tions with the general features of (2).[10] In addition, a generalized treatment of phonon collisions, going beyond the Born approximation in the Boltzmann equation, may also be necessary (cf. Ref. 4).

The improvement of the Ne result presented here over those of the harmonic and quasiharmonic approximations indicates the value of extending the self-consistent approach to encompass phonon lifetime effects. Further study of such effects, and their full incorporation into the renormalization formalism, seem desirable. New, constant-volume measurements of the Ne conductivity should now be able to provide a more stringent test of any anharmonic theory, by producing a higher maximum at lower temperature than that shown in Fig. 1.

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AUGER-LIKE RESONANT INTERFERENCE IN RAMAN SCATTERING FROM ONE- AND TWO-PHONON STATES OF $BaTiO_3$

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Resonant interference between one- and two-phonon states has been observed in $BaTiO_3$, and has been shown to obey the quantum mechanical formalism developed by Fano for Auger processes. By selecting different components of the differential polarizability tensor and by changing the propagation direction, the degree of interference could be varied over a wide range. The linewidth and line-profile parameters were determined for several different crystal orientations.

When a discrete energy state is superimposed on a broad continuum, the well-known phenomenon of resonant interference (Auger processes) may occur. In general, Auger interactions are characterized by (1) decomposition of the excited species through electron ejection or molecular fragmentation; (2) broadening and distortion of the absorption, emission, and scattering line shapes; and (3) weakening of emission lines to lower states from the discrete state. The wide range of electronic-state Auger resonances observed by electron scattering and ultraviolet absorption has been discussed by Burke[1] and Herzberg,[2] and the quantum mechanical formalism describing Auger transitions has been thoroughly developed by Fano and Cooper.[3,4] In this Letter we wish to report the Raman-scattering observation of a resonant interference between one- and two-phonon states of $BaTiO_3$ and to show that this interference may be completely described by the Fano formalism for Auger processes. The particular importance offered by Raman-spectroscopic observation of such processes is the ability to select a diversity of phonon propagation directions and differential polarizability tensors, and thereby drastically vary the degree of interference.

Recently there have been several Raman-scattering investigations of ferroelectric solids.[5-7] Since these materials have very large dielectric constants they exhibit very strong multiple-phonon scattering. For example, the Raman spectrum of ferroelectric $BaTiO_3$ (C_{4v}^1) consists of very intense and broad multiple-phonon processes,[6] obeying the wave-vector relation $\sum_i \vec{k}_i \cong \vec{q}_0 \cong 0$, in addition to the relatively sharp $\vec{k} \cong \vec{q}_0 \cong 0$ one-phonon processes. ($\vec{k}$ and $\vec{q}_0$, respectively, refer to the phonon and photon wave vectors.) The broadness of the multiple-phonon scattering is accounted for by relaxed wave-vector conservation rules which allow scattering from overtones and combinations of both optical and acoustical modes throughout the Brillouin zone. In $BaTiO_3$ at room temperature the two-acoustical-phonon processes (2LA, 2TA, LA + TA) are a dominant feature of the spectrum,[6] appearing as a broad band extending from close to the exciting line to ~300 cm^{-1} with a not well defined peak at ~250 cm^{-1}. The structure of this band is dependent on both the polarization and the propagation direction. In this crystal there is also an infrared and Raman allowed one-phonon process[8] at ~175 cm^{-1} so there is an overlap in energy between the discrete one-phonon process and the very broad two-phonon scattering.[6] As each process has a different differential polarizability tensor, scattering geometries can be selected so as to vary independently the transition probability of each. Because of this superposition, as the scattering geometry is changed, a strange series of line shapes, that sometimes resemble absorptions in the two-phonon continuum, appear.[6]

Since the one-phonon state can interact with the two-phonon state through anharmonic terms in the potential function, we may discuss the interaction in terms of a phonon energy level diagram such as that in Fig. 1. In this diagram Ψ_0 is the wave function of the ground state; φ and E_φ are the unperturbed wave function and eigenvalue of the one-phonon discrete state; ψ_E is the wave function for a member of the two-phonon continuum of states, associated with an eigenvalue E; and W is the transition rate between the one- and two-phonon states and is proportional to the anharmonicity of the potential function. It can be measured by the linewidth of the one-phonon process.

This quantum mechanical picture of the interaction between these one- and two-phonon states is exactly analogous to the Auger-type electronic transitions treated by Fano.[3,4] By applying his formalism to this phonon problem, we can describe the Raman transition matrix element from the initial state Ψ_0 to the final state Ψ_f as

$$\langle \Psi_f | \alpha_{ij} | \Psi_0 \rangle = \frac{W\langle \Phi | \alpha_{ij}^{(1)} | \Psi_0 \rangle + (E - E_\varphi - F)\langle \psi_E | \alpha_{ij}^{(2)} | \Psi_0 \rangle}{[(E - E_\varphi - F)^2 + \pi^2 |W|^4]^{1/2}}. \tag{1}$$

In this expression $\alpha_{ij}^{(1)}$ and $\alpha_{ij}^{(2)}$ are the differential polarizability tensor operators associated with the one- and two-phonon processes, and Φ is the wave function of the single-phonon state, φ, which has been slightly modified by an admixture of states of the continuum. This perturbation of the wave function φ results in a shift in the resonant position E_φ by the amount F.

Inspection of Eq. (1) reveals that as you pass through resonance (i.e., $E = E_\varphi + F$), there is a sharp variation in $\langle \Psi_f | \alpha_{ij} | \Psi_0 \rangle$. The effect of this variation on the scattering line shape can be best demonstrated by defining new functions q and ϵ where

$$q = \frac{\langle \Phi | \alpha_{ij}^{(1)} | \Psi_0 \rangle}{\pi W \langle \psi_E | \alpha_{ij}^{(2)} | \Psi_0 \rangle} \tag{2}$$

and

$$\epsilon = (E - E_\varphi - F)/\pi |W|^2. \tag{3}$$

The ratio of the transition probability to the final stationary state Ψ_f with a scattering cross section σ to that of the continuum ψ_E with a scatter-

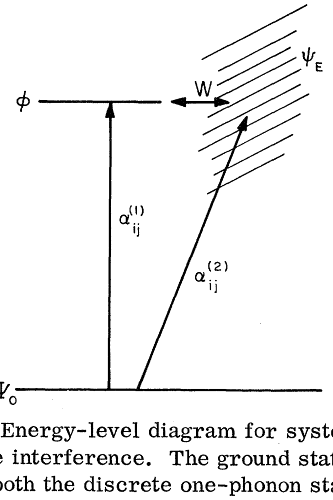

FIG. 1. Energy-level diagram for system exhibiting Auger-like interference. The ground state Ψ_0 is connected to both the discrete one-phonon state φ and the two-phonon continuum ψ_E by the polarizability tensor operators $\alpha_{ij}^{(1)}$ and $\alpha_{ij}^{(2)}$, respectively. W is the transition rate between the one- and two-phonon states.

ing cross section σ_2 then becomes

$$\frac{\sigma}{\sigma_2}=\frac{|\langle\Psi_f|\alpha_{ij}|\Psi_0\rangle|^2}{|\langle\psi_E|\alpha_{ij}^{(2)}|\Psi_0\rangle^2}=\frac{(q+\epsilon)^2}{1+\epsilon^2}. \tag{4}$$

Figure 2 shows a plot of Fano's curves for this function for various values of q. As shown by these curves the discrete state interacting with the continuum will distort the line shape and cause the transition probability to pass through zero.

In the case of $BaTiO_3$, however, there are several superimposed continua, i.e., 2LA, 2TA, LA + TA. Fano[3,4] has treated this case also, and has shown that the interaction occurs between the discrete state and one linear combination of the continua but not with the remaining orthogonalized continua. Therefore the resonance phenomenon will be superimposed on a continuum, and the intensity will not go to zero as predicted by Eq. (4). We may then rewrite the scattering cross section as

$$\sigma=\sigma_2\frac{(q+\epsilon)^2}{1+\epsilon^2}+\sigma_{2'}, \tag{5}$$

where $\sigma_{2'}$ is the scattering cross section for the underlying continuum which does not interact with the discrete state.

In conventional Auger processes as well as in a recently discussed resonance effect in excitons in nitrogen-doped GaP,[9] one sees only a fixed value of q, but in Raman spectroscopy of phonons the magnitude of q can be varied and the degree of resonant interference can therefore be changed In $BaTiO_3$ the one-phonon process at 175 cm^{-1} has both A_1 and E symmetries with differential polarizability-tensor components xz, yz, xx, yy, and zz different from zero. The two-acoustical-phonon processes, although observed in all orientations, are strongest in scattering with tensor components zz, xx, and yy.[6] Both the one- and two-phonon processes are also strongly dependent on the phonon propagation directions,[6] so there should exist a large range of values through which Fano's q can be varied. The complexity of the two-phonon spectrum makes an a priori determination of the value of q very difficult.

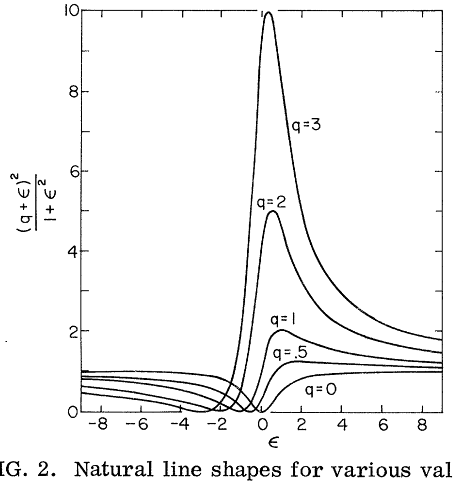

FIG. 2. Natural line shapes for various values of q (from Fano, Ref. 3). A negative value of q results in a mirror image of these curves about zero.

In Fig. 3 we show several Raman spectra of the 175-cm^{-1} region of $BaTiO_3$ on which are superimposed calculated Fano curves. These spec-

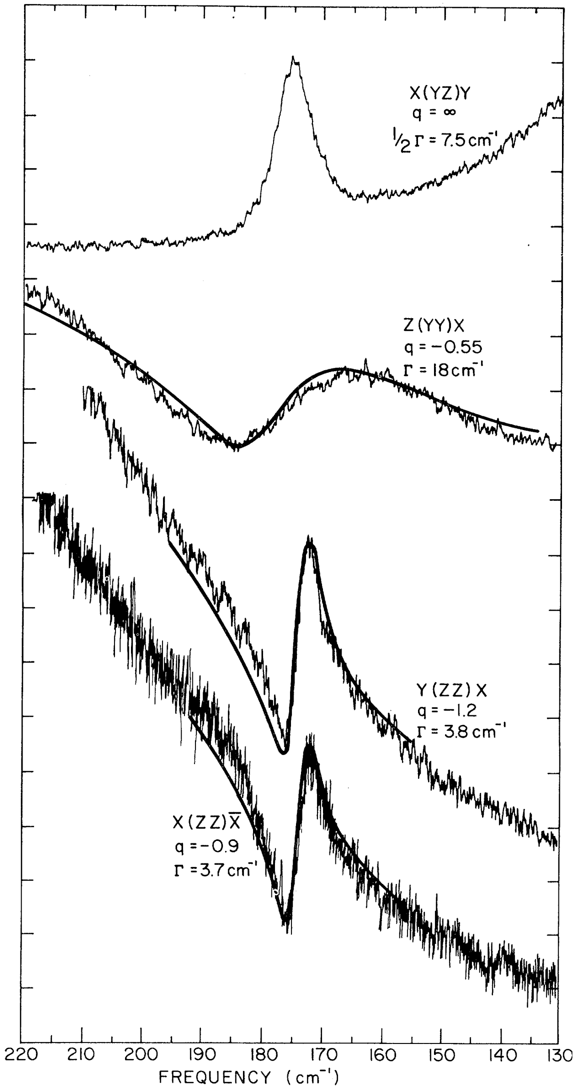

FIG. 3. Raman spectra of 175-cm^{-1} region of $BaTiO_3$. The notation used is described in the text and the line-profile parameter, q, and linewidth parameter, Γ, were obtained from the smooth curves fitted to the data.

tra were taken using the 4880-Å output from a Spectra-Physics argon laser as the exciting source and the scattered light was dispersed by a Spex double monochomator. The notation used here is that of Damen, Porto, and Tell[10] and describes the scattering geometry of the spectrum. The letters inside the parentheses are the polarization directions of the incident and scattered beams and the letters outside the parentheses are the respective propagation directions.

In each spectrum a two-phonon continuum baseline has been extrapolated through the interference region so that Fano curves could be fitted to the spectra. The deviations of the experimental results from the theoretical curves probably result from uncertainties in the precise characteristics of the two-phonon continuum and from finite spectrometer resolution (4 cm^{-1}). The large difference in the value of $\Gamma = 2\pi|W|^2$ between the $z(yy)x$ spectrum and the two zz spectra is a point of considerable interest. One might expect that by changing orientations the degree of interference, q, would vary but the linewidth Γ would remain constant. However, large differences were observed in the value of Γ for phonons propagating in different directions. The small value of Γ in the $y(zz)x$ and the $x(zz)\bar{x}$ spectra indicates that when the A_1 phonon is propagating in the xy plane it has a very long lifetime while the very large value of Γ in the $z(yy)x$ spectrum indicates that the A_1 phonon is very rapidly destroyed when propagation is in the xz direction. Furthermore, this large value of Γ in the $z(yy)x$ spectrum suggests that in one-phonon decay only specific two-phonon states make a significant contribution to the linewidth. Further analysis of such interferences should elucidate this point and yield valuable information about phonon interactions and lifetimes.

The occurrence of this type of resonant interference has no doubt gone unnoticed in several infrared and Raman experiments in both solids and liquids. Resonant interference should be a general phenomena, and whenever broad and discrete vibrational states have the same symmetry and energy this Fano-type interference should occur through anharmonic coupling in the potential energy expansion.

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