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NEW METHODS FOR APPLYING THE SYMMETRY THEORY OF STEREOREGULAR POLYMERS FOR QUANTUM-MECHANICAL MODELLING OF PHOTOVOLTAIC TYPE MATERIALS

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It is well-known, that the detailed experimental and theoretical investigation of basic structural and physical properties of different types of carbon nano - tubes plays a role of continuously increasing importance in the whole condensed matter physics, because of the very promising experimental investigation results about solar energy applications, too. Among them, the very powerful symmetry analysis methods based on the representation theory of symmetry groups of the ideal, and infinitesimally long discrete chain-type subsystems accepted as the relevant ones. The adequate quantum mechanical analysis of the collective elementary excitations was developed by applications of the representation theory of line groups. In order to apply our own earlier theoretical results in this contemporary research area, we decided to extend them in more details, in order to give new, original significant contributions to the theoretical modeling of the basic optical properties of the stereoregular polymers and carbon nanotubes at the quantum-level.

***Keywords**: Alternative energetics, nanotechnology, symmetry theory, solar energetics, stereo-regular polymers*

INTRODUCTION

The applications of the projective representations [1] of crystallographic point groups in solid state physics are known for decades but they are absent even from the most complete recent works about applications of line groups in various types of structural investigations of condensed matter systems [2]. These seemingly purely theoretical studies in the condensed matter physics may have very promising future applications in the field of solar energetics, too. Therefore, we decided to fill this gap, and have succesfully introduced the concept of the projective representations of line groups (= symmetry groups of discrete, chain-type molecular systems, usually called quasi-one-dimensional (*Q1D*) systems in the literature) together with some basic applications into theory of the incommensurately modulated crystal structures. In the present work, we will demonstrate explicitly the applicability of the same technique in the cases of optical scattering processes in incommensurate systems, including multiple-type Raman processes.

According to the definition, the complete set of symmetry transformations leaving invariant a *Q1D* system belongs to one of the (discrete) infinitely many line groups gathered into 13 families. The irreducible representation $D^{(\mu)}(L)$ of a full line group L can be obtained from the irreducible representation of symmetry groups (concretely: point groups) of the motifs: $D^{(\nu)}(P)$. The construction of the complete irreducible representation matrices is usually realized by use of the induction technique

elaborated in the group representation theory for decades, and widely applied in solid state physics (e.g. [2]), usually denoted by $D^{(\mu)}(L)=D^{(\nu)}(P)\uparrow L$). From the point of view of the applications in this study, we point out here the importance of the basic (helical) line group $Ln_p=(n/r)\otimes C_q^a$, on the base of which the irreducible representations of its can be directly obtained as a product of the irreducible representations of the constitutive subgroups, i.e. of the cyclic discrete rotational point group: $A_m\left(C_q^s\right)=e^{ims\alpha}$ (where "α" is the discrete-valued, elementary, smallest rotation around the main axis of the actual *Q1D* system) and of the subgroup of generalized translations n/r is given by: $D\left(R|v_R\right)\equiv {}_kA\left(\left(C_n^r|v\right)^t\right)=e^{ikt\zeta}$, where $k\in\left(-\frac{\pi}{\zeta},+\frac{\pi}{\zeta}\right]$, and ζ is the distance between nearest-neighbour scattering centre motifs in the given actual helical system.

On the base of this formalism (according to which the irreducible representation matrix of the relevant general line group element can be given as ${}_kA_m\left(\left(C_n^r|v\right)^t C_q^s\right)=e^{ikt\zeta}e^{ims\alpha}$), the formulae necessary for quantum-mechanical selection rules between an initial (*i*) and a final (*f*) state in chain-type systems are (*k* denotes the absolute value of a wave vector, *j* is an integer number of the possible allowed integer translations along the main axis of a *Q1D* system being investigated) [2]:

$$\Delta k\equiv k_f-k_i=k+j\frac{2\pi}{\xi},\left(j\in\mathbb{Z}\right) \quad . \tag{1}$$

Furthermore, it is a unique feature of the representation theory of line groups, that analogous relations expressing conservation of quasi-angular momenta during propagation of collective excitations along the main axis of the actual chain-type system must also be respected [3], i.e.:

$$\Delta m\equiv m_f-m_i=m+zq, \tag{2}$$

where the symbol *m* denotes one of the possible discrete momentum values, *z* is an integer number again, while *q* is the order of a simple cyclic rotation group, also characterizing allowed integer translations along the main axis of the system. In the present study, all these selection rule relations will be generalized within frame of the projective representations of line groups relevant for incommensurately modulated structures and incorporated into correlation functions necessary for comparison of experimentally measured-, and theoretically derived light scattering intensity curves. From newest applications of the representation theory of line groups in the condensed matter physics, relevance of this powerful symmetry method in the rigid-layer dynamics with applications in the Raman-, and infrared activity [4] must be particularly pointed out, because it may induce further novel-type experimental methods in this rapidly developing experimental research area, according to the relevant recent review articles. Finally, it must also be emphasized here, that by applications of the contemporary theory of the irreducible representations of line groups, the modulation types characterized by both rational-, and irrational $\vec{k}$ -s in the first Brillouin zone, can be equally treated [3].

METHODS

The basic informations summarized in the previous sections will be applied in detail by a new formalism presented in this section. The most essential feature of the forthcoming calculations is the following: the very basic-type selection rules of type (1) and (2) will be directly incorporated into the matrix elements of types (4), relevant for the Raman-type optical scattering processes of emission-, or absorption characterized by the frequency change Ω. (At this point, relevance of the basic results published already in [1,2] must be particularly pointed out, because they also represent in detail the irreducible representations of polar vectors, which are necessary for systematization of the perturbation matrix

elements at optical absorption processes in dipole approximation.) Besides, as it has been mentioned in the introductory part of this paper, the useful applications of the projective representations will also be taken into account, wherever possible.
Then, as it is known (e.g. [2]), at the case of the inelastic light scattering processes from crystals, the basic relations relevant for the phonon impulse-, and energy changes, are the following ones:

$$\begin{aligned} &\vec{k}_0 \pm \vec{k} = \vec{q}, \\ &\omega_0 - \omega = \mp \Delta\omega, \end{aligned} \tag{3}$$

where $\vec{k}_0$ and $\vec{k}$ are the wave vectors of the incident-, and scattered polarized monochromatic light beam, and $\pm\vec{q}$ is the wave-vector change in the given scattering process. Similarly, the symbols $\omega_0, \omega, \mp\Delta\omega$ denote relevant frequency (and the: adequate energy-) changes in the same light beam. It must be emphasized, that the wave-vector change expression in (8) is a relation of basic importance, and for an adequate, accurate descriptions of the light-scattering processes, the orthogonal-type transformations of the wave vectors must also be applied, for obtaining correct selection formulae relevant for them. Then, the dipole moment component in the ground state is [2,4]:

$$p_i(t) = \langle 0 | p_i | 0 \rangle + \sum_j \left\{ \alpha_{ij}(\Omega) E_{+j} \cdot e^{i\Omega t} + \alpha_{ij}(-\Omega) E_{-j} \cdot e^{-i\Omega t} \right\}, \tag{4}$$

where $\alpha_{ij}(\Omega)$ denotes the (-Hermitian – type-) polarizability tensor, and $E_{\pm}$ are the electric field components of the polarized light beam. Accordingly, we have:

$$\hat{\sigma}_{\pm} = (\beta) \vec{E} \cdot e^{\pm i\Omega t}, \tag{5}$$

where β is an electro-elastic tensor, equivalent to the polarization tensor in isotropic active optical media. Then, in order to realize this analysis in the case of the incommensurately modulated crystal structures, we will here firstly summarize all the expressions, which are accepted as the basic quantum-mechanical tools necessary for an accurate description of the Raman-scattering processes. Accordingly, at the optical transitions, related to the initial-, and scattered electromagnetic waves polarized along the relevant unit vectors $\vec{e}_i$ and $\vec{e}_j$ correspond to $p_i = \vec{e}_i \cdot \vec{p}, p_j = \vec{e}_j \cdot \vec{p}$. Then, the relevant total perturbation expression is given by $p_f R^{fi} p_i$, where R^{fi} denotes a component of the actual Raman-tensor. The basic selection rules in this type of scattering processes is related to examination of the direct product

$$D^P(L) \otimes D^P(L) \otimes D^{\left(k_i^{ph} m_i^{ph} \Pi_i^{ph}\right)}(L), \tag{6}$$

according to which [2], the decomposition of (6) must contain the identity representation too, in order to the given quantum transition to be possible. For an accurate, precise description of the new method of modelling calculations to be realized in this study, the results originally published in [3] and [6] are to be applied here, too. In general case, the quasi-impulse conservation law can be written as [2,6]:

$$\vec{w}_1' + \hat{\alpha}_0 \vec{w}_1 = \vec{K}, \tag{7}$$

where $\hat{\alpha}$ denotes a general orthogonal symmetry transformation operator, and the reciprocal space vectors $\vec{w}_i \left(i = \pm 1, \pm 2, ...\right)$ are related to the actual phonon modes of crystals and/or actual subsystems

of them containing finite atomic and molecular *Q1D* chains incorporated into (in-)finite two-dimensional (*2D*) nanolayers.
Finally, in agreement with the basic results about collective excitations in modulated crystals summarized e. g. in [5,6,7], we may accept the detailed classifications of the spectral terms, which emanated from the generalized versions of the selection rule types, as it has been demonstrated above.

CONCLUSIONS

In the present study, a detailed calculation method, necessary for elaborating of more advanced modelling applications of the light-matter interactions at quantum mechanical level has been proposed. The fundamental mathematical tools emanating from the representation theory of the symmetry groups of infinitesimally long discrete chain-type systems have been applied in a novel manner. On the base of this new – type mathematical concept, the quantum-mechanical selection rules relevant for incommensurately modulated 3-dimensional crystal systems have been successfully incorporated into the already developed formalisms in this research field. By this way, a new mathematical research tool has been introduced; whose applicability limits may be to be far beyond of the problem solution area indicated by this paper.

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