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Raman Effect in Ferroelectric Sodium Nitrite Crystal. II. Dependence of B_2 Type Phonon Spectrum on Propagation Direction

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The Raman spectra corresponding to the (bc) component (B_2 type vibrations) of the polarizability tensor in the ferroelectric sodium nitrite crystal (C_{2v}^{20}) have been observed with various directions of the phonon propagation. It has been found that one of the B_2 Raman lines at 160 cm^{-1} splits into two components when the phonon propagates in a direction 45° from the c axis in the ac plane. This splitting has been ascribed to an interaction of a B_2 and B_1 type lattice-vibrations whose frequencies are accidentally equal to each other in the phonon propagation direction now in question.

A great improvement has been made in the Raman spectroscopy of crystals by the introduction of laser light sources. We can now easily distinguish Raman lines corresponding to different components of the polarizability tensor of a crystal, if its single crystal with a size greater than or comparable to the diameter of the laser beam is available. In addition, we can now examine whether each of the Raman frequencies changes depending upon the direction of the phonon propagation. In an ionic crystal, an appreciable frequency difference is often observed between the transverse and longitudinal waves of the same mode of vibration.[1,2] Such a frequency difference is observed only for an optical mode and is considered to be caused by a long-range electric field.[3,4]

We have been examining the Raman effect of ferroelectric sodium nitrite crystal ($C_{2v}^{20}-Im2m$) by use of helium-neon and argon ion lasers. In our previous paper,[5] we reported Raman frequencies observed with the orientations of the incident and scattered beams which allow the frequencies of the transverse waves to appear. In a further experiment, different frequencies have been found in general for different orientations. As was once reported by Tramer,[6] a marked shift (from 1230 to 1360 cm^{-1}) in one of the B_2 frequencies has been observed on changing the direction of the phonon propagation from a axis to c axis in the ac plane. One of the other two B_2-type Raman lines, on the other hand, shows a peculiar behavior in a similar change of the phonon propagation direction. This peculiar behavior will be described below with an interpretation for it.

Experimental

The single crystals of sodium nitrite ($NaNO_2$) used in our experiment were kindly provided by Dr. S. Hirotsu and Mr. K. Suzuki, Tokyo Institute of Technology. Final data were taken on two $NaNO_2$ crystals. One of the crystals was cut so that each of the a, b, and c axes is parallel to a sample edge. The other was cut so that the b axis is parallel to a sample edge and the a and c axes are parallel to a sample face and at 45°C to the sample edges.

Each Raman spectrum was recorded a number of times by use of three different setups: (1) a Perkin-Elmer LR-1 Raman Spectrometer with a 10 milliwatt He-Ne laser, (2) a Spex 1400-II Double-monochromator in combination with a 30 milliwatt He-Ne laser made by Japan Electron Optics Laboratory, Company, and (3) a Spex 1400-II Double-monochromator in combination with a 50 milliwatt argon ion laser made by Japan Electron Optics Laboraty, Company. Each laser beam is completely polarized along a certain direction. The scattered beam from the crystal was sent to the monochromator slit through a polarizer so that only a particular component of the scattered beam can be observed.

1) T. C. Damen, S. P. S. Porto and B. Tell, *Phys. Rev.*, **142**, 570 (1966).

2) B. Tell, T. C. Damen and S. P. S. Porto, *ibid.*, **144**, 771 (1966).

3) R. H. Lyddane, R. G. Sachs and E. Teller, *ibid.*, **59**, 673 (1941).

4) M. Tsuboi and A. Wada, *J. Chem. Phys.*, **48**, 2615 (1968).

5) M. Tsuboi, M. Terada and T. Kajiura, This Bulletin, **41**, 2545 (1968).

6) A. Tramer, *Compt. rend.*, **248**, 3546 (1959).

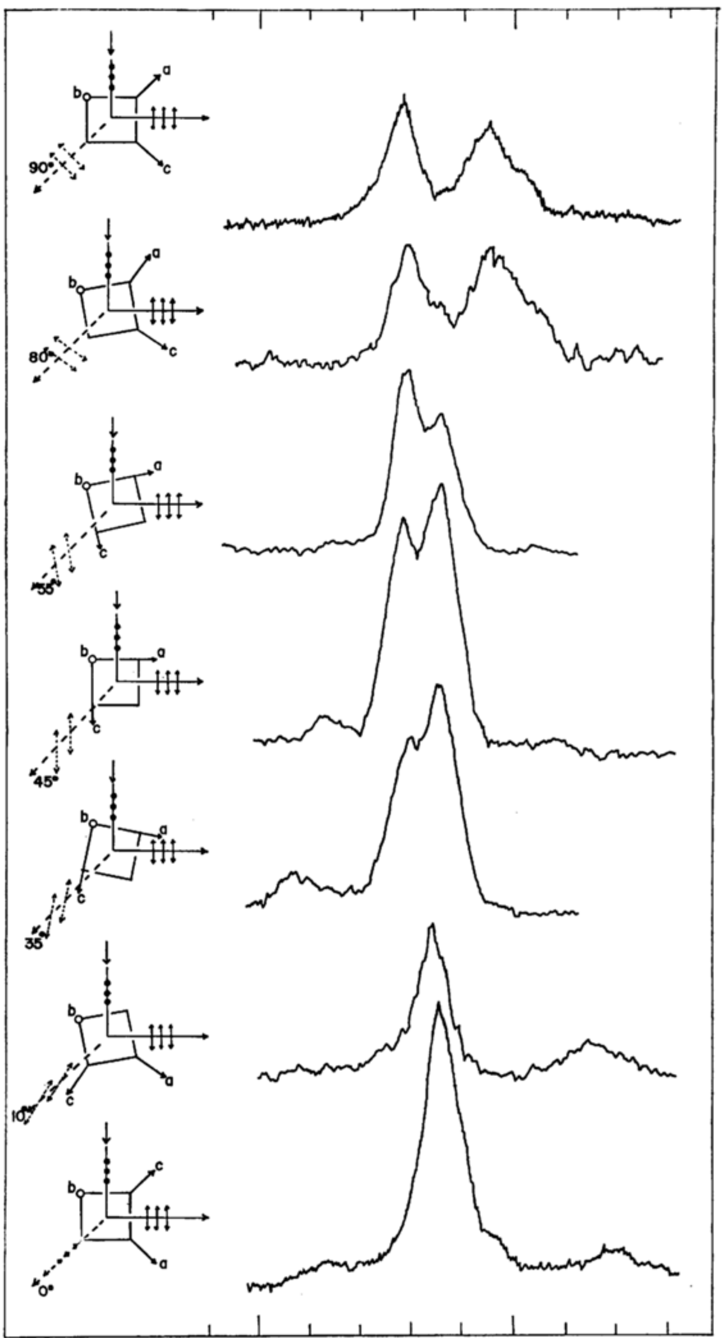

Fig. 1. Raman spectra of $NaNO_2$ crystal (C_{2v}^{20}) observed at room temperature. Orientations of the incident and scattered beams and their electric vectors are given in the left side of each spectrum. The broken lines indicate the direction of the phonon propagation and the direction of its electric polarization.

Result and Interpretation

Figure 1 shows the Raman spectra of the $NaNO_2$ crystal (C_{2v}^{20}) with various orientations in the 100—260 cm^{-1} region recorded at room temperature. Here, the incident and scattered beams are always set so that the Raman lines corresponding to the (bc) component in the polarizability tensor should appear. In this setting there should appear only the B_2-type vibrations, in which the dipole oscillation takes place along the c axis. The single crystal was placed so that the phonon propagation direction is in the ac plane and makes an angle θ indicated in the figure with the c axis. When θ is 90° (transverse wave) the B_2 Raman lines are at 157 and 190 cm^{-1}, while when θ is 0° (longitudinal wave) they are at 172 and 236 cm^{-1}. When θ is 55—35° the first Raman line splits into two at 157 and 171 cm^{-1}.

The splitting just stated is considered to be caused by B_1 vibration whose frequency comes accidentally in the vicinity of 165 cm^{-1}. In fact, there is a B_1 vibration whose frequency was located by Axe[7] at 149 cm^{-1} for the transverse wave and at 193 cm^{-1} for the longitudinal wave. It is true that any vibration belonging to the B_2 species cannot interact with a vibration belonging to the B_1 species as far as

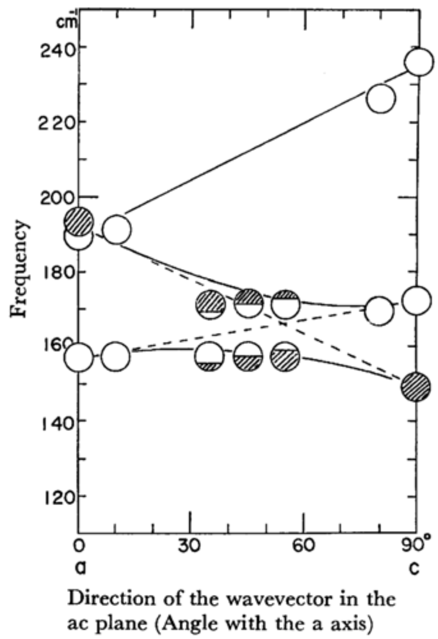

Fig. 2. Frequencies of a few Raman-active vibrations of $NaNO_2$ crystal plotted against the phonon propagation direction.

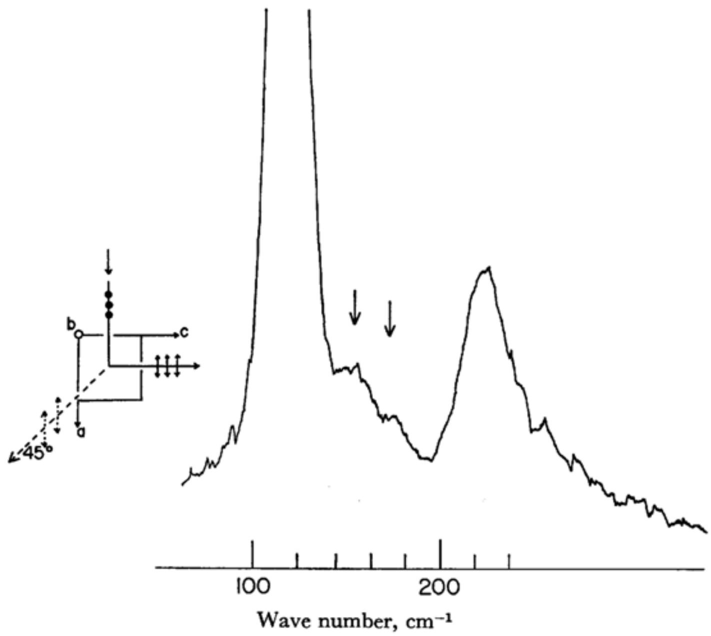

Fig. 3. Raman spectrum of $NaNO_2$ crystal (C_{2v}^{20}) observed at room temperature. Orientations of the incident and scattered beams and their electric vectors are shown in the left side of the figure. The broken lines indicate the direction of the phonon propagation and the direction of its electric polarization. A strong Raman line observed at 120 cm^{-1} is assigned to the A_2 type vibration.

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7) J. D. Axe, *Phys. Rev.*, **167**, 573 (1968).

these symmetry classifications are strictly valid. Actually, however, these are so only for vibrations whose wavevectors are exactly zero. What we are observing in the Raman spectra are vibrations with small but appreciable amounts of phase difference between the adjacent two unit cells, and therefore, an approximate "B_1" vibration may interact with an approximate "B_2" vibration through, for example, a long-range electric field. Figure 2 shows a relation of the frequencies of the Raman-active lattice vibrations with the direction of its phonon propagation direction in the ac plane. The broken lines indicate the frequencies expected when there were no interaction between the "B_1" and "B_2" vibrations, and the solid lines are what are expected when there is an interaction. The circles indicate the observed frequencies; white circles are those corresponding to the (bc) component (B_2-type vibration) and black circles to the (ba) component (B_1-type vibration) of the polarizability tensor. The partly-white, partly-black circles indicate Raman lines which are considered to have partly B_2 and partly B_1 character. The relative intensities observed of the doublet Raman lines in Fig. 1 may be taken as indicating the relative amount of the B_2 character, becuase the incident and scattered beams are set here so that almost only B_2 vibrations should appear.

On the basis that both of the 157 and 171 cm^{-1} Raman lines are due to lattice vibrations which have halfway B_2 and halfway B_1 character, these Raman lines should appear not only in a B_2 type phonon spectrum but also in a B_1 type phonon spectrum. This has been found to be actually the case as shown in Fig. 3. Here, the incident and scattered beams are set so that only Raman lines corresponding to the (ba) component (B_1 type vibrations) of the polarizability tensor should appear. The propagation direction of the phonon should be 45° with the a axis in the ac plane. Besides the Raman lines at 225 cm^{-1} (assigned to a B_1 vibration), there are two weak Raman lines observed at nearly 157 and 171 cm^{-1}, which are indicated by two arrows in Fig. 3. This result supports our interpretation of the splitting of the Raman line.

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