

Phase transition due to nonlinear resonance of lattice vibrations

K. S. Aleksandrov, I. P. Aleksandrova, G. M. Zaslavskii, A. V. Sorokin, and V. F. Shabanov

Kirenskiĭ Physics Institute, Siberian Division, USSR Academy of Sciences

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Raman spectroscopy in the polarized phase was used to observe, in a number of ferroelectrics of the order-disorder type, two low-frequency oscillations with strong temperature dependence of the frequencies as $T \rightarrow T_c$. This dependence is regarded as a result of nonlinear resonant interaction of two lattice vibrations near the Curie point, and a model is proposed for the phase transition due to this resonance.

In the course of the study of Raman spectra of light in ferroelectrics of the order-disorder type, we observed in a number of crystals a characteristic phenomenon that can serve as the starting point for the construction of a new model for the phase transitions in these compounds. The gist of the phenomenon is that low-frequency lattice vibrations in the ferroelectric phase have a critical behavior as $T \rightarrow T_c$. This is manifest in a strong temperature dependence of the oscillation frequencies ω_i , leading to their coincidence and, consequently, to a definite form of the degeneracy in the spectrum near T_c .

Figure 1 shows the temperature dependence of the frequencies of two type-B lines in a triglycinselenate (TGSeI) crystal, obtained by laser Raman spectroscopy with the setup in⁽¹⁾. As T_c is approached, as seen from Fig. 2, a redistribution of the intensities, measured relative to the intramolecular frequency 330 cm^{-1} , is observed between ω_3 and ω_4 . The ratio J_3/J_4 decreases from 1.8 at -60°C to 1.0 near the phase transition. A broadening of both lines is observed near the transition. All this points to an increase in the effective interaction of the modes. Similar results were obtained by us in the investigation of the Raman spectra in triglycinsulfate (TGS) crystals and $\text{NaNH}_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$. Thus, the frequencies corresponding to the modes ω_3 and ω_4 for TGS are equal to 60 and 75 cm^{-1} respectively at $T = -14^\circ\text{C}$ and to 62 and 70 cm^{-1} respectively at $T = 20^\circ\text{C}$, and then approach the value 66 cm^{-1} at $T = 49^\circ\text{C}$.

Owing to the low symmetry of the lattices (space

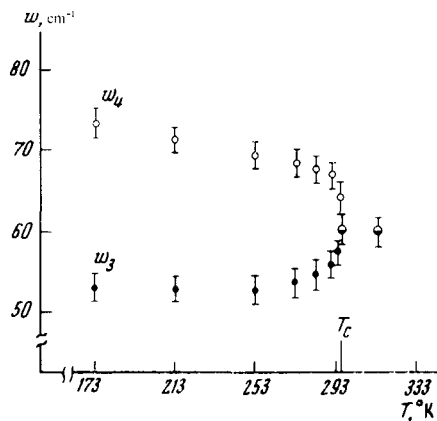


FIG. 1. Temperature dependence of the frequencies of the interacting mode in a triglycinselenate crystal.

groups $P2_1/m$ and $P2_1$ above and below T_c) and to the absence of pseudosymmetry in the arrangement of the groups, the observed behavior of the frequencies cannot be attributed to the usual lifting of the frequency degeneracy at $T < T_c$.

Investigations of the Raman spectra of TGS, of mixed TGS-TGSel crystals, and of their deuterated analogs have made it possible to establish uniquely that far from T_c the ω_3 mode is due primarily to translational vibration of the SeO_4 groups, while ω_4 is due to the orientational vibrations of the glycine groups. These data, and also the fact that $\Delta\omega_4 - \omega_3 \sim \omega_3$, ω_4 far from T_c , exclude the interpretation of the result as the splittings of the vibration frequencies of the same group in a two-minimum potential.

Above T_c , one observed in the investigated frequency region (Fig. 2) one intense line $\omega = 62 \text{ cm}^{-1}$ against the background of a broad band that spreads out with increasing temperature. On passing through T_c on the paraphase side, the lattice vibrations become modified and go over into coupled vibrations of the glycine group (ω_4) and SeO_4 group (ω_3).

The behavior of the investigated oscillations near T_c can be attributed to nonlinear resonance of these modes. Indeed, (see e.g.,⁽²⁾), for "capture" into nonlinear resonance it is necessary that the nonlinearity of at least one of the modes in the region be sufficiently large in comparison with the coupling constant between the modes. As seen from Fig. 1, as $T \rightarrow T_c$ and as $\Delta\omega \rightarrow 0$ we have $\partial\omega/\partial T \rightarrow \infty$, i.e., the anharmonicity increases and the condition for the capture is automatical-

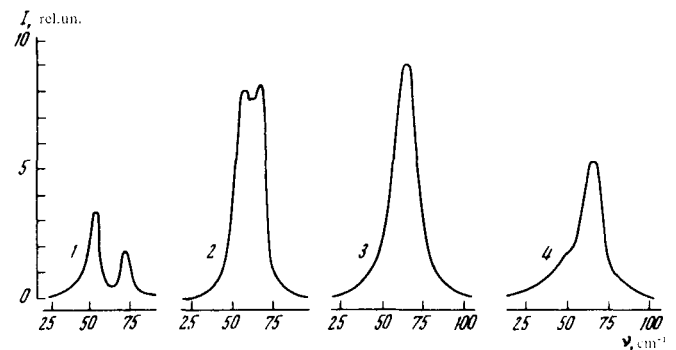


FIG. 2. Spectrograms of the interacting modes in a triglycinselenate crystal at various temperatures: 1— $T = 60^\circ\text{C}$, 2— $T = +18^\circ\text{C}$; 3— $T = +22^\circ\text{C}$, 4— $T = +63^\circ\text{C}$.

ly satisfied for the usual values of the coupling constants between the modes. Within the framework of these concepts, the unusual increase of ω_3 near T_c and other observed phenomena receive a natural explanation.

A model can be constructed for the considered transition on the basis of the Hamiltonian that describes the coupled nonlinear oscillations of the $\omega_3 = \omega_k$ and $\omega_4 = \omega_j$ modes in the vicinity of the resonance. The binding energy of the modes is

$$H_{int} = \sum_j V_{jk}(J_j, J_k, T) \cos(\theta_j - \theta_k). \quad (1)$$

The critical behavior of the separated modes becomes manifest in the resonance condition

$$\dot{\psi} = \dot{\theta}_j - \dot{\theta}_k = \omega_j(J_j, T) - \omega_k(J_k, T) = 0. \quad (2)$$

The quantity ψ characterizes the relative detuning of the phases of the oscillations, and condition (2) means that its time variation, due to the phase oscillation, is small. Excitation of the mode ω_k is accompanied by the appearance of long-range order (spatial coherence) of the phase oscillations. A competing mechanism are the thermal fluctuations. Calculation of the partition function with allowance for (1) and with minimization of the free energy with respect to J_k leads to the equation

$$\omega_k = \frac{\partial V}{\partial J_k} \frac{I_1\left(\frac{V}{T}\right)}{I_0\left(\frac{V}{T}\right)}, \quad (3)$$

where $V = V(J_j^{(0)}, J_k, T)$; $J_j^{(0)}$ is the solution of Eq. (2) near T_c ; I_0 and I_1 are Bessel functions of the imaginary arguments.

Equation (3) is analogous to the Curie-Weiss equation with

$$T_c = \frac{\partial V}{\partial J_k} \left/ \left[\frac{\partial}{\partial J_k} \left(\frac{\omega}{\frac{\partial V}{\partial J_k}} \right) \right] \right. \quad (4)$$

The quantity J_k is here a thermodynamic order parameter. At $T > T_c$ we have $J_k \equiv 0$ in accord with (3). At $T < T_c$ there exists a solution with $J_k \neq 0$, namely $J_k \sim (T_c - T)^{1/2}$.

Thus, the lattice instability that leads to the phase transition can result not only from the vanishing of one of the oscillation frequencies of the lattice (the soft mode⁽³⁾), but also from the capture of two modes of close frequency into a nonlinear resonance.

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