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## Raman-Active Resonance Modes, Overtones, and Anharmonicity in NaCl:Cu<sup>+</sup>

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The existence of an impurity-activated  $E_g$  resonance mode in NaCl:Cu<sup>+</sup> 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<sup>-1</sup> 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.<sup>1</sup> Most experimental studies have been on infrared-active resonance modes. Raman-active modes have been predicted, but only in KI:Ag<sup>+</sup> have they been found at very low frequency.<sup>2</sup>

The present work involves NaCl:Cu<sup>+</sup>, which has been known for some time to have an infrared-active ( $T_{1u}$ ) resonance mode at 23.5 cm<sup>-1</sup>.<sup>3</sup> Its far-infrared properties have been studied under applied electric fields<sup>4</sup> and uniaxial stress,<sup>5</sup> and the isotope splitting has been resolved.<sup>6</sup> It has a pronounced temperature dependence.<sup>3,7,8</sup> 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<sup>-1</sup>, and coupling it anharmonically to the 23.5-cm<sup>-1</sup> mode.<sup>8</sup> Additional indirect evidence for even-parity resonances in NaCl:Cu<sup>+</sup> comes from thermal-conductivity measurements. The observed conductivity depression cannot be explained by the presence of the 23.5-cm<sup>-1</sup> resonance alone.<sup>9</sup> It has been suggested that the data could be explained if an  $E_g$  resonance were present at a somewhat higher frequency.<sup>10</sup>

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<sup>+</sup> 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<sup>+</sup> impurity. There are peaks at 40 and 48 cm<sup>-1</sup> that are sensitive to temperature in a way reminiscent of the infrared mode.<sup>3,8</sup> The 40-cm<sup>-1</sup> peak was originally interpreted as an ordinary  $E_g$  resonance mode.<sup>11</sup> 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

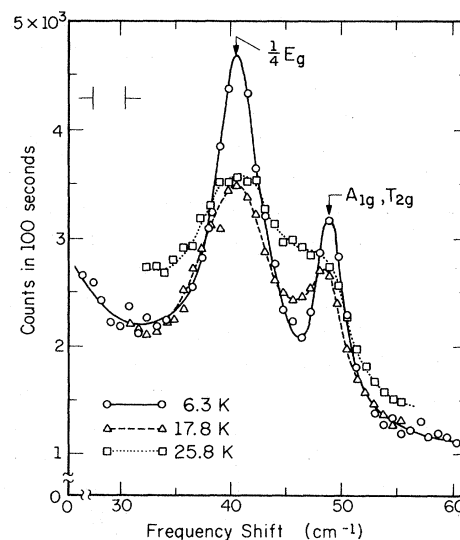


FIG. 1. Combined Raman spectrum of NaCl:Cu<sup>+</sup> at moderate resolution showing strong temperature dependence. Copper concentration:  $3 \times 10^{18}/\text{cm}^3$ .

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

We interpret the  $48\text{-cm}^{-1}$   $T_{2g}$  and  $A_{1g}$  peaks as two of the three components of the first overtone of the  $23.5\text{-cm}^{-1}$   $T_{1u}$  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  $\text{H}^-$  impurities.<sup>12,13</sup> 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  $48\text{-cm}^{-1}$  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  $40 \text{ cm}^{-1}$  seen in Fig. 1 and a weak

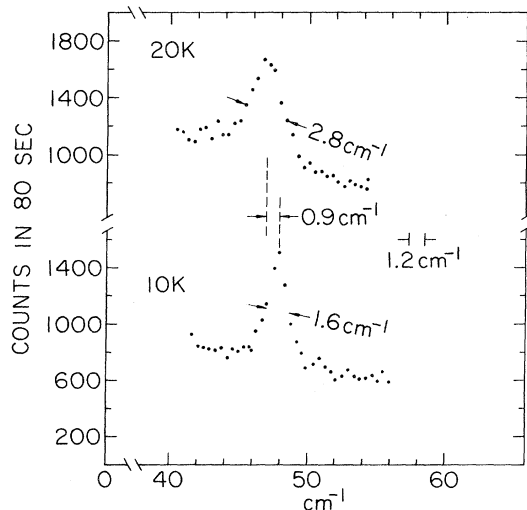


FIG. 2. High-resolution scan on a more heavily doped sample ( $7.5 \times 10^{18}/\text{cm}^3$ ) of the  $T_{2g}$  component of the  $48\text{-cm}^{-1}$  peak from Fig. 1.

asymmetric second peak at  $63 \text{ cm}^{-1}$ . 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,  $\omega_1$  and  $\omega_2$  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  $\lambda_1$  and  $\lambda_2$  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  $63\text{-cm}^{-1}$  peak in Fig. 3 is asymmetric and that there is a distinct minimum at  $54.6 \text{ cm}^{-1}$  (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.<sup>14</sup> Let the amplitude for a Raman transition to unperturbed state  $|1\rangle$  be  $P_1$  and to unperturbed state  $|2\rangle$  be

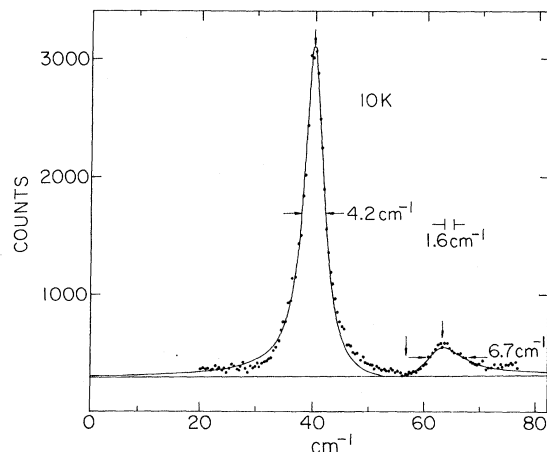


FIG. 3. High-resolution scan of the  $E_g$  Raman spectrum. The ordinate is the number of counts in 20 sec below  $48 \text{ cm}^{-1}$  and one half the number of counts in 40 sec above  $48 \text{ cm}^{-1}$ . The solid line is a theoretical curve described in the text. Copper concentration:  $7.5 \times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

$P_2$ . The  $P$ 's will be proportional to appropriate polarizability derivatives. The low-temperature Stokes-Raman intensity due to the coupled modes at frequencies  $\lambda_1, \lambda_2$  may be obtained by rewriting the energy  $\delta$  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

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

with

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

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

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

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),<sup>15</sup> 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  $40\text{-cm}^{-1}$  mode is a mixture of 65%  $E_g$  overtone and 35%  $E_g$  resonance, whereas for the  $62.5\text{-cm}^{-1}$  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  $54.5 \text{ cm}^{-1}$  with a full width at half-maximum of  $10.8 \text{ cm}^{-1}$  and a peak height 29% of the height of the  $40\text{-cm}^{-1}$  peak in Fig. 3. The  $E_g$  component of the overtone at  $48 \text{ cm}^{-1}$  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  $\text{NaCl:Cu}^+$  is provided by the existence of combination bands in the far infrared at 64 and  $69 \text{ cm}^{-1}$ .<sup>11</sup> A paper containing detailed discussions of the infrared work and of additional Raman results will be forthcoming.

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