Observation of light scattering by bound states of optical phonons trapped at neutral donor centers with a degenerate ground state

B. Kh. Baĭramov, G. Irmer, I. Monecke, and V. V. Toporov
Physicotechnical Institute, Academy of Sciences of the USSR

(Submitted 18 February 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **41**, No. 8, 349–352 (25 April 1985)

The first experimental observation of bound states of optical phonons trapped by neutral donor centers in crystals with a degenerate ground state is reported. These bound states were predicted previously on the basis of a general theory of weakly bound electron-phonon states for Jahn-Teller centers.

Kogan and Suris[1] have predicted a new type of spatially localized bound state of an optical phonon near an impurity center in a semiconductor in the case in which the energy of an electronic transition from the ground state to the excited state is approximately equal to the energy of a longitudinal optical phonon. The dielectric local modes corresponding to such bound states are active in the Raman effect and have been observed in the spectra of n-GaP with a nondegenerate impurity-center ground state.[2–4] Rashba has predicted the appearance of dielectric modes for degenerate electronic levels of Jahn-Teller centers with an electronic spectrum of arbitrary structure on the basis of a general theory of weakly bound electron-phonon states. In such systems, the interaction of the electrons with oscillations active in the Jahn-Teller effect gives rise to bound states even in the lowest approximation of the theory, in which all the excited electronic states are eliminated from consideration.[6] However, bound states of optical phonons of this type have not previously been observed experimentally for Jahn-Teller systems.

In this letter we report the first observation of bound states of longitudinal optical phonons trapped by neutral donor centers with a degenerate ground state; specifically, we have observed these states in GaP:Si crystals.

We studied the scattering of light by gallium phosphide single crystals doped with silicon, having an n-type conductivity and a density difference $N_D - N_A$ ranging from 1.6×10^{17} to 7.1×10^{17} cm^{-3}. The spectra are excited by various lines in the output from He-Ne and Ar^+ lasers in the geometry of backscattering from the (111) plane.

In addition to carrying out chemical, emission-spectrum, and neutron-activation analyses and measurements of the temperature dependence of the conductivity and the Hall coefficient, we identified and monitored the types of impurities in the samples by simultaneously measuring the luminescence of donor-acceptor pairs the electron Raman scattering due to transitions between impurity levels of silicon in gallium phosphide,[1)] and the Raman scattering by bound phonon-plasmon states.[7]

Figure 1 shows some representative spectra for several of the GaP:Si samples. With increasing density of donor centers, a new line "floats up" from the low-frequency side of the line corresponding to the $LO(\Gamma)$ phonon, and then the intensity of this

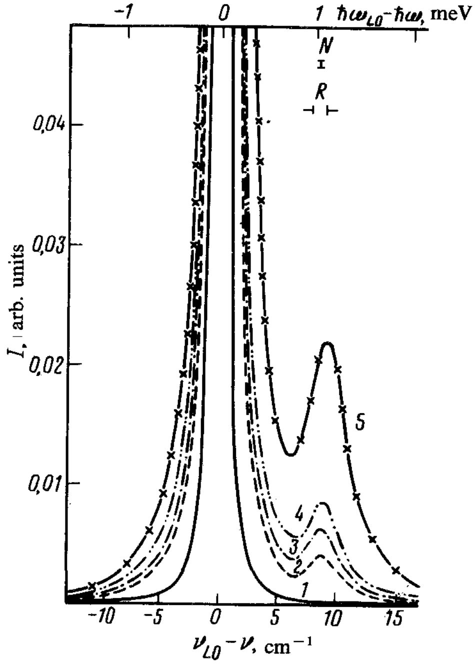

FIG. 1. 1—Spectrum of Raman scattering involving $LO(\Gamma)$ phonons in an undoped GaP sample with $n < 10^{15}$ cm^{-3}; 2–5—Raman scattering by bound electron-phonon states in GaP:Si with various densities of donor centers, $N_D - N_A$, in units of 10^{17} cm^{-3}; 2) 1.6; 3) 2.0; 4) 3.2; 5) 7.1. The polarizations of the incident light ($\lambda_i = 5145$ Å) and of the scattered light are horizontal. $T = 6$ K. Here N is the average noise level due to the scattered light.

new line increases. We interpret this new line as a local dielectric mode. The measured binding energy is 1.12 meV or 9 cm^{-1}.

The ground state of an impurity electron is triply degenerate for the conduction band of gallium phosphide, which has three equivalent minima at the edge of the Brillouin zone in the [100] direction. The nature of this degeneracy can be determined from the irreducible representations of the T_d group, under which the wave functions of the trapped electronic states transform.[8] For group-VI donors replacing phosphorus atoms, the wave functions have the symmetry of the X_1 minimum, and the degeneracy is lifted by the valley-orbit interaction, accompanied by the formation of a $1s(A_1)$ singlet and a $1s(E)$ doublet. The group-IV donors replace gallium atoms, and the wave functions of the trapped states have the symmetry of the X_3 minimum, and the ground state remains triply degenerate (the triplet T_2).[8] In the theory of weakly bound electron-phonon states,[3] there is a severe restriction: It is assumed that the ground state of the impurity center is nondegenerate. There is, however, the possibility of a generalization to the case of a degenerate ground state. We will not go into the details of the analysis of that problem[2)]; we simply note that if the interaction between different ground states through intermediate states is ignored (this interaction is responsible only for the small Jahn-Teller effect), we find a system of independent equations, one for each ground state, which are exactly the same as the Rashba equations.[5] For a spherically symmetric donor center, using hydrogen-like functions for the bound states corresponding to the transition $1s(T_2')\rightarrow 2p_{\pm}$ with a transition energy $E_{2p_{\pm}} - E_{1s(T_2)} = 93$ meV, we find a binding energy $W_{2p_{\pm}} = 0.87$ meV or 7.0 cm^{-1}. In view of the simplifications which we have made, we judge the agreement with the experimental value to be satisfactory.

TABLE I.

Sample	2	3	4	5
$(N_D - N_A) \cdot 10^{-17}$ cm^{-3}	1,6	2,0	3,2	7,1
I_{DLM}/I_{LO} theo	0,009	0,013	0,018	0,055
I_{DLM}/I_{LO} expt	0,010	0,013	0,021	0,046

Measurements of the intensity of the dielectric modes and various densities of donor centers have made it possible to experimentally test the conclusions of the theory of weakly bound electron-phonon states with regard to the absolute value of the intensity of the scattering by donor centers.[3,5]

According to Ref. 5, the ratio of the effective cross sections for the scattering of light by phonons trapped by neutral donors (per impurity center) and by lattice phonons (per unit cell, of volume d^3) in scattering in the same direction and with the same polarization is

$$\frac{(\sigma_{imp})_t}{\sigma_{intr}} = \left(1 - \frac{d\lambda_t}{d\lambda}\right)^{-1} \frac{4\pi\alpha(\hbar\omega_{LO})^2}{d^3(2m^*\hbar\omega_{LO})^{1/2}} \sum_{t'} |(\psi_0|x|\varphi_{t'})|^2 . \tag{1}$$

Here the summation over t' runs over the excited states. In the case of interest here, we have $(1 - d\lambda_t/d\lambda)^{-1} \approx 1$, and the wave functions are $\varphi_t = \psi_t A_{tt'}^{-1/2}$, where $A_{tt'} = [1/(2\pi)^3]\int d^3k \gamma_{t0}(k)\gamma_{0t'}(-k)$, and the γ_{t0} are the matrix elements of the electron-phonon interaction. Using hydrogen-like wave functions for the ground and excited states, we find the following expression for the ratio of the intensities of the light scattering by phonons trapped at the $N_D - N_A$ neutral donors and by the lattice scattering by N unit cells:

$$\frac{I_{DLM}}{I_{LO}} = \frac{N_D - N_A}{N} \frac{(\sigma_{imp})_t}{\sigma_{intr}} = \frac{8192}{63} \frac{\pi a_0^3}{d_3} \frac{N_D - N_A}{N}, \tag{2}$$

where a_0 is the first Bohr radius of the impurity center. The results of these calculations, listed in Table I, agree well with the experimental values.

We wish to thank B. P. Zhakharchenya and Sh. M. Kogan for useful discussions, and V. Sigel' and T. Kyunel' for carrying out the electrical measurements.

[1)]Three new lines have been discovered in the frequency interval 570–610 cm^{-1}. The detailed results on this scattering will be reported in a separate paper.
[2)]These results will be published in a separate paper.

[1]Sh. M. Kogan and R. A. Suris, Zh Eksp. Teor. Fiz. **50**, 1279 (1966) [Sov. Phys. JETP **23**, 850 (1966)].
[2]P. J. Dean, D. D. Mannchon, Jr., and J. J. Hopfield, Phys. Rev. Lett **25**, 1027 (1970).
[3]M. V. Klein, in: Light Scattering in Solids (ed. M. Cardona), Springer-Verlag, New York, 1975 (Russ. Transl. Mir, Moscow, 1976).

[4]B. Kh. Baĭramov, G. Irmer, I. Moneke, and V. V. Toporov, Pis'ma Zh. Eksp. Teor. Fiz. **38**, 238 (1983) [JETP Lett. **38**, 281 (1983)].
[5]É. I. Rashba, Zh. Eksp. Teor. Fiz. **71**, 319 (1976) [Sov. Phys. JETP **44**, 166 (1976)].
[6]B. G. Vekhter, V. Z. Polinger, Yu. B. Rozenfel'd, and B. S. Tsukerblat, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 84 (1974) [JETP Lett. **20**, 36 (1974)].
[7]G. Irmer, V. V. Toporov, B. H. Bairamov, and J. Monecke, Phys. Status Solidi **b119**, 595 (1983).
[8]T. N. Morgan, Phys. Rev. Lett. **21**, 819 (1968).

Translated by Dave Parsons