Experimental observation of spectral fine structure in the light scattered by local dielectric modes

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Fine structure has been observed for the first time in the spectra of the light scattered by local dielectric modes. The effect had been predicted previously on the basis of the general theory of weakly bound electron–phonon states. Transitions of the type $1S(A_1) \rightarrow 2P_0$ along with electronic transitions $1S(A_1) \rightarrow 2P_{\pm}$ are primarily involved in the scattering.

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Kogan and Suris[1] predicted a new type of local mode near impurity centers in a semiconductor on the basis of a two-level model. The interaction of an electron at an impurity center with an optical phonon can give rise to spatially localized bound states when the energy corresponding to a transition of the electron from the ground state to the excited state is approximately equal to the phonon energy. These states have been called "local dielectric modes."[1)] These modes are active in Raman scattering and have been observed in the spectra of *n*-GaP (Refs. 2 and 3). A singlet band split off from the line of the corresponding $LO(\Gamma)$ phonon has been observed. For many-level impurity centers, the appearance of a large number of local dielectric modes has been predicted in the general theory of weakly bound electron–phonon states without allowance for Rashba phonon dispersion.[4,5] It is natural to suggest that a set of additional lines corresponding to all values of the discrete electronic spectrum of the impurity can be expected in the Raman spectra of impure semiconductors.

In this letter we report the first results of our study of Raman scattering for several GaP:S crystals with a concentration difference $N_D - N_A$ ranging from 9×10^{17} to $\sim 1 \times 10^{19}$ cm^{-3}.

The Raman spectra were excited by various wavelengths from He–Ne and Ar^+ lasers with $\lambda_i = 6328$ Å, $\lambda_i = 5145$ Å, and $\lambda_i = 4880$ Å, so that lines not associated with the Raman effect could be eliminated from consideration. We studied the scattering from the (111) plane through an angle of 180°. The incident and scattered light was horizontally polarized. The samples were held in a metal helium cryostate. The scattered light was analyzed with a refined *DFS*-24 double monochromator. The spectral resolution was 0.8 cm^{-1} (0.1 meV) as $\lambda_i = 6328$ Å.

The types of impurities in our samples were identified and monitored by neutron activation analysis and by measurements of the Hall effect; in addition, we simultaneously recorded the luminescence spectra of donor–acceptor pairs and the electronic Raman scattering due to transitions between the ground and excited states of a donor, split by the valley–orbit interaction: transitions of the type[2)] $1S(A_1)$–$1S(E)$.

Figure 1 shows some representative Raman spectra of local dielectric modes for $T = 6 \pm 0.1$ K; the spectra were excited by the beam from an Ar^+ laser with

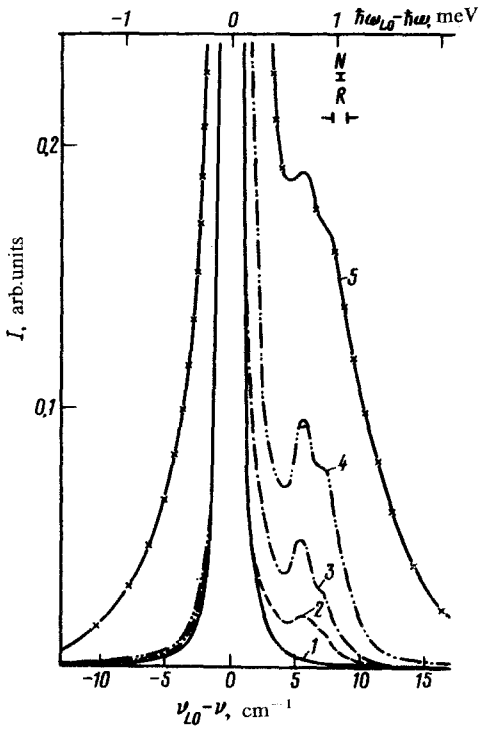

FIG. 1. Raman spectra. 1—Raman scattering involving an $LO(\Gamma)$ phonon in GaP which has not deliberately been doped; 2–5—scattering involving local dielectric modes for several GaP:S samples with various concentrations of neutral donors, N_D–N_A (in units of donors per cubic centimeter): 2—9.0×10^{17}; 3—2.3×10^{18}; 4—5.2×10^{18}; 5—$\sim1\times10^{19}$. $\lambda_i = 5145$ Å, $T = 6$ K. Here N is the average noise level.

$\lambda_i = 5145$ Å in GaP crystals (not deliberately doped; spectrum 1) with various concentrations of neutral donors. On the low-frequency side of the intense line of the $LO(\Gamma)$ phonon we can clearly see the well-defined structures of lines corresponding to local dielectric modes, lying 7.4 cm^{-1} (0.93 meV) and 5.4 cm^{-1} (0.68 meV) from the line of the $LO(\Gamma)$ phonon. Their intensities increase with increasing concentration of neutral donors.

For a discrete electron spectrum with a nondegenerate ground state, the problem of calculating the binding energy of the local dielectric modes, $W = \hbar\omega_{LO} - \epsilon$, where $\hbar\omega_{LO}$ is the energy of the optical phonon, reduces to the problem of finding the roots of the equation[4–6]

$$\left| A_{tt'} - \delta_{tt'} W(\epsilon_t - \hbar\omega_{LO} + W) \frac{\hbar\omega_{LO} + \epsilon_t}{2\epsilon_t} \right| = 0 \quad (t, t' = 1, 2, \ldots \infty). \tag{1}$$

Here the subscripts t and t' specify all the excited electronic states, the $\epsilon_t = E_t - E_0$ are the excitation energies, E_0 is the ground-state energy, and

$$A_{tt'} = \frac{1}{2\pi} \int d^3\mathbf{k}\, \gamma_{t0}(\mathbf{k})\, \gamma_{0t'}(\mathbf{k}), \quad \gamma_{t0}(\mathbf{k}) = (\lambda | \mathcal{H}_{\text{el-ph}} | k),$$

where γ_{t0} are the matrix elements of the electron–phonon interaction.

Direct calculations for a spherically symmetric donor center, carried out with hydrogen-like wave functions for the excited states $t = 2S$ and $2P$, show that the off-diagonal terms $A_{tt'}(t \neq t')$ vanish, and the roots of Eq. (1) are

$$W_{\pm t} = \frac{\epsilon_t - \hbar\omega_{LO}}{2} \pm \sqrt{\frac{2A_{tt}\epsilon_t}{\epsilon_t + \hbar\omega_{LO}} + \frac{(\epsilon_t - \hbar\omega_{LO})^2}{4}}. \quad (2)$$

For $t = 2P$ states we can write[7]

$$A_{2P,\,2P} = \frac{112}{6561}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\left(\frac{e^2}{2a_0}\right)\hbar\omega_{LO},$$

where $a_0 = \hbar^2\epsilon/m^*e^2$ is the first Bohr radius of the impurity center. The intensity of the Raman scattering of a local dielectric mode due to an electron transition between even states, $1S(A_1) \rightarrow 2S$, is small,[3] and the greatest contribution can come from transitions of the type $1S(A_1) \rightarrow 2P$. With increasing deviation of the gallium phosphide conduction band from a parabolic band near the χ_1^c minimum, the P states split into a P_0 singlet with a magnetic quantum number $m = 0$ and a $P_\pm$ doublet with $m = \pm 1$. According to the actual structure of the electronic levels for the donor centers of sulfur in GaP, the scattering may be caused primarily by transitions with a large oscillator strength: transitions of the types $1S(A_1) \rightarrow 2P_0$, $1S(A_1) \rightarrow 2P_\pm$, with excitation energies $E_{2P0} - E_{1S(A_1)} = 71.5$ meV and $E_{2P_\pm} - E_{1S(A_1)} = 97.0$ meV (Refs. 8–12). Under this assumption, for a sulfur donor impurity with an ionization energy $E_D = 108$ meV and $a_0 \approx 6$ Å, we find the following numerical estimates of the frequencies of the local dielectric modes: $\nu_{2P_0} = 8.5\ \text{cm}^{-1}$ (1.06 meV) and $\nu_{2P_\pm} = 4.5\ \text{cm}^{-1}$ (0.56 meV). These frequencies agree satisfactorily with the experimental observations.

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[1)]These modes should of course be distinguished from the ordinary local modes, which are related to the difference between the masses of the impurity and the host material and also to the change in the rigidities caused by changes in the valence-electron configuration.

[2)]The careful preparation of the samples also made it possible to observe some new aspects of this type of Raman scattering, which will be reported in a separate paper.

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