

# Comment on "Brillouin scattering studies of orientationally disordered sodium cyanide and potassium cyanide single crystals"

Cite as: J. Chem. Phys. **70**, 4437 (1979); <https://doi.org/10.1063/1.437990>

Published Online: 28 July 2008

S. K. Satija and C. H. Wang



View Online



Export Citation

Lock-in Amplifiers  
up to 600 MHz



Zurich  
Instruments



# Comment on "Brillouin scattering studies of orientationally disordered sodium cyanide and potassium cyanide single crystals"

S. K. Satija and C. H. Wang

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112  
(Received 6 November 1978)

Both sodium cyanide (NaCN) and potassium cyanide (KCN) undergo two successive order-disorder phase transitions upon cooling below the room temperature. The first order-disorder transition in these solids is characterized by softening of the shear acoustic mode associated with the elastic constant  $C_{44}$ .<sup>1</sup> Recent Brillouin scattering of NaCN<sup>2,3</sup> and KCN<sup>3</sup> single crystals have confirmed this result. In Ref. 3 the elastic constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  for the two cyanide crystals were determined as a function of temperature in the cubic disordered phase. For KCN our Brillouin scattering values for the elastic constants are in good agreement with the values obtained at 15 MHz from the ultrasonic technique by Haussuhl.<sup>1</sup> In the ultrasonic-hypersonic frequency range, there is negligible dispersion in the KCN crystal. Haussuhl has also published recently the elastic constants for NaCN using the ultrasonic technique.<sup>4</sup> While his  $C_{44}$  values for NaCN agree fairly well with our results, there is a significant discrepancy between his ultrasonic and our Brillouin scattering values for  $C_{11}$  and  $C_{12}$ . This discrepancy prompted us to repeat the Brillouin scattering measurement on NaCN.

We report in this communication the recent Brillouin scattering results on NaCN. In Ref. 3 the elastic constant  $C_{11}$  was determined by measuring the Brillouin spectra of the (100) longitudinal acoustic (LA) phonon using a 90° scattering geometry. In carrying out that experiment, NaCN crystal sample was prepared by cutting the crystal parallel to its (110) faces. Since NaCN crystals do not cleave naturally along the (110) direction, the cutting and subsequent polishing operation may introduce significant strain in the crystal. Furthermore, unless an x-ray diffractometer is used to monitor the cutting, there is a finite chance of making an error of few degrees in cutting the crystal. To circumvent these difficulties, we have in the present experiment deter-

mined the Brillouin frequency of the (100) LA phonon using the 180° scattering geometry. In this backscattering geometry, the incident light is directed perpendicular to the (100) face (which can be easily cleaved) and the scattered light is collected along  $(\bar{1}00)$ . While the 180° Brillouin scattering experiment is more difficult, the phonon frequency (which is proportional to  $\sqrt{C_{11}}$ ) obtained using this geometry is believed to be of greater accuracy as one does not need to cut the crystal in this case.

Having determined the (100) longitudinal acoustic phonon frequency by the back scattering technique, we have determined the  $C_{11}$  values from the index of refraction and the density data given in Refs. 3 and 4. With the availability of  $C_{11}$  one can then determine  $C_{12}$  from the LA frequency previously measured, as reported in Ref. 3. The elastic constants  $C_{11}$  and  $C_{12}$  for NaCN determined by this technique are given in Table I, along with our earlier results. Haussuhl's values for  $C_{11}$  and  $C_{12}$  are also included in Table I for comparison. One notes that the present values of the elastic constants differ considerably from the earlier ones; furthermore, all the present values are between 1% and 3% higher than Haussuhl's ultrasonic ones, despite the similarity in the overall temperature dependence for the elastic constants. It is not known at present whether the 1%-3% difference is due to the frequency dispersion or to the uncertainty in the density and the index of refraction data of the NaCN crystal.

However, we believe that our previously reported  $C_{11}$  and  $C_{12}$  values for NaCN are probably in error for the reason that the  $C_{11}$  value, which was determined by using the 90° scattering geometry involved the use of a crystal cut along (110), showed a somewhat stronger temperature dependence than that determined by 180° scattering. This suggests that in the earlier measurements of  $C_{11}$  we were not observing the pure (100) longitudinal

TABLE I. Elastic constants of sodium cyanide (units  $C_{ij}$  in  $10^{11}$  dyn  $\text{cm}^{-2}$ ).

T(°C)	Ref. 3			Present work			Ref. 4		
	$C_{11}$	$C_{12}$	$C_{44}$	$C_{11}$	$C_{12}$	$C_{44}$	$C_{11}$	$C_{12}$	$C_{44}$
20	2.102	1.195	0.036	2.557	1.463	0.036	2.534	1.444	0.033
30	2.129		0.045	2.565	1.447	0.045	2.545	1.424	0.0415
40	2.155	1.123	0.054	2.576	1.430	0.054	2.554	1.406	0.0495
50	2.182		0.063	2.583	1.413	0.063	2.560	1.390	0.0575
60	2.208	1.047	0.071	2.586	1.398	0.071	2.565	1.375	0.066
70	2.243		0.080	2.599	1.371	0.080	2.569	1.361	0.074
80	2.275	0.930	0.088	2.600	1.360	0.088	2.571	1.347	0.082
90	2.301		0.096	2.601	1.345	0.096	2.572	1.333	0.0905
100	2.322	0.911	0.105	2.602	1.330	0.105	2.572	1.319	0.099

phonon, due possibly to the error introduced in the cutting of the crystal. Apparently, an error of a few degrees and the strain introduced in cutting the NaCN crystal have a significant effect on the Brillouin frequency. Due to the fact that in Brillouin scattering  $C_{12}$  is not determined directly but through a combination of the quantity  $C' = (C_{11} + C_{12} + 2C_{44})/2$ , the temperature dependence of  $C_{11}$  also introduces a temperature dependence of  $C_{12}$ . The temperature dependences of  $C_{11}$  and  $C_{12}$  reported in Ref. 3 are thus exaggerated. Furthermore, the curve which shows the vanishing of  $(C_{11} - C_{12})/2$  for NaCN as the second phase transition temperature is approached also appears to be fortuitous. In the light of the present result, it is unlikely that the second phase transition in NaCN is related to the vanishing of the shear modulus  $(C_{11} - C_{12})/2$  as suggested in Ref. 3.

We thank Professor Robert Pick of the University of Paris for pointing out to us the recent NaCN ultrasonic results of Professor S. Haussuhl. The suggestion of making the  $180^\circ$  scattering experiment by Dr. R. Vacher is also acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for the support of this research.

<sup>1</sup>S. Haussuhl, *Solid State Commun.* **13**, 147 (1973).

<sup>2</sup>S. Satija and C. H. Wang, *J. Chem. Phys.* **66**, 2221 (1977).

<sup>3</sup>C. H. Wang and S. Satija, *J. Chem. Phys.* **67**, 851 (1977).

<sup>4</sup>S. Haussuhl, J. Eckstein, K. Recker, and F. Wallrafen, *Acta Crystallogr. A* **33**, 847 (1977).