

Effect of polarizability on excitation transfer in a disordered linear chain

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The state density of a quasi-one-dimensional vibrational exciton ω_2 has been studied experimentally in isotopically mixed crystals $\text{K}^{15}\text{N}_x^{14}\text{N}_{1-x}\text{O}_3$. The probability for the transfer for an excitation through the light impurity is found to be much higher than that for transfer through a heavy impurity. This effect is explained in terms of an interference of vibrational and electronic states.

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The spectrum of excitations of a disordered one-dimensional chain is usually analyzed in the single-level approximation of the interaction of nearest neighbors.¹ In this approximation the excitation spectra of chains containing a light impurity (L ; $\Delta > 0$) and a heavy impurity (H ; $\Delta < 0$) are similar (Δ is the energy defect at the impurity). In this letter we show, for the first time, that L and H impurities are not equivalent in a real quasi-one-dimensional system. This conclusion follows from an analysis of the state density spectra $g(\omega, x)$ of a quasi-one-dimensional vibrational exciton ω_2 in isotopically mixed crystals $\text{K}^{15}\text{N}_x^{14}\text{N}_{1-x}\text{O}_3$. The experiments were carried out by studying the Raman spectra of the completely symmetric transitions $\omega_2 + \omega_2$.

The possibility of directly determining $g(\omega, x)$ from the measured spectra of composite transitions was pointed out in Ref. 2; in the same study it was found that the ω_2 band is quasi-one-dimensional in KNO_3 . In this crystal the planar quasimolecular ions NO_3^- lie in stacks (or chains) parallel to the c axis. The internal vibration ω_2 is also polarized along the c axis. The isotopic shift of ω_2 caused by the replacement of ^{14}N by ^{15}N is $\Delta = -21.5 \text{ cm}^{-1}$. The anharmonic shift of the overtone level ω_{22} is negligible, $|\Delta_{22}| < 0.5 \text{ cm}^{-1}$. Since there is no anharmonic interaction and since the overtone transition is not an intramolecular transition, the spectrum of completely symmetric $\omega_2 + \omega_2$ transitions can be taken to be the same as the $g(\omega, x)$ spectrum, but stretched out twice as far as the frequency scale, in both pure and isotopically mixed crystals.

In the experiments we studied the Raman spectra of isotopically mixed $\text{K}^{15}\text{N}_x^{14}\text{N}_{1-x}\text{O}_3$ single crystals. The isotopic composition was determined within 1%. The spectra were excited with an argon laser ($p \approx 0.8 \text{ W}$, $\lambda_0 = 514.5 \text{ nm}$) and detected by a Spex Ramalog-6 spectrometer by a multiple-scanning method with data accumulation with the help of a microcomputer. The $\omega_2 + \omega_2$ spectra shown here are normalized to a constant integrated intensity and are transferred into the region of ω_2 states.

It can be seen from Fig. 1a that the experimental spectrum of the $\omega_2 + \omega_2$ transitions in KNO_3 is quite similar to the model spectrum $g(\omega, x = 0)$ of a one-dimensional exciton. The bandwidth is determined by the width of the exciton band, T_2 : $T_2 = 21.5 \text{ cm}^{-1}$ at 90 K. It falls off monotonically to 17.5 cm^{-1} at 300 K. Comparison of this

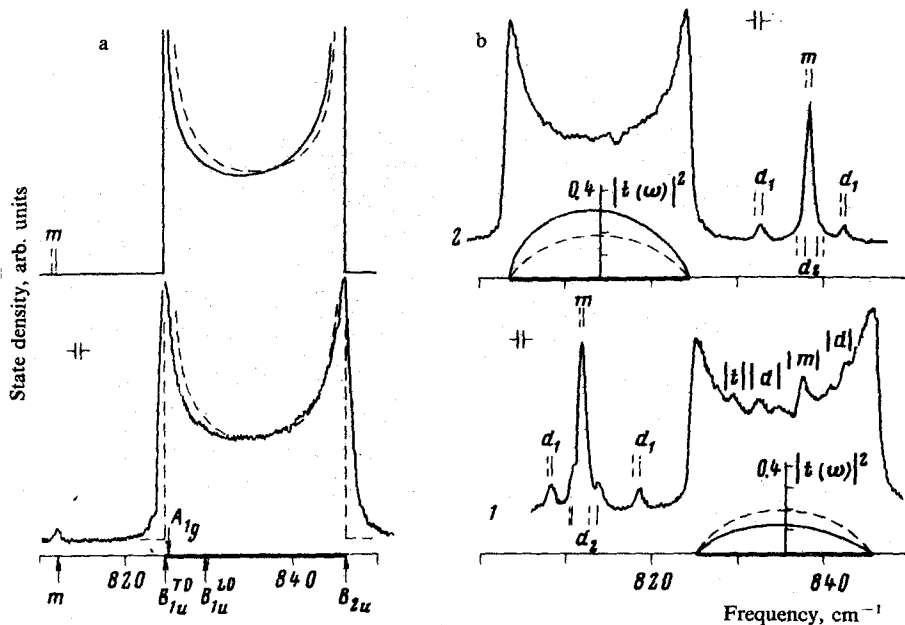


FIG. 1. Spectra of the density of ω_2 states in $\text{K}^{15}\text{N}^{14}\text{N}_{1-x}\text{O}_3$ crystals. The curves with the noise are the experimental Raman spectra of $\omega_2 + \omega_2$ transitions at 90 K, transferred into the region of ω_2 states. The results of calculations with $T_2 = 21.5 \text{ cm}^{-1}$ are shown by dashed curves ($\beta = 0$) and solid curves ($\beta = 0.13$). The vertical line segments are the calculated vibration frequencies of m , d_1 , and d_2 clusters. The calculation regions for the exciton bands are shown along the frequency axis. a—0.37% ^{15}N and calculation of $g(\omega, x = 0)$ [the arrows show the frequencies of the local vibration (m) of $^{15}\text{NO}_3^-$ and the frequencies of the Davydov components measured from the first-order spectra]; b—1—10% ^{15}N (H impurity); 2—10% ^{14}N (L impurity) and calculated curves of the probability $|t(\omega)|^2$ for excitation transfer through H and L impurities.

behavior with the thermal expansion of the crystal ($\alpha_c = 18 \times 10^{-5} \text{ K}^{-1}$, $\alpha_b \approx \alpha_a = 2.3 \times 10^{-5} \text{ K}^{-1}$; Ref. 3) shows that the interaction of the ω_2 vibrations falls off in proportion to $r^{-5.5 \pm 1}$; i.e., it is a short-range interaction.

The local vibration of an isolated impurity (m) is observed even in a crystal with the natural abundance (0.37%) of the isotope ^{15}N . At 10% ^{15}N , four new lines appear in this part of the spectrum (curve 1 in Fig. 1b); their positions and intensities demonstrate unambiguously that they belong to dimer vibrations $d_1(\dots\text{LLHHLL}\dots)$ and $d_2(\dots\text{LLHLHL}\dots)$. The splitting of the doublet d_1 is determined primarily by the direct interaction of the vibrations of adjacent molecules in the chain, while the splitting of d_2 is due to an indirect interaction of the impurities through the host molecule between them. The absence of components corresponding to clusters of molecules of adjacent chains proves that the interaction with a chain is at least 20 times stronger than that between chains.

Study of the concentration behavior of the spectrum $g(\omega, x)$ shows that the structure which appears against the background of the quasicontinuous spectrum of L states at a 10% H impurity is genetically related to vibrations localized at groups of one ($|m\rangle$), two ($|d\rangle$), and three ($|t\rangle$) L molecules. The existence of highly localized L

vibrations in a crystal containing 90% L molecules means that the H impurities almost completely block the transfer of excitations along the L chain, separating it into weakly coupled segments.

In the case of the 10% L impurity (curve 2 in Fig. 1b), the $g(\omega, x)$ spectrum also has m and d_1 lines. The d_2 doublet can be observed, however, only at the maximum resolution, since its splitting is half that in the case of the H impurity. The magnitude of the d_2 splitting is a measure of the probability for the transfer of an excitation through a molecule separating impurities. The probability for the transfer of H excitations through an L molecule is thus twice as high as that for the transfer of L excitations through an H molecule. Further evidence for this conclusion comes from the absence of any clearly defined structure in the continuous spectrum of H states in the crystal containing a 10% L impurity.

These experimental results thus prove the very nearly one-dimensional nature and short-range nature of the interaction of ω_2 vibrations. On the other hand, these results show that H and L impurities are not equivalent; this nonequivalence cannot be explained by the standard one-dimensional model. This contradiction can be resolved by taking into account the interaction and interference of vibrational (v) and electronic (e) states (NO_3^- has no other internal vibrations with the symmetry of ω_2). The contribution of the remote e state to the moment p_m induced at the m th molecule by the field $E_m = \gamma(p_{m-1} + p_{m+1})$ produced by the vibrations of the neighbors is $\alpha_0 E_m$, where α_0 is the background polarizability of the molecule. The magnitude and sign of the v contribution to p_m depend on the difference between the excitation frequency and the resonant frequency of the molecule, $\omega_m = \omega_0 + \delta_m \Delta$, where $\delta_m = 0$ for the host molecule and 1 for the impurity molecule:

$$p_m = \left(\alpha_0 + \frac{\mu^2}{\omega_m - \omega} \right) E_m = \gamma \left(\alpha_0 + \frac{\mu^2}{\omega_m - \omega} \right) (p_{m-1} + p_{m+1}). \quad (1)$$

Here $\mu = \partial p_m / \partial q_m$, and q_m is the normal coordinate of the vibration. From (1) we find the following expressions for the dispersion of the vibrations $\omega_{\mathbf{k}}$ of an ordered chain and for the probability $|t(\omega)|^2$ for the transfer of an excitation through the impurity:

$$\omega_0 - \omega_{\mathbf{k}} = \frac{\Gamma \cos ka}{1 - \beta \cos ka}, \quad (2)$$

$$|t(\omega)|^2 = \left| \frac{-iA'(\omega) \sin ka}{1 - A'(\omega) e^{ika}} \right|^2, \quad (3)$$

where

$$\Gamma = 2\gamma\mu^2, \beta = 2\gamma\alpha_0, A'(\omega) = \beta + \frac{\Gamma}{\omega_0 + \Delta - \omega_{\mathbf{k}}},$$

and a is the constant of the chain. The width of the exciton band is $T_v = 2\Gamma / (1 - \beta^2)$. Expressions for $g(\omega, x = 0)$ and for the frequencies of the m , d_1 , and d_2 states can be found from (2). Figure 1 shows results calculated with $\beta = 0$ and $\beta = 0.13$. We see that the polarizability strongly affects the calculated spectrum and leads to a complete agreement with experiment.

Our calculation has shown that the direct contribution of the e states to $g(\omega, x = 0)$ is small. On the other hand, the v and e moments induced at the impurity by the vibrations of the chain are comparable in magnitude. At $\Delta < 0$ these moments are out of phase and cancel each other. As a result, even an H impurity which is not very deep ($|\Delta| \approx T_v$) can completely block the transfer of excitations along the chain if $\beta \approx -\Gamma/\Delta$. On the other hand, at $\Delta > 0$, the v and e moments are in phase and significantly increase the probability for excitation transfer through the L impurity.

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