RAMAN AND FAR INFRARED SPECTROSCOPY OF THE INCOMMENSURATE
STRUCTURE Na$_2$CO$_3$

H. HUKKIN, K. HANSSON, A. JANSSER, T. JANSSER and P. HDER
Faculty of Science, University of Nijmegen, Toernooiwei
d 6525 ED Nijmegen, The Netherlands

A. RASING
Department of Physics, University of California, Berkeley,
CA 94720, U.S.A.

Abstract The lattice vibrations of Na$_2$CO$_3$ in the incommensurate
phase have been studied by means of Raman and far
infrared (F.I.R.) spectroscopy. The results exhibit strong
temperature dependences which can be related to those of the
modulation parameters.

INTRODUCTION

An incommensurate crystal structure is characterized by the fact
that labelling of its diffraction pattern requires more than three
(integer) indices. For a modulated structure this means that the
period of the modulation is rationally independent of the under-
lying lattice periodicity. Therefore, incommensurate crystal struc-
tures do not have 3-dimensional space group symmetry. A clear
indication of incommensurability is present if the modulation period
varies continuously with respect to the other periods as a function
of external parameters (temperature, pressure, etc.).

Consequently, in that case a rational approximation is physically
not meaningful.

Na$_2$CO$_3$ in its γ-phase is an example of an incommensurate modulated
structure with a strongly temperature dependent wave vector. This
phase exists below $T_1 = 820$ K. The modulation consists mainly of
rotations of the CO$_3$$^-$ ions. De Pater$^1$ has reported a lock-in trans-
formation at $T_0 = 120$ K. In the incommensurate phase, the modulation
amplitude and both length and direction of the modulation wave
vector vary with temperature. Therefore, γ-Na$_2$CO$_3$ is well suited
to study the effects of the modulation on the physical properties
of incommensurate crystal structures.
EXPERIMENTAL

The crystals were grown in a platinum crucible, using the Bridgman method, thus polycrystalline samples with one preferred direction along the crucible were obtained.

For the F.I.R. transmission experiments, different thin plates were cut perpendicular to the above mentioned direction (presumably the c-axis), whereas transparent regions were chosen for the Raman scattering.

The F.I.R. measurements were done between 5 K and 300 K, in a He-cooled continuous flow cryostat with a Fourier transform interferometer. The light source was a medium pressure mercury lamp. For the Raman experiments, the crystals were placed in a specially designed variable temperature cryostat, with working temperatures between 5 K and 700 K. An Ar laser (514.5 nm) served as exciting radiation source. The scattered light was analysed at right angles with a double grating monochromator, after which the signal was recorded with the usual photon counting techniques. No polarization analyzer was used, because of the lack of single crystals.

SELECTION RULES

The selection rules for I.R. absorption and Raman scattering are closely related to the crystal symmetry. In the case of an incommensurate structure, the lack of translational symmetry prohibits the use of ordinary space groups. De Wolff and Janner and Janssen have, however, shown that higher (3+1) dimensional so-called superspace groups can restore the translational symmetry for incommensurate structures. With the help of these superspace groups, one can find the appropriate selection rules (Janssen).

For the case of Na$_2$CO$_3$ (superspace group P2/m in the incommensurate phase and spacegroup C2/m in the normal phase), the results can be found in Table 1.

<table>
<thead>
<tr>
<th>Group</th>
<th>$n^{(y)}_{\text{opt}}$</th>
<th>$n^{(y)}_{\text{cut}}$</th>
<th>$n^{(y)}_{\text{vib}}$</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_g$</td>
<td>4 + 5</td>
<td>1 + 4</td>
<td>4 + 4</td>
<td>Raman</td>
</tr>
<tr>
<td>E$_g$</td>
<td>2 + 10</td>
<td>2 + 2</td>
<td>2 + 8</td>
<td>Raman</td>
</tr>
<tr>
<td>E$_u$</td>
<td>3 + 10</td>
<td>2 + 2</td>
<td>2 + 8</td>
<td>I.R.</td>
</tr>
<tr>
<td>B$_u$</td>
<td>6 + 5</td>
<td>1 + 4</td>
<td>4 + 4</td>
<td>I.R.</td>
</tr>
</tbody>
</table>

TABLE 1 Number of modes in both phases, indicated as $n^{(y)}_{\text{total}} = n^{(y)}_{\text{vib}} + n^{(y)}_{\text{rot}} + n^{(y)}_{\text{ext}}$, vibrational and rotational modes only concern the CO$_3^-$ ions.
EXPERIMENTAL RESULTS

Typical results of the measurements are the following.

F.I.R. Spectra

In Figure 1 a part of the low frequency F.I.R. spectrum is shown, together with the temperature dependence of the mode frequency (near 50 \text{ cm}^{-1}). For all modes observed, a shift with increasing temperature towards lower frequencies is seen. At temperatures above 300 K the transmission becomes too small for measurement. At 65 K there is a conspicuous change in the \( \omega(T) \) plot, which can also be seen in the width of the mode as a function of temperature. A comparable but less significant change in the slope of the \( \omega(T) \) plot is seen at 120 K for another (\( \omega \approx 63 \text{ cm}^{-1} \)) mode.

![Plot](image)

**FIGURE 1** Left: Temperature dependence of the frequency of the mode near 50 \text{ cm}^{-1}. Right: Low frequency F.I.R. transmission spectrum for various temperatures.

Raman Spectra

In Figures 2 and 3 some \( \omega(T) \) results are shown for the Raman measurements. A strong temperature dependence in particular at the highest temperatures can be seen for the internal modes (Figure 2). In fact many modes are ill-defined due to the large thermal broadening with increasing temperature. For the internal modes (two of which are plotted in Figure 3), a less strong but never-
Nevertheless obvious temperature dependence is observed. All internal modes appear in pairs or even triplets, the frequency difference for pairs tending towards zero on approaching $T_1$. The latter tendency is not observed for all internal modes.

The strange and strong temperature dependence of many modes could be explained by the combined influence of the temperature dependence of the modulation wave vector and the amplitude. The connection between the two can be found by considering a harmonic oscillator model for an incommensurate system. This model, applied to Rh$_3$P$_4$, has been discussed in ref. 5.

Summarizing, we have observed many modes with a strong temperature dependence. An explanation for these results is being worked on.

REFERENCES


Acknowledgement - This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Netherlands Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research).