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Loidl, Alois, S. Haussühl, and J. K. Kjems. 1983. “Elastic properties of CsCN.” Zeitschrift für Physik B Condensed Matter 50 (3): 187–92. https://doi.org/10.1007/bf01304126.

Elastic Properties of CsCN

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The temperature dependence of the elastic constants of CsCN exhibiting the CsCl structure was measured with ultrasonic and neutron techniques. The room temperature values were found to be $c_{11}=18.8$, $c_{12}=10.7$ and $c_{44}=2.95\ 10^{10}$ dyn/cm^2. The sound waves in T_{2g} and E_g symmetries exhibit anomalous temperature effects which are similar but definitively weaker than those in the NaCl type cyanides. In addition we measured the acoustic phonon dispersion along [100] and [110]. These results are compared with recent molecular dynamics calculations.

I. Introduction

Caesium cyanide is an ionic crystal with a pseudo-cubic (CsCl, Pm3*m*) high temperature phase in which the $(CN)^-$ ions are orientationally disordered. At 193 K CsCN transforms discontinuously into a trigonal ($R\bar{3}m$) structure [1-4]. The $(CN)^-$ ions are aligned now along the threefold axis, corresponding to what were the ⟨111⟩-axes in the cubic phase [2]. The space group of the low temperature phase implies that the $(CN)^-$ ions are still disordered with respect to head and tail. As no further phase transformation was found down to 14 K [2] the crystal exists in a non-equilibrium state where the electric ordering is suppressed by high hindering barriers leading to long relaxation times for 180° flips. This situation is strongly suggestive for a frozen-in state at the lowest temperatures [2]. A similar situation was proposed for the low temperature state of RbCN (with a high temperature NaCl structure) [5].

The special interest in CsCN lies in the fact that this salt exhibits the CsCl structure and it can be expected, that the reorientational dynamics differ significantly from those of the rocksalt-type cyanides NaCN, KCN and RbCN which have been studied extensively by ultrasonic, Brillouin and neutron techniques [6-19]. These investigations showed that the characteristic frequencies of the reorientational process are of the order of some meV, leading to anomalous dispersion effects in this frequency range in the acoustic branches. These effects are most pronounced in T_{2g} symmetry where in addition a drastic softening of the long wavelength phonons is observed as the transition temperature to the ordered phase is approached from above. Theoretically these results have been explained by a microscopic model of Michel and Naudts [20] where the translational modes are coupled to the rotational degrees of freedom of the system. In KCN there exists a controversy if a pure relaxational model or a model with a finite excitation energy accounts for the measured neutron line shapes [17, 18].

To our knowledge, the only published experimental work on the dynamic properties of CsCN is our previous inelastic neutron scattering investigation [21]. These experiments have established that the [100] TA branch displays no anomalous dispersion, in contrast to the experimental findings in KCN, NaCN and RbCN. However, on cooling towards the phase transition a drastic softening of the entire transverse acoustic branch was observed. The [110]

TA (E_g) phonons showed a clear interaction with a rotational excitation.

Very recently Klein et al. [22] reported molecular dynamics calculations for the orientationally disordered phase of solid CsCN. These calculations reproduced the anomalous low frequencies of the [100] TA phonons, but were unable to account properly for the behaviour of the TA phonons propagating along [110].

In this article we report the temperature dependence of the elastic constants c_{11} and c_{44} determined by ultrasonic techniques. In addition we present some new neutron data of transverse and longitudinal modes in the [100] and [110] directions.

II. Experiments and Results

The single crystal of CsCN was grown from the melt employing the Czochralski technique and originally had a volume of 0.3 cm^3. The ultrasonic and neutron measurements were carried out only down to temperatures of 195 K in order to avoid the first order transformation of the crystal. In very recent dielectric and X-ray measurements we determined the transition temperature from the disordered to the elastically ordered phase to be 186 K, 7 K below the value reported by Sugasaki et al. [2] for a crystal which has been grown from solution.

For the ultrasonic investigation we were able to prepare a slab of 3 mm thickness with parallel [100] faces which were grinded and polished. The sound velocity was determined by measuring the transit time of an ultrasonic pulse applying the pulse overlap method. The measuring frequency was 10 MHz. As bonding agents between quartz transducer and sample we used - dependent on the temperature and on the polarisation of the sound wave - Salol (Phenyl-Salicylate), Nonaq stopcock grease or Apiezon. The temperature was measured with a calibrated Silicon diode inside a continuous Helium flow cryostat. For the calculation of the elastic constants we used the room temperature density ($\rho = 3.41$ g/cm^3) and the room temperature lattice constant ($a = 4.26$ Å).

The results for c_{11} and c_{44} are shown in Fig. 1. These data summarize the results of different runs. The relative temperature dependence of the elastic constants determined from these runs was essentially the same and always inside the scatter of the data, but the absolute values differed as much as 8%. Note that c_{44} is the pure T_{2g} symmetry mode, while c_{11} contains A_{1g} and E_g contributions. Of course it would have been desirable to measure also $(c_{11} - c_{12})/2$, the pure E_g symmetry mode directly, which is determined by the velocity of sound waves propagating along [110] and being polarized in the $[1\bar{1}0]$ direction. But the crystal was too small to prepare slabs of reasonable size with [100] and [110] faces respectively. However, from our experience with the NaCl type cyanides we expect the bulk modulus (A_{1g} symmetry) to be unaffected by the rotational-translational coupling [23] and therefore the temperature dependence of c_{11} should be entirely due to E_g contributions.

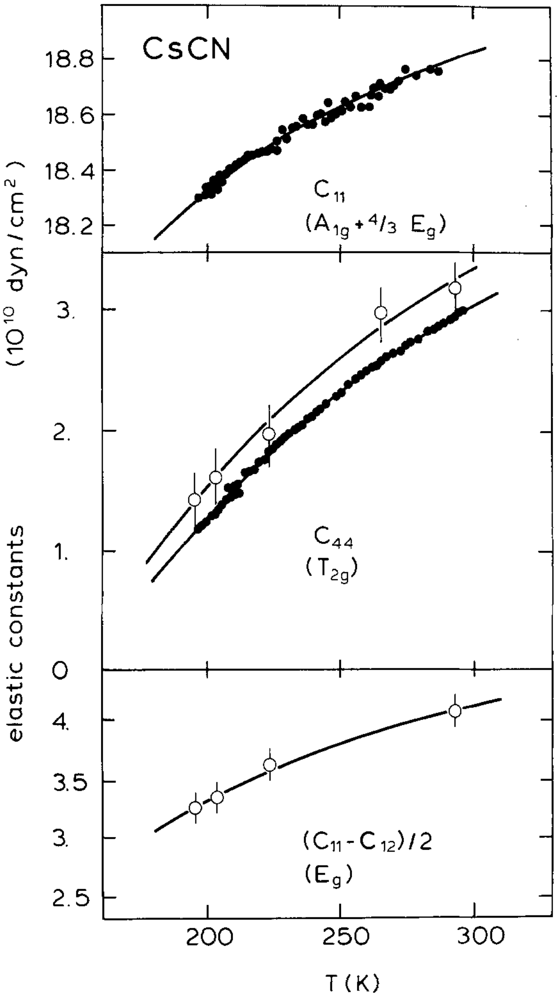

Fig. 1. The elastic constants c_{11}, c_{44} and $(c_{11} - c_{12})/2$ versus temperature: ultrasonic results (●), neutron results (o). The solid lines are the result of a Curie law fitted to the experimental data

From room temperature down to 195 K the shear modulus decreases by more than 60%. The softening of c_{11} is only moderate; its decrease is only of the order of 2-3%. Both effects are similar but definitively weaker than those observed in potassium cyanide which exhibits a similar transition temperature (168 K).

The inelastic neutron scattering experiments were carried out on a triple axis spectrometer situated at the cold neutron source of the reactor DR3 at Risø. Fixed incident neutron wave numbers k_i of 1.55 Å^{-1} and 2.66 Å^{-1} were used with pyrolytic graphite monochromator and analyser in connection with common filter techniques. A typical horizontal collimation was 60′-40′-40′-40′ along the path of the neutrons. The scans were performed in the constant E- and in the constant $\vec{Q}$-mode of operation within the (001)-plane. In Fig. 1 we plotted the temperature dependence of the elastic constants c_{44} and $c''=(c_{11}-c_{12})/2$ as determined from the slope of the phonon dispersion in a phonon wave number region $0.05 \leqq q/q_{ZB} \leqq 0.15$.

In T_{2g} symmetry we measured the temperature dependence of the sound wave by ultrasonic and by neutron scattering techniques. The relative temperature dependence is very similar with no indication of dispersion effects in the whole temperature range. The discrepancy between the neutron and the ultrasonic results on the absolute values of c_{44} might be due to systematic errors: no corrections have been made for the influence of the resolution ellipsoid in analysing the neutron results (due to the vertical focusing monochromator especially the vertical divergence is quite large). In the ultrasonic measurements large absolute errors can be introduced by the small path length and the relatively poor surface quality of the CsCN crystal.

In pure E_g symmetry only the neutron data are available. They indicate a softening to a much lesser degree than that observed in c_{44}. This is consistent with the ultrasonic results comparing c_{11} and c_{44}. Analogous to the results in the alkali cyanides with NaCl structure also CsCN shows the strongest coupling of translational modes with the internal molecular states of the CN dumb-bell in T_{2g} symmetry. Obviously it is this interaction that drives the phase transition, consistent with the symmetry of the low temperature phase.

Figures 2 and 3 show the very different behaviour of the transverse acoustic modes in E_g and T_{2g} symmetries. At small q-values well defined neutron groups are measured in both directions. Along [110] they broaden and finally anticross a rotational exci-

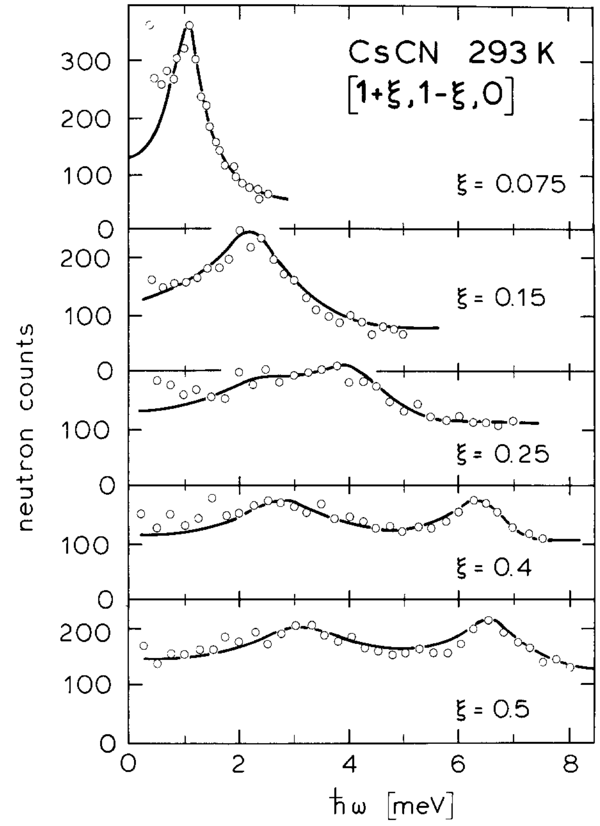

Fig. 2. Neutron groups along [110] TA polarised in the [1$\bar{1}$0] direction (E_g symmetry). The lines are the results of the mode-mode coupling model

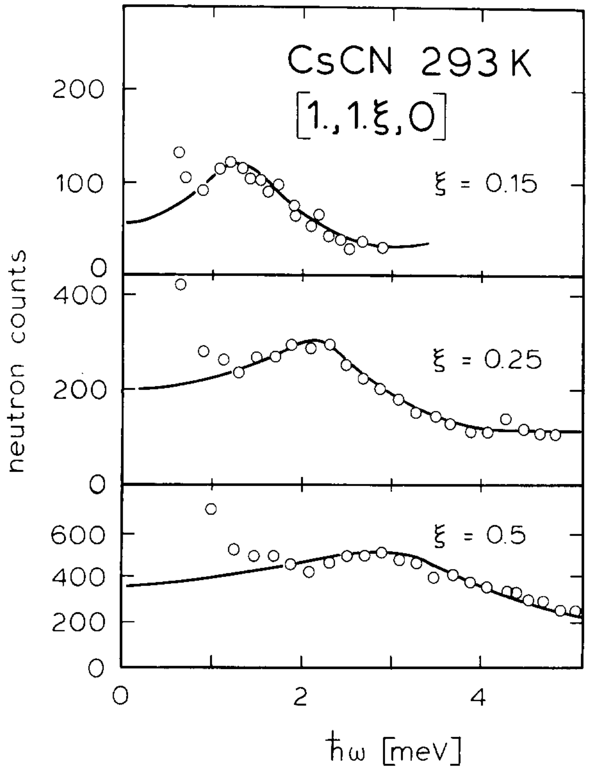

Fig. 3. Neutron groups along [100] TA. The lines are the results of the Silverman model in the relaxation limit ($\Delta \ll \Gamma$)

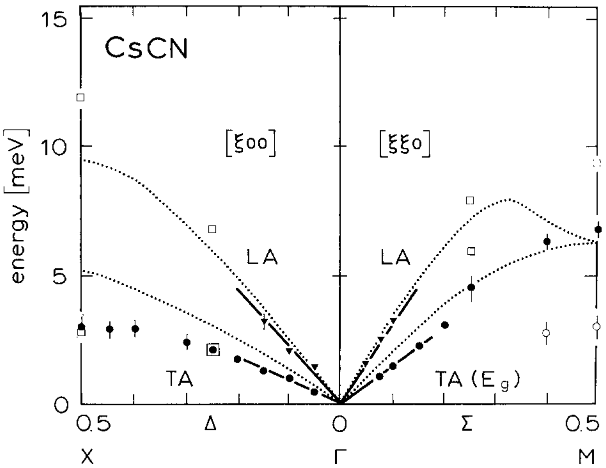

Fig. 4. Dispersion relation in CsCN at room temperature along [100] and [110]: transverse phonons (♦), longitudinal phonons (▼), rotational excitations (E_g symmetry) (ϕ). The full lines represent the long wavelength dispersion as being calculated from the elastic constants. The dotted lines show the experimental phonon dispersion in CsBr [28]. The open squares (□) are the results of a molecular dynamics calculation by Klein et al. [22]

tation. Near the zone boundary an acoustic phonon at 6.75 meV and a broad molecular excitation at 3 meV are observed. Along [100] the line width increases with increasing phonon wave number, but in contrast to the observations in E_g symmetry no molecular excitation is located in a frequency region from one to five meV. The line shapes remind of a system of purely relaxational character.

In Fig. 4 we show all the room temperature neutron results of the phonon dispersion in the [100] and the [110] directions. Here we include also some results on long wavelength longitudinal phonons.

III. Analysis of the Experimental Results and Discussion

In the analysis of the experimental data we follow the pseudospin approach by Silverman [24]. Assuming a two level system the molecular (pseudospin) susceptibility is written as [24]

$$\chi(\omega)=\frac{\alpha^2 \operatorname{tgh}\left(\frac{\hbar\Delta}{2k_BT}\right)\left[\Delta+\frac{\Gamma}{\Delta}(i\omega+\Gamma)\right]}{(i\omega+\Gamma)\left[i\omega+\Gamma\left(1-\frac{2J\alpha^2}{\Delta}\operatorname{tgh}\left(\frac{\hbar\Delta}{2k_BT}\right)\right)\right]+\Delta\left(\Delta-2J\alpha^2\operatorname{tgh}\left(\frac{\hbar\Delta}{2k_BT}\right)\right)}. \tag{1}$$

Here the two levels are separated by an energy $\hbar\Delta$ and connected with the transition matrix element α. Γ is the linewidth of the rotational excitation. J is an effective interaction between the CN dumb-bells which can be either direct (electric dipolar or quadrupolar coupling) or indirect (the molecules are coupled through optical branches).

This model was used to calculate the coupled proton-phonon system in KDP [24]. However, similar pseudospin theories have been used to account for phase transitions in Jahn-Teller systems and in a variety of molecular crystals where the spin variable specifies the orientational configuration of the aspherical ions [25]. The phonon propagator of a particular mode (E_g, T_{2g}) in the coupled pseudospin-phonon system is given by

$$D(\vec{q},\omega)=\frac{2\omega_0(\vec{q})}{\omega_0^2(\vec{q})-\omega^2-g^2\,\omega_0^2(\vec{q})\,\chi(\omega)+i\gamma\omega} \tag{2}$$

where $\omega_0(\vec{q})$ is the undisturbed phonon frequency of a phonon with wave vector $\vec{q}$ and g is the rotational translational coupling constant. γ is an additional damping constant due to the normal phonon anharmonicity. The dynamic structure factor $S(\vec{q},\omega)$ yields the shape of the scattered neutron groups. It is given by

$$S(\vec{q},\omega)=\left[1-\exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]^{-1}\operatorname{Im}D(\vec{q},\omega). \tag{3}$$

The poles of (2) determine the excitation frequencies. The limit of vanishing frequencies ($\omega\to 0$) yields the well known Curie-Weiss law for the elastic constants

$$c=c_0\,\frac{T-T_S}{T-T_C} \tag{4}$$

with the characteristic temperatures $T_S=\frac{\hbar}{k_B}\,g^2\alpha^2+T_C$ determining the temperature were the elastic constant c vanishes and $T_C=\frac{\hbar}{k_B}\,\alpha^2 J$ the clamped transition temperature. At T_C the pseudospins would order in absence of a coupling to the acoustic phonons ($g=0$). c_0 is the undisturbed 'background' elastic constant.

The pseudospin approach outlined above neglects the temperature dependence of the single site potential. This effect is explicitly taken into account in the microscopic model of Michel and Naudts [20] and yields a temperature dependence of the parameters

$T_S \sim y(T)(g^2\alpha^2 + T_C)$ and $T_C \sim y(T)\alpha^2 J$ [20, 26]. In CsCN $y(T)$ decreases with decreasing temperature by a factor of 1.15 in T_{2g} symmetry and increases by a factor of 1.07 in E_g symmetry in the experimental temperature range [27]. These numbers are of the same size as the effects of anharmonic renormalization of the elastic constants. For a first inspection and especially for a test if neutron scattering and ultrasonic results can be explained with the same set of coupling parameters it seemed reasonable to neglect these contributions. This treatment is very similar to the formalism we used in previous publications [18, 21]. However, the molecular susceptibility of (1) has the great advantage that it yields a relaxational behaviour in the limit $\Gamma \gg \Delta$. So, simply by increasing the linewidth Γ of the molecular excitation one finds a crossover from a coupled mode to a relaxational behaviour. In the latter case the dynamics of this coupled pseudospin-phonon system is solely determined by Γ independent of the level separation Δ as long as $\Gamma \gg \Delta$ is warranted.

Using this formalism and by adjusting the free parameters T_S, T_C, Δ, Γ and c_0 we tried to find a consistent description of both, the elastic and the neutron results. Best fits to the lineshapes of the inelastic scattered neutron groups were achieved with T_C values of about 0 K. This is documented in Fig. 2 where the rotational excitation at 3 meV is dispersion free, while large values of T_C describe dispersive propagating rotational excitations. A fit to the elastic constants with $T_C = 0$ K is acceptable. However, if one assumes a temperature dependence of the background elastic constants due to phonon anharmonicity – we performed calculations assuming that c_0 follows the thermoelastic behaviour of pure CsBr – the best fit values of T_C are of the order of -300 K, a value suggesting collective molecular excitations in contradiction to the experimental observations. Therefore the best overall description of ultrasonic and neutron results was achieved by setting $T_C = 0$ K which means that one neglects the coupling between the $(CN)^-$ ions.

The solid lines in Figs. 1–3 are the results of these fits using (3) and (4). The values of the best fit parameters are listed in Tables 1 and 2. Each constant $\vec{Q}$ scan in Figs. 2 and 3 was fitted using a separate set of parameters. The error bars in Table 2 are due to the scatter of the parameters for the different scans.

In T_{2g} symmetry the parameters c_0 and T_S determined from ultrasonic measurements agree very well with both, the long wavelength neutron results (Fig. 1) and the results from a fit to the neutron lineshapes covering the whole Brillouin zone (Fig. 3).

Table 1. Parameters determined by fitting (4) (with $T_C = 0$ K) to the temperature dependence of the elastic constants

Elastic constant	(Symmetry)	c_0 (10^{10} dyn/cm^2)	T_S	Experimental technique
c_{11}	$(A_{1g} + 4/3\,E_g)$	20.0	18.0	ultrasound
c_{44}	(T_{2g})	6.5	160.5	ultrasound
c_{44}	(T_{2g})	7.0	156.0	neutrons
$(c_{11} - c_{12})/2$	(E_g)	5.7	82.0	neutrons

Table 2. Parameters of the pseudospin model fitted to the observed neutron lineshapes of Fig. 2 and 3

Symmetry	c_0 (10^{10} dyn/cm^2)	Δ (meV)	Γ (meV)	T_S (K)
E_g	6.7 ± 0.4	3.3 ± 0.3	1.4 ± 0.4	98 ± 11
T_{2g}	6.5 ± 0.2	$\Delta \ll \Gamma$	5.0 ± 1.0	155 ± 05

In E_g symmetry the agreement is less satisfactory but still reasonable.

The values of the parameters listed in the Tables 1 and 2 are comparable with the results of our previous analysis [21] with the exceptions of c_0 and Δ in T_{2g} symmetry. The former analysis yielded $\Delta = 7$ meV. This value was forced by a model that produced a relaxational behaviour in the limit $\Delta \gg \Gamma$. We found no evidence for a rotational excitation in this frequency range and we believe that the model of Silverman [24] used in the present analysis is more reliable.

In CsCN all the phonon frequencies of the [100] TA branch fall into the range of fast relaxation $\omega \ll \Gamma$. With decreasing temperature the whole branch softens [21]. This also explains the absence of any anomalous dispersion effects in this branch contrary to the experimental findings in NaCN [16], KCN [16, 17, 18] and RbCN [19]. In all these NaCl-type cyanides the frequencies in the [100] TA branch show a transition from a fast to a slow relaxational case.

The phonons along [110] TA with a polarisation in the $[1\bar{1}0]$ direction show a clear interaction with a molecular excitation at 3 meV. A similar coupled mode behaviour along [110] has not been found in the other cyanides, but so far a systematic study has not been performed in these crystals.

A summary of the present experimental status in CsCN is given in Fig. 4 where we plotted all the measured excitations at room temperature together with the long wavelength phonon dispersion as calculated from the elastic constants determined with ultrasonic techniques. The dotted lines show the measured phonon dispersion in CsBr [28]. Taking into account the different coupling mechanism in T_{2g} and E_g symmetry it seems that CsBr is a reasonable 'background system' describing the uncoupled phonon frequencies. The open squares are the results of the molecular dynamics calculations of Klein et al. [22]. There is excellent agreement with the measured [100] TA phonons. The discrepancies in the other branches could arise from the model that ignores the polarisation of the ions, a conclusion that thas been drawn already by Klein et al. [22].

IV. Summary

We investigated the elastic properties of CsCN in the paraelastic phase utilizing ultrasonic and neutron techniques. The room temperature values of the elastic constants are: $c_{11}=18.8$, $c_{12}=10.7$ and $c_{44}=2.95\ 10^{10}$ dyn/cm^2. In calculating c_{12} we used $(c_{11}-c_{12})/2$ as determined from the long wavelength neutron results. Anomalous temperature effects appear in E_g and T_{2g} symmetries, with the most drastic softening of the elastic constant c_{44}. These results are very similar to the experimental findings in the NaCl-type cyanides. In T_{2g} symmetry we have a direct comparison of the temperature dependence of the elastic constant measured at 10 MHz and at THz frequencies. In both cases the thermoelastic behaviour is essentially the same and we found no indications for dispersion effects.

At room temperature we followed the phonon dispersion in the main symmetry directions in the (001)-plane throughout the Brillouin zone. Along [110] TA a rotational excitation at 3 meV causes a mixed mode behaviour. In the [100] TA direction the observed translational excitation shows a fast relaxational behaviour. For the inverse relaxation time we found $\Gamma=5$ meV. These characteristic frequencies of the molecular susceptibility are responsible for dispersive effects in the sound wave propagation. In CsCN they are at 3 and 5 meV. Therefore, ultrasonic, Brillouin and longwavelength neutron results should yield the same thermoelastic behaviour, consistent with our experimental findings.

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