Ultrasonic study of the quasi-one-dimensional spin fluctuations in $CsNiCl_3$ in the presence of a magnetic field

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High-resolution ultrasonic-velocity and -attenuation data are used to characterize the paramagnetic phase of $CsNiCl_3$ as a function of temperature, frequency, and magnetic field (both amplitude and orientation). The interpretation of the results is based on a classical treatment of a compressible spin chain. Qualitative agreement is obtained but the experimental data put into question the validity of the classical approach for spin fluctuations in this system.

I. INTRODUCTION

In recent years, hexagonal magnetic ABX_3 compounds have been widely investigated both theoretically and experimentally. These crystals may be considered to be quasi-one-dimensional magnetic insulators but, at low temperature, many competing magnetic interactions produce three-dimensional ordering and yield very rich phase diagrams. Multicritical points have been found in many systems[1] and controversies about the nature of their universality classes exist.[2]

Because of the quasi-one-dimensional magnetic character at high temperatures, in general the physical properties are largely affected by the one-dimensional fluctuations whose effects can be monitored on a large temperature scale. It is then very important to fully characterize these fluctuations in order to understand the subsequent magnetic ordering. A good candidate for such a study is $CsNiCl_3$, an easy-axis antiferromagnet which is ordered below 4.85 K.[3] Above 10 K, the quasi-one-dimensional character is clearly established ($J_\parallel=-33$ K, $J_\perp=-0.6$ K) (Ref. 4) and associated anomalies have been observed in the temperature range 10–60 K on the magnetic susceptibility,[5] the thermal expansion,[6] and the elastic constants;[7] other anomalies, associated instead with the three-dimensional ordering, are present at lower temperatures.

The existence of a strong magnetoelastic coupling in $CsNiCl_3$ has been shown by previous ultrasonic[7–10] and Brillouin[10] scattering measurements. Longitudinal waves propagating along the hexagonal axis have revealed a pronounced anomaly on the elastic constant C_{33} centered around 40 K with a consequent attenuation peak. A classical model, developed by Fivez, De Raedt, and De Raedt[11,12] introduces the magnetoelastic coupling via a modulation of the parallel exchange integral by the interspin separation. This model yields a softening peak for C_{33} centered at a temperature near $|J_\parallel|/k_B$ and an attenuation one at approximately the same temperature. The amplitude of the attenuation peak varies as the square of the frequency ω. The effects of the magnetic field and of its orientation relative to the hexagonal axis (c axis) on the ultrasonic velocity have never been included in Fivez's study. The investigation of such effects should be considered in order to fully acknowledge such a magnetoelastic coupling model and the validity of the classical approach for treating one-dimensional spin fluctuations.

We will thus report, in this paper, experimental data for the temperature (4–200 K) and frequency (30–150 MHz) dependences of the ultrasonic velocity and attenuation of longitudinal waves propagating along the hexagonal axis in $CsNiCl_3$ crystal. These data are obtained in magnetic fields ranging from 0 to 8.5 T, oriented parallel and perpendicular to the easy magnetization axis. In order to appreciate these data we have extended Fivez's model for the acoustic velocity by the addition of a single-ion magnetic anistropy field and a magnetic field. Comparison of experimental data with the predictions of the model supports qualitatively the coupling of spin fluctuations with phonons. Some important deviations are, however, observed and they put into question the classical approach for spin fluctuations in $CsNiCl_3$.

II. THEORETICAL MODEL

The interpretation of our experimental data is based on an extension of Fivez's model to take into account the single-ion magnetic anisotropy field and the magnetic field. We report here only the outline of the model, the details of the theoretical development being presented elsewhere.[13]

The Hamiltonian used by Fivez expresses the modulation of the superexchange integral by a compressional acoustic wave. We can separate it into three parts, one for the phonons, $\mathcal{H}_P$, one for the spins, $\mathcal{H}_S$, and finally for the spin-phonon coupling, $\mathcal{H}_{SP}$:

$$\mathcal{H}=\mathcal{H}_P+\mathcal{H}_S+\mathcal{H}_{SP}$$

with

$$\mathcal{H}_P = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \tfrac{1}{2}\alpha \sum_{i=1}^{N-1} (x_{i+1}-x_i)^2 ,$$

$$\mathcal{H}_S = -J \sum_{i=1}^{N-1} \mathbf{S}_i \cdot \mathbf{S}_{i+1} ,$$

$$\mathcal{H}_{SP} = -\varepsilon \sum_{i=1}^{N-1} (x_{i+1}-x_i) \mathbf{S}_i \cdot \mathbf{S}_{i+1} .$$

α is the longitudinal restoring force constant, J is the parallel exchange integral ($J_\parallel \gg J_\perp$), and ε characterizes the strength of the magnetoelastic coupling. The index i identifies the momentum p, the displacement from equilibrium x, and the spin vector $\mathbf{S}$ at a particular site along the chain made of N sites. To this Hamiltonian, we have added a term for the single-ion magnetic anisotropy field

$$\mathcal{H}_{an} = D \sum_{i=1}^{N} (S_i^z)^2 .$$

The accepted value for D in $CsNiCl_3$ is quite small at -0.62 K,[4] compared with $J_\parallel$ (-33 K). As a consequence large magnetic-field-orientation effects are not expected. External magnetic-field effects are introduced via a Zeeman term

$$\mathcal{H}_Z = -g\mu_b \mathbf{H} \cdot \sum_{i=1}^{N} \mathbf{S}_i .$$

Due to the presence of these additional terms in the Hamiltonian, the expression giving the acoustic velocity is similar to the expression of Fivez's but the term appearing in the denominator now includes the summation over all neighbors. We now have

$$v = \frac{v_0}{\left[1 + Au \sum_j [\langle (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1})(\hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_{j+1}) \rangle - \langle \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} \rangle \langle \hat{\mathbf{S}}_j \cdot \hat{\mathbf{S}}_{j+1} \rangle] \right]^{1/2}} , \tag{1}$$

where

$$A = \frac{[S(S+1)]^2 \varepsilon^2}{\alpha |J_\parallel S(S+1)|}$$

is the magnetoelastic coupling constant. Also,

$$u = \beta |J_\parallel S(S+1)|, \quad \beta = 1/k_B T ,$$

and v_0 is the acoustic velocity in the absence of the magnetic interaction. The spins $\hat{\mathbf{S}}_i$ are assumed to be classical unit vectors. This expression is solved numerically using a transfer operator method and it yields, in the absence of the single-ion magnetic anisotropy and magnetic field ($D = |\mathbf{H}| = 0$), the same results as obtained from the analytical solution by Fivez. We may summarize the predictions of expression (1) according to the following: the magnetoelastic interaction produces a softening peak, centered at $T \sim J_\parallel / k_B$, whose amplitude is controlled by the parameter A; the presence of a magnetic field accentuates further the softening but the addition of the small single-ion anisotropy field has no direct measurable effect on the peak. A parallel treatment for the acoustic attenuation has not been done yet.

III. EXPERIMENT

The ultrasonic velocity was measured with a pulsed acoustic interferometer whose operating principle is based on the measurement of the phase difference between the ultrasonic wave and a reference signal.[14] This phase difference is inversely proportional to the ultrasonic velocity v according to the relation

$$\phi = \frac{2\pi f n L}{v} ,$$

where n, L, and f are, respectively, the number of back-and-forth trips executed by the acoustic pulse, the length of the sample, and the radiofrequency. During the experiment, when the external parameters (H, T) are modified, the phase difference is maintained constant by a frequency feedback loop. The relative velocity variation is then given by

$$\frac{\Delta v}{v} = \frac{\Delta f}{f} + \frac{\Delta L}{L} .$$

We can obtain the thermal expansion from the literature[6] so that a measurement of the frequency that keeps the phase constant yields directly the relative velocity variation. Since the magnetostriction[15] is usually orders of magnitude smaller than the variation of velocity due to the magnetic field, it is neglected. The attenuation is obtained from the amplitude of the first acoustic transmitted pulse at the output of the sample. Particular care has been necessary to take into account the nonparallelism and the finite bandwidth of the transducers. These effects can be evaluated correctly for frequencies up to 150 MHz and temperatures below 60 K.

The single crystal used for this experiment was grown by the Bridgman method. Its tendency to cleave along the $\{1120\}$ plane facilitated its orientation for acoustic propagation along the c axis [0001]. Parallel faces, approximately 10 mm apart with normals parallel to the c axis, were polished to receive the acoustic transducers. In this work we have used Y-cut coaxially plated $LiNbO_3$ piezoelectric transducers, having fundamental frequencies of 10 and 30 MHz, to produce the longitudinal acoustic pulses. Precisions better than 1 ppm for the acoustic velocity and 10% for the total attenuation are easily obtained with this interferometer.

In the present work, we have used longitudinal ultrasonic signals at 30, 50, 90, and 150 MHz propagating along the hexagonal axis. The orientation of the crystal in the magnetic field was controlled by a gearing system which allows all angles from 0 to 90°. The sample temperature was monitored with a carbon glass resistance sensor (weak magnetoresistance) and controlled by a Lakeshore DRC-93C system.

IV. RESULTS

Typical data of relative acoustic velocity and attenuation, at 150 MHz, in zero magnetic field, are presented in Fig. 1. The reference of the attenuation curve is taken at a temperature of 4.2 K in zero magnetic field. The acoustic velocity shows a 0.6% softening (decrease) between 10 and 40 K while the attenuation shows a broad maximum centered around 25 K. In the absence of a magnetic field, the ultrasonic data obtained are similar to those reported by Mountfield and Rayne[7] and by Almond and Rayne.[9] It has also been verified that the attenuation is proportional to ω^2 as mentioned by Almond and Rayne.[9] These dependences as a function of the temperature and frequency have been the object of earlier investigations; they are presented here for reference and because of their higher resolution, they will be used later in the discussion. We will now show how these data are modified by the application of a magnetic field.

The application of a magnetic field, parallel or perpendicular to the hexagonal axis, increases both the softening and attenuation. This can be seen in Fig. 2 where the relative velocity and attenuation data are plotted as a function of the magnetic field at field temperatures. Both sets of data follow a quadratic dependence on field and we may write

$$\frac{v(H)-v(0)}{v(0)}=\beta(T,\omega)H^2 ,$$

$$\alpha(H)=\gamma(T,\omega)H^2 .$$

The parameters β and γ are temperature and frequency dependent and they also vary with field orientation. These parameters are plotted in Figs. 3 and 4 as a function of the temperature for, respectively, parallel and perpendicular field relative to the hexagonal axis at various

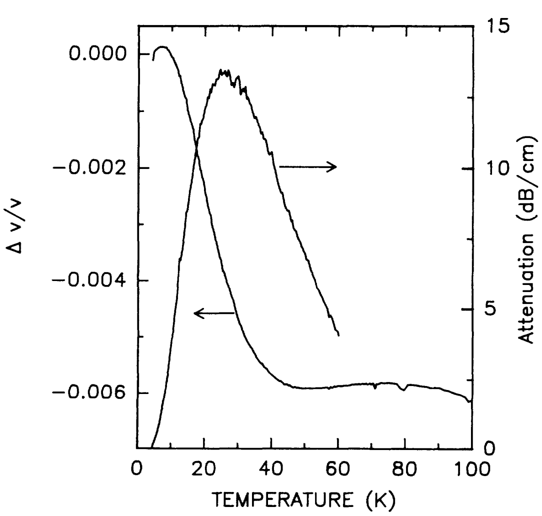

FIG. 1. Acoustic velocity and attenuation as a function of temperature in zero magnetic field and at 150 MHz.

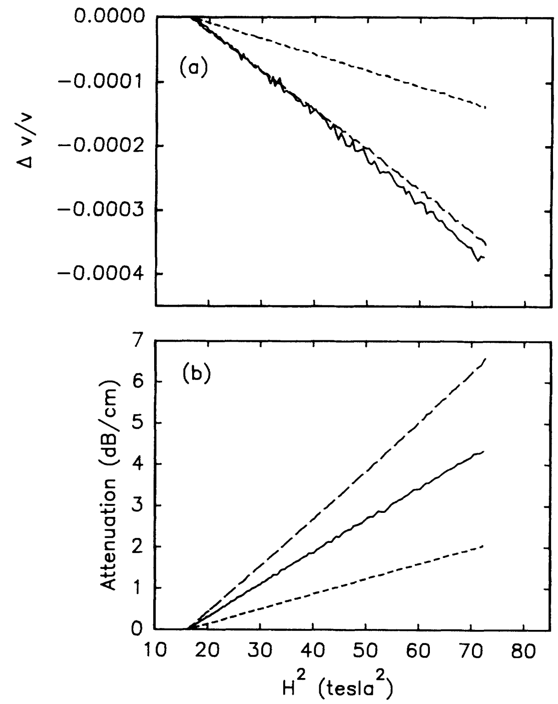

FIG. 2. Acoustic velocity (a) and attenuation (b) as a function of the magnetic field: ——, 10 K; — —, 25 K; and - - - -, 50 K.

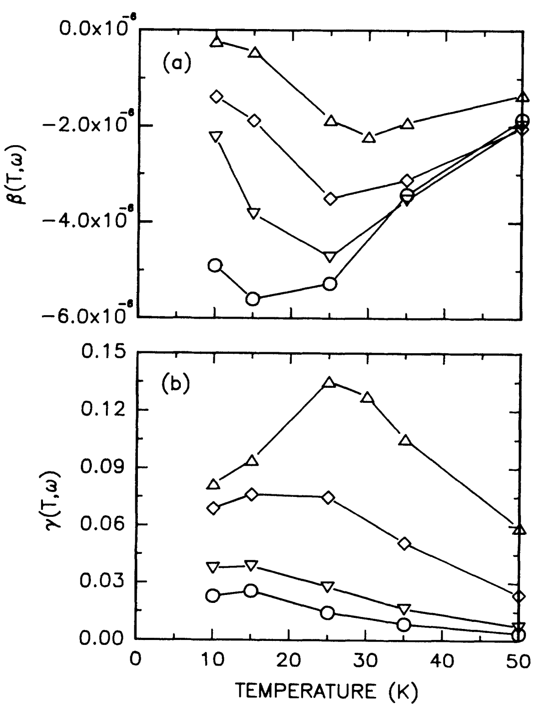

FIG. 3. Magnetic-field dependences of relative velocity and attenuation for field parallel to the hexagonal axis: ○, 30 MHz; ▽, 50 MHz; ◇, 90 Mhz; and △, 150 MHz. (a) $\beta(T,\omega)$ (T^{-2}); (b) $\gamma(T,\omega)$ (dB T^{-2}).

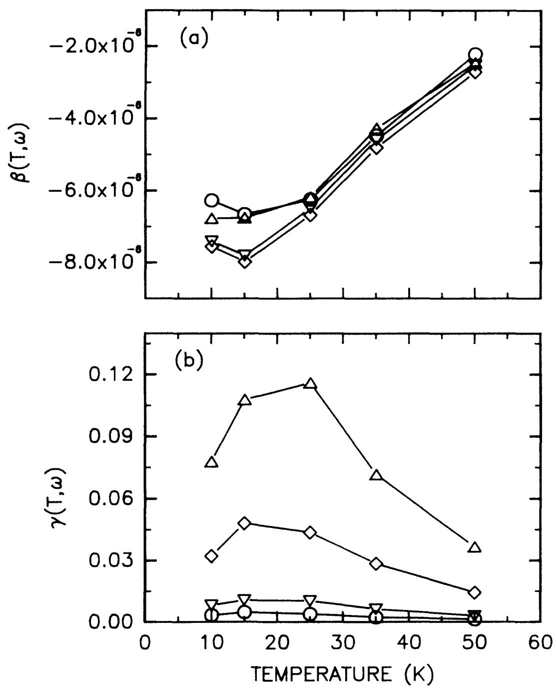

FIG. 4. Magnetic-field dependences of relative velocity and attenuation for field perpendicular to the hexagonal axis: ○, 30 MHz; ▽, 50 MHz; ◇, 90 MHz; and △ 150 MHz. (a) $\beta(T,\omega)$ (T^{-2}); (b) $\gamma(T,\omega)$ (db T^{-2}).

frequencies. In the first configuration (parallel), the absolute values of parameters β and γ show a broad maximum structure; when the frequency is increased, the maximum for the parameter β is shifted toward higher temperature along with a diminution of its amplitude; a similar temperature displacement can be observed on the maximum of the parameter γ but its amplitude increases with frequency in a way which is not parabolic. The picture is somewhat different in the perpendicular configuration (Fig. 4): there is no longer a shift of the temperature of the maximums as a function of frequency for both parameters while the amplitude is frequency independent for the parameter β and shows a more normal ω^2 dependence for the parameter γ. The observation of frequency effects on the velocity is not predicted by the theoretical model as well as the magnetic-field angular dependence because of the small amplitude of the single-ion anisotropy field in $CsNiCl_3$. These observations for the frequency and magnetic-field-orientation dependences should be considered to evaluate the validity of the theoretical model to explain the magnetoelastic coupling.

V. DISCUSSION

Before attempting to compare the experimental acoustic velocity data with the predictions of the theoretical model, we must isolate the contribution due to the magnetoelastic interaction. This means, in the first place, that we should subtract the elastic anharmonic contribution to the velocity, a contribution which is not directly accessible in $CsNiCl_3$. To conduct such a subtraction we have tried to find an equivalent crystal for which the magnetism, if there is any, does not affect the elastic constant C_{33}. In $CsNiF_3$, this elastic constant shows no anomaly[16] and it is quasilinear in the temperature range (4–300 K). This temperature behavior for C_{33}, after adjusting the slope by a factor of 5, has been used to isolate the magnetic contribution to the relative variation of acoustic velocity. This treatment is shown in Fig. 5(a). The magnetoelastic contribution deduced along this procedure is compared to the prediction of Fivez's model in Fig. 5(b) in the absence of a magnetic field; the magnetoelastic coupling constant A has been adjusted to 0.027 with $J_\parallel = -33$ K. The agreement is qualitatively good. The experimental softening peak has its maximum at a higher temperature and its width is much smaller than it is predicted. As it was said before, the single-ion magnetic anisotropy field D is very small in $CsNiCl_3$ ($D/J_\parallel \sim 0.02$) and its addition in the model does not affect the softening peak. According to this we should not expect the orientation of the magnetic field to be a relevant parameter for interpreting the data.

Considering the magnetic-field dependence, no subtraction of the anharmonic contribution is needed and the comparison with the model should be made easier. The inclusion of a Zeeman term in the model predicts[13] a quadratic H^2 field dependence for the acoustic velocity. This is shown in Fig. 6(a) for the parallel configuration where we have used the same parameter $A = 0.027$ at the reduced temperature $u = 1$ and with $g = 2.23$.[5] The straight line helps to show the quadratic dependence. This field dependence of the velocity has been verified at all temperatures, all frequencies, and magnetic field orientations. Although the same dependence was found for

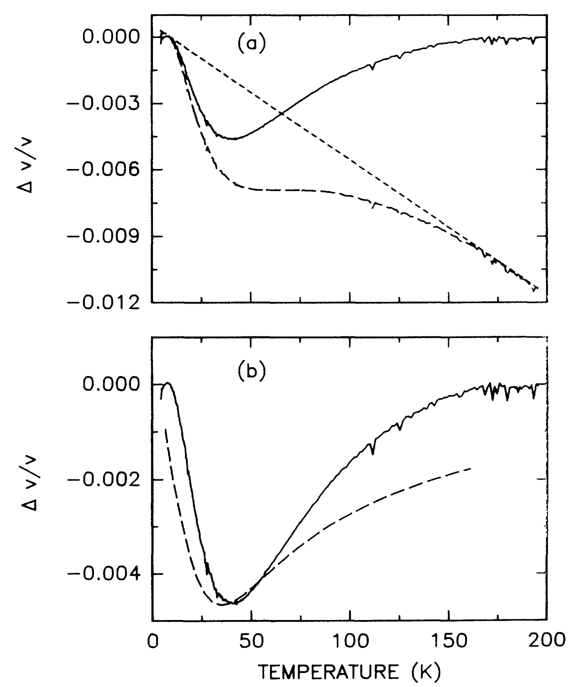

FIG. 5. (a) Process of subtraction of the anharmonic contribution from the experimental data: — —, experimental data; (- - -), anharmonicity; and ——, magnetic velocity. (b) Comparison between the experimental and theoretical magnetic softening: ——, experimental and — —, theoretical.

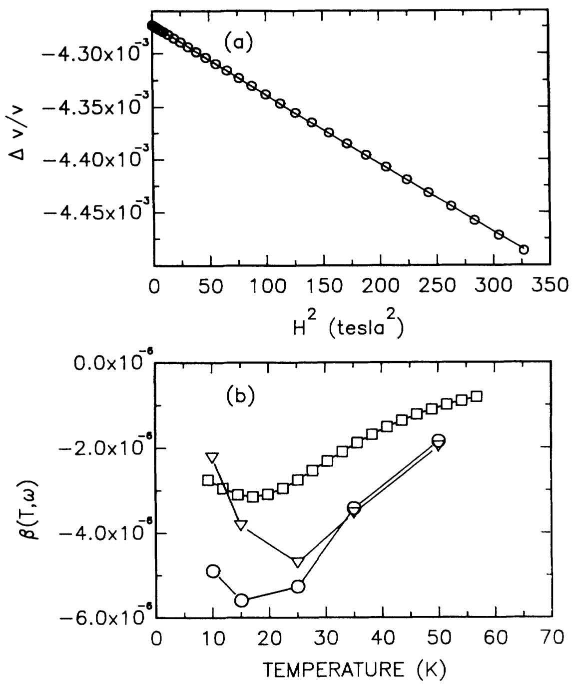

FIG. 6. (a) Theoretical velocity as a function of the magnetic field. (b) Comparison between theoretical and experimental β for $H\|c$: ○, 30 MHz; ▽, 50 MHz; and □, theoretical.

the attenuation, no theoretical predictions are available at this time. The temperature dependence of the theoretical parameter β (Ref. 13) (expressing this quadratic H^2 dependence on the field) is shown in Fig. 6(b). It is compared with experimental data obtained at 30 and 50 MHz for the parallel configuration. The agreement is qualitatively good at the lowest frequencies but the predicted amplitude is much smaller than measured. When the frequency is increased or if the orientation of the field is perpendicular to the hexagonal axis, the qualitative agreement is no longer valid.

Even if good qualitative agreement is found between the experimental data and the predictions of the model, important observations cannot be reconciled regarding the frequency and the field orientation dependences. These observations are possible indications that something is missing in the theoretical model. This could be the higher-order terms in the development of the exchange integral[13] since the large value of the magnetic Grüneisen constant would lead one to expect that the second-order constant will be larger than the first-order one. This second-order term was, however, neglected in the theoretical treatment. Another important approximation made in the development of the model was the use of classical spins ($S\rightarrow\infty$). As a consequence important quantum effects might have been neglected. In fact, the whole comparison as a function of the temperature relies on an arbitrary subtraction of the elastic anharmonic contribution to the velocity. This subtraction gives anomalies of the velocity and attenuation which are displaced from each other in temperature by ~ 15 K; from Fivez's model this temperature separation is at most 7 K. This difference cannot be attributed to the particular details of the anharmonic contribution chosen to obtain a softening peak for the velocity. We must remember that according to Kramers-Kronig relations, one should expect anomalies to be centered at the same temperature for any model. This fundamental discrepancy between the experience and the model suggests to us that there may be another way of analyzing the ultrasonic data. With a simple anelastic model in mind, it is possible to interpret the data of Fig. 1 as a softening step for the velocity (a step of 0.6%) when raising the temperature between 10 and 40 K accompanied by an attenuation peak centered exactly at the center of the velocity step. Such anomalies are often encountered in physical acoustics. The elastic anharmonic contribution that should be subtracted then will be similar to what is generally found in insulators at low temperatures. It is plausible that such a behavior is linked to quantum effects because, in $CsNiCl_3$, there is a relevant quantity in this range of energy, the Haldane gap[17] [$\Delta\sim 13$ K (Ref. 4)]. In this picture, at low temperatures the magnetism is frozen by the Haldane gap and the softening will come from the excited spin waves above the gap which would start at a temperature near to the value of the gap and will be maximum when the spin waves reach their full energy spectrum at $T\sim|J_{\|}|/k_B\sim 33$ K. The development of a quantum model would be needed to verify this hypothesis but the classical approximation may still be valid in systems where there is no Haldane gap such as $CsNiF_3$ (a ferromagnetic chain) or where there is a very strong easy axis, such as $CsCoCl_3$ ($D\sim J$, $S=\frac{1}{2}$).

VI. CONCLUSION

In this work, high-resolution data for the acoustic velocity and attenuation in $CsNiCl_3$ have been reported as a function of the temperature. We note that this is an acoustic investigation of this system in the paramagnetic phase in the presence of a magnetic field. Interesting frequency and magnetic-field-orientation effects have been found. These data have been compared with a model based on the longitudinal compression of a spin chain developed by Fivez and completed[13] to take into account the magnetic field and single-ion magnetic anisotropy field. In general, the comparison between the experimental and theoretical data is good qualitatively, but the model cannot explain the frequency and field orientation effects. There is some evidence that quantum effects may play an important role, especially those related to the Haldane conjecture. The development of a quantum model will be needed in order to fully appreciate the acoustic data in $CsNiCl_3$. However, the classical model can still be useful in systems that do not correspond to the Haldane conjecture. Experiments in such systems will be necessary if one wants to go any further in testing the validity of the classical model.

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