

Phonon Coupling and Angular Dispersion in Biaxial NaNO_2 [†]

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A detailed Raman investigation of the angular dispersion of the five phonons, propagating in oblique directions in the ac plane of biaxial NaNO_2 , is reported. It is shown that this dispersion is caused by the coupling of all the vibrational modes through the induced longitudinal electric field. When the polarization configurations used in the Raman measurements are along the principal axes of the crystal, all the coupled modes are then detectable, leading to apparent selection-rule violations. For two dimensions the analysis yields a frequency-gap picture, which accounts quantitatively for the experimental results. An expression for the Raman intensities of the oblique phonons is also given.

Recent Raman experiments upon oblique phonons (polar phonons which are propagating at oblique angles to their ionic polarizations) have shown curious phenomena.¹⁻³ In biaxial NaNO_2 , oblique phonon spectra have revealed^{1,2} more lines in a particular polarization configuration than are predicted by the standard group-theory analysis for the fundamental modes. Furthermore, the frequencies of these phonons have shown unexplained angular dispersion. In another investigation, the oblique-phonon angular dispersion³ of uniaxial LiIO_3 has been shown to fit the Loudon approximation,⁴ determined by the assumption of anisotropy dominance over the long-range electrostatic field, even when the inequality of frequencies that necessitates this assumption was not satisfied. As a part of a general survey of the connection between the ferroelectric properties and the lattice dynamics of NaNO_2 ,⁵ we had to measure LO frequencies, using a near-forward Raman scattering experiment. We then encountered similar anomalies; more lines appeared than were expected, and they showed shifted frequencies that were neither the pure LO nor TO values. We were thus motivated to survey the behavior of the oblique phonons in this biaxial crystal. This paper presents a detailed investigation of the angular dispersion and mode coupling of the five B_1 and B_2 Raman-active polar modes, traveling in the ac plane of NaNO_2 . A classical macroscopic model, based upon the coupling of any number of modes presented by the long-range induced electric field, is developed and shown to describe the experiments. This analysis is applicable to crystals of orthorhombic or higher symmetry.

At room temperature, NaNO_2 is orthorhombic with space-group symmetry C_{2v}^{20} (one molecule per primitive cell). Group theory allows the following irreducible modes⁵:

$$3A_1(aa, bb, cc): b + 1A_2(ac) + 3B_1(bc): c + 2B_2(ab): a,$$

where a , b , and c refer to conventional designations

of the biaxial-crystal's axes.⁶ The Raman activities are put in parentheses. The polarization direction of each mode is indicated in the letter following the bracket.

Raman scattering from a zero-degree cut NaNO_2 single crystal has been applied to detect the oblique phonons.⁵ By controlling the incident light beam direction, different oblique phonons could be selected for observation. The following scattering geometries, which allow the detection of B_1 and B_2 phonons propagating in the ac crystallographic plane, were used: $(xc + ya)(ba)c$, $(xc + ya)(ba)a$, and $(xc + ya)(a + c, b)a$ (x, y are arbitrary). The scattering-tensor components (bc) and (ba) used in the experiment may be regarded as filters that select either B_1 or B_2 phonons, respectively. The behavior of A_1 and A_2 phonons is not reported, because it adds no additional insight to the oblique-phonon clarification. The angle ϕ , which will be used to parametrize the angular dispersion, is the angle between the direction of the phonon propagation in the ac plane and the c axis.

Figures 1(a)–1(f) present some of the anomalous Raman spectra that we observed in the external-mode region. In Figs. 1(a) and 1(d), two resonances are seen, which correspond to pure fundamental TO modes of B_1 and B_2 character, as is expected for transversal scattering configurations with (ab) and (bc) polarization filters, respectively. In Figs. 1(b) and 1(c), and Figs. 1(e) and 1(f), which show the spectral results of some oblique phonons, four, or sometimes three, resonances with unidentified frequencies are observed with the (ab) and (bc) polarization filters. The additional lines are apparent violations of selection rules based upon standard group-theory analysis for the fundamentals of the B_1 and B_2 modes, and are not due to crystal misorientation, crystal birefringence, or to the finite solid angle of the gathering lens. The angular dispersion values of the three B_1 and two B_2 oblique modes, traveling in the ac plane, are given in Fig.

PLICIT expression for the angular dispersion:

$$\tan^2 \phi = -\frac{\epsilon_{\omega_c}}{\epsilon_{\omega_a}} \prod_{i=1}^{N_a} \prod_{j=1}^{N_c} \frac{(\omega_{ia}^2 - \omega_{\phi}^2)(\omega_{jc}^2(\text{LO}) - \omega_{\phi}^2)}{(\omega_{jc}^2 - \omega_{\phi}^2)(\omega_{ia}^2(\text{LO}) - \omega_{\phi}^2)}, \quad (3)$$

where ϕ is defined as above. Inspection shows that any angular-dispersion curve ω_{ϕ} that satisfies (3) has the properties stated in the experimental observations (ii), (iii), and (iv).

The theoretical angular-dispersion curves (3) for NaNO_2 ($N_a = 2$; $N_c = 3$) are plotted in Fig. 2, showing an excellent fit with the experimental values. The five observed TO frequencies⁵ for B_1 and B_2 used in (3) correspond well with previous measurements.^{6,9} The LO frequency values are not accurately known^{5,6,9} and were treated as adjustable parameters in order to achieve the best fit with the experimental points throughout the angular range. Thus, the oblique-phonon frequency-dispersion study provides a more accurate method to determine the LO values, which is especially important for cases where the Raman scattering intensity of the LO mode tends to diminish. The resulting TO and LO frequencies of B_1 and B_2 modes are denoted in Fig. 2.

At any angle ϕ , the oblique phonon of branch j is a mixture of the fundamental modes. In the classical limit, we expect the amplitude of the oblique-phonon Raman scattered wave, seen through a polarization filter which selects fundamental modes polarized parallel to axis k , to be linear in the amplitudes of the ionic polarizations P_{ik} of the fundamental modes:

$$I_{j\vec{q},k} = 2\pi \left[\sum_i (A_{ik}/S_{ik}^{1/2}) P_{ik}(\omega_{j\vec{q}}) + B_k E_k / 4\pi \right]^2. \quad (4)$$

B_k is related to the electro-optical coefficient, and the dielectric transition strength S_{ik} is given by

$$S_{ik} = \epsilon_{\omega_k} \prod_j [\omega_{jk}^2(\text{LO}) - \omega_{ik}^2] / \omega_{ik}^2 \prod_{j \neq i} (\omega_{jk}^2 - \omega_{ik}^2). \quad (5)$$

The factors A_{ik} can be found experimentally (up to a sign) from the intensities of the Stokes lines at

the fundamental TO modes,

$$I_{ik}(\text{TO}) = A_{ik}^2 (\bar{n}_{ik} + 1) \hbar \omega_{ik},$$

where \bar{n}_{ik} is the thermal population factor for frequency ω_{ik} . For arbitrary \vec{q} ,

$$I_{j\vec{q},k} = \frac{\alpha_k^2 \left(\sum_{i=1}^{N_k} \frac{A_{ik} S_{ik}^{1/2} \omega_{ik}^2}{(\omega_{ik} - \omega_{j\vec{q}})} + B_k \right)^2}{\sum_m \alpha_m^2 \sum_{i=1}^{N_m} \frac{S_{im} \omega_{im}^2 \omega_{im}^2}{(\omega_{im} - \omega_{j\vec{q}})^2}} (\bar{n}_{j\vec{q}} + 1) \hbar \omega_{j\vec{q}}. \quad (6)$$

There is qualitative agreement between (6) and our experimental results.

In conclusion, the problem of multioblique phonons confined to propagate in a plane is easily interpreted by the previous analysis, giving a gap-frequency-type picture. For a noninteracting mode, the oblique phonon will scan between its pure TO and LO frequencies. In case of frequency-overlapping modes, which electrostatically interact, the destinations of the angular-dispersion curves can be predicted by (3) and will depend only on the relative positioning of the pure TO and LO frequencies of all the modes involved. The previous ideas of dominance of electric field over anisotropy or vice versa^{4,10,11} to describe the angular-dispersion behavior are only special cases, which are usually not applicable to the general oblique-phonon behavior. Indeed, better agreement was obtained between the experimental angular-dispersion results of uniaxial LiIO_3 ³ and the predictions of (3) than with the earlier theory. Also, the relative intensities, observed by a polarization filter, of the TO and LO frequencies in cubic NaClO_3 for oblique propagation¹² conform to (6). The general analysis described above is, therefore, a very powerful tool for investigating the oblique-phonon behavior in cubic uniaxial and biaxial crystals of orthorhombic symmetries.

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