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Order-disorder phenomenon in sodium nitrate studied by low-frequency Raman scattering*

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The low-frequency Raman spectrum of a single crystal of $NaNO_3$ has been measured for temperatures from 25 to 300°C covering both ordered and disordered phases. The crystal is partially disordered below the transition temperature and the corresponding Raman spectra are interpreted in terms of the theory developed by Loveluck and Sokoloff.

I. INTRODUCTION

In recent years, the study of the optical properties of randomly disordered solids has increased substantially.[1-5] Some crystals are inherently disordered or may exist as such over a certain temperature range. In most cases, the disorder is orientational in character and there is positional long-range order, but orientational long-range disorder. The study of such crystals provides a useful route of approach to the understanding of the properties of amorphous materials in which neither of the long-range orders exist.

In the disordered molecular crystals, the $\vec{k} = 0$ selection rule is lifted and the Raman spectrum essentially reflects the orientational correlation of the molecules. In particular, the Raman spectrum of the disordered molecular crystal shows certain features of the one-phonon density of states of the ideal crystal.[6-8]

We have studied the low-frequency Raman spectrum of sodium nitrate at different temperatures and noticed that the Raman spectrum becomes complicated as the temperature is raised. This complication is caused by the presence of disordering. The observed spectrum is actually a combination of two parts, one is the ordinary first-order Raman spectrum and the other is the disorder-induced spectrum. By using the theory developed by Loveluck and Sokoloff,[5] we have interpreted the temperature dependence of the Raman spectrum in a self-consistent manner.

II. EXPERIMENTAL

Sodium nitrate undergoes an order-disorder phase transition at 276 °C.[9-12] At low temperatures, sodium nitrate crystalizes in the ordered calcite structure. It belongs to the D_{3d}^6 space group ($R\bar{3}C$) with two formula units of $NaNO_3$ per unit cell. Successive nitrate groups are rotated 60° relative to one another. When the crystal is heated, the structure changes into the high-temperature form by a gradual transition ending at about 276 °C. Many different models have been proposed for the disordered $NaNO_3$ structure, among them are rotationally disordered structure,[9] disordered aragonite structure,[13] disordered calcite structure,[14] and the mixture of the last two.[15] In any case, the disordering is caused by the reorientation of the NO_3^- ions, and we are only interested in the effect of this disordering on the low-frequency Raman spectrum. The disordering of NO_3^- ions has also induced sidebands on some internal modes.[16,17] The change from complete order to complete disorder for $NaNO_3$ is spread out over a wide temperature range of nearly 100 °C. It is this wide temperature range which makes sodium nitrate a good example for applying the theory of Loveluck and Sokoloff.

Raman spectra were excited by the 4880-Å laser line of a Coherent Radiation Model 52G argon-ion laser with a power output of 400 mW. The light scattered at 90° was collected and spectrally analyzed by a Spex Industries Model 1400 double-grating monochromator. The light was detected by a cooled ITT-FW130 photomultiplier tube. The electrical signal output was processed by a standard photon counting technique. The system resolution was about 4 cm^{-1}. The crystal, which was grown by slow evaporation of a saturated solution, was mounted inside a small oven with a temperature control within ±0.5 °C. The temperature was measured by a copper-constantan thermocouple.

III. RESULTS AND DISCUSSION

Since the two Raman active modes at 185 and 98 cm^{-1}, identified as long-wavelength librational and translational modes, respectively, belong to the E_g representation,[18,19] we have only studied the Raman spectrum in the $z(xz)y$ scattering configuration. Some of the spectra are displayed in Fig. 1. We have noticed a progressive disappearance of the band at 98 cm^{-1} as the transition temperature was approached. The increasing background intensity and the appearance of some irregular peaks may be attributed to the disorder-induced spectrum.

Following the treatment of Loveluck and Sokoloff[5] for the optical properties of phonon systems with disordered force constants, the Raman spectrum in the lattice region of a partially disordered solid may be written as

$$I(\omega, T) = I_1'(\omega, T) + I_2'(\omega, T), \tag{1}$$

with

$$I_1'(\omega, T) = m^2(T) I_1(\omega, T), \tag{2}$$

and

$$I_2'(\omega, T) = [1 - m^2(T)] I_2(\omega, T), \tag{3}$$

where $I_1(\omega, T)$ is the first-order Raman spectrum for a completely ordered crystal at temperature T; $I_2(\omega, T)$ is the first-order Raman spectrum of a completely disordered crystal at the same temperature; and $m(T)$ is the order parameter. The presence of the disorder-induced spectrum I_2' makes it difficult to clearly discern the zone-center phonon behavior (which is important in the understanding of the phase transition) directly from the Raman spectrum below the transition temperature. The two terms I_1' and I_2' have to be separated before further analysis can be accomplished. This method had been used to interpret the Raman spectra of some ammonium halides.[20,21] By using the Bragg-William's approximation,[20] the order parameter $m(T)$ can be related to the configuration enthalpy H_c in the following manner:

$$1 - m^2(T) = \frac{2}{\epsilon\gamma} \int_0^T \delta C_p \, dT = \frac{2}{\epsilon\gamma} H_c , \tag{4}$$

where δC_p is the additional molar specific heat due to the disordering of NO_3^- ions, γ is the number of nearest neighbors at any NO_3^- site, and ϵ is the interaction energy.

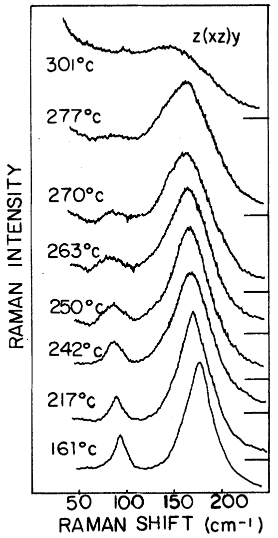

FIG. 1. $z(xz)y$ Stokes Raman spectra of $NaNO_3$ in the lattice-mode region at several temperatures. The horizontal bars on the right-hand side indicate the zero intensity levels at different temperatures.

The first-order Raman spectrum $I_1(\omega, T)$ of an ordered structure with two uncoupled modes can be expressed as[22]

$$I_1(\omega, T) = R X''(\omega)[n(\omega, T) + 1] , \tag{5}$$

where

$$X''(\omega) = \text{Im}\left(\frac{\rho_1^2}{\omega_1^2 - \omega^2 + i\omega\Gamma_1} + \frac{\rho_2^2}{\omega_2^2 - \omega^2 + i\omega\Gamma_2}\right), \tag{6}$$

$$n(\omega, T) = \frac{1}{e^{\hbar\omega/kT} - 1} , \tag{7}$$

and R is a constant. $\omega_{1,2}$, $\Gamma_{1,2}$, and $\rho_{1,2}$ represent the oscillator frequencies, widths, and relative strengths, respectively.

For a completely disordered crystal, the Raman intensity $I_2(\omega, T)$ is related to the density of vibrational states, $\rho(\omega)$ by the following relation[23]:

$$I_2(\omega, T) = [c(\omega)/\omega][n(\omega, T) + 1]\rho(\omega), \tag{8}$$

where c is a frequency-dependent coupling factor.

We assume that for temperatures above 276 °C, the crystal is completely disordered (i.e., $m = 0$), and thus the corresponding Raman spectrum is just $I_2'(\omega, T)$ in Eq. (1). The reduction in intensity of the first-order Raman spectrum, as the temperature was raised further, is probably associated with the increased thermal broadening due to pho-

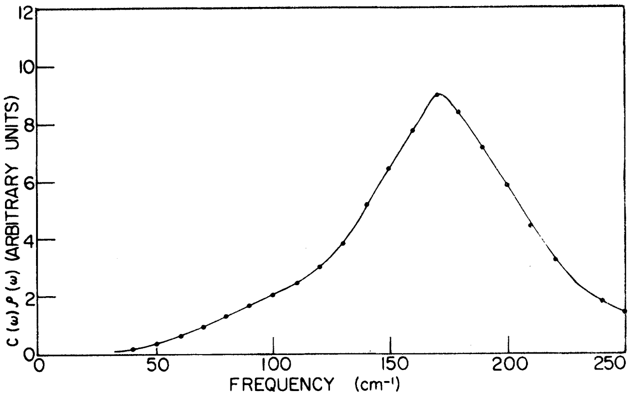

FIG. 2. Reduced density of states of $NaNO_3$ at 277 °C.

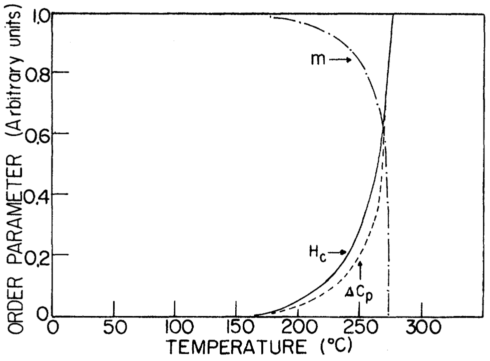

FIG. 3. Plots of the normalized configurational enthalphy H_c, residual specific heat ΔC_p, and the order parameter m, as functions of temperature.

non-phonon interaction which occurs at higher temperatures.[5] After having subtracted the Rayleigh background which was approximated by a Gaussian shape, we multiply the spectrum at high temperatures by the factor $\omega/[n(\omega, T)+1]$ [see Eq. (8)] and obtained the weighted one-phonon density of states of $NaNO_3$ crystal, as shown in Fig. 2. Since the factor $\omega/[n(\omega, T)+1]$ suppresses the low-frequency range, the error introduced during subtracting the Rayleigh background is also reduced.

The order parameter $m(T)$ is obtained by using Eq. (4). ΔC_p values of $NaNO_3$ were obtained by subtracting from the measured specific-heat curve[12] a baseline representing all the non-configurational contributions to C_p[12]. The normalized curves of ΔC_p and H_c for $NaNO_3$ are shown in Fig. 3. The order parameter $m(T)$ is also plotted in the same graph. It has to be mentioned that Sato *et al.*[24] have used an empirical method to ob-

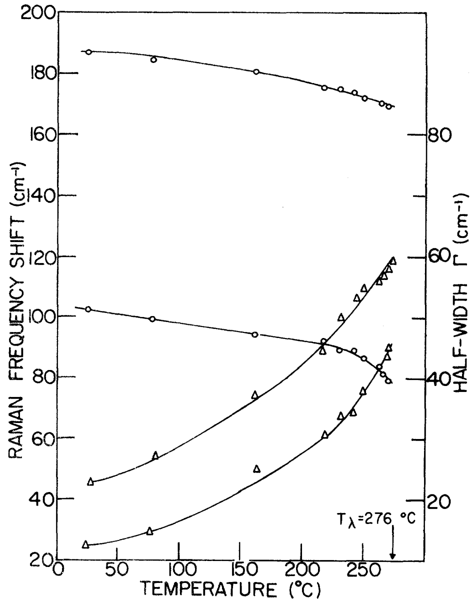

FIG. 4. Temperature dependence of the frequencies (circles) and half-widths (triangles) of the translational and librational modes.

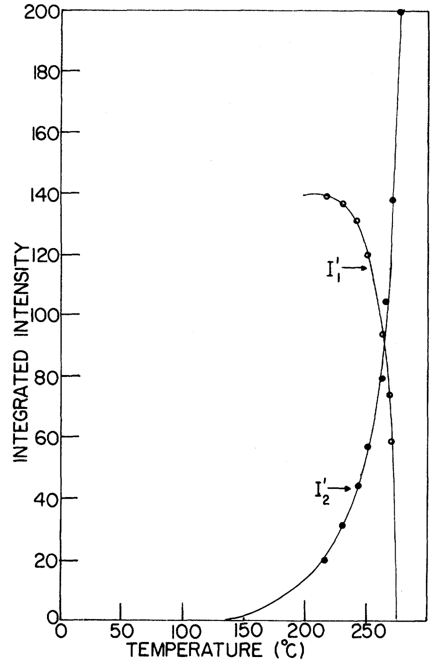

FIG. 5. Temperature dependence of integrated intensities I_1' and I_2'.

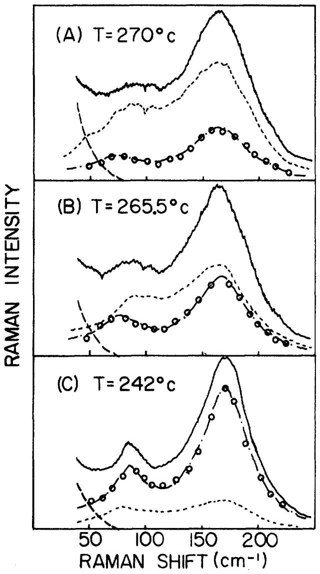

FIG. 6. Raman spectra of $NaNO_3$ at 270, 265.5 and 242 °C separated into I_1' and I_2' according to Eq. (1). The solid curve represents experimental results; the dashed-dotted curve, calculated I_1'; the open circle, experimental I_1'; the dotted curve, I_2'; the dash curve, the Rayleigh wing.

tain the order parameter by analyzing the infrared absorption spectrum of one internal mode of $NaNO_3$. Their order parameter, which is unrelated to other physical observations, is, however, quite different from ours.

Since the Raman spectrum obtained above the transition temperature reflects the density of states at that particular temperature only, some modifications are required in order to get $I_2(\omega, T)$ at a lower temperature from extrapolation of the high-temperature one. Typical modifications are the shifts of peak positions, changes in band shape, etc. Multiplying the proper density-of-states spectrum by $(1-m^2)$ and subtracting it from the Raman scattering cross section $I(\omega, T)$ below the transition temperature will determine the first term in Eq. (1). The calculated spectrum of $I_1'(\omega, T)$ is obtained from a least-square fit[25] of Eq. (5) to the resulting spectrum. The parameters ω_1, ω_2, Γ_1, and Γ_2, determined from the fit are plotted in Fig. 4. The integrated intensities of $I_1'(\omega, T)$ and $I_2'(\omega, T)$ are displayed in Fig. 5. The spectra of $I(\omega, T)$, $I_1'(\omega, T)$, and $I_2'(\omega, T)$ are shown in Fig. 6 for three different temperatures.

The calculated results are in very good agreement with the experimental ones. The introduction of the last term in Eq. (1) improves remarkably the analysis of the Raman spectrum below the transition temperature. We had tried to fit the entire spectrum with coupled and uncoupled damped oscillators only, but the results were rather poor.

In summary, the Raman spectrum of $NaNO_3$ in the lattice-mode region can be interpreted very satisfactorily by using the method developed by Loveluck and Sokoloff. The presence of the disorder-induced spectrum makes it difficult to observe the zone-center phonon behavior directly from the Raman spectrum below the transition temperature. We have successfully isolated the spectrum due to the zone-center phonon only.

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