Raman scattering in crystals with order-disorder type phase transition

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The theory based on the "operator" two-time Green functions formalism applied for the construction of the polarizability operators entering the general expression for the effective cross-section of Raman scattering is developed. The presented microscopic scheme is applied to the investigation of the ferroelectrics with hydrogen bonds.

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1. Raman scattering tensor

The main characteristics of Raman scattering is the effective cross-section which can be expressed by Raman tensor [1]

$$\frac{1}{2\pi}\int\limits_{-\infty}^{+\infty}\mathrm{d}t e^{i(\omega_1-\omega_2)t}\langle\hat{P}^{\beta'\alpha'}_{\vec{k_2},-\vec{k_1}}(-\omega_1,t)\hat{P}^{\beta\alpha}_{-\vec{k_2},\vec{k_1}}(\omega_1,0)\rangle = H_{\beta'\alpha',\beta\alpha}(\omega_1\omega_2) \qquad (1.1)$$

where

$$\hat{P}^{\beta'\alpha'}_{\vec{k_2},-\vec{k_1}}(-\omega_1,t) = \mathrm{i}\int\limits_{-\infty}^{t}\mathrm{d}s\left[\hat{M}^{\beta'}(\vec{k_2},t),\hat{M}^{\alpha'}(-\vec{k_1},s)\right]e^{\mathrm{i}\omega_1(s-t)} \qquad (1.2)$$

is the polarizability operator; ω_1, ω_2 are frequencies; $\vec{k_1}$, $\vec{k_2}$ are wave vectors of the incident and the scattered light, respectively; α, β, α', β' are coordinate indices.

Here, $\hat{M}^{\beta}(\vec{k}) = \sum_n e^{\mathrm{i}\vec{k}\vec{R}_n}\hat{M}^{\beta}_n$ are the Fourier transforms of the dipole momenta operators of the unit crystal cell (n is the cell number).

$$\hat{\vec{M}}_n = \sum_k(e\hat{\vec{D}}_{nk} + z_k\vec{U}_{nk}) \equiv \sum_k\hat{\vec{M}}_{nk}, \qquad (1.3)$$

where $\hat{\vec{D}}_{nk}$ are the electronic operators; $\vec{U}_{nk}$ are the ionic displacements. The summation in (1.3) is fulfilled over ionic species in the cell (z_k is the ionic charge, k is the ionic type index); in (1.2) the operators are given in Heisenberg representation. In the semiphenomenological description of the Raman scattering the polarizability operators are presented as the expansions in vectors of ionic displacements. Equation (1.2) enables us to obtain the explicit form for the operator $\hat{P}^{\beta\alpha}_{-\vec{k}_2,\vec{k}_1}$; its specific features are determined by the Hamiltonian of the system. In the following we use the polarizability operator presented in terms of the "operator" Green functions [2]:

$$\hat{G}_{\hat{A}\hat{B}}(t,s) \equiv \left\{\left\{\hat{A}(t)|\hat{B}(s)\right\}\right\} = -\mathrm{i}\theta(t-s)\left[\hat{A}(t),\hat{B}(s)\right]. \tag{1.4}$$

where $\hat{A}(t), \hat{B}(s)$ are the operators written in Heisenberg representation. The statistical averaging of the $\hat{G}_{\hat{A}\hat{B}}(t,s)$ operator leads to the retarded two-time Green function $\left\langle\left\langle\hat{A}(t)|\hat{B}(s)\right\rangle\right\rangle$.

After the Fourier transformation we have

$$\hbar\omega_1\left\{\left\{\hat{A}|\hat{B}\right\}\right\}_{\omega_1,\omega_2} = \frac{\hbar}{2\pi}\left[\hat{A},\hat{B}\right]_{\omega_1-\omega_2} + \left\{\left\{\left[\hat{A},\hat{H}\right]|\hat{B}\right\}\right\}_{\omega_1,\omega_2}. \tag{1.5}$$

In the presence of small parameters, the equation of the (1.5) type makes it possible to construct the operator expansions for the Fourier transformants $\left\{\left\{\hat{A}|\hat{B}\right\}\right\}_{\omega_1,\omega_2}$.

By means of (1.3) and (1.4) the expression (1.2) for the polarizability operator may be presented as follows

$$\hat{P}^{\beta'\alpha'}_{\vec{k}_2,-\vec{k}_1}(-\omega_1,t) = -2\pi\sum_{nn'}\sum_{ll'}\mathrm{e}^{\mathrm{i}\vec{k}_2\vec{R}_n}e^{-\mathrm{i}\vec{k}_1\vec{R}_{n'}} \cdot \int\limits_{-\infty}^{+\infty}\mathrm{d}\omega'_1\left\{\left\{\hat{M}^{\beta'}_{nl}|\hat{M}^{\alpha'}_{n'l'}\right\}\right\}_{\omega'_1,-\omega_1}\mathrm{e}^{-\mathrm{i}(\omega_1+\omega'_1)t}. \tag{1.6}$$

Thus, the problem of the explicit expression for the polarizability operator is reduced to determining the Fourier transformant $\left\{\left\{\hat{M}|\hat{M}\right\}\right\}_{\omega'_1,-\omega_1}$.

2. Raman scattering on internal vibrations of ionic groups in crystals of KH_2PO_4

In the problem of Raman scattering by the crystals with a complicated structure, we dwell upon the scattering by the internal vibrations of ionic groups which can be in different configurations. Configurations are considered to mean different location of the structural elements which form an ionic group including the structural elements which can be ordered at phase transition. In the case when the vibrations of internal and external (translational and librational) modes differ essentially they may be considered independently.

Consider the case when characteristics of vibrations and related electron states depend on the configurations of some of the ionic complexes in the unit cell. Then

the Hamiltonian is written:

$$\hat{H} = \sum_{nk}\sum_{i}\left(\sum_{s_i}\lambda_{ks_i}^{(i)}\hat{X}_{nk}^{s_is_i}\right)N_{nk}^{ii} - \sum_{\substack{nk\\ \nu\alpha}}\sum_{i}\left(\sum_{s_is_i'}\theta_{k\nu\alpha}^{s_is_i'}\hat{X}_{nk}^{s_is_i'}U'_{nk\nu}^{i\alpha}\right)N_{nk}^{ii} + \hat{H}_{\text{ph}}. \quad (2.1)$$

Here, N_{nk}^{ii} is the occupation number of the i-th configuration of the complex (n,k); $\hat{X}_{nk}^{s_is_i'}$ are the Hubbard operators (see [3]) acting based on the electron states of the groups; $\lambda_{ks_i}^{(i)}$ denotes energy of the state s_i of the group k. We confine ourselves to the account of electron-vibrational interaction within individual ionic groups; $U'_{nk\nu}$ are the vectors of ion displacement from equilibrium positions (ν is the number of the ion in a group); $\theta_{k\nu\alpha}^{s_is_i'}$ is the interaction matrix. Beside the terms in (2.1) the total Hamiltonian includes the interaction energy of ionic groups (dependent on their configurations) which is responsible for the transition to the order state (in the case of the crystal possessing the order-disorder type phase transition).

Expression for the scattering cross-section can be written in terms of the Green function constructed of the polarizability operators [4].

In order to describe the one phonon Raman scattering by internal vibrations of ionic groups in the ferroelectric crystals with hydrogen bonds we apply configurational averaging and the approach of mean field type. As an example we consider the crystals of KH_2PO_4 (KDP)-type. In such crystals the various configurations of H_nPO_4 groups (n=0, 1,...,4) can be realized depending on the character of proton location in the double potential wells on the hydrogen bonds. The most probable between them are the configurations with two protons in the neighbourhood of the given complex PO_4 [5,6]. Confine ourselves to the account for such configurations only; their number is six, more preferable energetically are two of them with protons near the upper or lower (with respect to the crystal c-axis) oxygen atoms (figure 1). We consider the case $T > T_c$.
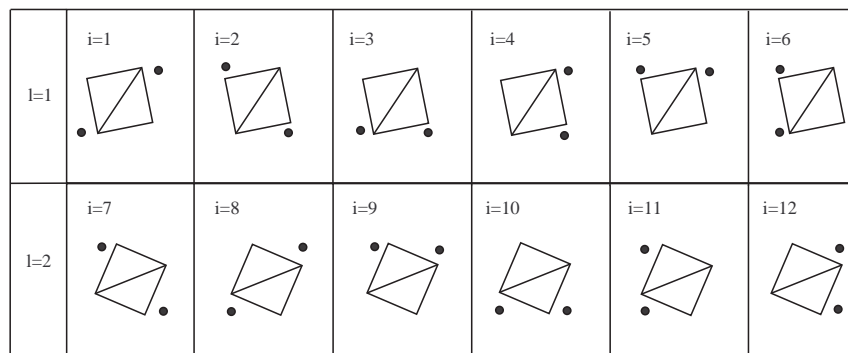

Figure 1. H_2PO_4 configurations for two sublattices of PO_4 groups in KDP crystal (projection to xy-plane).

For isolated PO_4 complex of the point symmetry T_d the internal vibrations are classified in terms of irreducible representations A_1 (ν_1 frequency); E (ν_2 frequency); F_2 (ν_3 and ν_4 frequencies). In the case of configurations i=1,2 (l=1), i=7,8 (l=2) they reduce to the modes of the symmetry A_1, B_1, B_2; $2A_1$, $2B_1$, $2B_2$; A_1, B_1, B_2, $4E$ respectively, and for configurations i=3,...,6 (l=1) and i=9,...,12 (l=2) into the modes with symmetry A_1, B_1, B_2, $2E$; $2A_1$, $2B_1$, $2B_2$, $4E$; $3A_1$, $3B_1$, $3B_2$, $6E$. Splitting of the frequencies ν_2, ν_3, ν_4 is insignificant when symmetry lowers and its value is not established experimentally, although it is quite possible that the splitting of the mode ν_3 observed in [7] is configurational. The electronic spectrum of PO_4 groups is more sensitive to the location of the nearest proton.

The configurationally averaged expression for the effective Raman scattering cross-section contains contributions from different configurations of $H_n PO_4$ groups. If the correlation corrections are neglected the specific weights of such contributions are proportional to the mean occupation numbers $\langle N_l^{ii} \rangle$ and to the scattering tensor elements and are determined by the proton distribution on the hydrogen bonds [8].

The possible situations for $H_2 PO_4$ groups with account of the contributions of different configurations are presented on table 1; the symmetry of phonon modes arising due to both configurational and Davydov splitting is shown.

Since $H_2 PO_4$ configurations possess lower symmetry as compared to the S_4 symmetry of the position of PO_4 groups in the crystal, it is possible that the lines may appear which are forbidden by the site symmetry. In particular, such a situation takes place at the (zz) - scattering ($\mathbf{e_1}|\mathbf{oz}, \mathbf{e_2}|\mathbf{oz}$) [9]. As it follows from table 1, at a given scattering geometry, besides the lines with ν_1 and ν_2 frequencies, the lines ν_3 and ν_4 should appear too (that are missing both for T_d symmetry and for S_4). This result agrees with experimental data [10]; ν_3 and ν_4 lines that are observed in Raman scattering spectra are considerably weaker in comparison with the principal ones and appear at the temperatures near T_c only.

The lines forbidden by the symmetry of PO_4 groups may appear also in the cases of (xy) – scattering (ν_1 and ν_2 frequencies), of (xz) – or (yz) – scattering (ν_1 and ν_2 frequencies) and of (xx) – or (yy) – scattering (ν_3, ν_4 frequencies). The former of these cases for ν_1 frequency is investigated experimentally in [10]. The second one is of interest, because "lateral" $H_2 PO_4$ configurations contribution are only (i=3,...6, 9,...,12). This is investigated experimentally in [11]. One of the peaks of Raman intensity, observed in this work, may correspond to the frequency ν_1. However authors of this work connect this peak to the splitted mode ν_3 and think, that these "lateral" configurations of the symmetry C_1 do not manifest itself in the Raman scattering spectra.

As to the possible usage of the proton ordering model for describing the ferroelectric phase transition in crystals of KDP group the attention should be paid to a more thorough experimental investigation of the cases (see table 1) when "lateral" configurations of protons, possessing C_1 symmetry, appear in the scattering since the model given allows for the existence of this kind of configuration (and configurations with different proton number). This problem is of importance in connection with the possibility of another interpretation of the phase transition in $KH_2 PO_4$ which

Table 1. Scattering geometry of the configurationally splitted modes ($T > T_c$ case). First column is the Davydov splitting. Fourth column is the configurational splitting. Symbols * denote the presence of non-zero components of scattering tensors; $\otimes$ correspond to the scattering in the case of isolated PO_4 complexes of T_d symmetry. Two last columns show the symmetry of modes arising from different configurations.

$D_{2\alpha}$ $\left\{{k \atop \bar{x}}\right\}$	S_4 $\{\bar{x}\}$	T_α $\{\bar{x}\}$	$D_{2\alpha}$ $\left\{{k(i) \atop \bar{x}_i}\right\}$	(xx)	(yy)	(zz)	(xy)	(xz)	(yz)	i=1, 2,7,8	i=3,..., 6,9, ...,12
A_1	A	A_1	$2A_1$	$\otimes$	$\otimes$	$\otimes$				A_1	A_1
+			$2A_2$							A_2	A_2
A_2			$2B_1$	*	*					B_1	B_1
			$2B_2$				*			B_2	B_2
			$2E$					*	*		$2E$
$2E$	E	F_2	$2A_1$	*	*	*					$2A_1$
			$2A_2$								$2A_2$
			$2B_1$	*	*						$2B_1$
			$2B_2$				*				$2B_2$
			$8E$					$\otimes$	$\otimes$	$4E$	$4E$
B_1	B	F_2	$2A_1$	*	*	*				A_1	A_1
+			$2A_2$							A_2	A_2
B_2			$2B_1$	*	*					B_1	B_1
			$2B_2$				$\otimes$			B_2	B_2
			$2E$					*	*		$2E$
A_1	A	E	$2A_1$	$\otimes$	$\otimes$	$\otimes$				A_1	A_1
+			$2A_2$							A_2	A_2
A_2			$2B_1$	*	*					B_1	B_1
			$2B_2$				*			B_2	B_2
			$2E$					*	*		$2E$
B_1	B	E	$2A_1$	*	*	*				A_1	A_1
+			$2A_2$							A_2	A_2
B_2			$2B_1$	$\otimes$	$\otimes$					B_1	B_1
			$2B_2$				*			B_2	B_2
			$2E$					*	*		$2E$

has been discussed recently – as a transition related with ordering of H_2PO_4 groups with protons near the "upper" or the "lower" oxygen ions (with C_2 symmetry). This point of view is presented in [10, 12]. We note that practical realization of such a model causes some difficulties due to the violations in the case of disordered state of the "ice rule" (one proton on the bond and two protons near PO_4 group). On the other hand, the idea of ordering H_2PO_4 groups was not confirmed in the experiments for investigating the nuclear quadrupole resonance in KH_2PO_4 [13] as well as the isotopic frequency shift in $K(D_xH_{1-x})_2PO_4$ [14]; the data obtained support the proton ordering model.

Finally, the approach proposed in this paper may be applied in the analysis of Raman scattering in other ferroelectric crystals with hydrogen bonds as well as in the crystals of another type with the phase transition of the order-disorder type. In the framework of the theory developed the interactions between electrons and lattice anharmonisms [15] may be taken into account. More detailed investigation of phonon spectrum of the crystals considered is of interest.

In particular, the systems of equations for the averaged phonon Green functions determining the shapes of the lines in Raman scattering spectra are obtained in the coherent potential approximation [4]. Configurationally splitted components of the Raman scattering lines are studied using a simple model. For KH_2PO_4 and CsH_2PO_4 type ferroelectrics, the possibility to observe experimentally the configurational splitting is discussed.

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Раманівське розсіяння у кристалах з фазовими переходами типу лад-безлад

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На основі формалізму двочасових функцій Ґріна розвинуто теорію побудови оператора поляризованості, що входить у загальний вираз для ефективного поперечного перерізу раманівського розсіяння. Представлена мікроскопічна схема використовується для дослідження сегнетоелектриків з водневими зв'язками.

Ключові слова: *раманівське розсіяння, фазові переходи типу лад-безлад*

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