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STUCTURES WITH BROKEN TRANSLATIONAL SYMMETRY

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ABSTRACT

This paper reviews the results of few years of research on effects created in structures with broken translational symmetry along one direction. The research is carried on the different systems: phonons, excitons and ferroelectrics. It is shown that the existence of boundaries drasticaly changes the system with respect to the threedimensional non-broken system. Existence of surface states, changes in dispersion laws, and specific temperature dependences on the ordering parameters, are observed in broken symmetry structures.

INTRODUCTION

In theory of condensed matter, the structures which are spatially homogeneous and have translational invariance are most frequently analysed. The fact that, these structures conserve momentum (or quasimomentum) simplifies the mathematical analysis. In reality, ideally pure structures do not exist. Every crystal, regradless of fineness and purity, contains number of impurities and defects which break the translational invariance and momentum is not conserred. Besides, the crystals have boundary surfaces and with them the specific effects which cannot be investigated by methods for ideal structures. The standard method cannot be used for amorphous structures, or liquids. All of this points to the significance of analysis of structures with broken symmetry. The mathematical analysis of these structures is much more complicated than the analysis used for ideal structures, so that the contributions in mathematical methods in this area are most wellcome. From this point of view the research of the effects of broken symmetry structures becomes significant in the sense of opening the new mathematical

methods which would not only contribute to the development of theory of broken symmetry structures but the development of mathematics as well.

Here, we will analyse some effects of broken symmetry in molecular crystals, ferroelectrics and metallic structures.

1. PHONONS IN STRUCTURES WITH BROKEN SYMMETRY

The analysis of phonons in structures with broken symmetry is useful since phonons are always present as a subsystem regardless of weather we have excitons, electrons, excitations in ferroelectrics or any other type of elementary excitations in crystal. Besides, phonons in structures of broken symmetry are somewhat simpler, so the analysis in this paragraph could be taken as an introduction to mathematicaly rather complicated analysis found in excitonic and ferroelectric excitations in structures with broken semmetry.

Observing the collective mechanical oscillations in a simple cubic structure where we assume that the breaking is along just one of the axis (z-axis). In the planes normal to the z-axis the crystal will be treated as an ideal continuous structure, i.e. without symmetry breaking, in order to simplify the calculations, we assume the strain coefficients of elasticity to be equal to zero, i.e. $C^{\alpha\beta} = 0$; $\alpha \neq \beta$, $\alpha,\beta = (x,y,z)$. Using the mentioned assumptions, the Hamiltonian of the phonon system, in nearest neighbours approximation, as in |1| , can be written in the form:

$$H = \sum_{\vec{n}\beta} \frac{1}{2M_{\vec{n}}} (\vec{p}^{\beta}_{\vec{n}})^2 + \frac{1}{4} \sum_{\vec{n}\vec{\lambda}\beta} C^{\beta\beta}_{\vec{n}}(\vec{\lambda}) (u^{\beta}_{\vec{n}} - u^{\beta}_{\vec{n}-\vec{\lambda}})^2 \qquad (1.1)$$

Our aim is to investigate the displacements $u^{\beta}_{\vec{n}}$ in broken symmetry structures. Symmetry breaking in expression (1.1) comes from the assumption that the structure is composed of difetent types of atoms (the dependence of M on the lattice point $\vec{n}$), and the strain coefficients $C^{\beta\beta}_{\vec{n}}(\vec{\lambda})$ dependence on the lattice vector $\vec{n}$. On the basis of the morement equations for the operators p and n we obtain the equation which regulates the behaviour of displacements in the observed system.

$$\omega^2 u_{\vec{f}}^{\alpha} = \frac{1}{2M_{\vec{f}}} \sum_{\vec{\lambda}} C_{\vec{f}}^{\alpha\alpha}(\vec{\lambda})(2u_{\vec{f}}^{\alpha} - u_{\vec{f}+\vec{\lambda}}^{\alpha} - u_{\vec{f}-\vec{\lambda}}^{\alpha}). \qquad (1.2)$$

Expressing the lattice vector $\vec{f}$ as:

$$\vec{f} = (f_x, f_y, f);\ -\frac{N_x}{2} \leqslant f_x \leqslant \frac{N_x}{2};\ -\frac{N_y}{2} \leqslant f_y \leqslant \frac{N_y}{2};\ 0 \leqslant f \leqslant N$$

where $(N_x+1)(N_y+1)(N+1)$ represents a total number of atoms (molecules) in the crystal, we will look for the solution of (1.2) in the form:

$$u_{f_x,f_y,f}^{\alpha} = u_f^{\alpha} \cos(f_x k_x + f_y k_y)a, \qquad (1.3)$$

where a is the lattice constant.

The result of the preceding procedure is the following system of equations:

$$u_{f+1}^{\alpha} + u_{f-1}^{\alpha} - Q_f^{\alpha\alpha} u_f^{\alpha} = 0;\quad f = 1,2,\ldots, N-1 \qquad (1.4)$$

$$u_1^{\alpha} - Q_o^{\alpha\alpha} u_o = 0;\quad f = 0 \qquad (1.5)$$

$$u_{N-1}^{\alpha} - Q_N^{\alpha\alpha} u_N^{\alpha} = 0;\ f = N \qquad (1.6)$$

The value Q which stands in (1.4,6) is separately defined for bulk and surface layers. Different forms of Q give different types of symmetry breaking. The simplest form of symmetry breaking we have, in the case of semi-infinite structures where the boundary condition in the layer N (eq. 1.6) is not taken into account since $N \sim 10^8$ is a rather large value. Other would be thin films ($N \sim 10^2 - 10^3$) where besides eq.(1.4), we must use both boundary conditions (1.5; 6). The analysis of the structures show that they posses both the surface and volume phonon states |3|. Finally we can investigate the case of multi layer structures, where we assume that the values Q change on the outer boundary surfaces and on the contact layers, where as in the interior they are independent of position. All of the mentioned cases of broken

symmetry will be investigated in further paragraph, where the system of excitons will be analysed, and primarily because the difference equations of the (1.4; 6) type, are for the excitonic system more general than in the case of phonons. So it is better to analyse first the general equations, since the obtained results could serve for simpler equations as their special cases.

We will investigate now the continual approximation for a system of phonons, and this formaly means that from difference equation (1.4) we will go over to the corresponding differential equation. From the physical point of view it is clear that this change is justified only for the case of mechanical oscillations for the large wave lengths. Going over to a continuum is achived formally in a following way: $f \to z$; $N \to L$ where z is a continuous variable, equations (1.4-6) become respectively:

$$\frac{d^2u}{dz^2} + \left[\frac{\omega^2 M(z)}{a^2 C(z)} - k^2 \right] u(z) = 0 \qquad (1.7)$$

$$u(a) - 2\left[\left(1 - \omega^2 \frac{M(0)}{C(0)} + a^2k^2 \right] u(0) = 0 \right. \qquad (1.8)$$

$$u(L-a) - 2\left[1 - \omega^2 \frac{M(L)}{C(L)} + a^2k^2 \right] u(L) = 0 \qquad (1.9)$$

Basic problem in further calculations is the definition of the function $\frac{M(z)}{C(z)}$ which stands in (1.7). Determining proper dependence requires formation of a model based on the character of deformations in the investigated case. We supposed that $M(z) = M = \text{const.}$, $C = \text{const.}$, and on both outer surface symetric conditions are demanded, and due to these conditions on the boundaries we have $C(0) = C(L) = C+C'$, where the correction C' could be both positive or negative value. Finally, we take the function $\frac{M}{C(z)}$ to have the same value as in the ideal structure in the middle of the layer where $z = \frac{L}{2}$, and towards the boundaries it change according to the parabolic law:

$$\frac{M}{C(z)} = \frac{M}{C} - \alpha^2(z - \frac{L}{2})^2;\ \alpha^2 = \frac{4M}{L^2C}\frac{C'-C}{C'+C} \qquad (1.10)$$

It is evident that parabolic model makes sense only in the case where on the boundaries $|C'| > C$, and which we will assume further on. After the substitution of (1.10) into (1.7-9) we find that phonon displacements satisfy the Hermite-Weber equation, i.e. the solution can be written in the form:

$$u_n(\xi) = A_o e^{-(1/2)\xi^2} H_n(\xi);\ \xi = \frac{1}{\Lambda}(z - \frac{L}{2});\ \Lambda = (a/\alpha\omega)^{1/2} \qquad (1.11)$$

where $H_n(\xi)$ are Hermite polynomials, with the condition (see |4| for details):

$$\Lambda^2(\frac{M\omega^2}{Ca^2} - k^2) = 2n + 1;\ n = 0,1,2, \ldots$$

which defines the allowed phonon frequencies in the observed structure.

$$\omega_n = (2n+1)\frac{a}{L}\left(\frac{C}{M}\left|\frac{C'-C}{C'+C}\right|\right)^{1/2} + \left(\frac{a^2C(2n+1)^2}{L^2M}\frac{C'-C}{C'+C} + \frac{Ca^2k^2}{M}\right)^{1/2} \qquad (1.12)$$

Due to the presence of boundary conditions, it is evident that parameters M,C,C′ and L are not mutually independent.

In order to investigate the conditions of existence of phonon states with energies (1.12) we will restrict ourselves to energies of the ground state, i.e. the states when n = 0.

$$\omega_o = \frac{a}{L}\left(\frac{C}{M}\left|\frac{C'-C}{C'+C}\right|\right)^{1/2} + \left(\frac{a^2C}{L^2M}\left|\frac{C'-C}{C'+C}\right| + \frac{Ca^2k^2}{M}\right)^{1/2} \qquad (1.13)$$

$$u_o = A_o \exp\left[-\frac{1}{2}\frac{(z-(L/2))^2}{\lambda^2}\right] \qquad (1.14)$$

In the basis of (1.13) we can conclude that, contrary to the ideal structure in which dispersion law for phonons is given by $\hbar\omega = \hbar ak\sqrt{\frac{C}{M}}$; $k = \sqrt{k_x^2+k_y^2+k_z^2}$, the phonons in investigated

structures have gap in the dispersion law which in of the order $G = \frac{a\hbar}{L}(\frac{C}{M}|\frac{C'-C}{C'+C}|)^{1/2}$. This, on the other hand means that the average number of phonons bahaves according to $e^{-(G/\theta)}$ law, where θ is the temperature in energy units while the average number of phonons in the ideal structure bahaves according to the θ^3 law and increases much faster with the temperature increase. This conclusion is very important if we have a case of metallic superconducting structure. In the structure which we investigated here we found only one phonon branch existing, being of the optical type and therefore the average number of phonons in these structures is rather small. Besides, regulating the pressure we can increase the gap G (the difference $|C'-C|$ increases) and therefore decrease the average number of phonons to the desired value. The results are very useful for synthesis of more effective superdonducting structures from the one known presently.

2. SYMMETRY BREAKING AND EXCITONIC STATES

Here, we will give a short review of analysis of excitonic states in crystals with broken translational symmetry. Symmetry breaking manifests itself, first, in the excitation energy of isolated molecules and matrix elements of the dipol-dipol interaction which change from lattice point to lattice point. Symmetry breaking arises on the boundary layers of the crystal, or, if we speak of a multi layered structure the breaking occurs along the boundaries of entire structure as well as on the contact surface between the layers. We will analyse here the case of planar symmetry breaking, i.e. the symmetry breaking on the boundaries of the crystal or symmetry breaking in the multi-layer structures.

Hamiltonian of the excitonic system (taken in harmonic approcimations) for the structures with broken symmetry has a standard form |5|:

$$H = \sum_{\vec{n}} \Delta_{\vec{n}} B^{+}_{\vec{n}} B_{\vec{n}} + \sum_{\vec{n}\vec{m}} W_{\vec{n}\vec{m}} B^{+}_{\vec{n}} B_{\vec{m}} \qquad (2.1)$$

The consequences of the symmetry breaking are analysed by single-particle excitonic wave function

$$|\psi\rangle = \sum_{\vec{g}} A_{\vec{g}} B^{+}_{\vec{g}} |0\rangle \tag{2.2}$$

Using analogous procedure as in the previous paragraph we get the following difference equations:

$$M_{f,f+1}A_{f+1} + M_{f,f-1}A_{f-1} - R_f A_f = 0 \tag{2.3}$$

$$f = 1,2,\ldots, N-1$$

$$M_{01}A_1 - R_o A_o = 0;\ f = 0 \tag{2.4}$$

$$M_{N,N-1}A_{N-1} - R_N A_N = 0;\ f = N \tag{2.5}$$

where

$$R_F = E - \Delta_f - 2M_f(\cos ak_x + \cos a k_y) \tag{2.6}$$

In general, difference equation (2.3) is rather complicated for solving, so we will investigate the simpler cases. Let us see first the semi-infinite structure [6-9] where we, due to the large number of N, neglect the effects on layer N ($N \to \infty$) and disregrad equation (2.5). Besides, we assume that on the layer f=0 the excitation energy of an isolated molecule changes for the value Λ_o, which can be both positive and negative, while it has the same value for all the other layers. For this case we get the spectrum of excitonic energies in the form:

$$E = \Delta + 2M(\cos a k_x + \cos ak_y) + 2M \cos a k, \tag{2.7}$$

and for probability amplitudes:

$$A_{f_x,f_y,f} = \left| e^{if_x ak_x + if_y ak_y} \left| \sin ak - \frac{1}{T - \Lambda_o} \sin(f-1)ak \right| \right. \tag{2.8}$$

Excitonic states with energies (2.7) and probability amplitudes (2.8) are called bulk states, since the probability $|A_f|^2$ possesses the equal distributed minimus and maximus along the crystal volume, which further means that excitonic excitations are evenly distributed over the whole crystal. Besides the volume states we can expect states localized on the level 0 and levels close to it. These states are called surface states.

For the case of thin film, i.e. case when N is not too large and renges from 100-1000, the calculations of coefficients A can be done using (2.3), with both boundary conditions (2.4) and (2.5). The excitonic energy for this case has the value:

$$E = \Delta + 2M(\cos ak_x + \cos ak_y) + \Lambda_o + \Lambda_N \qquad (2.9)$$

As can be seen, the excitons in films have two-dimensional zones in k-space and this represents the basic difference between the semi-infinite structures in which dispersion depends on three components. From the normalizing conditions for coefficients A we come to the existing conditions for bulk excitonic states in films

$$1 - \Lambda_o \Lambda_N = 1 - \frac{\Lambda_o \Lambda_N}{M} > 0 \qquad (2.10)$$

We can conclude that in films the excitonic excitations could be localized on one or the other or simultaneously on both boundary surfaces. In the last case it is necessary that he conditions on both voundaries be the same $\Lambda_o = \Lambda_N = \Lambda$ where $\left| \frac{\Lambda}{M} \right| > 1$.

In this section we will also analyse the case of the structure which is composed on two layers where one layer has L+1 molecules of one type and N-L molecules of the other type. We suppose that in layer 0 there is a change in excitation energy and interaction for molecules of the first type. In the inside of the first layer up to the layer with the index L-1 the excitation energy and interactions have the same values. In the layer L we have change in the excitation energy and interaction. Finally in N-th layer the molecules of the other type change the excitation energy and interaction since it represents the boundary layer. The case which corresponds to the described scheme is represented by general difference equation (2.3), which can be written in this form:

$$A_{f+1} + S_f A_{f-1} - K_f A_f = 0; \quad S_f = \frac{M_{f,f-1}}{M_{f,f+1}}; \quad K_f = \frac{R_f}{M_{f,f+1}} \qquad (2.11)$$

This type of mathematical problem is analysed by continnous fractions. From the continuons fraction we can calculate the coefficients A using generalized Chebyshevs polynomials of the type F |10| where the presented schematic approach could be generally applied to multi-layer structures. Specific calculations require use of a computer, although this numerical part of analysis is rather simplified due to the fact that in it we can use analytic formulas for the generalized Chebyshevs polynomials.

3. SYMMETRY BREAKING IN FERROELECTRICS

Here we observe the semi-infinite one dimensional ferroelectric where we will try to include into the calculation the effects of the broken symmetry structures on the boundaries and the temperature dependence. We decided to work with the one-dimensional structure, since in ferroelectrics properties of threedimentional system appear as a result of dynamic of one-dimensional structures composed of O-H-O bonds.

Hamiltonian of ferroelectrics can be written in the form (as in |11,12|):

$$H = \sum_n \Delta_n P_n^+ P_n - \frac{1}{2} \sum_{nm} X_{nm} P_n^+ P_m - \frac{1}{2} \sum_{nm} I_{nm} P_n^+ P_n P_m^+ P_m \qquad (3.1)$$

I_{nm} are the interactions between O-H-O bonds while the value X_{nm} which is one order of magnitude smaller than I_{nm} characterizes the tunneling of protons through bonds and transfer the excitation from lattice point to lattice point.

In order to include temperature effects and having in mind Tyablikov's decoupling of Greens functions |13| we go over to the equivalent Hamiltonian (more details about this in |12|) where we still have to change from Pauli to Bose operators (using |14|)

$$H_{eq} = \sum_n (\Delta_n - \sum_m L_m I_{nm}) B_n^+ B_n - \frac{1}{2} \sum_{nm} X_{nm} (1-2L_n) B_n^+ B_m \qquad (3.2)$$

where $L_m = P_m^+ P_m$, and B^+ and B are Bose operators.

It is simple to show that Hamiltonian (3.2) gives the same dispersion law as Hamiltonian (3.1) if we use Tyablikov's approximation using (3.1), and equivalence of these two Hamiltonians is meant only in this sense. For further analysis of ferroelectrics we will use Hamiltonian (3.2) assuming that for atom 0, the values I_{01} changes, while the change in value X_{01} will be neglected since $X_{01} << I_{01}$. For the interior atoms the values $I_{n,n\pm1}$ and $X_{n,n\pm1}$ have for every n the same value. The boundary effects on N are neglected since $N \sim 10^8$. The analysis will be done analogously to the previous paragraph, and this means that we will search the probability amplitudes A for a single particle wave function (2.2). If we are restricted to the nearest neighbour approximations and take into consideration the previously mentioned assumptions about I and X changings, we come to the following difference equations:

$$A_{f+1} + A_{f-1} + TA_f = D;\ f = 2,3,\ldots,N \tag{3.3}$$

where

$$T = \frac{2(E - \bar{T})}{\sigma X};\ \sigma = 1 - 2\bar{L} = 1 - 2 < p^+p > \tag{3.4}$$

We took the average numbers of I in the interior of the structure not to depend upon the index of O-H-O bond. For a bond of index 0 we take that $I_{01} = I + I'$ and $X_{01} \approx X$. The average number of excitations on the point 0 we will denote by I_o and this number is different from the average numbers in the interior of the structure. I we look for the solution of equation (3.3) in the form:

$$A_f = \alpha \sin f\,a\,k + \beta \sin(f-1)\,a\,k \tag{3.5}$$

so the energies are given in the following form:

$$E = \sigma(I - X\cos a\,k) \tag{3.6}$$

If were express eq (3.3) for f = 0 and f = 1, and on the basis of (3.4) and (3.5), we come to a relation which regulates the question of existence of excitation in semi-infinite ferroelectric.

$$I' = \left(\frac{\sigma}{\sigma_o} - 1\right)I. \tag{3.7}$$

Since $\frac{\sigma}{\sigma_o}$ is temperature dependent value it is evident that excitations can happen only for some fixed temperature

for which the condition (3.7) is satisfied and the values of the temperature regulated by the relation of the values I and I′. Besides, it must be stressed that condition (3.7) gives a connection between the ordering parameter σ of the interior of the structure and ordering parameter σ_o on the boundary. Explicitly written this connection (given obtained in |5|) has the form:

$$\sigma = \frac{\sigma_o}{1 + I'/I}, \qquad (3.8)$$

which means that in thermodynamic calculations we do not have to calculate both ordering parameters, one of them is just enough.

CONCLUSION

This paper gives a short review on the effects of symmetry breaking for molecular crystals, ferroelectrics and phonons. For molecular crystals we investigated the surface and bulk states for the semi-infinite structures and thin films. For ferroelectrics we investigated the bulk and surface states but differing from the excitonic system, here we calculated also the thermodynamic effects. Besides excitonic and ferroelectric excitations we investigated also phonons in thin films. The model of parabolic deformation is formulated, which can be practically achived with proper distribution of external pressure.

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