

Experimental investigation of the density of states of a quasi-one-dimensional vibrational exciton in isotopically mixed KNO_3 crystals

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(Submitted 16 July 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **36**, No. 5, 152–155 (5 September 1982)

The possibility of directly measuring the density of states of a disordered crystal from the spectrum of compound transitions is noted and studied experimentally for the first time. The unusual behavior of the spectrum studied as a function of concentration is explained by the quasi-one-dimensional nature of the band.

PACS numbers: 71.20. + c, 71.35. + z

There are now no methods for experimentally measuring the density of states in disordered crystals. In addition, it follows from an analysis of the vibronic and band-band transitions¹ as well as two-phonon transitions² that it is possible to measure directly the density of state of an isotopically mixed crystal from the spectrum of compound transitions. The simplest situation occurs for transitions with the participation of a "narrow-band" state, whose energy does not change with isotopic substitution. If, in so doing, it is possible to neglect the interaction of the two-particle states investigated, then their spectrum coincides with the spectrum of the density of "wide-band" states, both in the pure and in the isotopically mixed crystal.

The polarized ($\mathbf{E}||\mathbf{c}$) IR absorption spectra in the region of $\omega_1 + \omega_2$ transitions in $\text{K}^{15}\text{N}_x^{14}\text{N}_{1-x}\text{O}_3$ crystals (aragonite structure, D_{2h}^{16} , four molecules per cell) were studied experimentally. According to previously obtained data,^{3–5} the transition investigated satisfies the conditions formulated above. Vibrational excitons (intramolecular phonons) in the crystal KNO_3 correspond to isolated bands and, in addition, the width of the bands $\omega_2(\mathbf{k})T_2 = 21 \text{ cm}^{-1}$ greatly exceeds the width of the band $\omega_1(\mathbf{k})$, $T_1 \approx 1 \text{ cm}^{-1}$. When ^{14}N is replaced by ^{15}N , the frequency of the completely symmetrical vibration ω_1 does not change, while the shift in the frequency of the extraplanar vibration ω_2 is equal to $\Delta_2 = -22 \text{ cm}^{-1}$, i.e., $|\Delta_2|/T_2 \approx 1$. The anharmonic interaction of the states examined is small ($\Delta_{12} \approx -2 \text{ cm}^{-1}$, i.e., $|\Delta_{12}|/T_2 \ll 1$) and for this reason it has almost no effect on the shape of the $\omega_1(\mathbf{k}) + \omega_2(-\mathbf{k})$ band.

The optical density spectra obtained as a function of the content of the isotope ^{15}N are presented in Fig. 1. A wide band, whose shape reflects the distribution on the density of $\omega_2(\mathbf{k})$ states, is observed in the crystal with a natural isotopic content (lower curve).⁵ On the low-frequency side of this band, a weak line corresponding to local vibration of an isolated impurity (monomer) can be seen. As the impurity content increases, the intensity of the monomer line increases and a doublet arises at the same time, whose components are naturally assigned to the symmetrical (2^+) and antisymmetrical (2^-) dimer vibrations. When the impurity content exceeds 50%, the spectrum

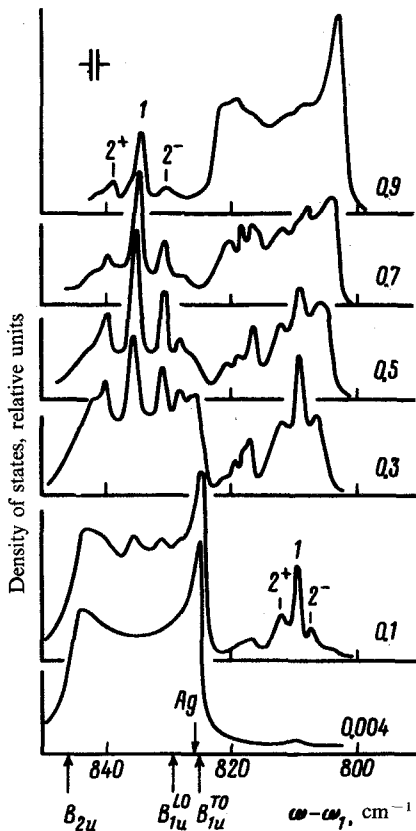


FIG. 1. Spectra of the density of $\omega_1(\mathbf{k}) + \omega_2(-\mathbf{k})$ states in isotopically mixed KNO_3 crystals at $T \approx 100$ K. The curves are shifted in frequency by $\omega_1 = 1050 \text{ cm}^{-1}$ into the region $\omega_2(\mathbf{k})$ states. The relative content of the isotope ^{15}N is indicated in the figure. The arrows mark the frequencies of Davydov components $\omega_2(\mathbf{k} \approx 0)$ in the natural crystal. 1, 2^+ , and 2^- are lines corresponding to local vibration of the monomer, as well as the symmetrical and antisymmetrical vibrations of the dimer.

acquires a quasicontinuous character, which indicates delocalization of vibrations and formation of a new band.

The most distinct property of the picture observed is the surprising stability of the monomer and dimer peaks, whose existence is observed up to 90% impurity content. Of the examples studied in the literature, the exciton spectrum of the isotopically mixed naphthalene crystal (nd_0 - nd_8), where $|\Delta|/T \approx 0.7$, the resonance interaction is short-ranged, while the excitonic band is two dimensional, is most similar to the examples studied here. The computed⁶ and experimental⁷ absorption spectra, as well as the computed spectra of the density of states,⁸ show (see also Ref. 1) that in naphthalene the cluster structure disappears with $x \gtrsim 0.3$, while the monomer peak washes out with $x \gtrsim 0.5$, i.e., near the percolation threshold for the two-dimensional lattice. The anomalous stability of localized states discovered in this work forces the conclusion that the $\omega_2(\mathbf{k})$ band is quasi-one-dimensional.

The appearance of a one-dimensional band in the three-dimensional crystal KNO_3 can be explained by examining its structure. Replacing the ions NO_3^- by linear oscillators, polarized like ω_2 along the \mathbf{c} axis, the crystal KNO_3 can be represented as a slightly distorted hexagonal lattice with constants $c = 0.32$ nm and $a = 0.54$ nm. The one dimensionality of $\omega_2(\mathbf{k})$ indicates that the interaction of nearest neighbors along the \mathbf{c} axis greatly exceeds the interaction of neighbors in planes perpendicular to \mathbf{c} . The high degree of one-dimensionality of the $\omega_2(\mathbf{k})$ band is supported by the fact that in the natural crystal the shape of the band $\omega_1(\mathbf{k}) + \omega_2(-\mathbf{k})$ (lower curve in Fig. 1) is similar to that of the spectrum of the density of states of a one-dimensional chain and, in addition, the Davydov components, which correspond to the center (B_{1u}^{TO} , B_{1u}^{LO}) and boundaries (A_g and B_{2u}) of the expanded Brillouin band, fall into the low-frequency and high-frequency band edges.

We note also the difference in the splitting of the ^{14}N -dimer (5 cm^{-1}) and ^{15}N -dimer (9 cm^{-1}) doublets, as well as the considerably different form of the high-frequency and low-frequency bands with equal isotopic composition. These apparently interrelated effects qualitatively agree with the results obtained for naphthalene,⁶⁻⁸ but are much more distinct.

The simplicity of the investigations of the system suggests that it can be described in detail by a model, which together with additional experimental study of the first and second order of spectra, will yield complete information concerning the nature of the interaction of vibrations, as well as the nature of the observed pattern not discussed here.

We note that the conditions necessary for directly measuring the density of states are also satisfied in a number of other crystals with impurity and thermoactivated disorder. The range of objects can be greatly broadened by examining cases when the isotopic shift of the narrow-band state differs from 0 (see Ref. 1), as well as by studying the pure overtone transitions [for example, $\omega_2(\mathbf{k}) + \omega_2(-\mathbf{k})$ in KNO_3]. We can hope that the development of the theory of interaction of quasiparticles in disordered crystals will allow analyzing more complicated situations as well, when these interactions cannot be ignored.

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