Investigation of acoustic phonons in $CsNiF_3$ by Brillouin scattering

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Brillouin scattering measurements were made to determine the velocities of acoustic phonons and the values of the elastic coefficients of $CsNiF_3$. Temperature dependence of C_{11} and C_{33} was investigated between 4 and 300 K. In contradiction with the earlier measurement of Young's modulus along the c axis of the crystal, C_{33} was found to have a negative thermoelastic coefficient. In connection with these measurements the dispersion of the refractive index was also determined.

Physical properties of the one-dimensional ferromagnet $CsNiF_3$ have recently been subject to much investigation. Low dimensionality can also be seen in the hexagonal $P6_3/mmc$ structure[1] of the crystal where Ni^{2+} ions form chains along the c axis. The spins lie in the xy plane but there is a ferromagnetic coupling along the chains. When the temperature is lowered the weak interchain interactions become more important and the crystal changes to a three-dimensional (3D) antiferromagnetic state at $T_N=2.6$ K.[2] It has been suggested that a chain structure of a low-dimensional material may cause specific elastic anisotropy.[3] Accordingly, Young's moduli of $CsNiF_3$ were investigated by using a vibrating reed technique over the frequency range $1-4$ kHz.[4] The results show a large softening of the modulus measured along the c axis when the temperature is lowered from 300 to 30 K. Whether this softening should be connected to the 1D magnetic interactions, or even to the chain structure along the c axis, is not clear. Below T_N a sharp anomaly pertaining to the magneto-elastic interactions is clearly seen. When measured perpendicular to the c axis, the Young's modulus was found to slowly increase upon cooling the sample, which is a common feature of many materials.

The macroscopic elastic properties of $CsNiF_3$ are very anisotropic. The crystal has a cleavage plane which contains the a and c axes and it breaks up easily to needles which have their axes parallel to the c crystallographic direction. This suggests that the values of the elastic coefficients may depend on the experimental method used. In the present work we investigate the velocities of hypersonic phonons in $CsNiF_3$ by the Brillouin scattering method and compare the results with those obtained by low-frequency measurements.[4]

$CsNiF_3$ is fairly transparent in the green region of the spectrum. Hence, the investigation of spin dynamics by observing light scattering from pumped magnons[5] may be feasible in this crystal. If the magneto-elastic interactions are strong enough, enhanced light scattering near certain phonon frequencies may be anticipated. The present Brillouin scattering data for acoustic phonons would be helpful in planning these kinds of experiments.

The sample crystals were cut from a block of $CsNiF_3$ to a typical size of $5\times5\times5$ mm^3. To slice the crystal perpendicular to the c axis, it was first casted in "plastic padding" and carefully cut with a wire saw. The final polishing was made with diamond paste. Both an Ar and a Kr laser were used as the light source in the Brillouin spectrometer. The spectrum of the scattered light was analyzed by using a triple-pass Fabry-Perot interferometer. In order to be able to calculate the velocity of phonons from the observed Brillouin shifts, the refractive indices of the sample crystal must be known. These were measured by using both the minimum deviation method and the method based on the observation of Brillouin scattering itself.[6] The results are quoted in Table I for some laser wavelengths.

The Brillouin shifts ν_B and the velocity of phonons v are related with the formula

$$\nu_B=\frac{v}{\lambda}(n_i^2+n_s^2-2n_in_s\cos\phi)^{1/2}\ , \tag{1}$$

where λ is the wavelength of the incident light. The refractive indices n_i and n_s are defined for the directions of the incident and scattered light propagating with the mutual angle ϕ. Some examples of the scattering geometries used and the related Brillouin data, obtained at the 514.5-nm Ar line, are collected in Table II. In the notation $a(bc)d$,

TABLE I. Refractive indices of $CsNiF_3$ measured at different laser wavelengths, $T=300$ K, and at 514.5 nm, $T=4$ K. $dn_{o,e}/dT=-2.59\times10^{-5}$ K^{-1} between 4 and 300 K.

λ (nm)	n_o	n_e
528.7	1.4812	1.5130
514.5	1.4815	1.5140
514.5	1.4892 (4 K)	1.5217 (4 K)
501.7	1.4822	1.5150
488.0	1.4830	1.5158
454.5	1.4858	1.5186

the first and last symbols stand for the directions of the incident and scattered lights and those in parentheses their polarizations, respectively. The density $\rho=4693$ kg^{-3}, used to calculate C_{ij} from v, was estimated from the x-ray results $a=6.23$ and $c=5.22$ Å.[1] There is some variation in the published values of the lattice constants of $CsNiF_3$. The corresponding changes in ρ will be, however, less than 1%. The room-temperature values of C_{ij} are given in Table III. Some elastic coefficients of $CsNiF_3$ have been determined earlier from neutron scattering data observed at 85 K.[7] Except for C_{11}, these results ($C_{11}=4.7$, $C_{33}=6.7$, and $C_{44}=0.5\times10^{10}$ dyn/cm^2) deviate to some extent from our values. However, the coefficients derived from the neutron scattering data may involve some inaccuracy due to the difficulty in determining the slope of the dispersion curves at small values of the wave vector.

The elastic anisotropy of $CsNiF_3$ can be described by the ratios $(C_{33}/C_{11})=2.2$ and $(C_{66}/C_{44})=6.1$. C_{11} and C_{33} are related with the longitudinal modes propagating along the a and c axes of the crystal and C_{44} and C_{66} with the transverse modes propagating perpendicular to the c axis but vibrating in the basal plane or along the c axis, respectively. Although these ratios clearly indicate elastic anisotropy, the phonon dynamics of $CsNiF_3$ still has essentially three-dimensional character. Starting from the expressions for the velocity of phonons in different crystal symmetries[8] and our experimental data, the velocity was further investigated in the ac plane. As shown by Fig. 1, the strongest asymmetry in this plane is related with C_{44}.

Figure 2 shows the temperature dependence of C_{11} and C_{33}. The strong softening upon cooling was the essential feature of the measurement of the Young's modulus $E_{||}$ along the c axis of $CsNiF_3$.[4] It can be shown, by using the connections between elastic compliances and stiffnesses in the hexagonal system,[9] that $E_{||}$ and C_{33} are related by the equation

$$E_{||}=\frac{C_{33}(C_{11}+C_{12})-2C_{13}^2}{C_{11}+C_{12}}\ . \tag{2}$$

Taking into account the relation $C_{13}<<C_{33}$, we can write $E_{||}\sim C_{33}$. However, when the measured temperature dependence of C_{33} is compared with that of $E_{||}$, it is seen that the behavior of these parameters is quite different. Instead of softening, we found C_{33} to increase by about 3% upon cooling from 300 K down to 4 K. While $E_{||}$ showed hysteresis between cooling and heating periods, the values of C_{33} seem not to depend on thermal cycling of the sample. It is not easy to understand

TABLE II. Examples of the Brillouin scattering measurements at $\lambda=514.5$ nm and $T=300$ K. The wave vector of the phonon is denoted by $\vec{q}$. L, T, and M represent the longitudinal, transverse, and mixed phonon modes.

Case	$\vec{q}$				
$\bar{x}(yy)x$	(100)	L	17.71	3075	C_{11}
$\bar{z}(xx)z$	(001)	L	26.10	4531	C_{33}
$\bar{z}(yy)x$	$(101)/\sqrt{2}$	L	13.35	3277	γ_{13}
$\bar{z}(yy)x$	$(101)/\sqrt{2}$	M	8.94	2195	γ_{14}
$\bar{z}(yz)x$	$(101)/\sqrt{2}$	T	5.55	1348	$\frac{1}{2}(C_{44}+C_{66})$
$\bar{x}(zy)y$	(110)	T	2.97	721	C_{44}

$$\gamma_{13}=\tfrac{1}{4}\{C_{11}+C_{33}+2C_{44}+[(C_{11}-C_{33})^2+4(C_{13}+C_{44})^2]^{1/2}\}$$
$$\gamma_{14}=\tfrac{1}{4}\{C_{11}+C_{33}+2C_{44}-[(C_{11}-C_{33})^2+4(C_{13}+C_{44})^2]^{1/2}\}$$

TABLE III. Values of the elastic coefficients of $CsNiF_3$ at 300 K.

C_{ij}	in units of 10^{10} N/m^2
C_{11}	4.45±0.10
C_{12}	1.50±0.10
C_{13}	0.74±0.10
C_{33}	9.66±0.10
C_{44}	0.24±0.05
C_{66}	1.47±0.10

why the methods used to measure $E_{||}$ and C_{33} give so different temperature dependences. It is possible that the structural properties of $CsNiF_3$, including the high tendency to break up to thin needles, are involved in a different way in the measurements of a low-frequency and high-frequency elastic mode in this crystal. It is worth noting that $E_{\perp}$ has rather similar temperature dependence to that measured by us in the case of C_{11}.

The magnetic properties of a 1D magnet are controlled by short-range order, which is temperature dependent. The regions over which the spins are correlated can be described by the correlation length $\xi(T)$ which in $CsNiF_3$ at 10 K is about 20 Å.[2] This value is 2 orders of magnitude smaller than a typical wavelength of phonons detected by Brillouin scattering. The short-range order is described by the spin-correlation function, which governs both quasistatic and dynamic properties of a magnetic system. In a number of 3D and 2D magnets, an anomaly in the velocity and absorption of phonons can be observed near a magnetic phase transition point.[10,11] The size of the anomaly of velocity is usually limited between 0.1% to 1% but it may be even smaller.[11] The dominating coupling mechanism is the spin-phonon energy-density interaction. Although the lack of long-range order leads to the condition $\langle M \rangle \equiv 0$, magneto-elastic interactions may become possible if the correlation length ξ approaches the wavelength of a phonon. As mentioned above, this requirement is not met in the present measurements. Therefore it is understandable that when measuring $\nu_B(C_{11})$ and $\nu_B(C_{33})$ below 60 K, we found no indication of coupling between magnetic correlations and phonons.

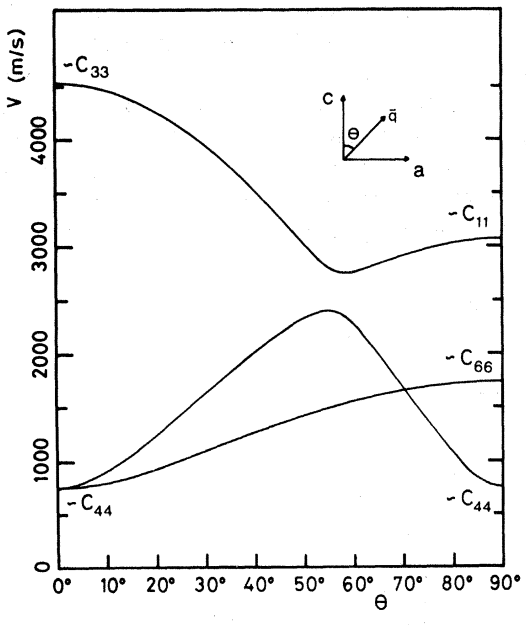

FIG. 1. Velocity of phonons propagating in the *ac* plane of $CsNiF_3$. The direction of the wave vector $\vec{q}$ of phonons is defined by an angle θ. The indicated elastic coefficients refer to propagation along the axial direction of the crystal.

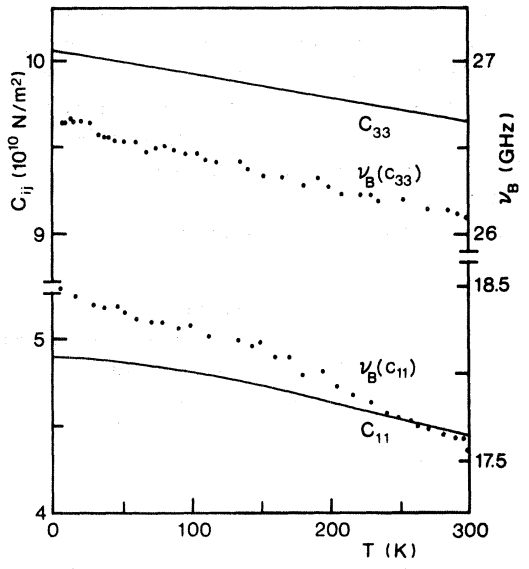

FIG. 2. Temperature dependence of Brillouin shifts (dots) for the longitudinal phonons propagating perpendicular (C_{11}) or along (C_{33}) the *c* axis of $CsNiF_3$. The values of the elastic coefficients calculated from these data (solid lines) are corrected for the temperature dependences of the refractive indices and of the density of the crystal.

Note added. After the manuscript was sent for publication a new crystal of $CsNiF_3$ was received from Cristal Tec, France. The elastic coefficients measured from this material agree very well with those reported in this paper.

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