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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 fields[4] 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 linewidth, 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

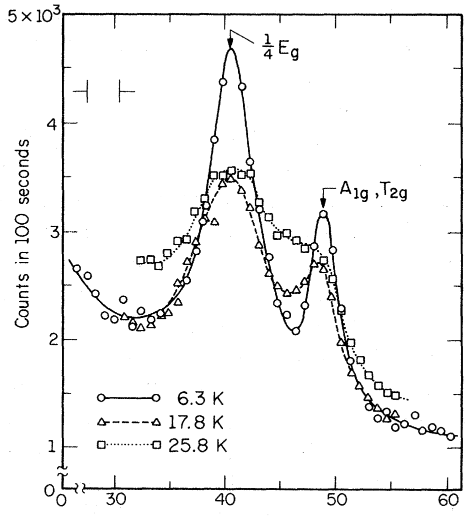

FIG. 1. Combined Raman spectrum of NaCl:Cu$^+$ at moderate resolution showing strong temperature dependence. Copper concentration: 3×10^{18}/cm^3.

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 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 $|1)$ and $|2)$ 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 $(1|H|1) = \omega_1$, $(2|H|2) = \omega_2$, and $(1|H|2) = (2|H|1)^* = V$. Its eigenvalues λ_1 and λ_2 obey the equations

$$\lambda_1 + \lambda_2 = \omega_1 + \omega_2, \tag{1}$$

$$\lambda_1\lambda_2 = \omega_1\omega_2 - |V|^2. \tag{2}$$

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

$$\omega_1 = 55 \text{ cm}^{-1}, \tag{3}$$

$$|V| = 11 \text{ cm}^{-1}. \tag{4}$$

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 $|1)$ be P_1 and to unperturbed state $|2)$ be

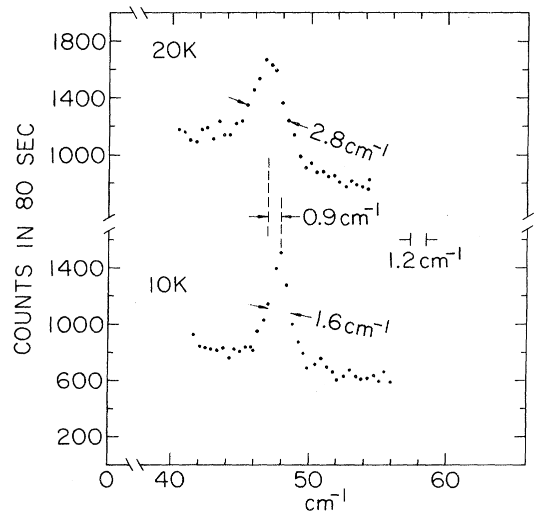

FIG. 2. High-resolution scan on a more heavily doped sample (7.5×10^{18}/cm^3) of the T_{2g} component of the 48-cm^{-1} peak from Fig. 1.

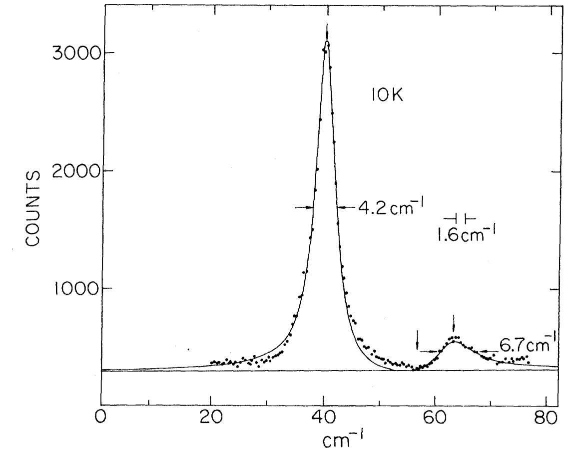

FIG. 3. High-resolution scan of the E_g Raman spectrum. The ordinate is the number of counts in 20 sec below 48 cm^{-1} and one half the number of counts in 40 sec above 48 cm^{-1}. The solid line is a theoretical curve described in the text. Copper concentration: 7.5×10^{18}/cm^3.

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

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

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

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

with

$$D=1-(1|G_0|1)(2|G_0|2)|V|^2. \tag{7}$$

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

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

and

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

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

$$\omega_0\equiv\omega_2-P_2V/P_1. \tag{10}$$

We have assumed that P_2V/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

$$\omega_1=54.5\ \text{cm}^{-1}, \tag{11}$$

$$V=10.8\ \text{cm}^{-1} \tag{12}$$

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

$$P_2/P_1=-0.63 \tag{13}$$

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 between 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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