

Reconstruction of the density of states from the one-phonon spectrum of a mixed crystal

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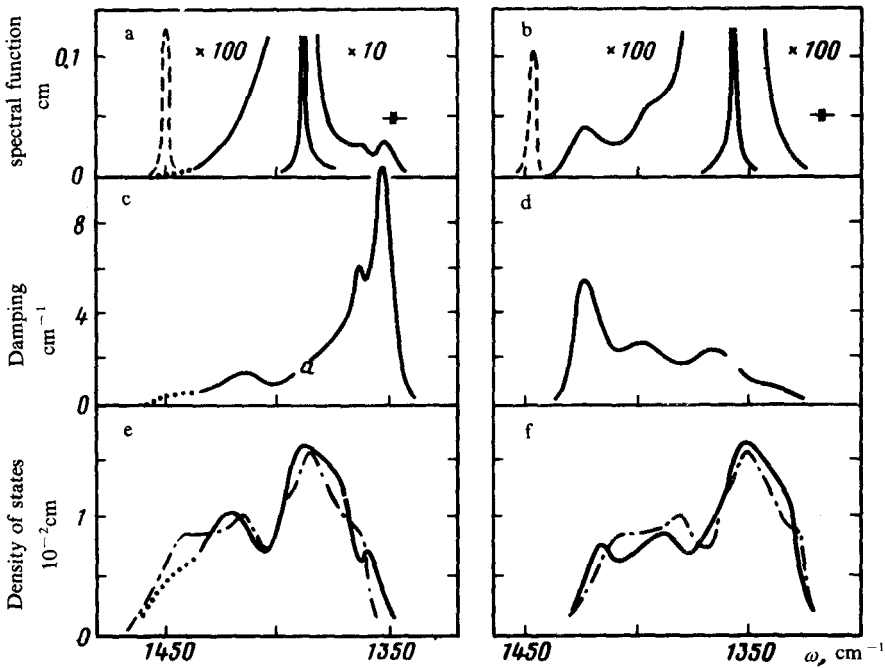
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A method is proposed for determining the density of one-phonon states, which is based on determination of the shape of the vibrational spectrum of an isotopically mixed crystal. Its correctness is experimentally verified by analyzing the spectra for Raman scattering of light (RSL) in the $\text{Na}^{15}\text{N}_x^{14}\text{N}_{1-x}\text{O}_3$ crystals.

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The spectra of crystals containing impurities and also two-phonon spectra of perfect crystals are an important source of information on the density of one-phonon states. Their role is especially large in high-frequency, intramolecular phonons which are difficult to investigate by using the neutron-scattering method. In this case the following approach is usually used to obtain quantitative information on dispersion and density of states. The first stage involves a calculation of the model of a perfect harmonic crystal. Then the perturbation caused by the impurity (or by anharmonism, if a two-phonon spectrum is calculated) is taken into account. A comparison of the calculated spectrum with the experimental was used as the criterion for the accuracy of the models used at both stages of calculation. A more effective approach was proposed by Rabin'kina *et al.*¹ who, by using the vibronic spectra, showed that the density of excitonic states can be reconstructed directly from the experiment. This approach was used successfully in Refs. 2–4 to reconstruct the density of states from two-phonon spectra. It is much more difficult to obtain quantitative information on the density of states from the spectrum of a mixed crystal. In this paper we show for the



first time that the density of states can be reconstructed in many cases by analyzing the profile of the one-phonon band in mixed crystals.

The one-phonon Green's function of an isotopically mixed crystal $A_{1-x}B_xC$ in a one-place approximation can be written in the following form⁵:

$$G_n(\mathbf{k}, \omega, x) = [\bar{\omega} - \omega_{n\mathbf{k}} - x \Delta_n + i\delta - \Sigma(\omega, x)]^{-1}, \quad (1)$$

where $\omega_{n\mathbf{k}}$ is the phonon frequency with the wave vector \mathbf{k} in a AC crystal, Δ_n is the frequency shift due to substitution of the B isotopes for the A isotopes, δ is the anharmonic damping, and $\Sigma(\omega, x)$ is the mass operator whose imaginary part describes the phonon damping due to scattering by impurities. In terms of a one-place approximation of the average T matrix (ATM) $\Sigma(\omega, x)$ and the complete Green's function $G_n(\omega)$ of a pure AC crystal are related by a simple relation⁵:

$$\Sigma(\omega, x) = x(1-x)\Delta_n^2 [G_n^{-1}(\omega - x\Delta_n) + (1-2x)\Delta_n]^{-1} \quad (2)$$

Thus, the spectral function of a mixed crystal $g_n(\mathbf{k}, \omega, x) = -\pi^{-1} \text{Im}G_n(\mathbf{k}, \omega, x)$ can be calculated if the density of states of a pure crystal is known $g_n(\omega) = -\pi^{-1} \text{Im}G_n(\omega)$.

By comparing it with the results of a numerical calculation using Dean's method⁵ and also with the experiment,^{4,6} we can show that the ATM approximation correctly describes the shape of the spectrum of a mixed crystal when the long-range interaction is dominant, that the concentration behavior of the spectrum has a single-mode (or almost a single-mode) nature, and that the impurity content is small (up to 10%). In this case the density of states can be reconstructed in the following manner. The

Green's function $G_n(\mathbf{k} = 0, \omega, x)$ can easily be calculated from experimental data, since its imaginary part coincides with the measured RSL spectrum (or with the spectrum of IR conductivity) with an accuracy to the normalization factor, and the real part is related to the imaginary part by the Kramers-Kronig relation. If $G_n(\mathbf{k} = 0, \omega, x)$ is known, then $\Sigma(\omega, x) = \omega - \omega_{nk=0} - x\Delta_n + i\delta - G_n^{-1}(\mathbf{k} = 0, \omega, x)$ and the damping spectrum [i.e., $\text{Im}\Sigma(\omega, x)$] can easily be calculated. The relation (2) in turn can be rewritten in such a way that the sought-for density of states can be expressed in terms of $\Sigma(\omega, x)$:

$$g_n(\omega - x\Delta_n) = -\pi^{-1} \text{Im} [x(1-x)\Delta_n^2 \Sigma^{-1}(\omega, x) - (1-2x)\Delta_n]^{-1} \quad (3)$$

To obtain reliable results, the damping due to scattering by impurities must greatly exceed the anharmonic damping, and the impurity-induced spectrum must be recorded over the entire region of single-phonon states.

For experimental verification, we selected a sodium nitrate crystal (D_{3d}^6 space symmetry, two formula units in the unit cell) that was isotopically substituted by nitrogen $\text{Na}^{15}\text{N}_x^{14}\text{N}_{1-x}\text{O}_3$ with $x = 0.1$ and 0.9 . This selection was contingent on the availability of reliable data for the density of vibrational states ω_3 ,^{2,3} which produce a zone of width 110 cm^{-1} in this crystal. As a result of substitution of ^{15}N for ^{14}N , the isotopic shift is $\Delta_3 = -32 \text{ cm}^{-1}$.

The RSL spectra excited by an argon laser ($\lambda_0 = 514.5 \text{ nm}$, power up to 1.5 W) were recorded by using a Spex-Ramalog 6 double monochromator with holographic gratings at spectral gap widths in the range 0.25 to 2.5 cm^{-1} .

At $T = 80 \text{ K}$ the half-width of the line ω_3 is 0.5 cm^{-1} in the RSL spectrum of a natural NaNO_3 crystal. The line is broadened to 2.8 cm^{-1} at $x = 0.1$ and to 3.8 cm^{-1} at $x = 0.9$ in the RSL spectrum of a mixed crystal [Figs. 1(a) and 1(b)]. The spectrum produced in its wings has a structure which is genetically related to the local vibration (for $x = 0.1$) or quasi-local (for $x = 0.9$) vibration, and also to the peculiarities of the density of states. These peculiarities are more clearly visible in the damping spectrum [Figs. 1(c) and 1(d)], which was calculated according to the procedure described above. Figures 1(e) and 1(f) show the curves for the density of states, which were calculated from the damping spectrum according to Eq. (3). For comparison, they also show the density of states taken from Refs. 2 and 3. Notice a small quantitative difference between the curves in the 1360 cm^{-1} region (for $x = 0.1$) and those in the 1420 cm^{-1} region (for $x = 0.9$), i.e., in those frequency intervals in which the cluster effects are expected to occur. However, a generally good agreement between the density of states reconstructed from the spectrum of a mixed crystal and the more accurate data^{2,3} obtained from two-phonon spectra indicates that the proposed method is correct and that it can be used effectively.

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