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The elastic anomaly of NaCN at 284 K

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Résumé. — Nous avons mesuré la fréquence et la largeur Brillouin de phonons longitudinaux ($\mathbf{q} \parallel \mathbf{e} \parallel (1, 0, 0)$) et de phonons transverses mous ($\mathbf{q} \parallel (1, 1, 0)$; $\mathbf{e} \parallel (0, 0, 1)$) dans la phase cubique de NaCN, au-dessus de la transition de phase élastique. Les résultats sont discutés sur la base de la théorie semi-phénoménologique proposée pour décrire les variations des constantes élastiques et des largeurs de phonons dans KCN. On montre que les effets anormaux liés à la dilatation du cyanure ne permettent pas une analyse quantitative cohérente de l'ensemble des résultats.

Abstract. — The Brillouin frequency and linewidth of longitudinal phonons ($\mathbf{q} \parallel \mathbf{e} \parallel (1, 0, 0)$) and soft transverse phonons ($\mathbf{q} \parallel (1, 1, 0)$; $\mathbf{e} \parallel (0, 0, 1)$) have been measured in NaCN in its cubic phase above the elastic phase transition temperature. The results are discussed on the basis of the semi-phenomenological model which explains the temperature variation of both the elastic constants and the linewidths of phonons in KCN. It is shown that the anomalous effects related to dilatation of the cyanide do not allow a coherent quantitative analysis of the whole set of results.

1. Introduction. — Since the discovery by Haussühl [1] of the anomalous behaviour of the C_{44} elastic constant in the orientationally disordered (ODIC) crystalline phase of potassium cyanide, the elastic properties of this material [2, 4] and of NaCN [3, 5, 6, 7] have been extensively studied by ultrasonic and Brillouin scattering techniques. In contrast, our study of KCN gives the only measurement presently available of the width of the Brillouin lines in this material [4]. This linewidth, which is nearly proportional to the attenuation of hypersonic waves, increases with decreasing temperature when approaching the phase transition temperature from the ODIC phase (or phase I) to the quasi-ordered phase II. In [4] we proposed a semi-phenomenological theory which accounts for the variation with temperature of both elastic constants and hypersonic attenuations in KCN. The purpose of the present paper is to describe an extension of this work to NaCN.

2. Experimental results. — The experimental arrangement is similar to that described in reference [4]. Two samples were used for this study. One was grown at the Département de Recherches Physiques by the Bridgman method. The second, grown by the Czochralski method, was obtained from F. Rosenberger at University of Utah-Salt Lake City. The samples were cleaved with faces parallel to the cubic planes. The longitudinal mode propagating along $\mathbf{q} = (1, 0, 0)$ was studied in a backscattering experiment, while the transverse and longitudinal modes propagating along $\mathbf{q} = (1/\sqrt{2}) (1, 1, 0)$ were studied in a right angle scattering configuration.

For calculating the elastic constants, the density was taken from reference [6]. The index of refraction at room temperature was 1.452 for $\lambda = 4880 \text{ \AA}$. The temperature dependence of the refractive index was calculated using the relation

$$(n^2 - 1)/\rho(n^2 + 2) = \text{const.}$$

Our measurements of C_{11} are shown in figure 1, together with the Brillouin scattering values obtained by Satija and Wang [7] and the ultrasonic results given by Haussühl *et al.* [6]. Our values agree within

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Fig. 1. — Variation with temperature of the C_{11} elastic constant : (+) this work ; (○) Ref. [6] ; (×) Ref. [7].

the accuracy of the experiments with the recently corrected results of Satija and Wang; the hypersonic values (Brillouin scattering) are slightly higher than the ultrasonic measurements, and the slope of the hypersonic curve is also higher. The ultrasonic and Brillouin scattering measurements of C_{44} are shown in figure 2. Here also, the hypersonic values and the slope of the hypersonic curve are higher. As already pointed out in references [3, 5, 6], in the whole recorded temperature range C_{44} varies linearly with temperature :

$$C_{44} = A(T - T_c^*) \quad \text{with} \quad T_c^* = 253 \text{ K}$$

while the actual transition temperature is $T_c = 284 \text{ K}$. In contrast, the surprising intersection of ultrasonic and Brillouin scattering curves shown by Love *et al.* [5] is not observed in figure 2.

Fig. 2. — Variation with temperature of the C_{44} elastic constant : (+) this work ; (○) Ref. [6] ; (×) Ref. [7].

The measurements of the linewidth for longitudinal and transverse phonons are shown in figures 3 and 4, respectively. The results are very similar to those obtained for KCN. The linewidth of the longitudinal phonon mode strongly increases with decreasing temperature when approaching the phase transition. In contrast, for the transverse mode, our measurements exhibit only a small increase in linewidth under the same conditions.

Fig. 3. — Half-width at half-maximum of the longitudinal Brillouin line (frequency $\approx 22 \text{ GHz}$; phonons propagating along (100)).

Fig. 4. — Half-width at half-maximum of the transverse Brillouin line (frequency ranging from 1.7 to 3.3 GHz; phonons propagating along (110)).

3. Discussion. — Various models [4, 8, 9] have been recently proposed for explaining the rather unique behaviour of the elastic constant $C_{44}(T)$ of KCN in the vicinity of the phase I-phase II transition but they basically contain the same ingredients, namely a linear coupling between the ordering of the CN^- ion orientation and an elastic constant. In particular, Michel and Naudts [8] based their analysis on a microscopic description of this coupling and, also, of the CN^- potential well. On the other hand, in [4], we started from a phenomenological free energy which assumes, at the onset, a temperature T_0 at which the CN^- ion

would order without any coupling with the elastic strain. In both descriptions, the transition temperature is increased by the linear coupling, leading in our case, to the following expressions :

$$C_{44}(T) = C_{44}^0 - \frac{b_{44}^2}{T - T_0}, \quad \Gamma_{44} = \Gamma_{44}^0 + \frac{\gamma_{44}^2}{(T - T_0)^2}$$

$$C_{11}(T) = C_{11}^0 - \frac{b_{11}^2}{(T - T_0)^{1/2}},$$

$$\Gamma_{11} = \Gamma_{11}^0 + \frac{\gamma_{11}^2}{(T - T_0)^{3/2}}$$

where Γ_{44} and Γ_{11} are the Brillouin linewidth reported in figures 3 and 4, the coefficients C^0 , b , Γ^0 and γ being adjustable parameters [10]. In the Michel and Naudts treatment, T_0 does not appear, but the b coefficients are temperature dependent.

Clearly, the former description is not strictly applicable in the present case because, as already noted, $C_{44}(T)$ has a linear variation with T from 10 to 100 °C, i.e. in the temperature range where the model should be applicable. Within the experimental accuracy, this would lead to a very large negative value for T_0 (i.e. $T_0 < -5 \times 10^3$ K) which is clearly unphysical. No direct comparison with the Michel and Naudts description is possible because the temperature variation of their coefficients has not been computed in the NaCN case.

A major difficulty with those treatments lies in the fact that they end up with a linearization of some set of equations, and such a linearization implies the neglect of many anharmonic properties. In particular C_{44}^0 the bare elastic constant, is supposed to be temperature independent. This is certainly not true, particularly in a constant pressure experiment, and the lowest possible approximation would consist in writing that C_{44}^0 is a linear function of the lattice parameter a . But in the vicinity of a phase transition, a is not a linear function of T , and the temperature derivative, $d\lambda(T)/dT$ of the expansion coefficient $\lambda(T)$ turns out to have a different sign, close to T_c , for KCN and NaCN [6]. A subtle cancellation effect could thus happen in the latter substance preventing any determination of T_0 from the $C_{44}(T)$ measurement.

This explanation is in line with the numerical analysis which can be made for the other data. Indeed, in the KCN case, $C_{44}(T)$ was the only data through which T_0 could be properly determined : large variations of T_0 and correlated changes of the remaining coefficients always led to good fits for the three other quantities $C_{11}(T)$, $\Gamma_{44}(T)$ and $\Gamma_{11}(T)$. The reported value for T_0 could thus be in error (due to the neglect of the unpredictable effect of anomalous thermal expansion) without affecting the main conclusions of [4]. Similarly, there exists a large range of T_0 (-500 K $< T_0 < 50$ K) for which $C_{11}(T)$, $\Gamma_{44}(T)$ and $\Gamma_{11}(T)$ can be fitted in NaCN.

4. Conclusion. — In view of these facts and of the similarity between the overall temperature behaviour of the three preceding quantities in NaCN and KCN, we suggest that the same basic mechanism, namely the coupling between fluctuation of F_{2g} symmetry of the orientational probability distribution $P_0(\Omega)$ with an elastic constant with the same symmetry, is responsible in both substances for the phase transition, characterized by the softening of the elastic constant C_{44} . Seen from an elastic point of view, the difference between both substances is minor : the fact e.g. that $P_0(\Omega)$ exhibits in phase I, maxima in the [100] directions in NaCN, and in the [111] ones in KCN does not show off at this level. In both cases, the residence time τ_0 of a CN^- dumbbell in one potential well is much shorter than the period related to a Brillouin experiment, so that the hypersonic and ultrasonic measurements give essentially the same results ; the small differences reported here between the two types of values are possibly due to impurities or domain wall effects between regions with different internal stresses [11] but are much smaller than those found between both measurements and the neutron ones [12] where for instance around 30 cm^{-1} the phase velocity of the transverse acoustical branch in the (100) direction is twice as large as the one obtained in the present measurements. This enormous difference is, of course related to the fact that, in the neutron experiment, one deals with a clamped crystal where there is no more coupling between an elastic deformation and the change of the static probability distribution function $P_0(\Omega)$.

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