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COOPERATIVE TUNNEL EFFECT IN CRYSTALS

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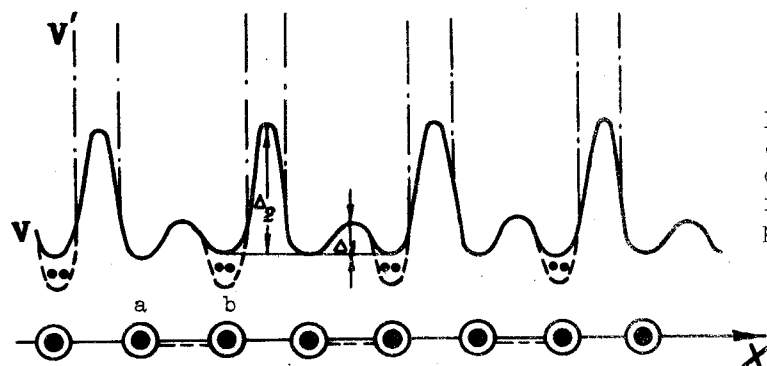
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In crystals consisting of one-dimensional molecular chains, alternation of the internuclear distances can occur both as the result of configuration instability and as a consequence of the energy features of the packing of the molecules in the crystal.

The purpose of the present paper is to show that in systems of this type, when the three-dimensional interaction is important, one can observe the effect of ordered localization of the electrons over the atomic centers; this effect is due to a cooperative process. If each center of the chain supplies the system with one electron, then ordered localization of electron pairs may arise¹⁾.

We separate in the crystal an infinite chain $(A)_\infty$ consisting of weakly-coupled groups of atoms (complexes) A, which supply one electron for the formation of the bond in the chain. The real potential function of the chain V will be approximated by a one-dimensional potential V' (see the figure), which separates a pair of complexes A-A with a tunneling pair of electrons. Such an approximation is natural and is the limiting case of alternation. The exchange interaction between the electron pairs will be taken into account later. To describe the electron system V', we use the quasispin formalism proposed by



Potential curve for a polyene chain $(A)_\infty$. The dashed line denotes the potential curve in the case of a cooperative process.

¹⁾In the case when two neighboring centers deliver to the system one electron, ordered localization of one electron will take place.

De Gennes [1], and write the Hamiltonian per unit cell, consisting of the interacting fragments of one-dimensional chains,

$$H = 2\Omega \sum_i X_i - \sum_{ij} I_{ij} Z_i Z_j, \quad (1)$$

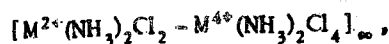
where 2Ω is the reciprocal of the tunneling frequency, and represents the difference between the energies of the last occupied and the first free electron states in the complex pair A-A; I_{ij} describes the electrostatic interactions between the pairs of electrons in neighboring double wells in the unit cell of the crystal; X_i and Z_i are the components of the quasispin operator. The Hamiltonian H is diagonalized in the stated manner. The Heisenberg equation for the components of the quasispins has two solutions, one of which corresponds to the ordered state, when the pairs of electrons are either in even (a) or in odd (b) wells. In this case, owing to the cooperative interaction of the well, a and b become non-equivalent and a dipole moment directed along the chain axis occurs. Such a situation corresponds to the solution $\sin \theta = \eta_0/\eta$, where θ is the angle of rotation in the plane XZ, η determines the degree of non-equivalence, and $\eta_0 = 2\Omega/I$, where $I = \sum_{ij} I_{ij}$. The second solution corresponds to the disordered state. In the molecular-field approximation, the critical temperature of the order-disorder transformation is determined by [2]

$$kT_k = \frac{\Omega}{\arctanh[2\Omega/I(1-x)]}, \quad (2)$$

where $x = p_i/p_{i+1}$ is the degree of delocalization of the electrons over the chain, characterizing the height of the barrier Δ_2 (see the figure), and p_i and p_{i+1} are the electron densities at the bonds (A-A)_i and (A-A)_{i+1}. In a weakly bound chain $\Delta_1 \neq \Delta_2$ owing to the configuration instability. Assuming a linear dependence of the bond length on the population, $r_i = L - \omega p_i$, and an exponential dependence of the binding integral $\beta(r_i) = \beta_0 \exp(-r_i/a)$, we obtain

$$p_i - p_{i+1} = \frac{a}{\omega} \ln \frac{\beta(r_i)}{\beta(r_{i+1})} = \frac{a}{\omega} \ln \gamma.$$

If γ is close to unity, then the alternation of the populations is strong when $a/\omega \gg \ln \gamma$. This condition is realized in a weakly bound chain, where $a \gg \omega$. There exists a critical value of the degree of delocalization, $x_{cr} = 1 - 2h\Omega/I$, when $x > x_{cr}$ the ordered state is impossible. The proposed model of electron localization as the result of cooperative ordering at $T < T_k$ explains the anomalously high value of the dielectric constant of the chains. The described effect of electron-pair localization is realized in chains of semiconductor crystals with forbidden-band widths $2\Omega = 0.1 - 0.5$ eV, of the type



where $M = Pd, Pt$ [3, 4], and possibly also in the crystals $D_2SbCl_6^{(2)}$, where $D = Cs, Rb, NH_4$, and in crystals of tetracyanoquinodimethane (TCQM) [5], which have a high dielectric constant at helium temperatures.

²⁾The results of the investigation will be published in JETP Lett. in 1971.

The crystals D_2SbCl_6 consist of individual octahedra, the centers of which are spaced $7.5 - 10.66 \text{ \AA}$ apart, so that two-electron delocalization is perfectly realistic, as is the case in Josephson tunnels [6]. The method of nuclear γ resonance (NGR) at liquid-nitrogen temperature has made it possible to establish the presence of antimony ions with different degrees of oxidation (Sb^{3+} and Sb^{5+}), thus indicating the effect of localization of electron pairs as a result of the cooperative process. We note that in those cases when the phase-transition temperature exceeds the critical temperature of the cooperative tunnel two-electron transition, the latter temperature can be determined by the NGR method from the coalescence of the two absorption maxima into one (in the absence of quadrupole splitting).

In subsequent papers we shall present estimates of T_k for concrete systems, for the case of strong electron-phonon interaction.

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SUPPRESSION OF STIMULATED RAMAN SCATTERING IN A DISPERSIVE MEDIUM WITH A NON-LINEAR REFRACTIVE INDEX

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1. We report here the results of a theoretical and experimental investigation of the features of SRS of intense and picosecond and nanosecond light pulses in self-focusing liquids. The anomalous broadening of the pulse spectra, due to the nonlinearity of the refractive index, is accompanied by an appreciable decrease in the SRS intensity, and in many cases by its complete suppression. It has been established that this effect is due to simultaneous influence of rapid phase modulation of the pump, resulting from the nonlinearity of the medium, and the dispersion of the medium. The corresponding generalization of the nonstationary SRS theory makes it possible to obtain quantitative relations for this regime, which heretofore has not been investigated.

The decrease of the SRS intensity in liquids in self-focusing beams was observed in [1 - 3], but the reason of this effect was not established. It was noted in the theoretical papers [4, 5] that this can be caused by simultaneous influence of the dispersion of the medium and phase modulation of the pump, but no concrete results are given in the cited papers.

2. Experiments on SRS in self-focusing media were performed by us with the second harmonic of a neodymium laser operating in the single-mode regime (pulse duration $\tau_p \sim 10^{-8}$ sec) and in the mode-locking regime ($\tau_p \sim 3 \times 10^{-12}$ sec). Anomalous broadening of the spectrum, reaching 1000 cm^{-1} in nanosecond pulses and more than 1000 cm^{-1} in picosecond pulses were observed in carbon disulfide in a collimated beam (see Fig. 1). At a cell length $l = 10 \text{ cm}$, a broadening larger than 500 cm^{-1} leads to a practically complete suppression of the first Stokes component of the SRS. To determine the cause of the