Soft acoustic modes in NaN$_3$

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Brillouin scattering measurements in the high-temperature phase of NaN$_3$ are reported. A five-pass Fabry-Perot interferometer was used to analyze the scattered radiation. Soft modes whose velocity extrapolated to zero at $T_C - 2\,°C$ were observed. Here T_C is trigonal to monoclinic transition temperature. No appreciable line broadening in the Brillouin spectra nor changes in intensity of the central scattering peak were observed. The measurements provide the first data on these soft modes. They indicate that the transition is almost a prototype displacive rather than an order-disorder transition.

We report here some Brillouin scattering measurements in the high-temperature trigonal phase of sodium azide NaN$_3$. This crystal undergoes a nearly second-order phase transition to a monoclinic phase near 20 °C.[1-6] There have been uncertainties as to the physical mechanism responsible for the transition. The measurements reported here provide the first data on the soft acoustic modes associated with this transition. They indicate that the transition is almost a prototype displacive rather than an order-disorder transition. The velocities of some of the acoustic modes were observed to decrease by more than a factor of 3 as this transition temperature was approached. These velocities extrapolated to zero about two degrees below the transition temperature T_C. No appreciable extra broadening of the associated Brillouin peaks was observed. These are presumably acoustic soft modes associated with the phase transition. Of interest, none of the soft modes have a strain with the symmetry of the strain used as an order parameter in modeling the transition.[7] No marked changes in the central peak in the Brillouin spectra were observed near the transition temperature.

Single crystals of NaN$_3$ were grown using a precipitation-infusion method.[8] A number of clear thin plate-shaped crystals 0.1–0.5 mm thick and a few mm across were obtained from each growth attempt (see Fig. 1). The

birefringence of NaN$_3$ crystals is very large, $n_0 = 1.368$, $n_e = 1.720$.[9] Our measurements were made using unpolished crystals in dried acetone, $n = 1.359$, using a 90° scattering configuration. An index-matched nearly ordinary ray was used as input. It was necessary to make complex refraction corrections for the scattered ray. All in all, the highly unfavorable sample sizes and physical properties of NaN$_3$ crystals made the measurements quite difficult.

A 10- to 30-mw beam obtained from a single-mode Coherent argon laser INNOVA 90 operating at 514 nm was used for the input radiation. The scattering was analyzed using a microprocessor to control a Burleigh RC110 multipass Fabry-Perot interferometer operated in the five-pass mode. The microprocessor was programmed as a data accumulator as well. A cooled RCA model C31034 photomultiplier with a GaAs photocathode with a background count rate near four photoelectrons per second was used. In our selected samples near the transition temperature, the scattering from the soft mode exceeded that of the central peak scattering (see Fig. 2). This signal in Fig. 2 could be observed on an oscilloscope without signal averaging. The width of the peak was equipment limited.

We found the Brillouin spectra of the different crystals to be quite variable. In the majority of clear cyrstals we were unable to even observe the well-defined Brillouin spectra. For the crystals selected for our measurements, the higher frequency lines in the Brillouin spectra were strong, narrow,
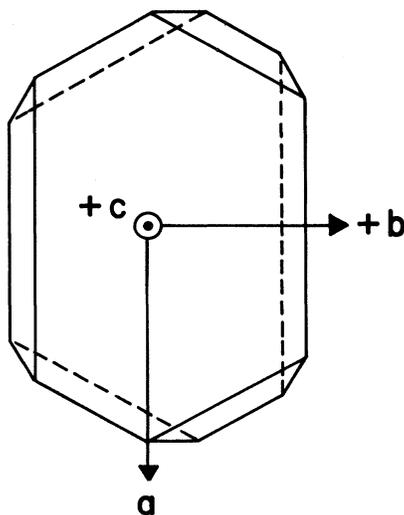
FIG. 1. Crystal habit for NaN$_3$ with the axes indicated. The signs are based on Cady's convention (Ref. 19).
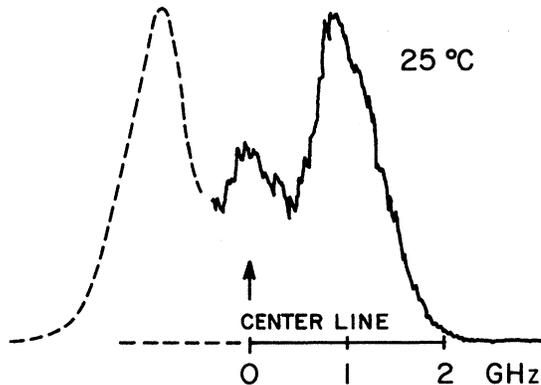
FIG. 2. Low-frequency peak in the Brillouin spectra of NaN$_3$ at 25 °C observed by scanning a five-pass Fabry-Perot interferometer with free spectral range of 9.65 GHz. The scattered radiation was polarized at right angles to the incident laser beam.
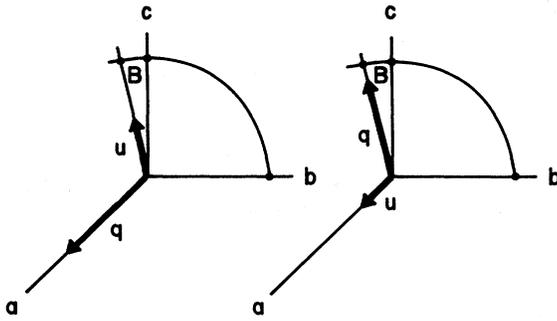
FIG. 3. Predicted propagation vectors $\vec{q}$ and displacement vector $\vec{u}$ for a pair of soft modes of NaN$_3$ at the transition temperature, where $C_{44}C_{66} - C_{14}^2 = 0$ and $\tan\theta = -C_{44}/C_{14}$. Both modes of the pair have the same strain. The crystal has threefold symmetry around the c axis. The other two pairs of soft modes can be found by rotating the pair shown by $\pm 120°$ around the c axis.

and symmetric. However, the spectrum for these crystals changed after a few hours of irradiation in acetone. The area under the peaks would decrease with little broadening and sometimes the peaks would split into two or more peaks. There are a few reports on the twinning of NaN$_3$ crystals in the trigonal phase. Twinning is easily induced by shock.[10] In one careful x-ray study[11] it is reported that all the crystals were twinned to the point that a double set of diffraction spot was always observed. Presumably the varia-

FIG. 5. Measured elastic stiffness at 25 °C for the transverse-acoustic waves polarized along the a axis and propagating at an angle θ to the c axis. The curve was calculated assuming $C_{66} = 16.1$, $C_{44} = 0.60$, and $C_{14} = 2.70$ all in units of 10^{10} dynes/cm^2.

bility in the spectra that we observed was due to elastic inhomogeneities connected with twinning.

Consistent measurements were obtained after the crystal selection process. The soft modes were observed to occur in pairs—one in the ab plane and one close to the c direction (see Fig. 3). This was expected from a general analysis[12] as the two modes would have the same strain at the transition temperature. The observed temperature dependence of the Brillouin scattering for the soft mode with its propagation vector $\vec{q}$ along the a direction is shown in Fig. 4. The angular dependence of the elastic stiffness deduced from measurements of the frequency of the transverse modes with its displacement vector $\vec{u}$ along the a direction is shown in Fig. 5. Figure 6 is a plot of the deduced elastic stiffness for both soft modes versus temperature. The straight line through the data goes through zero about two degrees below T_0.[13]

The stability conditions[14] for NaN$_3$ crystals in the trigonal

FIG. 4. Observed low-frequency Brillouin spectra as a function of temperature with the generated transverse-acoustic waves propagating along the a axis.
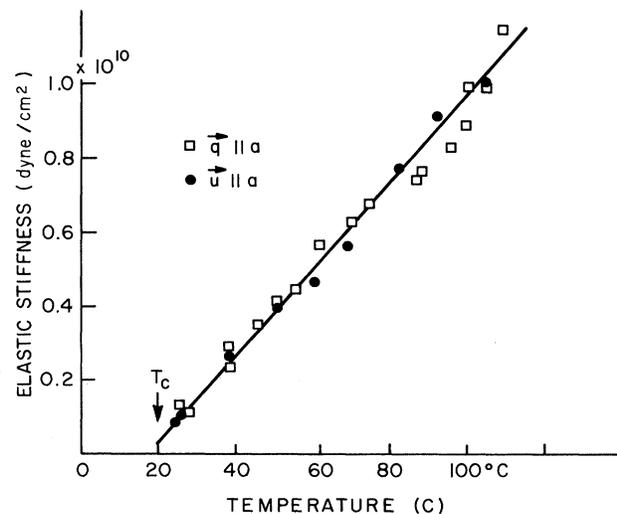
FIG. 6. Measured elastic stiffness for a pair of soft modes as a function of temperature.

phase require that the following combinations of the elastic coefficients be greater than zero: $C_{11} + C_{12}$, C_{33}, C_{44}, C_{66}, $C_{33}(C_{11} + C_{12})/2 - C_{13}^2$, and $C_{44}C_{66} - C_{14}^2$, with $C_{66} = (C_{11} - C_{12})/2$. The elastic instability associated with the NaN_3 phase transition occurs when $(C_{44}C_{66} - C_{14}^2)$ approaches zero.[14,15] The angular dependence of effective elastic stiffness C for pure transverse waves with $\vec{u}$ along a and $\vec{q}$ at an angle θ to the c axis is given by[16]

$$C = \sin^2\theta\, C_{66} + \cos^2\theta\, C_{44} + 2\sin\theta\cos\theta\, C_{14} \ . \qquad (1)$$

C is minimum when $\theta = \frac{1}{2}\tan^{-1}[2C_{14}/(C_{44} - C_{66})]$. The data shown in Fig. 5 were fitted with Eq. (1) setting $C_{66} = 16.1$, $C_{44} = 0.60$, and $C_{14} = 2.70$ all in units 10^{10} dynes/cm^2. These and some measurements at other temperatures indicate that the minimum would occur at $\theta = -10°$ at the transition temperature.

The width of the Brillouin scattering peak associated with the soft modes changed little, if any, with temperature. There were no obvious changes in the central line as the transition temperature was approached. These observations make the likelihood of large domain formation as precursors of the transition improbable. Also, we observed no temperature dependence of the frequency of the other peaks in the Brillouin spectra as great as 30%.

We are continuing our measurements. We plan to publish a longer paper with data sufficient to determine all the elastic constants and their temperature dependence. This includes observing the soft modes closer to the transition temperature. We also plan to observe the Raman spectra of our selected crystals. Elastic inhomogeneities in the crystals could well also explain the strong intensity of components not allowed by crystal symmetry observed in earlier Raman studies.[17,18]

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