PHYSICAL REVIEW B VOLUME 14, NUMBER 6 15 SEPTEMBER 1976

Resonant interaction of acceptor states with optical phonons in silicon*

H. R. Chandrasekhar,† A. K. Ramdas, and Sergio Rodriguez
Department of Physics, Purdue University, West Lafayette, Indiana 47907
(Received 7 June 1976)

This paper presents a study of the broadening and splittings of bound-hole excitation lines in silicon when the excitation energy is comparable to that of optical phonons. The approach utilized is a generalization of a similar study for donors in which the degeneracies of the ground and excited states do not play an essential role. However, the specific excitation considered in this work is a $\Gamma_8 \rightarrow \Gamma_8$ transition which is in resonance with the Γ_5^+ zone-center optical phonon of frequency ω_0, a situation which obtains for line 2 of Si(Ga). The hole-phonon interaction gives rise to a mixing of the Γ_8 excited states of the acceptor with the states in which the acceptor is in its Γ_8 ground state and the optical phonons are excited. The mixing of these states is governed by matrix elements which are linear functions of two phenomenological constants. The experimental observation that the expected line 2 of Si(Ga) is replaced with a broad feature and a sharp spike on the high-frequency side of ω_0 can be explained using this model. Futher, the model accounts for the striking sharpening of spectral features observed under uniaxial stress as well as the differences in this behavior when this stress is applied along different crystallographic directions. In the theory, the nonlinear stress dependence of the stress-induced components, the "pinning" of some components to $\hbar\omega_0$, and the possibility of observing the otherwise infrared-inactive zone-center optical phonons find a natural explanation.

I. INTRODUCTION

The excitation spectra of group-III acceptors in silicon have similar spacings, but are displaced with respect to one another as a result of the chemical shifts experienced by their ground states.[1,2] This is customarily understood within the frame work of the effective-mass approximation[1,3-5] which accurately describes the excited states. The ground state, however, is significantly altered by the departures from the effective-mass potential in the vicinity of the impurity; this is called the central-cell correction to the potential. The excitation spectra of the different group-III acceptors in silicon are displayed in Fig. 1. Figure 2 shows the excitation spectrum of the gallium acceptors recorded under improved experimental conditions; a weak sharp line, X, at 64.9 meV and a broad feature peaked at ~62 meV are seen. It is found experimentally that typical linewidths of the excitation lines are ~0.1 meV. Line 2 of gallium acceptors is a striking exception. Figure 1 shows that a broad feature replaces line 2 at the expected position. This behavior was first noticed by Hrostowski and Kaiser[6] and attributed to an interaction of the hole excitation with the silicon-oxygen bending mode; these authors used crucible-grown silicon which contains dispersed oxygen. However, this broadening is also present in oxygen-free floating zone silicon doped with gallium. Onton *et al.*[7] ascribed the anomalous broadening to a resonant interaction of the excitation with the zone-center optical phonon of the host. Under uniaxial stress the hole excitation lines split and shift; such effects are, in comparison, two orders of magnitude smaller for the optical phonons. It is thus possible to exploit piezospectroscopic effects to tune the hole excitation in and out of resonance with the optical phonons. The present authors discussed such effects in a recent communication,[8] where new features such as "mixed" hole-phonon excitations, pinning effects, and intensity changes were demonstrated. In this paper we develop the theoretical basis for the understanding of these and in addition provide an interpretation of other features such as polarization effects. We also present additional experimental results.

II. THEORY

Piezospectroscopic studies[9,10] have established that line 2 in the excitation spectra of acceptors in silicon is an optical transition from the Γ_8 ground state to a Γ_8 excited state.[11] One can describe the electronic excitation by a Hamiltonian H_0 and the fourfold ground and excited states by the wave functions ϕ_μ and $\psi_{\mu'}$, respectively, with $\mu, \mu' = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. These states behave, under T_d, like atomic states of angular momentum $j = \frac{3}{2}$. The phonon Hamiltonian is of the form $\sum_{qi} \hbar\omega_{qi} a_{qi}^\dagger a_{qi}$, where ω_{qi} is the frequency of a phonon of wave vector $\vec{q}$ belonging to branch i. The operators $a_{qi}^\dagger$ (a_{qi}) are phonon creation (destruction) operators. We shall consider here only those phonons which are in approximate resonance with the excitation of line 2. For Ga acceptors in Si these are the zone-center optical phonons. Of course, one must also take into account the optical-phonon branches in the vicinity of $\vec{q} = 0$. Because of the absence of translational symmetry the $\vec{q}$-conservation rule

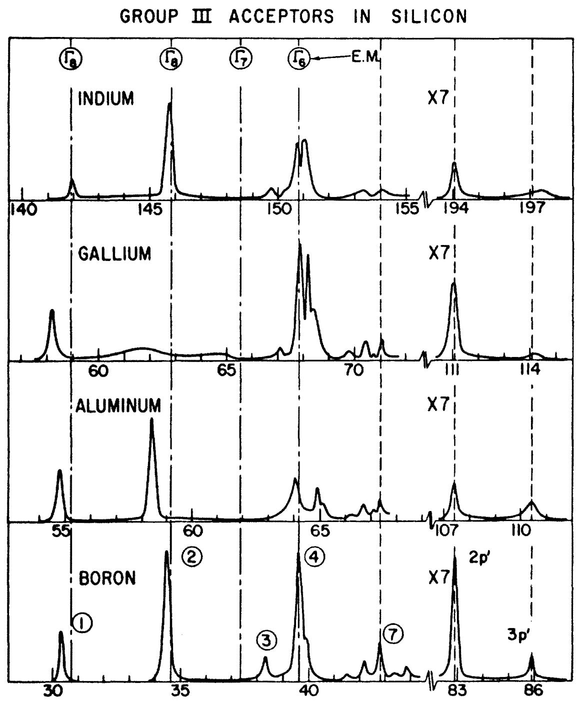

FIG. 1. Sketch of the group-III acceptor excitation spectra in silicon. The sketch shows the positions of the lines accurately. The relative intensities of the lines within a given spectrum are representative; note that the intensities of the $p_{1/2}$ lines compared to those of the $p_{3/2}$ lines have been scaled up by a factor of 7. The $2p'$ lines of the various spectra have been brought into coincidence, and the discontinuities in the horizontal scales have the same magnitude. The effective-mass excited states calculated by D. Schechter [J. Phys. Chem. Solids 23, 237 (1962)] for $B<0$ are also shown; the Γ_6 state has been aligned with line 4 of the boron spectrum. (See Ref. 9.)

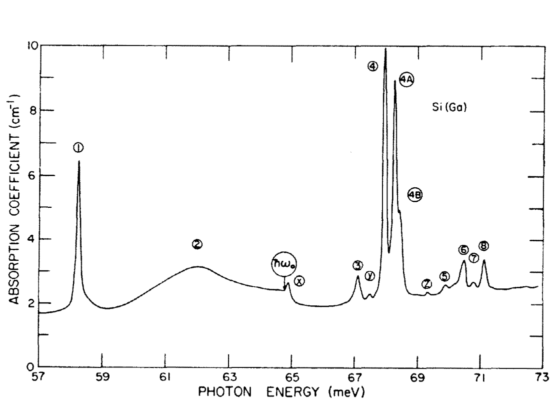

FIG. 2. Excitation spectrum of gallium in silicon, Si(Ga). Liquid helium was used as coolant. p(300 °K) $=2.6\times10^{15}$ cm^{-3}. Note the lines 2 and X on either side of the zone-center optical-phonon energy $\hbar\omega_0$.

need not be satisfied. However, since the acceptor states extend over several unit cells of the crystal, wave-vector conservation holds to within the reciprocal of a length of the order of the extension of the acceptor states.[12]

We describe the hole-phonon interaction by

$$H' = \sum_{qi} (Q_i^\dagger a_{qi}^\dagger + Q_i a_{qi}). \tag{1}$$

The operators $Q_i^\dagger$ (Q_i) act on the hole states. We restrict the summation over $\vec{q}$ and i to the optical phonons near $\vec{q}=0$ because of the approximate validity of the $\vec{q}$-conservation law, and hence make the approximation that $Q_i^\dagger$ and Q_i are independent of the wave vector. The zone-center optical phonons have symmetry Γ_5^+; hence, the operators Q_i transform, under the action of the operations of T_d, according to the irreducible representation Γ_5 of this group.[13] It follows that the matrix elements governing the coupling of the hole excitations with the optical phonons are the same as those for optical transitions in the dipole approximation.

We shall now study this interaction in some detail. Later, we will require results in which the excitation lines have been split by the application of a uniaxial stress. Thus, we assume that the Γ_8 quadruplets associated with line 2 have been split into two doublets characterized by quantum numbers[14] $\pm\frac{3}{2}$ and $\pm\frac{1}{2}$.

We now solve the eigenvalue problem by diagonalizing the Hamiltonian

$$H = H_0 + \sum_{qi} \hbar\omega_{qi} a_{qi}^\dagger a_{qi} + H' \tag{2}$$

in the subspace formed by single phonons and hole excitations. We find the eigenvalues W of the Schrödinger equation

$$H\psi = W\psi, \tag{3}$$

with states ψ of the form

$$\psi = \sum_{\mu'} c_{\mu'}\psi_{\mu'}\chi_0 + \sum_{qi\mu} b_{\mu i}(\vec{q})\phi_\mu \chi_i(\vec{q}), \tag{4}$$

where $\chi_i(\vec{q})$ is a state in which a single phonon of wave vector $\vec{q}$ and in branch i is present and χ_0 is the phonon vacuum state. Substitution of (4) into (3) and use of Eqs. (1) and (2) yield

$$c_{\mu'}E_{\mu'} + \sum_{qi\mu} \langle \mu'|Q_i|\mu\rangle b_{\mu i}(\vec{q}) = W c_{\mu'} \tag{5}$$

and

$$\sum_{\mu'} \langle \mu|Q_i^\dagger|\mu'\rangle c_{\mu'} + \hbar\omega_{qi} b_{\mu i}(\vec{q}) = W b_{\mu i}(\vec{q}). \tag{6}$$

From Eqs. (5) and (6) we obtain

$$c_{\mu'}(E_{\mu'} - W) + \sum_{i q \nu'} \frac{c_{\nu'}}{W - \hbar\omega_{qi}} \langle \mu' | Q_i Q_i^\dagger | \nu' \rangle = 0. \quad (7)$$

Since Q_i and $Q_i^\dagger$ belong to Γ_5, the quantities $Q_i Q_i^\dagger$ belong to $\Gamma_1 + \Gamma_3$. We can, thus, write

$$Q_i Q_i^\dagger = K + M(J_i^2 - \tfrac{1}{3}J^2), \quad (8)$$

where K and M are real constants, K being nonnegative. The operators J_i $(i = x, y, z)$ are the angular momentum matrices for $j = \frac{3}{2}$ and $J^2 = \frac{15}{4}$. This shows that the states $\psi_{\mu'}$ are mixed by the hole-phonon interaction according to the selection rule $\Delta\mu' = 0, \pm 2$. Thus, $\mu' = \frac{3}{2}$ and $\mu' = -\frac{1}{2}$ are hybridized as are $\mu' = \frac{1}{2}$ and $\mu' = -\frac{3}{2}$. For $\vec{q} = 0$, $\omega_{0i} = \omega_0$ is triply degenerate. If we neglect the separation of the optical-phonon branches for $q \neq 0$, i.e., if we set $\omega_{qi} = \omega_q$, Eq. (7) becomes

$$E_{\mu'} - W + \sum_q \frac{3K}{W - \hbar\omega_q} = 0. \quad (9)$$

Equation (9) can be solved graphically as exhibited in Fig. 3. The X line in Fig. 2 can be associated with the largest solution of Eq. (9). The intensity of the line is proportional to the amount of admixture of hole excitation in the phonon state, i.e., it is proportional to $\sum_{\mu'} |c_{\mu'}|^2$ in the absence of strain. In the presence of a uniaxial stress the Γ_8 levels split into doublets, leading to a structure in line X. At sufficiently high stresses, only the lower Γ_8 ground-state sublevel is populated and the X line splits into two. Their relative intensities are governed, however, by the proximity of the resonance. In Fig. 3 we show schematically how this splitting occurs. Another interesting feature arises from the admixture of the $\mu' = \pm \frac{3}{2}$ with the $\mu' = \mp \frac{1}{2}$ levels which follows from Eqs. (7) and (8).

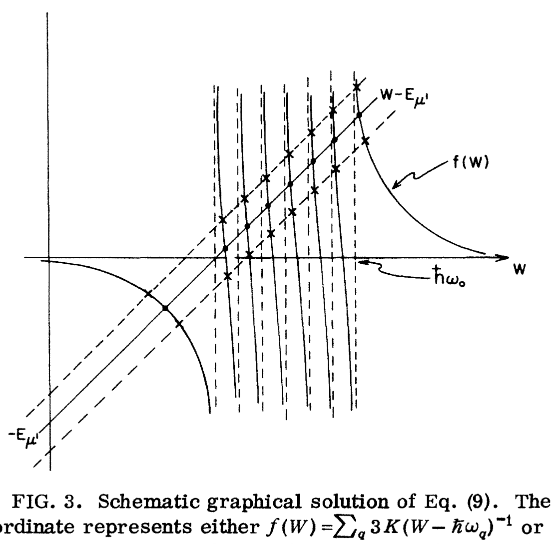

FIG. 3. Schematic graphical solution of Eq. (9). The ordinate represents either $f(W) = \sum_q 3K(W - \hbar\omega_q)^{-1}$ or $W - E_{\mu'}$. The vertical dashed lines are at the optical-phonon energies and are asymptotic to $f(W)$. The intersections of $f(W)$ with $W - E_{\mu'}$ yield the energy eigenvalues of the "mixed" hole-phonon excitations. The dashed inclined lines represent the splitting of the excited Γ_8 state under uniaxial stress into two sublevels, and their intersections (crosses) give the corresponding solutions of the mixed excitations.

This admixture occurs if we do not make the approximation $\omega_{qi} = \omega_q$. In such a case the eigenvalues are obtained by solving a 2×2 secular equation. We can write

$$A_{11} c_{3/2} + A_{12} c_{-1/2} = 0 \quad (10)$$

and

$$A_{12} c_{3/2} + A_{22} c_{-1/2} = 0, \quad (11)$$

with

$$A_{11} = E_{3/2} - W + (K - \tfrac{1}{2}M) \sum_q \left(\frac{1}{W - \hbar\omega_{qx}} + \frac{1}{W - \hbar\omega_{qy}} \right) + (K + M) \sum_q \frac{1}{W - \hbar\omega_{qz}}, \quad (12)$$

$$A_{12} = -\tfrac{1}{2} M\sqrt{3} \sum_q \left(\frac{1}{W - \hbar\omega_{qx}} - \frac{1}{W - \hbar\omega_{qy}} \right), \quad (13)$$

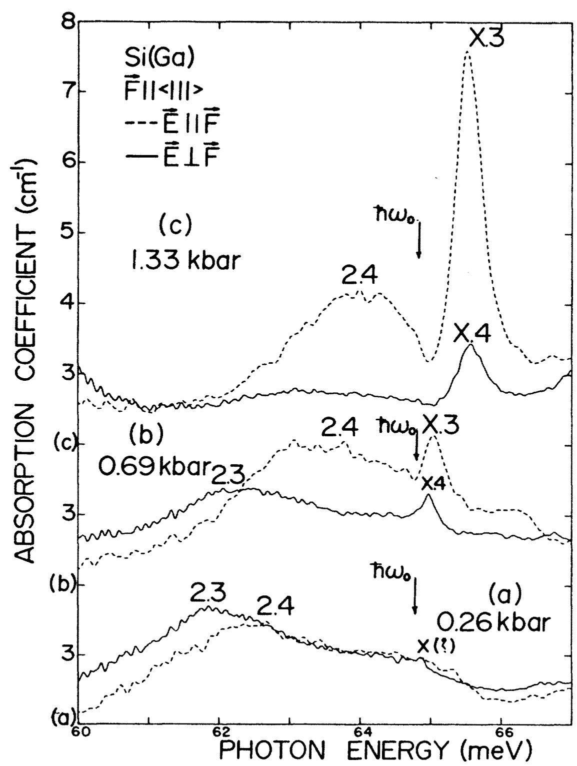

FIG. 4. Effect of a ⟨111⟩ compression on the lines 2 and X of Si(Ga) for different magnitudes of stress. The electric vector $\vec{E}$ is either parallel or perpendicular to the applied force $\vec{F}$. Measurements made with liquid helium as coolant.

and

$$A_{22} = E_{1/2} - W + (K + \tfrac{1}{2}M) \sum_q \left(\frac{1}{W - \hbar\omega_{qx}} + \frac{1}{W - \hbar\omega_{qy}} \right) + (K - M) \sum_q \frac{1}{W - \hbar\omega_{qz}}. \quad (14)$$

As we shall see in Sec. III, this admixture allows us to explain certain polarization features of the excitation spectra in the presence of uniaxial stress in different crystallographic directions.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The excitation spectra were recorded with a Perkin-Elmer double-pass grating monochromator (model E-1). A Perkin-Elmer wire-grid polarizer with AgBr substrate and a zinc-doped germanium detector operating at liquid-helium temperature were employed in the measurements. The data were directly converted to a digital form and punched on standard IBM cards. In several experiments, averages of multiple scans and optimum smoothing were performed on a computer.[15]

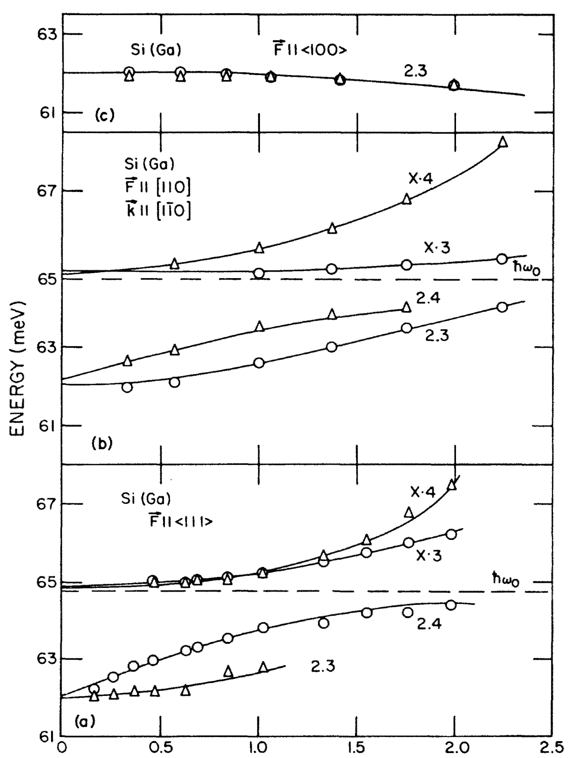

FIG. 5. Stress dependence of the components of lines 2 and X of Si(Ga) for (a) $\vec{F} \parallel \langle 111\rangle$, (b) $\vec{F} \parallel [110]$, and (c) $\vec{F} \parallel \langle 100\rangle$. For $\vec{F} \parallel [110]$, the direction of light propagation $\vec{k}$, was parallel to $[1\bar{1}0]$. The triangles and circles represent data points for $\vec{E} \perp \vec{F}$ and $\vec{E} \parallel \vec{F}$, respectively.

The low-temperature quantitative stress cryostat with modified sample-mounting procedure has been described elsewhere.[15,16]

The experimental results for a portion of the excitation spectrum, with compressive force $\vec{F}$ along a $\langle 111\rangle$ axis are shown in Figs. 4 and 5. Line 2 in the excitation spectrum of Si(B) splits into four components for $\vec{F} \parallel \langle 111\rangle$. In the Si(Ga) spectrum only two broad features are observed. At the higher stresses these can be identified as 2.3 and 2.4, the other two (2.1 and 2.2) not being observed because of thermal depopulation of the upper ground state. The polarization features of 2.3 and 2.4 are identical to those of the corresponding components of line 2 of other group-III acceptors. In the light of the interpretation for line X given Sec. II, it should split in a manner similar to line 2. The components labeled $X.3$ and $X.4$ show dramatic increases in intensity as the stress increases. Lines $X.1$ and $X.2$ possess negligible oscillator strengths since, even if allowed by population of the upper ground state, their excitation energies in the absence of the hole-phonon interaction are farther from resonance than those of $X.3$ and $X.4$. The polarization features of $X.3$ and $X.4$ are anomalous, however, in that $X.3$ appears strongly in $\vec{E} \parallel \vec{F}$, and $X.4$ in $\vec{E} \perp \vec{F}$, where $\vec{E}$ is the electric vector of the incident radiation, whereas the opposite should be

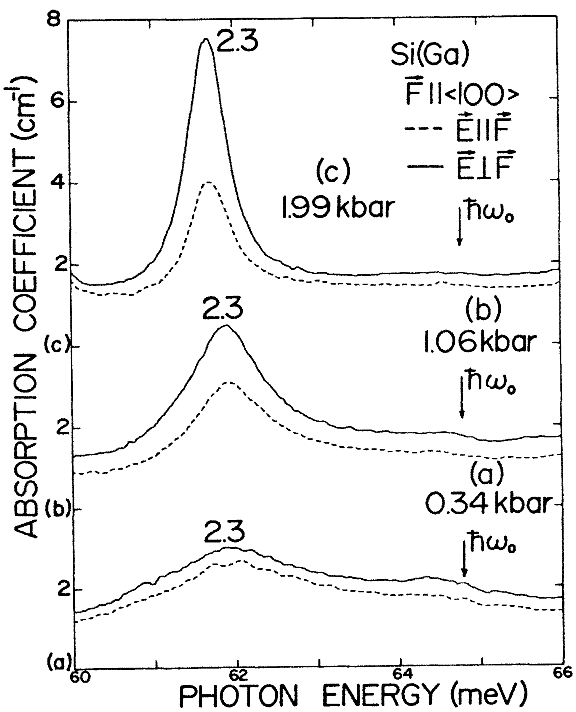

FIG. 6. Effect of a $\langle 100\rangle$ compression on the lines 2 and X of Si(Ga) for different magnitudes of stress. Liquid helium was used a coolant.

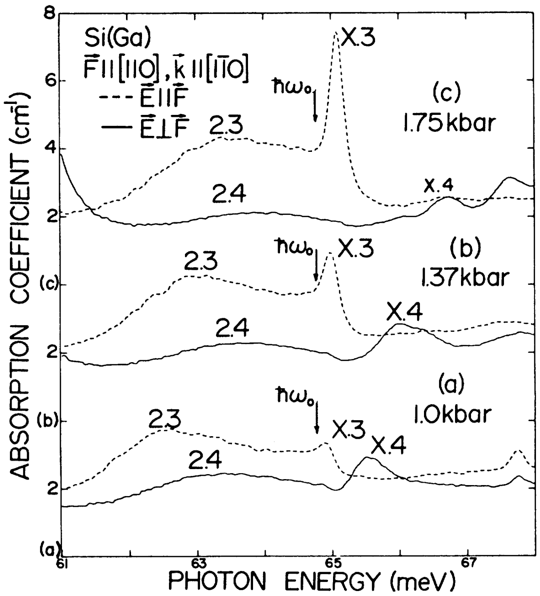

FIG. 7. Effect of a uniaxial compression with $\vec{F} \parallel [110]$ and direction of light propagation $\vec{k}$ along $[1\bar{1}0]$ on lines 2 and X of Si(Ga). Liquid helium was used as coolant.

the case.[14] We attribute this to the mixing of the $\Gamma_4(\pm\frac{1}{2})$ and $\Gamma_{5+6}(\mp\frac{3}{2})$ levels of the excited state of the 2.3 and 2.4 lines as discussed in Sec. II. The disappearance of 2.3 at the highest stress is to be understood as a consequence of level crossing effects with line 1.[10] The nonlinear stress dependence of 2.4, X.3, and X.4 seen in Fig. 5 is a direct consequence of the nature of the secular equation (9). On the scale of Fig. 5, the effect of uniaxial stress on the zone-center optical phonon is negligible and is therefore ignored.[17] Notice that the component 2.4 in this figure approaches $\hbar\omega_0$ asymptotically. This "pinning" in effect allows the observation of the otherwise infrared-inactive zone zone-center optical phonon in infrared absorption. Figures 5 and 6 show the results for $\vec{F} \parallel \langle 100\rangle$. The line labeled 2.3 moves to lower energies. The polarization features are consistent with the corresponding components of line 2 of other group-III acceptors. The components 2.1 and 2.4 which occur only in $\vec{E} \perp \vec{F}$ are of low intensity (see Fig. 3 of Ref. 14 and Fig. 19 of Ref. 9.). The sharpening of 2.3 with increasing stresses is due to the departure of the excitation from the resonance with $\hbar\omega_0$ and the weakening of the hole-phonon interaction for $\vec{q} \neq 0$. The results for $\vec{F} \parallel [110]$ and $\vec{k}$, the propagation direction, along $[1\bar{1}0]$ are shown in Figs. 5 and 7. The polarization features are the same as those observed for other acceptors without the resonant hole-phonon interaction.

We wish to draw attention to the fact that at zero stress, line X is sharp whereas line 2 is very broad. This is a consequence of the dispersion curves of the optical phonons which are not flat but have a maximum at $\vec{q} = 0$. It can be shown that had the dispersion curves been flat, lines X and 2 would have been equally sharp and intense when in resonance. The observed sharpness of line X is thus to be understood as a result of a maximum in the dispersion curve; line 2, however, acquires its breadth due to interaction with all the phonons below this maximum.

---

*Work supported by the NSF under Grant Nos. GH 32001A1 and DMR 76-04775 and MRL Program Nos. DMR-7203018A03 and DMR-7203018A04.

†Present address: Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany.

[1] W. Kohn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.

[2] P. Fisher and A. K. Ramdas, *Physics of the Solid State*, edited by S. Balakrishna, M. Krishnamurthi, and B. Ramachandra Rao (Academic, New York, 1969), p. 149.

[3] F. Bassani and G. Pastori Parravicini, *Electronic States and Optical Transitions in Solids* (Pergamon, Oxford, England, 1975).

[4] A. Baldereschi and N. O. Lipari, Phys. Rev. B 8, 2697 (1973).

[5] F. Bassani, G. Iadonisi, and B. Preziosi, Rep. Prog. Phys. 37, 1099 (1974).

[6] H. J. Hrostowski and R. H. Kaiser, J. Phys. Chem. Solids 4, 148 (1958).

[7] A. Onton, P. Fisher, and A. K. Ramdas, Phys. Rev. Lett. 19, 781 (1967).

[8] H. R. Chandrasekhar, A. K. Ramdas, and S. Rodriguez, Solid State Commun. 18, 405 (1976).

[9] A. Onton, P. Fisher, and A. K. Ramdas, Phys. Rev. 163, 686 (1967).

[10] H. R. Chandrasekhar, P. Fisher, A. K. Ramdas, and S. Rodriguez, Phys. Rev. B 8, 3836 (1973).

[11] The energy levels of an acceptor are labeled by the double-valued irreducible representations of the point group T_d. The notation is that of G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz [*Properties of the Thirty-Two Point Groups* (MIT U.P., Cambridge, Mass., 1963), pp. 88, 89, 103, and 104].

[12] See a similar discussion for donors in silicon given by S. Rodriguez and T. D. Schultz [Phys. Rev. 178, 1252 (1969)].

[13] Γ_5^+ of O_h is compatible with Γ_5 of T_d. See Ref. 11, p. 104.

[14] Details can be found in S. Rodriguez, P. Fisher, and F. Barra, Phys. Rev. B 5, 2219 (1972).

[15] N. R. Butler, Ph.D. thesis (Purdue University, 1974) (unpublished).

[16] V. J. Tekippe, H. R. Chandrasekhar, P. Fisher, and A. K. Ramdas, Phys. Rev. B 6, 2348 (1972).

[17] E. Anastassakis, A. Pinczuk, E. Burstein, F. H. Pollak, and M. Cardona, Solid State Commun. 8, 133 (1970).