OBSERVATION OF OPTICAL PHONONS BOUND TO NEUTRAL DONORS

P. J. Dean and D. D. Manchon, Jr.*
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

and

J. J. Hopfield†
Department of Physics, Princeton University, Princeton, New Jersey 08540

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We have observed new "local-mode lattice vibrations" in GaP, both in Raman scattering and as cooperating phonons in optical transitions. The modes are best qualitatively described as a particle—the LO phonon—bound to a neutral donor, which provides an effective attractive interaction for the phonon. In this analogy, bound states having various angular momenta around the donor can be expected, and both *S* and *P* states have been identified experimentally.

We have observed new local modes which are due to single, isolated neutral donors. The vibrational energies of these modes are between 0.8 and 1.9 meV lower than the $\vec{k}=0$ LO phonon energy, depending on the donor and the symmetry of the local mode. These modes are closely related to the exciton-phonon complex discussed by Toyozawa and Hermanson.[1] Our mathematical starting point is the same interaction as used by Toyozawa and Hermanson, but the physics of the present case permits closed expressions for local-mode energies and wave functions for states of several symmetries. The simplicity of our system permits quantitative comparison with a theory involving no adjustable parameters. These modes do not show the systematics of mass-defect local modes of the type described by Elliott and Dawber.[2]

The modes were observed in 90° Raman scattering with 5145-Å light from an Ar^+ laser focused on polished and oriented samples cooled to ~20°K, when the donors in GaP are completely frozen out ($E_D \gtrsim 65$ meV).

Liquid encapsulated Czochralski-grown (LEC) crystals containing $(0.1 \text{ to } 2.0)\times 10^{18}$ cm^{-3} neutral S, Te, and Sn donors, and solution-grown platelets heavily doped with Si donors, were used in the Raman studies. Luminescence was excited by 4880-Å Ar^+ light from crystals containing 10^{16} to 10^{17} cm^{-3} neutral P-site donors S and Te.

The peaks labeled S, Te, and Sn in Fig. 1, occurring just below $\hbar\omega_{\mathrm{LO}}$, are attributable to Raman scattering from the neutral-donor, LO-phonon bound state. The binding energies E_B of this quasiparticle are listed in the right-hand column of Table I for several donors. Strong evidence that these impurity modes are connected with the dielectric effects of the neutral donors, rather than with in-band resonance local lattice vibrations involving the mass defects of the substituents,[2] comes from the observation of similar shifts and scattering intensities for both light and heavy substituents on both Ga and P lattice sites. In addition, we could not find a similar component in scattering from a crystal containing 6×10^{17} cm^{-3} of the isoelectronic trap Bi, which does not affect the charge density in the crystal.

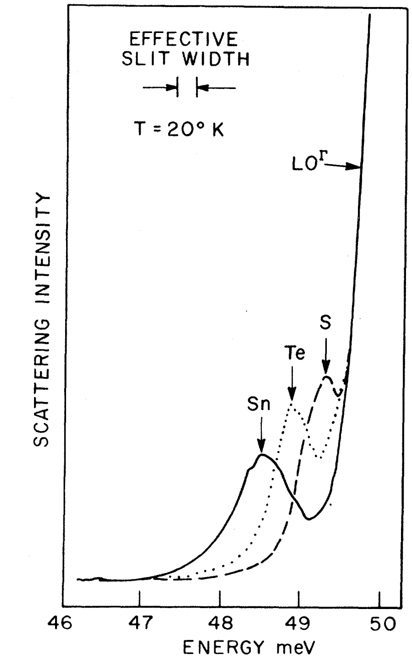

FIG. 1. Raman scattering of 5145-Å Ar^+ laser light from GaP containing ~10^{18} cm^{-3} neutral Sn, Te, or S donors, recorded just below the $\vec{k}=0$ LO phonon at 50.2 meV, showing the new local modes. These modes can be seen easily at donor concentrations as low as 10^{17} cm^{-3}, although their strengths relative to the LO$^\Gamma$ lattice normal mode decrease in proportion to the neutral donor concentration.

Table I. Experimental and calculated binding energies E_B of LO phonons localized at neutral donors in GaP observed through Raman scattering, $(E_B)^p$, and as sidebands in the luminescence of excitons bound to neutral donors, $(E_B)^s$.

Donor	(meV)	$E_{1s(A_1)} \rightarrow E_{2s(A_1)}$ (meV)	$E_{1s(A_1)} \rightarrow E_{2p}$[e] (meV)	$(E_B)_{\text{calc}}{}^s$ (meV)	$(E_B)_{\text{exp}}{}^s$ (meV)	$(E_B)_{\text{calc}}{}^p$ (meV)	$(E_B)_{\text{exp}}{}^p$
S	104.2[a]	82.6[a]	94.0[f]	0.98	1.2 ± 0.2	0.58	0.8 ± 0.2
Te	89.8[b]	68.2[b]	79.9[b]	1.40	1.9 ± 0.2	0.70	1.2 ± 0.2
Si	82.5[a]	70.2[d]	72.3[a]	1.16	?	0.82	1.3 ± 0.2
Sn	65.5[c]	53.2[c]	58.5[c]	[3.6][g]	?	[1.35][g]	1.6 ± 0.2

[a] From Onton (Ref. 3).

[b] From Onton and Taylor (Ref. 4).

[c] From Dean *et al.* (Ref. 5).

[d] Assuming that $E_{2s(A_1)}$ is the same as for Sn.

[e] Calculated as weighted mean of $E_{1s(A_1)} \rightarrow E_{2p_0}$ and $E_{1s(A_1)} \rightarrow E_{2p_\pm}$.

[f] Assuming that $E_{2p_0} \rightarrow E_{2p_\pm}$ is the same for S and Te.

[g] Using degenerate perturbation theory.

The donor-induced peaks in Fig. 1 have a few percent of the intensity of the normal LO modes for 10^{18} cm^{-3} neutral donors. The intensities of the new modes relative to the LO phonon are independent of geometry and polarization, and are proportional to the donor concentrations.

The virtual process

Donor + LO phonon $\vec{k} \rightarrow$ Excited donor $\rightarrow$ Donor + LO phonon $\vec{k}'$

produces an effective interaction of an LO phonon with a donor site. The effective scattering-matrix element $H_{kk'}$ is (neglecting the small curvature of the LO branch near $k = 0$) proportional to

$$\sum \frac{(E_j - E_0)\langle 0|e^{i\vec{k}\cdot\vec{r}}|j\rangle\langle j|e^{i\vec{k}'\cdot\vec{r}}|0\rangle}{[(E_j-E_0)^2-(\hbar\omega)^2]kk'},$$

where $|0\rangle$ is the donor ground state wave function and the sum is over excited donor states j. The interaction is attractive when $\hbar\omega_{\text{LO}}$ is less than the relevant excitation energies of the donor. If a spherical approximation is used for the donor, this interaction will produce bound states for each angular momentum of the LO phonon (viewed as a particle) around the donor. When, as in GaP, the lowest donor excitation energy is comparable with the phonon frequency, an approximation in which only the lowest donor excited state is kept will give a reasonable approximation and a lower bound to the binding energy for the eigenvalue problem defined by $H_{kk'}$.

In this approximation, the integral equation for the binding energy has a separable kernel. The results obtained for the phonon crystals wave functions and energies for S and P states are, for S states,

$$E_B = \left(\frac{32}{729}\right)\hbar\omega_{\text{LO}}\left(\frac{\epsilon_0}{\epsilon_\infty}-1\right)\left(\frac{e^2}{2a\epsilon_0}\right)\frac{E_{2s}-E_{1s}}{(E_{2s}-E_{1s})^2-(\hbar\omega_{\text{LO}})^2}, \tag{1}$$

$$\psi_K \propto k/[(3/2a)^2+k^2]^3; \tag{2}$$

for P states,

$$E_B = \left(\frac{224}{6561}\right)\hbar\omega_{\text{LO}}\left(\frac{\epsilon_0}{\epsilon_\infty}-1\right)\left(\frac{e^2}{2a\epsilon_0}\right)\frac{E_{2P}-E_{1S}}{(E_{2P}-E_{1S})^2-(\hbar\omega_{\text{LO}})^2}, \tag{3}$$

$$\psi_K \propto \cos\theta_k/[(3/2a)^2+k^2]^3. \tag{4}$$

In these expressions, ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants of the Fröhlich electron-phonon interaction. The donor Bohr radius is a, and the donor binding energy is $e^2/2a\epsilon_0$ for a hydrogenic donor. The energies E_{1S}, etc., are the energies of the donor ground and excited states. By combining results known from two-electron transitions of bound excitons,[5] and infrared absorption of donors,[3,4] all the energies in (1) and (3) can be evaluated with great accuracy (Table I). There are no unknown parameters in (1) and (3). The correction to the binding energy due to anisotropy of the donors is about 10% for the S bound states, so will be ignored. The theoretical binding energies from (1) and (3) are included in Table I.

Conventional Raman scattering theory would lead one to believe that both these local modes might be observed, each with the elementary selection rules appropriate to its symmetry (S or P). This expectation is unfulfilled in two ways. First, only one mode is seen. Second, its intensity relative to the LO phonon is independent of geometry. However, the LO mode in a zinc-blende structure has a characteristic Raman-scattering tensor associated with the LO-TO splitting caused by long-range Coulomb effects. The observed local mode apes this characteristic scattering behavior of LO phonons instead of having selection rules appropriate for an S or P local mode. This anomaly is present in spite of the fact that the scale of the local mode is comparable with that of a donor—about 6 to 10 Å radius in GaP, dependent on the donor.

The explanation of these paradoxes is contained in the wave functions (2) and (4) of the local modes. For scattering with large changes of wave vector $\Delta\vec{k}$ (compared with a Reststrahlen photon) the scattering rate for a weakly bound LO phonon in a crystal of volume V is related to the normal LO Raman scattering rate in the same geometry by the proportionality constant $|\psi_{\Delta\vec{k}}|^2$. This fact explains the peculiar selection rules observed. For P states, the normalization integral for the bound states can easily be done, yielding

$$|\psi_{\Delta k}|^2{}_{\Delta k\ \mathrm{small}} = \frac{256\pi}{9}\,\frac{a^3}{V}.$$

For 10^{18} cm^{-3} Sn ($a = 10$ Å) or Te ($a = 7.3$ Å) donors the predicted scattering intensities are 9% and 3.5% of the LO scattering, in excellent agreement with the experimental values, which are 10% (Sn) and 4% (Te).

For S states, the bound-state wave function is linear in the wave vector for small wave vectors. The S-state cross section will be about $(\Delta ka)^2 \sim 10^{-4}$ times the P-state cross section. We have therefore identified the observed states as being of P symmetry. The comparison of the measured and calculated binding energies (Table I) shows that the calculations uniformly give a result which is about $\frac{2}{3}$ the measured binding energy. Since contributions involving higher donor excited states would increase the calculated E_B, we regard the agreement as satisfactory.

Since the S-state local modes were not visible in Raman scattering, we were led to re-examine other experiments in which such modes might be expected to be observed. A strong vibronic sideband due to the creation of $\vec{k} = 0$ LO phonons appears in the luminescence of excitons bound to neutral P-site donors in GaP,[6] but is insignificant for Ga-site donors.[3] Because the LO coupling mechanism has the appropriate symmetry to couple to S-state bound LO phonons, they can be expected to be visible in the vibronic spectrum. Vibronic lines involving interactions with phonons of slightly lower energy appear in the S spectrum [Fig. 2(b)] and in the Te spectrum [Fig. 2(a)]. The binding energies of these states are again larger than the theoretical prediction, by a factor of about 1.3 (Table I). In addition to these S-like bound LO phonons, shifted components much closer to the ordinary LO replica occur in the exciton spectra in Fig. 2. These may involve D-like bound phonons.

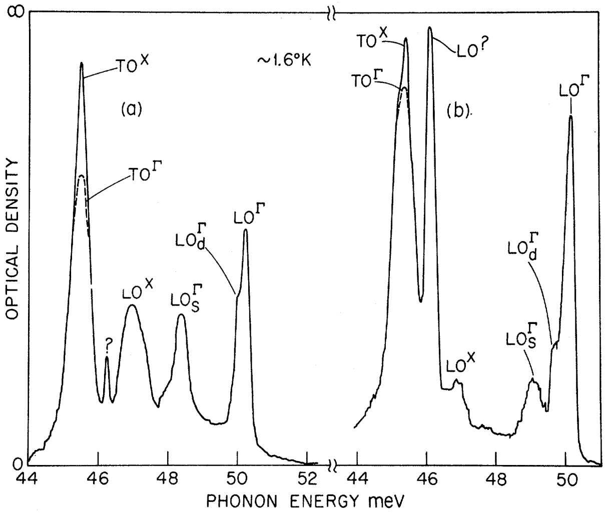

FIG. 2. Portions of the vibronic sidebands in the low-temperature luminescence spectra of excitons bound (a) to neutral Te donors and (b) to neutral S donors in GaP. Superscripts X denote replicas involving phonons selected for conservation of momentum in the recombination of indirect excitons in GaP (Ref. 6). Long-wavelength (zone-center) phonons are superscripted Γ. Subscripts s and d denote the symmetries of local modes around the neutral donors. The assignments of the d states are tentative.

Mass-defect local-mode theory could not account for the modes we see even if large changes in short-range spring constant were assumed. The observed modes fall in a region of high density of lattice normal modes, rather than in the low-density gaps in the normal-mode spectrum[7] as expected from such "local perturbation" theory.[2] The "local perturbation" modes must exist, but are presumably too weak to be seen because of the small k-space overlap of the LO phonon and the short-range perturbation. The coupling mechanism we describe successfully accounts for the large Raman scattering cross section observed.

Note added in proof.—Further evidence for the validity of this coupling mechanism comes from our recent observation that the intensity of the new local mode decreased to less than 4% of its original value as a result of close compensation by Cu diffusion in a crystal initially containing 1.5×10^{18} neutral Te donors.

We wish to express our appreciation to C. H. Henry for several stimulating discussions of the effects reported here. Good quality LEC single crystals of GaP containing controlled doping levels were kindly provided by H. W. Verleur. Expert technical assistance was given by G. Kaminsky and S. Bortas.

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*On assignment from Bell Telephone Laboratories, Reading, Pa. 19604.

†Consultant, Bell Telephone Laboratories, Murray Hill, N. J. 07974.

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FRENKEL EXCITON SUPEREXCHANGE, PAIR INTERACTIONS, AND DISPERSION RELATION: $^1B_{2u}$ NAPHTHALENE CRYSTAL*

Hwei-Kwan Hong and Raoul Kopelman
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104

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Guest-host-guest exciton exchange (superexchange) is appreciable in the $^1B_{2u}$ state of a $C_{10}H_8$-$C_{10}D_8$ mixed crystal. The experimental resonance pair fine structure in this system has been satisfactorily fitted, resulting in three sets of six pairwise exciton interactions, consistent with all known experimental data. A point multipole expansion, limited to nonoverlapping charge distributions and truncated after the transition-octupole–transition-octupole term, is only consistent with one set, whose values are presented. Using these values, the exciton band structure is completely determined within the restricted Frenkel limit.

Reported here is what we believe to be the first reliable determination of a complete exciton band structure in a molecular crystal. Potential applications include energy transfer and dynamics in molecular aggregates: pure crystals, mixed crystals, solutions, and synthetic or natural polymers.

The first excited electronic singlet state ($^1B_{2u}$) of the naphthalene crystal has been a prototype system for Davydov exciton splittings,[1] and recently for the experimental density-of-states determination.[2] This $^1B_{2u}$ exciton state in isotopically mixed naphthalene crystals has also yielded monomer (single guest) quasiresonance interactions,[3] resonance pair interactions,[4] and band spectra of heavily doped crystals,[5] all in agreement with the restricted Frenkel-Davydov model[6,2] (short-range interactions). However, the mixed-crystal resonance pair results[4] did not agree well with the pure-crystal density-of-states function,[3] nor with the translational shift,[3,1c] casting doubt on the separability of exciton and phonon contributions[2] and/or on the validity of the traditional first-order approach.[1]

We have now shown that the indirect guest-host exciton exchange contribution to the guest-guest "resonance-pair" line structure is of the same order as (or more than!) the direct resonance contribution for most observable splittings in the isotopically mixed naphthalene crystals (specifically $C_{10}H_8$ in $C_{10}D_8$—see Table I). These indirect or superexchange interactions can furthermore be utilized to assign experimentally observed splittings to specific pairwise interac-