of the spin-gap Δ_{SP} .

$$\frac{\Delta V}{V_o} = - \frac{M}{1 + N|\Delta_q|^2} \quad (2)$$

with parameters $M = h^2/2bC_o$ and $N = 3f/2b$. According to this expression, the value of the parameter M can be directly obtained by measuring the amplitude of the jump at T_{SP} where $\Delta = 0$ meV. The results of figure 3 indicate that this parameter is more or less pressure independent and equal to 1340 ± 10 ppm. We can also estimate the value of the other coefficient N using the measured value of $\Delta V/V_o$ at 4.2 K for ambient pressure and the accepted energy gap value ($\Delta = 2$ meV^{10,28-30}). We obtain $N = 0.155$ meV⁻². Assuming that pressure has no effect on the coefficient N , we have transformed our sound velocity data below T_{SP} according to equation 2 in order to obtain the temperature dependence of the spin-gap at different pressures. The results of that transformation are shown in figure 4. In the vicinity of T_{SP} , the gap $\Delta(T) = \Delta(0)(1 - T/T_{SP})^\beta$ has a mean field critical exponent $\beta = 0.40 \pm 0.02$ that is pressure independent. The inset of figure 4 shows the extrapolated zero temperature pressure dependence of the gap, from which $d\Delta/dP = 0.11 \pm 0.01$ meV/kbar, a result in good agreement with that obtained by Nishi et al.¹⁰. This analysis holds as long as the coefficient N is independent of pressure. This hypothesis is in fact questionable since according to the expressions derived recently by Dumoulin et al.¹¹, we should rather use that $N \propto T_c(p)^{-2}$. Taken that into consideration in equation 2, we rather obtain $d\Delta/dP = 0.20 \pm 0.02$ meV/kbar, a result that is practically twice the value obtained previously. Therefore, we

do in fact obtain a much better agreement for $d\Delta/dp$ ¹⁰ in the first scenario. However, whether N is pressure independent or not remains to be confirmed experimentally.

To summarize, we have measured the sound velocity temperature dependence of CuGeO₃ under pressure. We have shown that the magnetoelastic coupling along the c-axis remains relatively unchanged with pressure and thus cannot be responsible for the rapid increase of T_{SP} with pressure. Moreover, we were also able to extract from the measured sound velocity the temperature and pressure dependences of the SP order parameter. The pressure dependence of the spin-gap is in qualitative agreement with previous results and indicates that the ratio $2\Delta_{SP}/k_B T_{SP}$ increases with pressure.

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