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Raman-Active Resonance Modes, Overtones, and Anharmonicity in NaCl:Cu⁺

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The existence of an impurity-activated E_g resonance mode in NaCl:Cu⁺ has been suggested by several previous experiments. Raman data presented here reveal this resonance directly and also reveal the three components of the first overtone of the 23.5-cm⁻¹ infrared resonance mode. The frequencies of the E_g resonance and the E_g component of the overtone are shifted as a result of a strong anharmonic coupling. Their line shapes and strengths are considerably altered by an interference between the Raman amplitudes. A reasonable fit to the data has been obtained using a simple theory.

Substitutional impurities often introduce resonance modes into the lattice vibration spectrum of a crystal.¹ Most experimental studies have been on infrared-active resonance modes. Raman-active modes have been predicted, but only in KI:Ag⁺ have they been found at very low frequency.²

The present work involves NaCl:Cu⁺, which has been known for some time to have an infrared-active (T_{1u}) resonance mode at 23.5 cm⁻¹.³ Its far-infrared properties have been studied under applied electric fields⁴ and uniaxial stress,⁵ and the isotope splitting has been resolved.⁶ It has a pronounced temperature dependence.^{3,7,8} The measured shift in peak position, increase in line-width, and decrease in absorption strength with temperature could be explained by assuming the existence of an E_g resonance mode at about 31 cm⁻¹, and coupling it anharmonically to the 23.5-cm⁻¹ mode.⁸ Additional indirect evidence for even-parity resonances in NaCl:Cu⁺ comes from thermal-conductivity measurements. The observed conductivity depression cannot be explained by the presence of the 23.5-cm⁻¹ resonance alone.⁹ It has been suggested that the data could be explained if an E_g resonance were present at a somewhat higher frequency.¹⁰

We now present direct evidence for such an E_g resonance mode. It is not seen in its "bare" harmonic form; it is strongly affected by an anharmonic interaction with a nearby E_g component of the first overtone of the T_{1u} mode. Raman data for all three first overtone modes will be presented to support this picture.

Figure 1 shows part of the Raman spectrum of NaCl:Cu⁺ taken with the 4880-Å argon-laser line and a scattering geometry that yields all three Raman-active symmetries for the O_h point group of the substitutional Cu⁺ impurity. There are peaks at 40 and 48 cm⁻¹ that are sensitive to temperature in a way reminiscent of the infrared mode.^{3,8} The 40-cm⁻¹ peak was originally interpreted as an ordinary E_g resonance mode.¹¹ We have made calculations using lattice Green's functions derived from realistic NaCl shell models that give an E_g resonance at about the correct frequency and width using force-constant

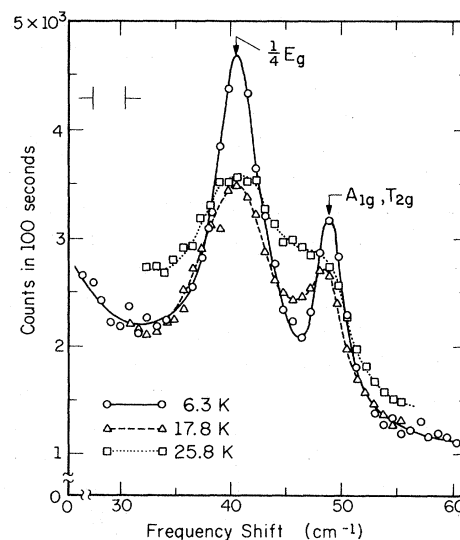


FIG. 1. Combined Raman spectrum of NaCl:Cu⁺ at moderate resolution showing strong temperature dependence. Copper concentration: $3 \times 10^{18}/\text{cm}^3$.

changes consistent with the existence of the infrared mode at 23.5 cm^{-1} . The A_{1g} and T_{2g} peaks at 48 cm^{-1} cannot be so explained. If they were resonance modes, their widths should be even greater than that of the 40-cm^{-1} mode. Furthermore, the existence of a 48-cm^{-1} A_{1g} resonance mode would require force constant changes sufficient to make the lattice unstable against E_g and T_{1u} displacements.

We interpret the 48-cm^{-1} T_{2g} and A_{1g} peaks as two of the three components of the first overtone of the 23.5-cm^{-1} T_{1u} mode. The third, E_g , component will be discussed below. Raman scattering from first overtones of an infrared-active *localized* mode have been seen in alkaline-earth fluorides and alkali halides containing H^- impurities.^{12,13} Because of anharmonicity the three lines, T_{2g} , A_{1g} , and E_g , occur at slightly different frequencies from each other and from twice the fundamental. In the present case our identification is based on the near factor of 2 in frequency and on similarities between the temperature dependence of the peak position and linewidth of the 48-cm^{-1} line and the infrared line. This is shown for the T_{2g} component in Fig. 2. Within the experimental uncertainties, the widths and shift are consistent with the data shown in Fig. 3 of Ref. 7 for the T_{1u} mode if the assumption is made that the width of the overtone and its shift are twice those for the infrared mode.

Where then is the missing E_g component of the overtone? Figure 3 gives a detailed E_g Raman spectrum and shows that there are two peaks; the one at 40 cm^{-1} seen in Fig. 1 and a weak

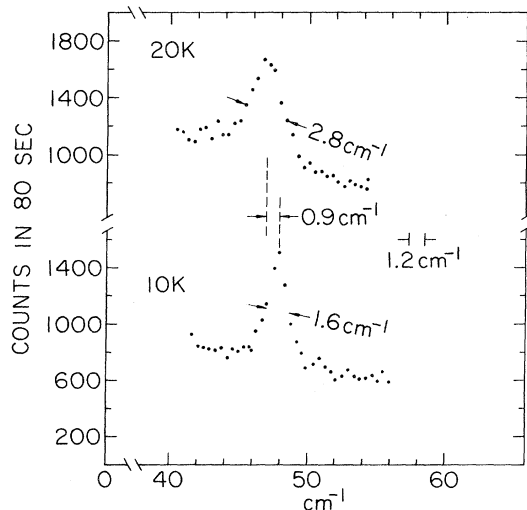


FIG. 2. High-resolution scan on a more heavily doped sample ($7.5 \times 10^{18}/\text{cm}^3$) of the T_{2g} component of the 48-cm^{-1} peak from Fig. 1.

asymmetric second peak at 63 cm^{-1} . We believe that these peaks result from anharmonic coupling and mixing of an E_g resonance mode and the E_g component of the first overtone of the T_{1u} mode.

To make a preliminary analysis of this coupling, we let $|1\rangle$ and $|2\rangle$ denote excited states corresponding to the E_g resonance and E_g overtone, respectively, ω_1 and ω_2 the corresponding unperturbed frequencies, and V the matrix element of the anharmonic perturbation coupling them. Then in a system of units where $\hbar = 1$, the Hamiltonian H has matrix elements $\langle 1|H|1\rangle = \omega_1$, $\langle 2|H|2\rangle = \omega_2$, and $\langle 1|H|2\rangle = \langle 2|H|1\rangle^* = V$. Its eigenvalues λ_1 and λ_2 obey the equations

$$\lambda_1 + \lambda_2 = \omega_1 + \omega_2, \quad (1)$$

$$\lambda_1 \lambda_2 = \omega_1 \omega_2 - |V|^2. \quad (2)$$

Inserting $\omega_2 = 48 \text{ cm}^{-1}$, $\lambda_1 = 40 \text{ cm}^{-1}$, $\lambda_2 = 63 \text{ cm}^{-1}$, we find from Eqs. (1) and (2)

$$\omega_1 = 55 \text{ cm}^{-1}, \quad (3)$$

$$|V| = 11 \text{ cm}^{-1}. \quad (4)$$

Note that the 63-cm^{-1} peak in Fig. 3 is asymmetric and that there is a distinct minimum at 54.6 cm^{-1} (arrow) that could well correspond to a zero in intensity. These features are strongly suggestive of an interference process. A discussion of this interference requires a calculation of the line shape for the coupled levels.¹⁴ Let the amplitude for a Raman transition to unperturbed state $|1\rangle$ be P_1 and to unperturbed state $|2\rangle$ be

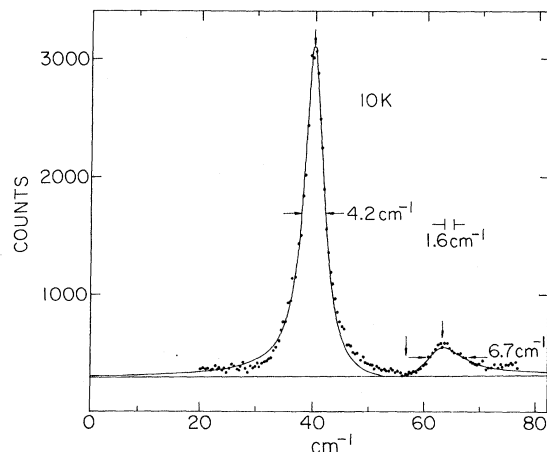


FIG. 3. High-resolution scan of the E_g Raman spectrum. The ordinate is the number of counts in 20 sec below 48 cm^{-1} and one half the number of counts in 40 sec above 48 cm^{-1} . The solid line is a theoretical curve described in the text. Copper concentration: $7.5 \times 10^{18}/\text{cm}^3$.

P_2 . The P 's will be proportional to appropriate polarizability derivatives. The low-temperature Stokes-Raman intensity due to the coupled modes at frequencies λ_1, λ_2 may be obtained by rewriting the energy δ function in Fermi's "golden rule" to yield

$$W(\omega) = \text{Im} \sum_{i,j=1,2} P_i^*(i|G|j)P_j, \quad (5)$$

where the operator $G \equiv (H - \omega - i\epsilon)^{-1}$, $\epsilon \rightarrow 0^+$, can be shown to have matrix elements

$$\begin{aligned} \langle 1|G|1\rangle &= \langle 1|G_0|1\rangle D^{-1}, \\ \langle 2|G|2\rangle &= \langle 2|G_0|2\rangle D^{-1}, \\ \langle 2|G|1\rangle^* &= \langle 1|G|2\rangle = -\langle 1|G_0|1\rangle\langle 2|G_0|2\rangle VD^{-1}, \end{aligned} \quad (6)$$

with

$$D = 1 - \langle 1|G_0|1\rangle\langle 2|G_0|2\rangle|V|^2. \quad (7)$$

We assume that the unperturbed E_g resonance level has a finite halfwidth at half-maximum denoted by γ and that the unperturbed second harmonic is very narrow. This gives

$$\begin{aligned} \langle 1|G_0|1\rangle &= (\omega_1 - \omega - i\gamma)^{-1}, \\ \langle 2|G_0|2\rangle &= (\omega_2 - \omega - i\epsilon)^{-1}, \end{aligned} \quad (8)$$

and

$$W(\omega) = \frac{|P_1|^2 \gamma (\omega - \omega_0)^2}{(\lambda_1 - \omega)^2 (\lambda_2 - \omega)^2 + \gamma^2 (\omega_2 - \omega)^2}, \quad (9)$$

where $\lambda_{1,2}$ obey Eqs. (1), (2) and where

$$\omega_0 \equiv \omega_2 - P_2 V / P_1. \quad (10)$$

We have assumed that $P_2 V / P_1$ is a real number.

The solid line in Fig. 3 is calculated from Eq. (9) with $\lambda_1 = 40 \text{ cm}^{-1}$, $\lambda_2 = 62.5 \text{ cm}^{-1}$, $\gamma = 5.9 \text{ cm}^{-1}$, and $\omega_0 = 54.8 \text{ cm}^{-1}$. The fit is not perfect, but it represents a good compromise involving the relative peak heights, shapes, and the position of the minimum. Equations (1) and (2) then give

$$\omega_1 = 54.5 \text{ cm}^{-1}, \quad (11)$$

$$V = 10.8 \text{ cm}^{-1} \quad (12)$$

(V assumed real and positive),¹⁵ and Eq. (10) then gives

$$P_2/P_1 = -0.63 \quad (13)$$

The wave functions for the perturbed modes are readily calculated and yield the result that the 40-cm^{-1} mode is a mixture of 65% E_g overtone and 35% E_g resonance, whereas for the 62.5-cm^{-1} mode these figures are reversed. The strength ratio 65:35 is strongly modified in the Raman spectrum by the $(\omega - \omega_0)^2$ factor in Eq. (9). This factor describes the result of the interference be-

tween the P_1 amplitude and the P_2 amplitude due to the anharmonic coupling provided by V .

If there were no anharmonic coupling, there would be an E_g resonance mode at 54.5 cm^{-1} with a full width at half-maximum of 10.8 cm^{-1} and a peak height 29% of the height of the 40-cm^{-1} peak in Fig. 3. The E_g component of the overtone at 48 cm^{-1} would have a width comparable to that of the T_{2g} overtone shown in Fig. 2 and an integrated area equal to $(P_2/P_1) = 40\%$ of that of the unperturbed E_g peak. The total area under the two unperturbed peaks would equal the area of the perturbed spectrum in Fig. 3.

Additional evidence for strong anharmonic coupling in NaCl:Cu^+ is provided by the existence of combination bands in the far infrared at 64 and 69 cm^{-1} .¹¹ A paper containing detailed discussions of the infrared work and of additional Raman results will be forthcoming.

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