

crystallization of the anthraquinone, and the lower corresponds to the illuminated section. Observation and photography were carried out in a polarization microscope in reflected polarized light. It is seen from the microphotograph that the illumination, without changing the direction of the texture axis (in both cases we have a uniaxial needle-like texture), changes the orientation of the crystals and decreases somewhat their concentration. Needle-like anthraquinone crystals on the illuminated section are turned through a certain angle around the texture axis compared with the crystals on the illuminated section. It is possible that what we have here is not a rotation but a change in the morphology of the faces of the [001] belt. This is seen from the fact that the extinction angle for both groups of crystals, when observed through an analyzer, turned out to be different. At the same time, when the crystals are observed in transmitted polarized light, the extinction angle is the same, since the optical indicatrices of the crystals are parallel. This, in particular, explains why the obtained images were more contrasty in reflected light than in transmitted light. Similar observations were performed also for images obtained on germanium.

We call attention to the analogy between the photoepitaxy on semiconductors, described above, and a phenomenon called by us earlier sensitized photolysis on semiconductors [2]. Apparently the change of the crystallization-center density is connected with optical charge exchange on the surface centers of the semiconductor, and the change of the orientation of the crystals is connected with the structure of the charge-exchanging centers. At any rate, this mechanism agrees with the recent notions concerning the role of charge centers in epitaxy [1]. The epitaxy phenomenon apparently has a general character and, in principle, should be observed for all semiconductors on the surface of which oriented crystallization takes place.

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CONNECTION BETWEEN CHARGE TRANSFER AND LASER SECOND HARMONIC GENERATION

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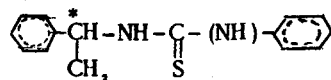
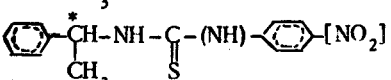
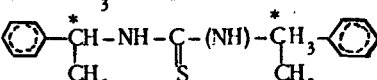
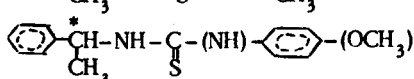
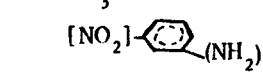
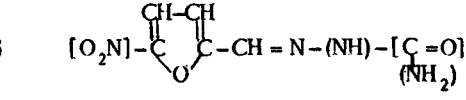
Several recent communications reported observation of intense second-harmonic generation of neodymium-laser emission in molecular crystals [1 - 3]. The choice of substances used for frequency doubling was in effect accidental. We report in this paper observation of a connection between the effective second-harmonic generation and the nature of the electronic transitions of the molecules. The observed connection enables us to estimate qualitatively the nonlinear properties of molecular crystals, by starting from the structure of its component molecules.

It is known that in order to obtain effective transformation it is necessary to match the phases of the first and second harmonics of the radiation and to have a sufficiently large nonlinear susceptibility, $\chi^{NL}(2\omega)$ [4].

$\chi^{NL}(2\omega)$ differs from zero only when the crystals have no symmetry center [1]. By virtue of the resonant character of this susceptibility, the largest contribution of $\chi^{NL}(2\omega)$ is made by the allowed electronic transition closest to the frequency 2ω . We can therefore confine ourselves in the analysis of frequency doubling to consideration of a two-level system.

For such a system $\chi^{NL}(2\omega)$ is proportional to the square of the matrix element of the transition and to the change of the diagonal component of the dipole moment. [4]. In order to make $\chi^{NL}(2\omega)$ large it is necessary that the electronic transition have a high intensity and be accompanied by a reorientation or by an appreciable change of the dipole moment of the molecules. Of all the known types of electronic transitions ($\sigma-\sigma^*$, $\pi-\pi^*$, $n-\pi^*$, intramolecular charge transfer, etc. [5]), intramolecular charge transfer satisfied these conditions most readily. It is usually observed in molecules that include benzene rings or other systems of conjugate bonds with substitutes of the donor (NH_2 , OH , OCH_3 , halogens, CH_3) or of the acceptor type ($\text{N}(\text{CH}_3)_3$, COOH , SO_3H , NO_2). The substitutes are listed in order of decreasing donor or acceptor properties [6]. If the presence of the intramolecular charge transfer actually is one of the conditions of effective second-harmonic generation, then the largest nonlinear susceptibility $\chi^{NL}(2\omega)$ should be possessed by molecules in which the donor and acceptor groups enter in a conjugate π -electron system.

To demonstrate experimentally the influence of the nature of the electronic transitions on the efficiency of second-harmonic generation, we investigated more than 100 organic compounds. The experiments were performed with substances in the powdered state, in a setup that differs from the system described in [2] in the presence of a monochromator used to separate the second-harmonic radiation. The excitation power density was $\sim 100 \text{ MW/cm}^2$. The conversion efficiency was determined by comparison with powdered lithium niobate. The connection between the efficiency of generation of the second harmonic with the charge transfer is best demonstrated by using the substances listed in the table as examples.

№ Structure formula	Second harmonic generation efficiency
1 	3
2 	10
3 	0.1
4 	0.1
5 	10
6 	10
7 LiNbO_3	10

The asterisks mark asymmetrical carbon atoms. The donors are in round brackets and acceptors in square brackets.

The first substance has a donor NH group, and the second, fifth, and sixth have donor and acceptor groups connected with the benzene ring. Excitation of such substances should be accompanied by intramolecular charge transfer [5]. All these substances have a noticeable second-harmonic generation efficiency. The third substance differs from the first in the presence of an additional

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, ω , 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