Raman Scattering in a Ferroelectric Sodium Nitrite Crystal

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Abstract—Raman spectra of the ferroelectric sodium nitrite are recorded over a wide spectral range at different temperatures, including the ferroelectric phase transition interval. The room-temperature Raman spectrum reveals the overdamped $A_1(z)$ soft mode which is attributed to the ferroelectric phase transition.

INTRODUCTION

Sodium nitrate ($NaNO_2$) is one of the structurally simplest ferroelectric crystals [1, 2]. At a temperature of 163°C, $NaNO_2$ crystals undergo a noncentrosymmetrical to centrosymmetrical ferroelectric phase transition [3]. In the ferroelectric phase at room temperature, this crystal is characterized by spatial symmetry group C_{2v}^{20}, while above the Curie point it exhibits a paraelectric phase with a structure corresponding to the spatial symmetry group D_{2h}^{25}.

The vibrational spectra of a $NaNO_2$ crystal were measured by means of infrared and Raman spectroscopy in [4–16]. The effect temperature has on the Raman spectra of this compound was studied in particular in [10, 11]. The $A_1(TO)$ polar soft mode responsible for the ferroelectric phase transition has yet to be observed in the Raman spectra of sodium nitrite.

The aim of this work was to perform a detailed analysis of the Raman spectra of sodium nitrite crystals at different temperatures in order to study the temperature dependence of the $A_1(TO)$ polar mode responsible for the temperature of the ferroelectric phase, and of the pseudo-scalar A_2 mode attributed to NO_2 group librations relative to the polar axis of a crystal.

EXPERIMENTAL

Raman spectra were recorded on a Horiba Jobin Yvon T64000 triple monochromator. A CCD matrix was used to receive the radiation and subsequently transmit a signal to a PC. The spectral resolution was 1 cm^{-1} when using diffraction gratings with 1800 gr/mm, and the entrance slit was 0.1 mm wide.

RESULTS AND DISCUSSION

Figure 1 shows the complete room-temperature Raman spectrum (lattice and intramolecular modes) of sodium nitrite polycrystals in the frequency range of 0 to 1500 cm^{-1}.

Figures 2a–2c show the low-frequency Raman spectra of sodium nitrate at temperatures of 123–283 K. The most intense low-frequency line is observed at 120–130 cm^{-1} as the temperature falls from 283 to 123 K. In addition, there are weak low-frequency bands at
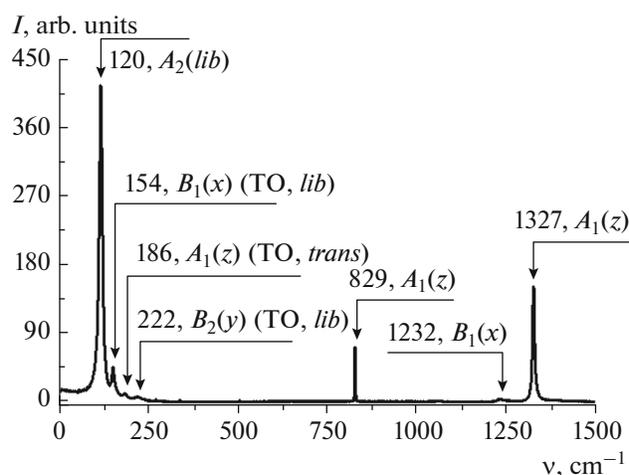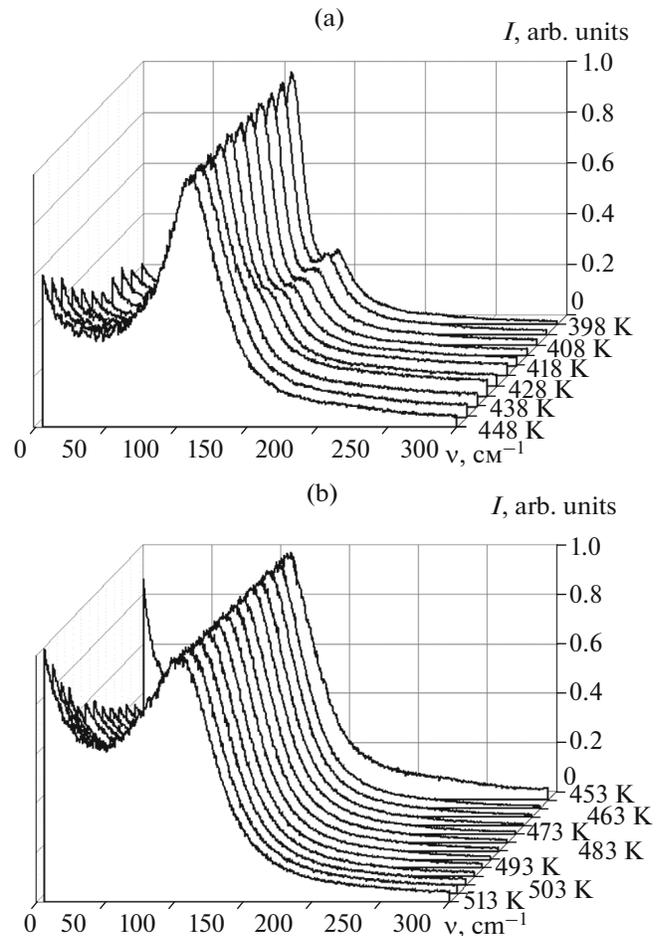

Fig. 1. Complete room-temperature Raman spectrum of sodium nitrite in the frequency range of 0 to 1500 cm^{-1}.
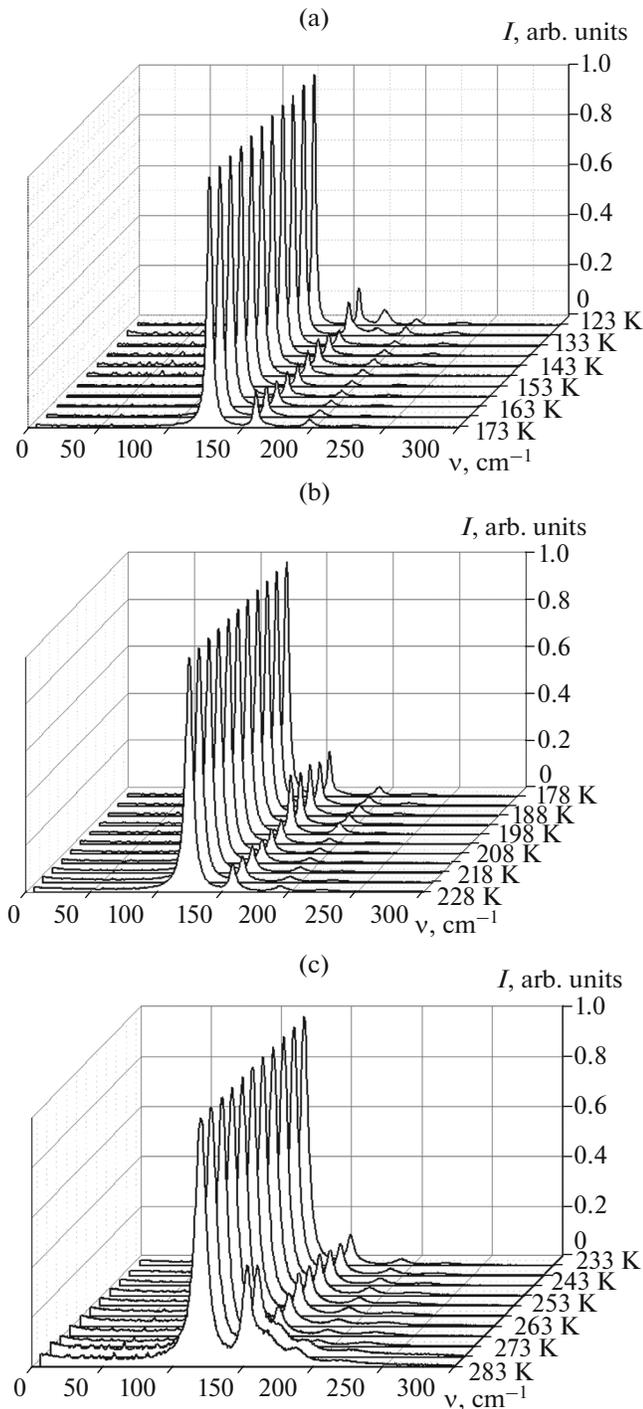
Fig. 2. Evolution of low-frequency Raman spectra at different temperatures: (a) 123–173 K, (b) 178–228 K, and (c) 223–283 K.

Fig. 3. Low-frequency Raman spectra as functions of temperature in the vicinity of the ferroelectric phase transition: (a) 398–448 K and (b) 453–513 K.

150–200 cm^{-1}, the intensities of which are redistributed when the temperature is altered.

Figures 3a, 3b show the changes in the low-frequency Raman spectra as the temperature rises in the area of the ferroelectric phase transition ($T_C = 436$ K).

As was found experimentally, a low-frequency wing of monotonically growing intensity emerges as we approach the ferroelectric phase transition ($T = 433$ K) (Fig. 3a; temperature range, 398–448 K), especially at 453 K (Fig. 3b, curve at $T = 453$ K). The rise in temperature ($T > 460$ K) is accompanied by a drop in the intensity of the low-frequency wing and its growth upon a further rise in temperature.

As can be seen from Figs. 3a, 3b, the low-frequency A$_2$ mode grows broader and shifts from 120 to 105 cm^{-1} as the temperature rises from 293 to 513 K. No pronounced changes in this mode are observed in the area of the ferroelectric phase transition ($T = 433$ K). Other modes arise in the form of diffuse and mutually overlapping bands upon heating the crystal.

According to a group theory analysis of the vibrational spectrum of sodium nitrite, the optical vibration

spectrum of the ferroelectric phase contains the following types of vibrations [17, 18]:

$$T_{opt} = [A_1(z) + B_1(x) + B_2(y)]$$
$$+ [A_2 + B_1(x) + B_2(y)] \qquad (1)$$
$$+ [A_1(z) + A_1(z) + B_1(x)].$$

The first square bracket is attributed to the translational (trans) lattice modes (the translational oscillations of the NO_2 group relative to the sodium ions); the second square bracket contains the libration modes (lib) of the NO_2 group relative to three axes; and the third bracket corresponds to intramolecular (inner) NO_2 vibrations. The $A_1(z)$, $B_1(x)$, and $B_2(y)$ polar modes should appear in the Raman spectra as transverse (TO) and longitudinal (LO) components.

In contrast to the data reported in the literature, our room-temperature Raman spectra reveal a lattice mode at 186 cm^{-1} that we attribute to the A_1(TO) translational polar transverse vibration responsible for the ferroelectric phase transition. Table shows the measured frequencies of the maxima in the low-frequency spectrum of sodium nitrite at $T = 123$ K. Note that the soft mode corresponding to the $A_1(z)$(TO) mode is overdamped away from the point of the ferroelectric phase transition, due to reorientation of the NO_2 group around the x axis, leading to the scaling of the $A_1(z)$(TO) phase. As a result, this mode is transformed into a relaxor and acquires the form of the broadband low-frequency wing typical of relaxation processes as the temperature rises.

In accordance with the table of characters of the irreducible C_{2V} groups [17, 18], the libration lattice vibrations are classified as pseudo-scalar A_2 symmetry. According to the theoretical concepts developed in [19−23], electromagnetic waves in a vacuum are accompanied by pseudo-scalar waves corresponding to the elementary particles known as axions. The resonant interaction between axions and pseudo-scalar phonons in a dielectric medium leads to the formation of hybrid quasi-particles known as axinons [24], which are analogous to polaritons. The law of axinon dispersion was derived in [24]:

$$\omega_{\pm}^2(k) = \frac{\left(\omega_{f\,ps}^2 + \omega_a^2 + c_0^2 k^2\right)}{2}$$
$$\times \left(1 \pm \sqrt{1 - \frac{4\left(\omega_{0ps}^2\omega_a^2 + \omega_{0ps}^2 c_0^2 k^2\right)}{\left(\omega_{f\,ps}^2 + \omega_a^2 + c_0^2 k^2\right)^2}} \right), \qquad (2)$$

where c_0 is the speed of light in a vacuum, ω_a is the vacuum axion frequency, $\omega_{0\,ps}$ is the characteristic frequency of the pseudo-scalar mode, ω_{fps} characterizes the efficiency of the interaction between the scalar photon field and the pseudo-scalar excitation in a medium: $\omega_{fps} = 2\pi c_0 \nu_{fps}$, $\omega_a = 2\pi c_0 \nu_a$, and $\omega_{0ps} =$
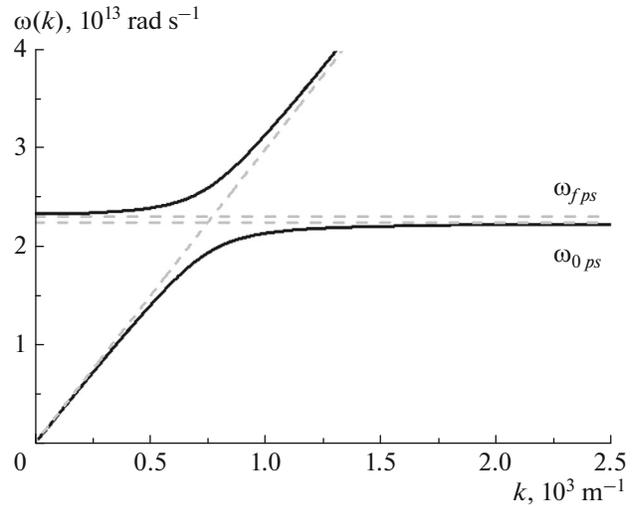

Fig. 4. Dispersion curves of axinon branches in sodium nitrite.

$2\pi c_0 \nu_{0ps}$. The following values of the parameters were used: $\nu_{fps} = 125$ cm^{-1}, $\nu_{0\,ps} = 120$ cm^{-1}, and $\nu_a = 1$ cm^{-1} [25]. Figure 4 shows the curves of dispersion in sodium nitrite, obtained using Eq. (2). The dashed lines in this figure correspond to the law of photon dispersion in a vacuum and determine the values of parameters ω_{fps} and $\omega_{0\,ps}$.

As can be seen from Fig. 4, the anti-intersection of the axion branch and the dispersion branch of the pseudoscalar mode of sodium nitrite, which is typical of hybridization of interplaying modes, is observed in the area of their maximum convergence.

Vibration frequencies and their attribution to types of symmetry in Raman spectra of sodium nitrite, recorded at temperature $T = 123$ K

Frequency, cm^{-1}	Symmetrical vibration	Phonon	Vibration
130	A_2		Libration
160	$B_1(x)$	TO, LO	Translation
178	$B_2(y)$	TO, LO	
201	$B_1(x)$	TO, LO	Libration
233	$B_2(y)$	TO, LO	
269	$A_1(z)$	LO	Translation

CONCLUSIONS

We established the presence of a transverse $A_1(z)$ polar mode in the Raman spectrum of sodium nitrite that is responsible for the ferroelectric phase transition in this crystal. This mode was clearly visible in the Raman spectra at low temperatures of a sample. It was overdamped as the temperature rose and could only appear as a central peak. As we approached the ferroelectric phase transition, a central peak emerged in the form of a broad relaxor wing near the exciting line. The intensity of this peak had a pronounced maximum at $T = 453$ K.

All Raman satellites predicted by group theory analysis were attributed to a source. The intensity of the low-frequency pseudo-scalar A_2 mode was found to be an order of magnitude higher than other lattice vibrations. The possible hybridization of pseudo-scalar phonons with axions was also discussed. The established laws for polar and pseudo-scalar modes in sodium nitrite can be used to monitor parametric processes with radiation generated in the terahertz range of the spectrum.

ACKNOWLEDGMENTS

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Translated by O. Maslova