

asymmetrical carbon atom, which separates the donor NH group from the benzene ring. This hinders the intermolecular charge transfer and is accompanied by a sharp decrease of the second-harmonic generation efficiency, in spite of the absence of a symmetry center. The fourth substance has a benzene ring with two substitutes of identical (donor) type in the para-position. In this case the dipole moments induced by the charge transfer cancel each other. The efficiency of second-harmonic generation then decreases. In all the remaining investigated compounds the effective frequency conversion (on the order of that of lithium niobate) is observed only in those cases when, owing to the presence of donor and acceptor substitutes bound with the conjugate system, the first allowed electronic transition is accompanied by charge transfer.

Thus, besides the requirement that there be no symmetry center, the existence of charge transfer upon excitation of the molecules is one of the most important conditions determining the magnitude of the nonlinear susceptibility  $\chi^{NL}(2\omega)$ , on which the efficiency of second laser harmonic generation in molecular crystals depends.

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#### SHIFT OF SINGULARITIES OF GERMANIUM LATTICE VIBRATION SPECTRUM UNDER PRESSURE

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As is well known [1, 2], a number of singularities of the lattice vibration spectrum becomes manifest in the tunnel characteristics of degenerate semiconductors. In germanium these are the energies of the TA, LA, LO, and TO modes of the [111] vibrations on the boundary of the Brillouin zone. Accordingly, these energies,  $\omega$ , can be determined with high accuracy from the tunnel characteristics. We present below results of an investigation, under hydrostatic pressure, of the shift of the indicated singularities of the germanium-lattice vibration spectrum. Similar measurements were carried out earlier only under uniaxial stresses [3].

The method of producing the hydrostatic pressure and of investigating the tunnel characteristics does not differ in the main from that employed earlier [4]. All the measurements were made at 1.3°K and pressures up to 18 kbar. Application of pressure did not cause any irreversible changes of the characteristics of the transitions in the entire investigated region. Plots of  $d^2U/dI^2$  at different pressures at one of the transitions are shown in Fig. 1. The energy of the singularity of the germanium lattice vibration spectrum was determined as the center of the corresponding maximum of  $d^2U/dI^2$ , with a possible error of about 0.04 meV.

A number of diodes revealed, besides the TA, LA, LO, and TO singularities typical of germanium, also a singularity near 38 meV (Fig. 1). It is obviously

due to the appearance of the frequency RO. The value of  $\omega_{RO}$  determined from the tunnel characteristics is in satisfactory agreement with the values obtained by the neutron-diffraction [5]  $\omega = 37.2 \pm 1.2$  meV and by optical measurements [6]  $\omega = 37.8$  meV.

Using similar diodes, it was possible to investigate the pressure-induced shift of five singularities of the germanium lattice vibration spectrum.

Figure 2 shows the values of  $\omega$  for different pressures. Similar results were obtained with diodes made of germanium doped with both Sb and As. In the latter case, however, the singularities were not so strongly pronounced, and the accuracy with which  $\omega$  was measured was lower. All the numerical values are listed in the table. In the calculation of the Gruneisen parameter  $\gamma = d \ln \omega / d \ln V$  we used the data of [7] on the compressibility of germanium.

The results evidently indicate that in germanium the optical vibration modes

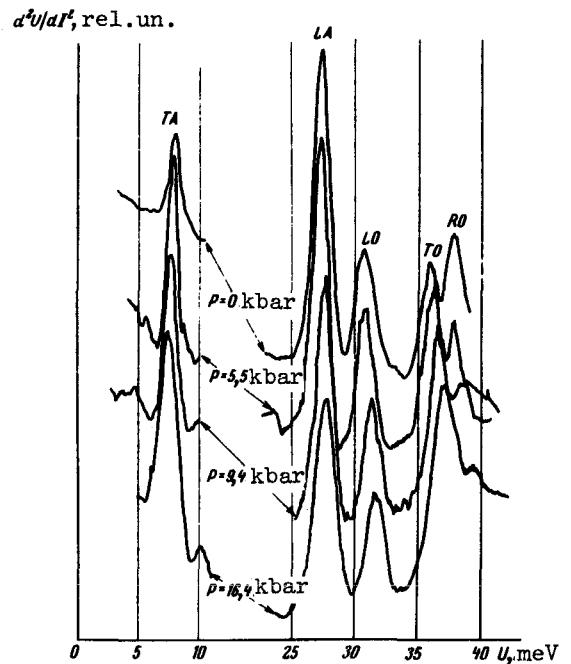


Fig. 1

	TA	LA	LO	TO	RO
Energy $\omega$ , meV	7.82	27.42	30.72	36.04	37.97
$d\omega/dP \cdot 10^{-5}$ , meV/bar	$-1.65 \pm 0.2$	$1.50 \pm 0.3$	$6.3 \pm 0.3$	$5.7 \pm 0.3$	$5.6 \pm 0.3$
$d \ln \omega / dP \cdot 10^{-6}$	$-2.11 \pm 0.25$	$0.545 \pm 0.008$	$2.05 \pm 0.08$	$1.57 \pm 0.08$	$1.48 \pm 0.08$
$\gamma = d \ln \omega / d \ln V$	$-1.6 \pm 0.2$	$0.42 \pm 0.06$	$1.57 \pm 0.06$	$1.21 \pm 0.06$	$1.13 \pm 0.0$

are shifted to a greater degree than the acoustic modes with changing interatomic distance. This result, and all the more the fact that  $\gamma$  has different signs for TA and LA, confirms the theoretical assumptions that the spectrum of the germanium lattice vibrations is determined by several forces of different character. Thus, for example, in Cochran's model [8, 9], each atom is subdivided into a heavy "core" and a weightless "shell," which are coupled by quasielastic forces. Analogous forces couple the core and the shell of each atom with the cores and shells of the neighbors. The interaction forces can accordingly be subdivided into those connected with the mutual arrangement of the cores, and the dipole forces due to the shift of the shells.

The negative value of  $\gamma_{TA}$  was to be expected from the results of [10, 11], in which the anomaly of the thermal expansion of germanium was analyzed phenomenologically [12]. The values of  $\gamma_{TA}$  calculated in these papers differ, however, by several times from the experimental value ( $\gamma_{\text{theor}} \approx -0.3$ ,  $\gamma_{\text{exp}} = -1.6$ ). To eliminate this disparity one could propose, for example, a stronger dependence of the dipole forces on the interatomic distance than is proposed in [10]. The change of the interatomic distance as a result of the

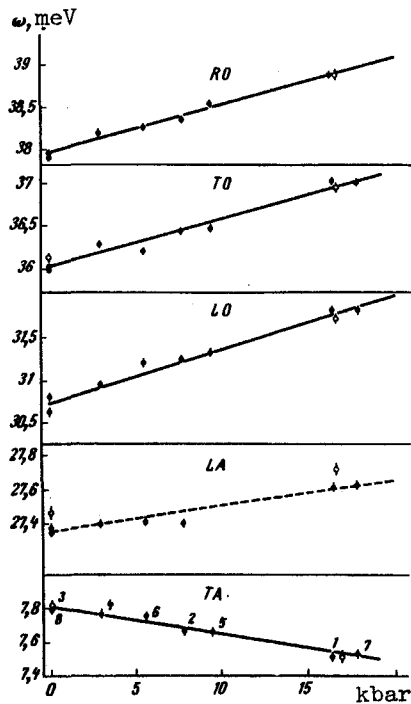


Fig. 2. Pressure dependence of the positions of the singularities of the germanium lattice vibration spectrum. The numbers on the TA curve show the sequence of the experiments.

thermal expansion also causes a shift of the lattice vibration frequencies. For germanium, the corresponding neutron-diffraction measurements were made in the interval  $100 - 700^\circ\text{K}$  [13]. For all the vibration modes,  $(\partial \ln \omega / \partial T)_P = (-7.5 \pm 0.8) \times 10^{-5} \text{ deg}^{-1}$ , which is much higher than the value  $d \ln \omega / dT$  that can be calculated from the obtained values of  $(d \ln \omega / dP)_T$  and the coefficient of thermal expansion. This contradiction can be eliminated by assuming that germanium is subject to an appreciable change of  $\omega$  as a result of the contribution from the phonon-phonon interaction (see [4]). The values of  $(\partial \ln \omega / \partial T)_V$  calculated from our data and from [13] are  $-11 \times 10^{-5}$ ,  $-7 \times 10^{-5}$ , and  $-5 \times 10^{-5} \text{ deg}^{-1}$  for TA, LA, and TO, RO singularities, respectively. Observation of a large value of  $(\partial \ln \omega / \partial T)_V$  and the complicated character of the shift of the spectrum under pressure are undoubtedly of interest. It is obvious that the lattice-vibration spectrum of the germanium and of similar substances deserves further study.

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#### ELECTRON SHOCK WAVES IN A COLLISIONLESS PLASMA

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Attention was called recently to the fact that the spreading of a bunch of hot electrons in a collisionless plasma can be strongly retarded by collective effects [1].