Ultrasonic evidence of a spin-Peierls transition in α'-NaV$_2$O$_5$

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We report the anomalous behavior of the C_{22} elastic constant in α'-NaV$_2$O$_5$ by studying the propagation of longitudinal ultrasonic waves along the chain direction. A stiffening anomaly is clearly seen at 35 K, which could be the signature of a spin-Peierls transition. The results are discussed and compared with the temperature dependence of the analogous elastic constant (C_{33}) in the CuGeO$_3$ system. Magnetic-field effects have also been investigated. Anomalously small shifts of the transition temperature are observed. [S0163-1829(98)00222-7]

The spin-Peierls (SP) instability is one of the interesting phenomena of low-dimensional quantum spin systems, where a structural phase transition is driven by magnetic interactions.[1] The synthesis of large single crystals of CuGeO$_3$, to our knowledge the only known inorganic SP compound up to now, gave the opportunity of a detailed experimental study of the magnetoelastic coupling between the one-dimensional (1D) antiferromagnetic chains and the 3D phonon field. However, departures from the theoretical predictions for an ideal one-dimensional $S = 1/2$ spin-Peierls system are observed in this system.[2] Therefore, the recent discovery of a second inorganic candidate α'-NaV$_2$O$_5$ to the spin-Peierls transition has attracted much interest. This vanadium oxide contains $S = 1/2$ spin chains isolated by nonmagnetic chains along the b direction.[3] Indeed, the temperature dependence of the magnetic susceptibility displays a broad maximum near 350 K that is well described by a Bonner-Fisher law[4] with a unique nearest-neighbor antiferromagnetic interaction ($J \sim 220$ K and $g \sim 2$).[5] To a certain extent, α'-NaV$_2$O$_5$ is therefore closer to the ideal one-dimensional $S = 1/2$ antiferromagnetic (AFM) chain than CuGeO$_3$. Therefore, this compound could give a better opportunity to test theoretical predictions of the ideal AFM $S = 1/2$ Heisenberg chains systems embedded in the 3D phonon field of the lattice, for which a progressive spin-lattice dimerization develops on lowering the temperature.

In α'-NaV$_2$O$_5$, a pronounced decrease of the magnetic susceptibility below $T_{sp} = 35$ K was the first evidence of a possible gap opening in the magnetic excitation spectrum at low temperature.[5] The exponential decrease was soon after found to be independent of the orientation of the applied magnetic field with respect to the crytallographic axes and the nature of the ground state was unambiguously established.[6] The structural signature of the SP transtion was then revealed by an x-ray-diffraction analysis.[7] Superlattice reflections were indeed observed below 35 K, reflecting the dimerization of the lattice along the chain direction. However, the low-temperature crystal structure has not yet been resolved to evaluate the atomic displacements. NMR measurements on ^{23}Na also reveal two distinct sites below T_{sp},

confirming the structural transition.[8] The amplitude of the gap is estimated to be about 98 K, in good agreement with neutron scattering experiments[7,9] or electron spin resonance analysis.[10] Further evidence of the SP transition is found by the typical appearance of new lines and a change of the line shapes in the IR (Ref. 11) and Raman[6] spectra.

The nature of the SP transition can be revealed efficiently by a direct investigation of the magnetoelastic coupling. For that purpose, ultrasonic experiments performed on CuGeO$_3$ single crystals[12,13] have already been successfully used to probe the temperature and magnetic-field dependence of various elastic constants, particularly sensitive to structural phase transitions. The C_{33} elastic constant obtained by measuring the velocity of longitudinal waves propagating along the chain axis displayed a unique anomalous temperature profile in the normal phase (near 100 K due to the magnetoelastic coupling with the 1D magnetic fluctuations) and the largest anomaly at the transition.[12] The signature of the SP transition was also confirmed by the typical shift, under a magnetic field, of T_{sp} to lower temperature and by the mapping of the phase diagram.

Considering the relevance of longitudinal ultrasonic wave propagation along the chain axis to probe the magnetoelastic coupling in a SP system, we report the temperature behavior of the C_{22} elastic constant of α'-NaV$_2$O$_5$. The results are discussed through a comparison with the temperature dependence of the analogous elastic constant (C_{33}) of CuGeO$_3$. Magnetic-field effects have been also investigated.

The α'-NaV$_2$O$_5$ single crystal used in this study was grown from a liquid phase using a flux method.[14] This compound crystallizes in the orthorhombic $P2_1mn$ space group.[3] The structure can be described as layers of VO$_5$ square pyramids sharing edges and corners, parallel to the ab plane, separated by sodium atoms along the c direction. Two crystallographically inequivalent vanadium sites define two kinds of VO$_5$ chains along the b axis: the V^{4+}O$_5$ magnetic chains ($S = 1/2$) are isolated by the nonmagnetic V^{5+}O$_5$ chains. The dimensions of the platelike crystal used in this study are approximately $2.3 \times 8.5 \times 1.1$ mm^3 along the a, b, and c directions, respectively. The ultrasonic velocity and attenua-
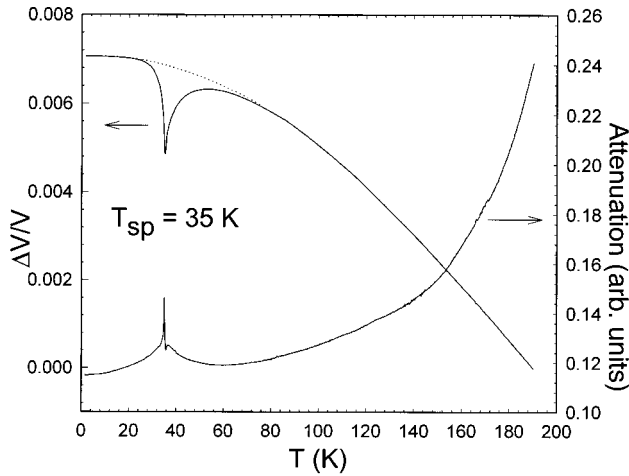
FIG. 1. Temperature dependences of the attenuation and the relative longitudinal velocity variations along the chain axis of α'-NaV$_2$O$_5$. The dotted line is an extrapolation of the normal elastic behavior.

FIG. 2. Comparision of the relative longitudinal velocity variations along the chain axis in α'-NaV$_2$O$_5$ (solid line) and CuGeO$_3$ (dotted line; see Ref. 12) as a function of T/T_{sp} when the normal elastic behaviors have been subtracted.

tion are measured with a pulsed acoustic interferometer[15] operated in a transmission mode. We will therefore only be concerned with relative variations of the elastic constant, which are directly related to the velocity variations through $\Delta C/C = 2\Delta V/V$. The precision of the velocity variation measurements is better than 2 ppm. Longitudinal waves along the chain axis are generated and detected at 30 MHz and odd overtones by two LiNbO$_3$ piezoelectric transducers which are bonded at each end of the crystal with a silicon glue. The amplitude of the first transmitted echo was monitored as the variations of the attenuation. The temperature is measured with either a Si diode or a capacitor sensor for magnetic-field measurements up to 14 T. The sample was sandwiched between the capacitor and the diode sensors to improve thermal contacts. However, accurate temperature measurements over a large temperature domain ($T_{sp} \sim 35$ K) and under high magnetic fields (up to 14 T) are particularly tedious since most usual sensors are either influenced by the field (diode) or sensitive to thermal cycling effects (capacitor). Therefore, the precision of the temperature measurement under magnetic field is about 0.20 K. The magnetic-field direction was set parallel to the chain axis.

The variations of the velocity and the attenuation between 5 and 200 K in zero field, recorded at 100 MHz, are displayed in Fig. 1. No frequency effects were detected on the velocity variations from 30 to 150 MHz. No thermal expansion corrections were performed since the thermal coefficient along the chain direction seems to be one order of magnitude smaller than the velocity variations.[5] No data were collected above 200 K since the transducer-sample link becomes less effective due to the softening of the silicon seal. An anomaly is clearly visible at 35 K on both the velocity and attenuation temperature dependences. On lowering the temperature from 200 K, the relative velocity variations and the attenuation first display a monotonic behavior typical of anharmonic contributions of the 3D phonon field: the velocity stiffens while the attenuation diminishes. As evidenced in Fig. 1, precursor effects of the SP transition begin to be observed below 70 K. A softening of the velocity progressively develops below 50 K and a rapid decrease is observed close to 35
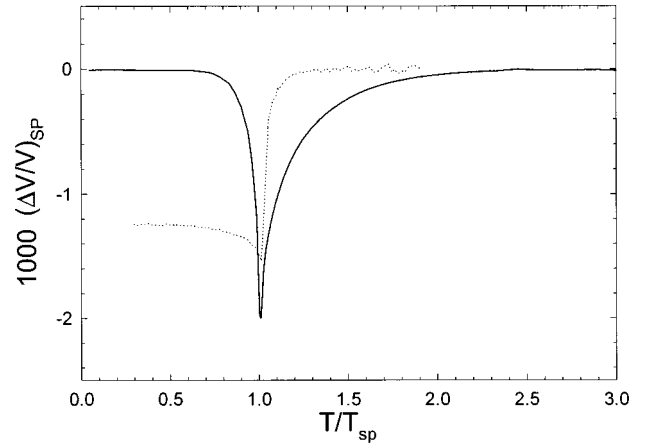
K. Concurrently, the attenuation reaches a minimum near 60 K and slowly increases on further cooling until an abrupt increase appears just above the transition. Below 35 K, a rapid stiffening of the velocity variation is observed while the attenuation quickly diminishes. At lower temperature, both the velocity and the attenuation tend to saturate. Since the transition observed at 35 K coincides with the drop of the magnetic susceptibility,[5,6] the anomaly of the C_{22} elastic constant has possibly a magnetoelastic coupling origin. In that case, this anomalous behavior is likely the signature of the SP transition and it is reminiscent of the temperature profile of C_{33} for CuGeO$_3$ in the transition region.[12] However, several distinctions are evidenced in the latter system, both in the dimerized and in the normal phases.

In order to gain a better appreciation of the differences between the two compounds in the transition region, it is important to isolate the magnetoelastic effect from the normal elastic behavior due to the anharmonic contributions. Therefore, the normal elastic behavior must be substracted from the raw data. For CuGeO$_3$, the normal behavior was first extrapolated from the high-temperature region and later experimentally confirmed.[16] For α'-NaV$_2$O$_5$ no experimental data are yet available. Therefore, using the procedure adopted for CuGeO$_3$, the anharmonic contributions have been guessed by an extrapolation from the high-temperature profile (above 70 K) of the velocity variations, as depicted by the dotted line in Fig. 1. The actual behavior might display some departures from our extrapolation, but they are expected to be small and the conclusions given below will not be fundamentally modified. A comparison between the two systems in the transition region is then reported in Fig. 2, where the relative velocity variations resulting from the SP contribution $(\Delta V/V)_{SP}$ are plotted versus the reduced temperature T/T_{sp}. In the dimerized phase and below about 20 K ($T/T_{sp} \sim 0.6$), no persistent softening is displayed for α'-NaV$_2$O$_5$: $(\Delta V/V)_{SP} \sim 0$. This contrasts with CuGeO$_3$, where a softening is still present at low temperature.[12] Above the SP transition, precursor effects are clearly observed in a wider temperature region in α'-NaV$_2$O$_5$, in contrast to CuGeO$_3$. In the former compound, departure from the nor-

mal elastic behavior starts below $T/T_{sp} \sim 2.3$. In the latter, fluctuations become effective much closer to the transition ($T/T_{sp} \sim 1.3$). These results suggest that the magnetoelastic coupling might be more effective in α'-NaV$_2$O$_5$ than in CuGeO$_3$ since the jump at the transition is greater and the fluctuation region is more extended.

In the framework of a spin-phonon coupling, the magnetoelastic anomaly at the spin-Peierls transition can be analyzed using the simple Landau formalism already developed for the CuGeO$_3$ compound.[12,17] To a first approximation, the elastic constant along the chain axis is given by

$$C_{22} = C_0 - \frac{h_1^2}{2b} + 2h_2\Delta^2,$$

where C_0 is the normal elastic constant and b, h_1, and h_2 are the coefficients used in the Landau expansion of the free energy. Δ is the SP gap. The first term reflects a linear coupling between the uniform elastic deformation e and Δ^2. It yields a jump at the transition. The second term is derived from a quadratic coupling ($\sim e^2\Delta^2$) and describes the hardening of the elastic constant in the dimerized phase with the opening of the gap. Since $\Delta C/C = 2\Delta V/V$ one obtains

$$\Delta V/V = M\Delta^2 + N,$$

where $M = h_2/C_0$ and $N = -h_1^2/4bC_0$. Therefore, the velocity variations should reflect the temperature dependence of the gap once the normal contributions have been substracted. The N coefficient can be estimated using the amplitude of the jump $(\Delta V/V)_{T_{sp}}$ at T_{sp} (where $\Delta=0$). The M parameter can be easily calculated if one considers that at low temperature, $C_{22} \sim C_0$ (i.e., the amplitude of the jump at the transition has been canceled by the stiffening due to the gap opening). Therefore, the temperature dependence of the gap becomes

$$\Delta = \Delta_0\left(1 - \frac{\Delta V/V}{(\Delta V/V)_{T_{sp}}}\right)^{1/2},$$

where Δ_0 is the gap value at $T=0$ K [$\Delta_0 \simeq 90$ K (Refs. 6 and 8–10)].

The temperature profile of the gap extracted from our ultrasonic measurements is displayed in Fig. 3. It is in excellent agreement with gap values deduced from inelastic neutron scattering data[7] also reported in Fig. 3 (filled squares). In the inset of Fig. 3, the temperature profile of the gap has been plotted as a function of the reduced temperature ($1-T/T_{sp}$) on a logarithmic scale. A linear variation in the vicinity of T_{sp} is clearly observed and can be accounted for by $\Delta(T)=\Delta(0)(1-T/T_{sp})^\beta$. The critical exponent is 0.34(8), which is very close to that of CuGeO$_3$ ($\beta_{\text{CuGeO}_3} \simeq 0.42$).[12]

A second difference from CuGeO$_3$ appears in the normal phase (above T_{sp}). It has already been observed and theoretically explained that in low-dimensional magnetic sytems, like the $S=1$ antiferromagnetic CsNiCl$_3$ material[18] or the $S=1/2$ CuGeO$_3$ compound,[12,19] 1D magnetic fluctuations couple to the lattice and usually induce anomalous behaviors of the elastic constant related to the chain axis direction. We recall that the energy scale of these fluctuations is of the order of J, the antiferromagnetic exchange constant. For our
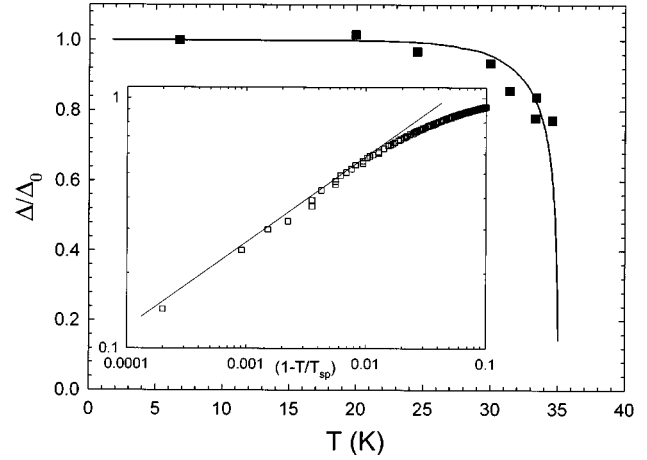

FIG. 3. Temperature profile of the gap determined from the relative velocity variations along the chain axis. Filled squares are the gap values deduced from the inelastic neutron scattering data of Ref. 7.

two systems of interest, J is about 70 K and 220 K in CuGeO$_3$ (Ref. 2) and α'-NaV$_2$O$_5$,[5] respectively. A better comparison between the behavior of these latter two systems is therefore performed in the normal phase if the relative velocity variations are plotted versus the reduced temperature T/J, as reported in Fig. 4. The curves have been shifted relatively to one another for a better appreciation of the variations. In the normal phase, the temperature dependence of the velocity variations of α'-NaV$_2$O$_5$ does not seem to display the magnetoelastic anomaly observed in CuGeO$_3$ above $T/J \sim 1$.[19] However, as recalled in the inset of Fig. 4, above T_{sp}, the derivative of the velocity curves tends to saturate on increasing the temperature. This could reflect the shift of the magnetoelastic anomaly to higher temperature due to a larger J value. This is also consistent with the stronger magnetoelastic coupling expected in this compound, as discussed previously. High-temperature data (above 300 K) are thus required to confirm its occurrence. Due to the limitations of our experimental setup, we could not study the high-temperature behavior.
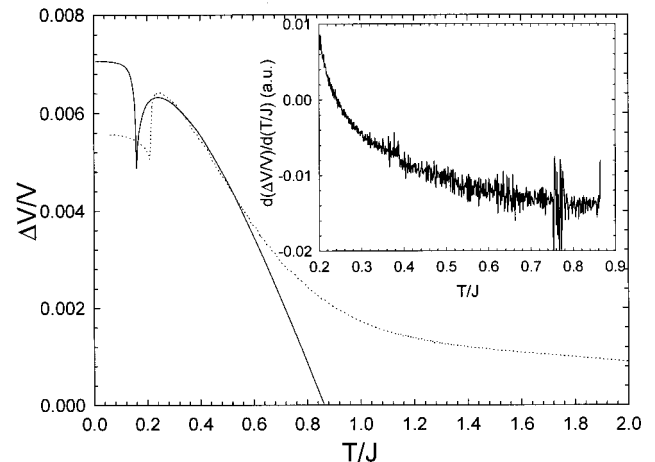

FIG. 4. Comparison of the relative longitudinal velocity variations along the chain axis in α'-NaV$_2$O$_5$ (solid line) and CuGeO$_3$ (dotted line; see Ref. 12) as a function of T/J (see the text).

When a magnetic field H is applied along the chain axis, the elastic anomalies observed on the velocity and the attenuation are hardly shifted to lower temperature. At 14 T and within the experimental precision, the shift of the transition temperature reaches -0.1 K. Such a small shift seems to contrast with the value deduced from magnetization measurements (-0.15 K at 5.5 T),[6] which was argued to be in fairly good agreement with the predictions of the theory of Bulaevskii et al.[20] and Cross[21] for SP systems. According to this theory, the expected shift is about -1 K at 14 T. Though the precision of the temperature determination was restricted in our study, the measured shifts are one order of magnitude too small from theoretical predictions for spin-Peierls systems and experimental artifacts can be excluded. Therefore, further investigations under a higher field are needed to confirm this unexpected behavior.

In conclusion, we report the temperature dependence of the elastic constant C_{22} of α'-NaV$_2$O$_5$ along the chain direction. An anomalous behavior is clearly observed at 35 K, which displays the same overall features as the elastic anomalies already detected in other SP systems. However, a comparison with the behavior of the well known CuGeO$_3$ inorganic SP compound has revealed differences, particularly in the dimerized phase. Furthermore, the decrease of the transition temperature when a static magnetic field is applied seems anomalously small. High-magnetic-field measurements are now required to detail the features of the phase diagram and clarify the actual nature of the observed transition at 35 K.

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