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Testing the lattice modes of NaCN by nuclear resonance photon scattering

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Abstract

A nuclear resonance photon scattering (NRPS) study of sodium cyanide (NaC¹⁵N) between 10 and 295 K is described. This temperature range covers the fully ordered phase I, the intermediate antiferroelectric phase II and the high temperature disordered cubic phase III. The scattering intensity from the 6324 keV level in ¹⁵N was measured versus temperature and a very good agreement with the calculated values has been obtained. In the calculations, one has to account for the zero-point kinetic energy of the internal vibration of the CN⁻ ion and the lattice modes of NaCN taken from infrared (IR), Raman and vibrational density of states (VDOS). In another approach, the external modes of motion of ¹⁵N in NaCN were accounted for by using an effective Debye temperature of $\Theta_0 = (310 \pm 5)$ K.

1. Introduction

Sodium cyanide (NaCN) belongs to the M⁺XY⁻ type polymorph compounds [1], which may be regarded as ‘hybrids’ between ionic and molecular crystals, combining features from both groups of materials [2–4]. Above 284 K, the *ionic* crystal is pseudocubic (O_h⁵ symmetry), having the sodium chloride structure (phase I) in which the CN⁻ ion directions are randomly distributed due to rapid reorientations. On cooling below 284 K, a disorder–order phase transition occurs and an orthorhombic monoclinic structure (phase II, D_{2h}²⁵) appears in which the CN⁻ ions lie along the (110) direction of phase I, but with an anisotropic distribution of their dipole moments. At $T < 172$ K, the CN⁻ ions become fully ordered, in a D_{2h}¹³ orthorhombic structure, and are parallel to each other with opposite head to tail directions (antiferroelectric phase III).

Intensive theoretical and experimental studies were focused mainly on attempts to interpret the lattice modes of the crystalline form of NaCN. Usually, vibrational density of states (VDOS) [5], IR and Raman spectroscopy techniques [6, 7], as well as theoretical lattice dynamic calculations [8, 9] were utilized for such studies, where the major attention was directed to the strong libron–vibron coupling.

In the present work the nuclear resonance photon scattering (NRPS) technique [10] is utilized for studying the lattice and the internal vibrations of the molecular NaC¹⁵N solid.

This is done by measuring the resonance scattered photon intensity from the 6324 keV nuclear level of ^{15}N in the form of a powdered NaCN sample. It turns out that this resonance scattering process is proportional to the Doppler broadening of the nuclear level, which in turn is governed by the zero-point kinetic energy of the N atom in the sample. This method can therefore be used for detecting the zero-point motion of the atoms in a solid. Contributions to the Doppler broadening come in part from the external vibrations of the molecular lattice and mainly from the internal vibration which has a much higher energy. A measure of the scattering cross section as a function of temperature may thus provide a very sensitive test of both the external and internal vibrational modes of the phonon spectrum of NaCN. It is of interest to note that the neutron Compton scattering (NCS) technique [11] can also be used for measuring the zero-point mean-square momenta of the atoms in the same or similar systems. The NRPS method may however be viewed as model independent, since all it requires is the knowledge of the Doppler broadening of the nuclear level; it is very sensitive to the zero-point motion of N-containing molecules.

In a molecular crystal of NaCN, the modes of motion consist of a single high frequency internal vibrational mode [8, 9, 12] of the CN^- ion at $\nu_0 \sim 2092 \text{ cm}^{-1}$ and low-energy lattice modes [6–9] in the spectral region 90–250 cm^{-1} . This means that the contribution of the internal vibration of the CN^- ion to the Doppler broadening of the 6324 keV nuclear level of ^{15}N is dominant in the range 12–295 K and is practically constant. Thus, the major *variation* of the scattering intensity with T arises from the external lattice modes only. It is thus very interesting to see to what extent the reported VDOS [5] lattice modes and the infra-red and Raman [6, 7] measured internal mode, could reproduce the measured NRPS data.

2. Principle of the NRPS technique

The nuclear resonance photon scattering process from ^{15}N involves a chance overlap between a γ line, generated by the $^{53}\text{Cr}(n,\gamma)$ reaction using a nuclear reactor, and the 6324 keV nuclear level. Both the incident γ line and the nuclear level are Doppler broadened and are separated by [10] $\delta = 29.5 \text{ eV}$ (figure 1). It turns out that the overlap between the two line-shapes (shaded areas in figure 1) gives rise to a resonance scattering signal whose cross section σ_r is proportional to the Doppler broadening of the resonance level. The Doppler width of the nuclear level is given by $\Delta_r = E(2kT_r/M_r c^2)^{1/2}$ where E is the excitation energy, M_r the nuclear mass, T_r the effective temperature of the scattering atom, k the Boltzmann constant and c the velocity of light. A similar definition holds for the Doppler width Δ_s of the incident γ line (with T_s and M_s referring to the effective temperature and mass of the source). The effective temperature T_r , which is a measure of the *total kinetic* energy of the N atom in NaCN, is very large and is contributed mostly by the zero-point motion. While T_s of the γ source is nearly constant during reactor operation, T_r varies between $T_r \sim 303 \text{ K}$ at 10 K and $\sim 444 \text{ K}$ at 295 K, and is responsible for the large difference between the corresponding Doppler broadenings (Δ_{r1} and Δ_{r2} in figure 1). The corresponding scattering cross sections, σ_{r1} and σ_{r2} (depicted by the shaded areas in figure 1), differ markedly from each other and are used for testing the reported phonon spectra of NaCN as explained in more detail below.

3. Theoretical remarks

3.1. Effective temperature of the ^{15}N atom in NaCN

The principal physical quantity measured in the present work is the resonance scattering intensity ratio, $R = I(T)/I(295 \text{ K})$, from the 6324 keV level of ^{15}N in NaC^{15}N . It is related

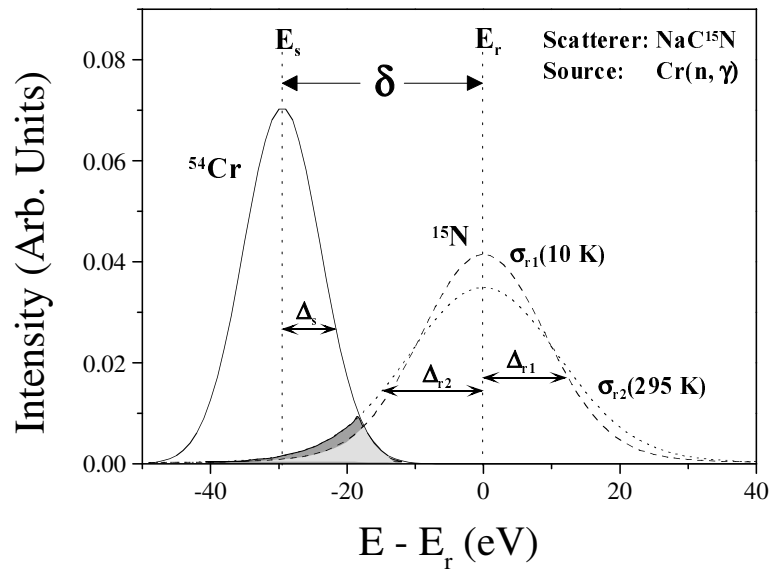


Figure 1. Calculated shapes of the Doppler-broadened γ line, emitted by the $^{53}\text{Cr}(n,\gamma)$ reaction, and the 6324 keV nuclear level of ^{15}N in a powdered NaCN scatterer at 10 K (dashed curve) and 295 K (dotted curve). The corresponding Doppler widths are indicated, where Δ_s was taken to be 8.0 eV, which corresponds to a γ source effective temperature ($T_s = 467$ K) during the measurements. The shaded areas, representing the overlap integrals, are related to the scattering cross sections and hence to the measured scattered intensities.

directly to the total kinetic energy of the ^{15}N -atom and hence to its *effective temperature* T_r . To calculate T_r , we note that NaCN is ionic where the $\text{Na}^+\text{--CN}^-$ bond is much weaker than the covalent $\text{C}\equiv\text{N}$ bond. Contributions to the kinetic energy of the N atom in NaCN (which should sum up to three kinetic degrees of freedom, $3kT_r/2$), come from the *external* modes of motion of NaCN, and from the *internal* stretching vibration ($k\alpha_v/2$) in the CN^- ion. The external modes consist of three translation–vibrations ($3kT_i/2$), and two rotation–librations (kT_R), where T_i and T_R are the corresponding effective temperatures of the entire NaCN molecule in the lattice, thus [10]:

$$3kT_r/2 = S_i(3kT_i/2) + S_R(kT_R) + S_vk\alpha_v/2. \quad (1)$$

S_i , S_R and S_v are the energy fractions shared by the ^{15}N atom in the various modes of motion of NaCN. The factor 1/2 in the last term is due to the fact that only half the vibrational energy ($k\alpha_v$) in the CN^- ion is *kinetic* and contributes to the Doppler broadening of the ^{15}N nuclear level and hence to T_r , where $k\alpha_v = h\nu_0[(e^{h\nu_0/kT})^{-1} + 1/2]$. The value of ν_0 for natural CN, taken from infra-red studies [8, 9, 12] is $\nu_0 = 2092 \text{ cm}^{-1}$ (where the spring constant [9] is $16.62 \times 10^5 \text{ dyn cm}^{-1}$). The corrected value for isotopic C^{15}N is $\nu_0 = 2016 \text{ cm}^{-1}$. In equation (1), $S_v = 12/27$ because the internal vibrational energy of CN is split between the C and N atoms inversely as their masses. Thus, to calculate T_r one has to deduce S_i , T_i and S_R , T_R for each mode of the lattice. The procedure for doing that is quite involved, thus to simplify matters, we took $T_i = T_R$, being the effective temperature of the N atom in the external modes and used equation (1) to define an energy fraction S_L of the external modes:

$$3S_L/2 = 3S_i/2 + S_R. \quad (2)$$

S_L may be easily calculated by using a ‘sum-rule’ [10] which requires the sum of all energy fractions of the N atom to add up to 1, namely, $S_L + S_v/3 = 1$, yielding $S_L = 0.8519$. The

expression for T_r may thus be written as

$$T_r = 0.8519T_t + 0.1491\alpha_v. \quad (3)$$

The values of T_t versus T may be obtained by integrating over the external vibrational density of states (VDOS) of the NaCN lattice measured in [5] at $T = 5, 100, 140, 200$ and 295 K, in the energy range 5 to 55 meV, covering all external modes. Thus [13],

$$T_t = \int_0^{v_m} g(v)\alpha(v) dv \left(\int_0^{v_m} g(v) dv \right)^{-1} \quad (4)$$

with v_m the maximum cutoff frequency of the molecular NaCN lattice. Equations (3) and (4) were used for calculating T_r and the corresponding scattering cross section σ_r against T .

It is of interest to note that a small correction was introduced to account for the higher isotopic mass of ^{15}N on the external modes of motion in NaCN which decreased the lattice frequencies by $\sim 1\%$. However, the calculated effect on the scattering cross section *ratios* (figure 3), which are our concern, was 0.2% at most.

An alternative method of deducing T_t (see below) was used where NaNO_2 was assumed to be a Debye solid having a Debye temperature Θ_0 , related to the external modes of motion of the ^{15}N atom in the sample. This is discussed in more detail elsewhere [14, 15].

We hereby give a brief description of the procedure used for calculating the scattering cross sections.

3.2. Scattering cross sections

For an *infinitely thin* ^{15}N sample, the scattering cross section σ_r is given by the overlap integral between the Doppler broadened shapes of the incident γ line (described by a Gaussian) and the nuclear level (represented by a ψ function) [15, 16]; it depends strongly on the effective temperatures T_s , and T_r (figure 1), through their Doppler widths. At 10 K and 295 K, the Doppler widths of the 6324 keV nuclear level are $\Delta_{r1} = 12.2$ eV and $\Delta_{r2} = 14.8$ eV (see figure 1), while that of the Cr γ source is $\Delta_s = 8.0$ eV (corresponding to a temperature $T \sim 171^\circ\text{C}$ where $T_s = 467$ K). In a *powdered* NaCN sample, the directions of the CN^- ions are randomly distributed with respect to that of the incident photon beam. While the scattering cross section from a CN^- ion oriented with its molecular axis parallel to the γ beam direction reaches a maximum, Δ_{max} , that from a perpendicular CN^- ion is minimum, Δ_{min} . Thus, the actual scattering cross section from ^{15}N , is a weighted average over all directions of the CN^- ions with respect to that of the γ beam.

$$\sigma_r = \int_0^{\pi/2} \sigma(\theta) \sin \theta d\theta \bigg/ \int_0^{\pi/2} \sin \theta d\theta. \quad (5)$$

This is calculated [17, 18] by considering a CN^- ion oriented at an angle θ relative to the γ beam direction and deducing its projected effective temperature, $T_\gamma(\theta)$, as follows:

$$T_\gamma(\theta) = S_L T_t + S_v \alpha_v \cos^2 \theta. \quad (6)$$

The factor $\cos^2 \theta$ reflects the variation of the effective temperature with the angle θ . This calculation was repeated for each T . The following parameters of the scattering process were used [15] for the calculations: $\Gamma = \Gamma_0 = 2.9$ eV; $\delta = 29.5$ eV; $J = 3/2$ and $J_0 = 1/2$ are the spins of the 6324 keV and the ground state of ^{15}N . The variations in the scattered intensities are due only to variations in T_r . This procedure of calculating σ_r is more accurate than that of previous studies where σ_r was directly obtained from an average value of T_r .

4. Experimental details

The photon beam was generated from the (n,γ) reaction on three chromium discs placed near the reactor core. The intensity of the 6324 keV γ line arising from the $^{53}\text{Cr}(n,\gamma)$ reaction is $\sim 10^4$ photons $\text{cm}^{-2} \text{s}^{-1}$ on the scatterer. More details concerning the experimental system may be found elsewhere [10]. A 1.390 g powdered isotopic NaC^{15}N sample (98% ^{15}N) containing ~ 409 mg ^{15}N was inserted in a pure aluminum cylindrical can (15 mm diameter, 30 mm high) fitted with a thermocouple to measure its temperature. The background was measured using a comparative natural NaCN sample (0.036% ^{15}N), inserted in an identical container. The scattered photons were detected using a 150 cm^3 hyper-pure Ge diode. Typical scattered radiation spectra from the 6324 keV level of ^{15}N using a powdered isotopic NaC^{15}N at 295 K (containing ~ 409 mg ^{15}N) are shown in figure 2. It is of interest to note that the scattering cross section from NaC^{15}N was compared to that of a similar $\text{Na}^{15}\text{NO}_2$ sample contained in an identical container [15]. The measured cross section ratio at 295 K was found to be $\sigma_r(\text{Na}^{15}\text{NO}_2)/\sigma_r(\text{NaC}^{15}\text{N}) = 1.18 \pm 0.06$, which is in very good agreement with a calculated ratio of 1.22 deduced from the calculated scattering cross sections [15]: $\sigma_r(\text{Na}^{15}\text{NO}_2) = 1.607 \text{ b}$, while $\sigma_r(\text{NaC}^{15}\text{N}) = 1.316 \text{ b}$.

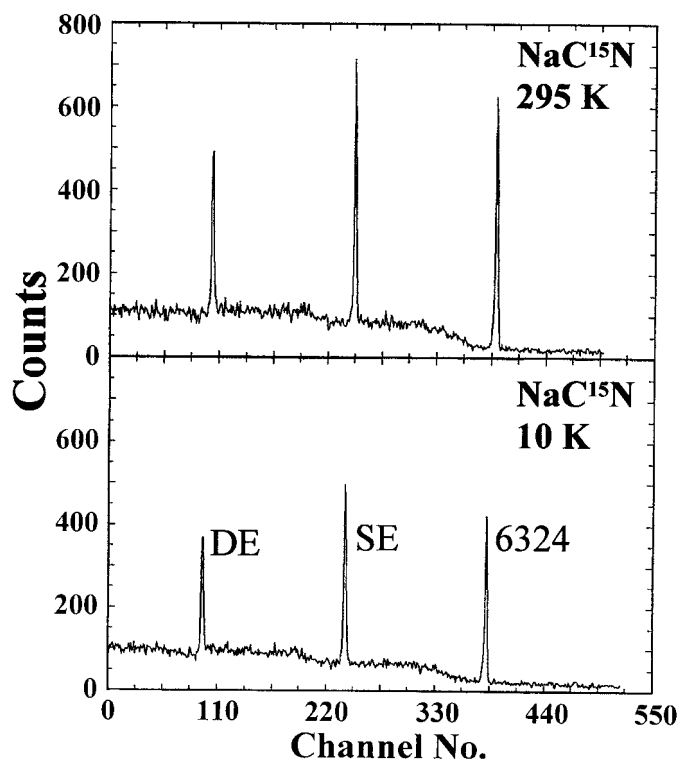


Figure 2. Typical scattered radiation spectra from the ~ 1.39 g isotopic powdered NaC^{15}N (containing ~ 409 mg ^{15}N), at 295 K and 10 K (upper and lower spectra respectively). The peak labelled '6324' is related to the photo-peak while SE and DE refer to the single- and double-escape peaks of the response function of the Ge detector. The scattered intensity is taken to be the integrated area under the energy region including these three peaks, where the measured relative intensity $I(10 \text{ K})/I(295 \text{ K})$ was 0.703 ± 0.010 .

5. Results and discussion

The measured scattered intensity ratios (relative to 295 K), $R = I(T)/I(295 \text{ K})$, obtained after background subtraction, are shown in figure 3(a) (error barred solid squares). The ratio R drops monotonically with T , reaching a plateau below 50 K, revealing a pure quantum effect caused by the zero-point motion of the N atom in the molecular crystal. Also depicted in figure 3(a) are the calculated values of R (open circles) obtained using the published [5] VDOS data at 10, 100, 150, 200 and 295 K (figure 3(b)) and equation (5).

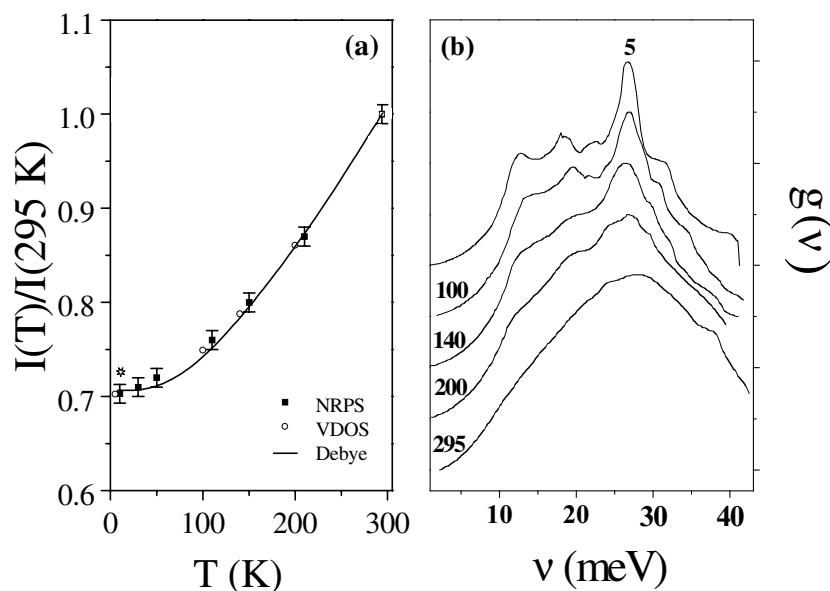


Figure 3. (a) Temperature variation of the scattered intensities relative to 295 K from the 1.39 g isotopic powdered NaC^{15}N sample. The solid line is a best fit to the NRPS data points (error barred solid squares), calculated using a Debye temperature of $\Theta_0 = (310 \pm 5) \text{ K}$. Open circles are the calculated values of R obtained by using the measured [5] phonon spectra of *natural* NaCN, and equation (5). The asterisk represents the calculated value of R at 10 K where a single-phonon spectrum (measured at 295 K) was used for the entire temperature region. (b) Experimental inelastic neutron scattering VDOS spectra of natural NaCN versus temperature (taken from [5]). For clarity, the spectra were shifted vertically with respect to each other.

It is of interest to note [5] that the phonon spectrum of NaCN is negligibly affected by the two phase transitions ($\text{I} \leftrightarrow \text{II}$, $\text{II} \leftrightarrow \text{III}$). However, it changes appreciably with T where at 5 K, the molecular crystal has five well resolved peaks at 12, 18, 22, 27 and 30 meV. This structure is washed out gradually towards higher temperatures approaching a broad bump at 295 K (see figure 3(b)). This variation in the shape of the phonon spectrum has a marked effect on the calculated effective temperature and hence on the ratio of the scattering cross sections. It is interesting to find that the present method is sensitive to such variations in the phonon spectra. This is illustrated in figure 3(a), which reveals an excellent agreement between the measured (solid squares) and calculated values of R (open circles). Moreover, if one uses the same VDOS (taken at 295 K) for deducing R at all temperatures appearing in figure 3(a), the resulting R at 10 K would deviate by 3% (asterisk in figure 3(a)), from the measured value.

The measured values of R were also used for deducing a Debye temperature Θ_0 related to the effective temperature T_i of the external modes of the ^{15}N atom in the NaCN lattice. The

value $\Theta_0 = (310 \pm 5)$ K best fits the measured values of R (solid curve in figure 3(a)) and is very close to those obtained using the reported VDOS spectra against T . Note that the Debye temperature obtained in this manner is unique in the sense that it is related purely to the motion of ^{15}N in NaCN. It is thus different from that quoted in the literature, which usually represents an average over the external modes of motion of all constituents of NaCN.

It may be remarked that while the present technique is very sensitive to the high-frequency modes of the atomic vibrations through their zero-point energies, it is less sensitive to phase transitions such as those occurring between 10 K and 295 K in NaCN. This is especially true if the phase transitions occur at relatively high temperatures such as 174 and 284 K, where the thermal motion is relatively large and overwhelms the small effects in the kinetic energy of the N atom occurring in phase transitions. This statement is not valid for phase transitions involving orientational changes in ordered system such as that of adsorbed gases (N_2 or N_2O) on Grafoil [17, 18], for which the NRPS technique was shown to be very sensitive.

6. Conclusions

We used the NRPS technique to study the temperature dependence of the scattered intensities from the 6324 keV nuclear level of ^{15}N in an isotopic powdered form of sodium cyanide (NaCN). This method is shown to be a powerful tool in testing the phonon spectra measured by inelastic neutron scattering. In particular, we illustrated the importance of accounting for the actual variation of the VDOS spectra with T that results in a good fit between the measured and calculated scattering cross section ratios.

Acknowledgments

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