Raman-scattering manifestation of a spatial modulation of the order parameter in a $NaNO_2$ crystal

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(Submitted 23 March 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 9, 420–422 (10 May 1987)

The Raman scattering induced by an orientational disordering of NO_2^- ions has been studied. Upon the transition to an incommensurate phase, the intensity of the Raman scattering by phonons with a wavelength equal to the period of the spatial modulation of the order parameter increases abruptly and then falls off gradually upon a transition to a paraelectric phase.

In the ordered ferroelectric phase of the $NaNO_2$ crystal all of the NO_2^- ions have an identical orientation (their dipole moments are parallel to the **b** axis, and their planes are perpendicular to **a**). When the crystal is heated, an orientational disorder gradually arises (the NO_2^- ions rotate 180° around the **a** axis). At $T_\lambda^+ = 163.8°$ C, this disorder results in a transition to an incommensurate phase and then, at $T \approx 165°$ C, in a transition to a paraelectric phase. A spatial modulation of the order parameter arises in the incommensurate phase. This modulation is characterized by a wave vector $k_{ic} = (2\pi/\lambda_{ic})s_{ic}$, where $s_{ic} \| a (|s_{ic}| = 1)$, and $\lambda_{ic} = (8 - 10)a$ specify the direction and period of the modulation.[1]

 0021-3640/87/090536-04$01.00

In this letter we report the first observation of a spatial modulation of the order parameter in the Raman scattering spectrum of the $NaNO_2$ crystal.

In the experiments we study the Raman-scattering spectra near ω_3 and the IR absorption spectrum near the frequency $\omega_2 + \omega_3$, where ω_3 and ω_2 are the frequencies of internal vibrations of the NO_2^- ion. The valence vibration ω_3 is polarized along the **c** axis and has a very large transition dipole moment. Corresponding to this vibration is a broad (≈ 140 cm^{-1}) band of single-phonon frequencies ($\omega^{TO}_{3,\mathbf{k}=0} = 1228$, $\omega^{LO}_{3,\mathbf{k}=0} = 1356$ cm^{-1} at $T = 20°$ C; Ref. 2). The completely symmetric vibrations $\omega_2 \approx 828$ cm^{-1} and $\omega \approx 1326$ cm^{-1} have a comparatively small dipole moment, which is directed along **b**.

After measuring the IR absorption in the region of two-phonon frequencies, $\omega_2 + \omega_3$, we incorporated the perturbation caused by the anharmonic interaction of phonons (see Ref. 3 for the calculation method; the constant of the anharmonic interaction is[4] $\Delta^{(23)} = -18$ cm^{-1}), and we reconstructed the spectral function $g^0_{23}(\omega, \mathbf{k} = 0)$ of the two-phonon states unperturbed by the anharmonicity. Since the width of the $\omega_{2,\mathbf{k}}$ band is small (≈ 2 cm^{-1}), the function $g^0_{23}(\omega, \mathbf{k} = 0)$ which we found is similar to the density function of single-phonon states, $g_3(\omega)$. The state density $g_3(\omega) = g_{23}(\omega_2 + \omega, \mathbf{k} = 0)$ found in this manner is shown in Fig. 1a. This figure shows a histogram of the state density $g_3(\omega)$ calculated in the dipole-dipole approximation with allowance for the anisotropic polarizability of the NO_2^-. The good agreement between the calculated and experimental state-density functions proves that the approximation used here is of satisfactory accuracy. Figure 1b shows $\omega_{3,\mathbf{k}}$ dispersion curves calculated in this approximation. The circle shows the frequency corresponding to $\mathbf{k} = \mathbf{k}_{ic}$.

Working from the data found on $g_3(\omega)$ and $\omega_{3,\mathbf{k}}$, we analyzed the spectrum of the Raman scattering induced by the orientational disordering of the crystal. Before we discuss the experimental results, we wish to point out that the flipping of the NO_2^- ion does not affect the dipole-dipole interaction, but it does change the sign of the Raman-scattering tensor of the ω_3 vibration ($\alpha_{bc} \to -\alpha_{bc}$). Consequently, the

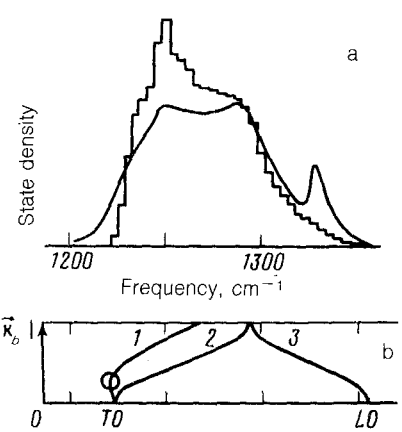

FIG. 1. (a) State-density function and (b) dispersion of the frequency $\omega_{3,\mathbf{k}}$ in a $NaNO_2$ crystal. a: The solid line has been reconstructed from the spectrum of $\omega_2 + \omega_3$ transitions measured at $T = 20°$ C, while the histogram is calculated. b: Calculations. 1—$\mathbf{k} \| \mathbf{a}$; 2—$\mathbf{k} \| \mathbf{b}$; 3—$\mathbf{k} \| \mathbf{c}$. Here $\mathbf{k}_b$ corresponds to the boundary of the Brillouin zone. The circle shows the phonon frequency $\omega_{3,\mathbf{k}}$ with $\mathbf{k} = \mathbf{k}_{ic}$. The state-density peak at the frequency ≈ 1325 cm^{-1} is a consequence of a resonant interaction of the ω_3 vibration with the ω_1 vibration. This interaction was disregarded in the calculation of $g_3(\omega)$ and $\omega_{3,\mathbf{k}}$.

Raman-scattering spectrum of the partially disordered crystal can be written

$$\kappa(\omega) \sim \int \Big(\sum_{n} p_n \alpha_{bc} e^{i\mathbf{kn}}\Big)^2 g_3(\omega, \mathbf{k}) d^3\mathbf{k} \sim p^2 \alpha_{bc}^2 g_3(\omega, \mathbf{k}=0) + (1-p^2)\alpha_{bc}^2 \int \xi_{\mathbf{k}} g_3(\omega, \mathbf{k}) d^3\mathbf{k}, \quad (1)$$

where $g_3(\omega,\mathbf{k})$ is the single-phonon spectral function, $p_n = \pm 1$ specifies the orientation of the ions, $p = \langle p_n \rangle$ is the long-range order parameter, and $\xi_{\mathbf{k}} \sim \Sigma_m \theta_m \exp(i\mathbf{km})$ is the Fourier transform of the orientation correlation function written in the form $\theta_m = \langle p_n p_{n+m} \rangle - p^2$ (under the normalization $\int \xi_{\mathbf{k}} d^3\mathbf{k} = 1$).

The first term in (1) describes the Raman scattering by phonons with $\mathbf{k} \approx 0$, which is allowed by the selection rules in the ordered crystal. The second term describes the Raman scattering by phonons with $\mathbf{k} \neq 0$, which is induced by the disorder. By comparing the Raman-scattering spectrum with $g_3(\omega)$ we can evidently evaluate the nature of the correlation in the orientations of the ions. In the absence of a correlation, we would have $\xi_{\mathbf{k}} = \text{const}$, so that the induced Raman-scattering spectrum would be similar to $g_3(\omega)$. A sinusoidal modulation of the order parameter which arises in the incommensurate phase should, according to (1), intensify the Raman scattering at frequencies corresponding to phonons with $\mathbf{k} = \mathbf{k}_{ic}$.

Figure 2 shows Raman-scattering spectra measured at frequencies $\omega_{3,\mathbf{k}}$. At room

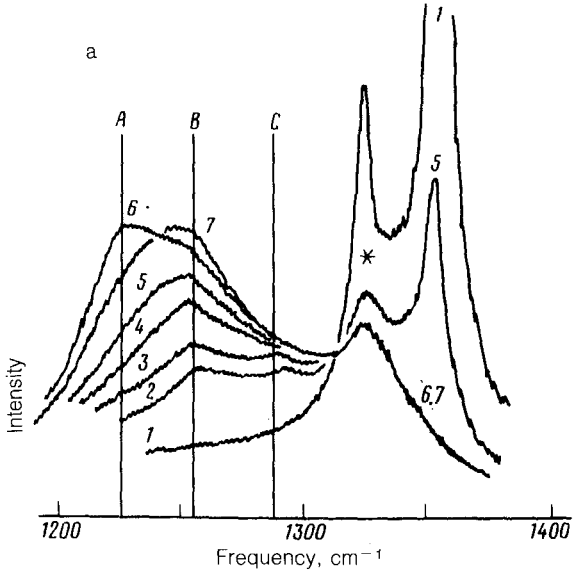

FIG. 2. Raman-scattering spectra of a $NaNO_2$ crystal measured near the frequency ω_3 at several temperatures: 1—20; 2—140; 3—150; 4—161; 5—162.8; 6—163.8; 7—168° C. The sample was cut at an angle of 45° with respect to the **a** and **c** axes; the scattering geometry was **c**′(**b** **c**′)**a**; the phonon wave vector was parallel to the **c** axis. The asterisk shows a parasitic line ω_1, observed here as a result of depolarization of the light. The vertical lines show the frequencies at which the temperature dependence of the intensity of the Raman scattering was measured.

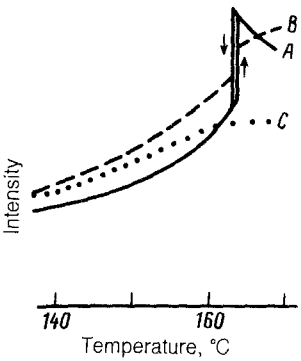

FIG. 3. Temperature dependence of the intensity of the Raman scattering at several frequencies. A—1225; cm^{-1}; B—1255 cm^{-1}; C—1285 cm^{-1}. The experimental conditions are described in the Fig. 2 caption.

temperature we see a narrow and intense line which corresponds to an LO phonon, $\omega^{LO}_{3,\mathbf{k}=0} = 1356\ cm^{-1}$; scattering by this phonon is allowed by the selection rules in this particular experimental geometry. As the temperature is raised, the LO line fades in intensity, and at $T = T_\lambda^+$ it abruptly vanishes. It follows from the experimental results that in the limit $T \to T_\lambda^+$ the integral intensity of the line varies in accordance with $(1 - T/T_c)^{2\beta}$, where $T_c = T_\lambda^+ + 0.5°$, and $\beta = 0.23 \pm 0.02$.

The broad band which appears in the Raman scattering spectrum during the heating of the crystal stems from the scattering of light by photons with $\mathbf{k} \neq 0$. At $T < 150°$ C, the induced Raman-scattering spectrum is similar to $g_3(\omega)$, implying that there is no correlation among the orientation defects. As the phase transition is approached, the shapes of the band change considerably (Fig. 2), and at $T > 150°$ C the intensity of the Raman scattering at frequencies below $\approx 1270\ cm^{-1}$ increases most rapidly. According to the estimates above, this behavior is evidence of the appearance of paired orientational defects.

The transition to the incommensurate phase leads to a sharp intensification of the Raman scattering at the frequency $\approx 1225\ cm^{-1}$ (curve A in Fig. 3), which corresponds to phonons with $\mathbf{k} = \mathbf{k}_{ic}$. As the temperature is raised further, and a transition occurs to a paraelectric phase, the intensity of the Raman scattering at this frequency falls off smoothly. At the same time, there is a smooth intensification of the Raman scattering at the frequency $\approx 1250\ cm^{-1}$ (curve B in Fig. 3).

In summary, it follows from the data on Raman scattering that a correlation arises amont orientational defects in $NaNO_2$ about 10° before the transition; the correlation changes sharply at the transition to the incommensurate phase and then varies smoothly during the transition to the paraelectric phase.

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Translated by Dave Parsons