RAMAN SCATTERING IN HEXAGONAL ICE INFLUENCED BY SYMMETRY OF CRYSTAL LATTICE

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ABSTRACT

Symmetries of phonon modes active in the first and the second order Raman scattering for the crystal of hexagonal ice and their influence on scattered polarized light are presented. Also examples of the depolarization ratios for the particular modes active in the first and second order scattering are given. Phonons for the points: Γ, L and M are from the low-energy part of the intensity spectrum. Only the translational modes of vibrations *i.e.* consisting of the displacements of the water molecules from the average positions on the lattice sites are considered here.

1 Introduction

Hexagonal ice belongs to a space group D_{6h}^{4} which describes the symmetry of arrangement of oxygen atoms. Water molecules in ice are tetrahedrally coordinated. They are arranged in puckered sheets perpendicular to the *c*-axis. The unit cell of this structure is a prism set on a rhombic base with inner angle 120° between the axes in the *xy*-plane. There are four molecules in a unit cell with four oxygen atoms in positions: $\pm(1/3, 2/3, z_o)$, $\pm(2/3, 1/3, 1/2+z_o)$ in units a_H in the *xy*-plane and c_H along the *z*-axis. The constant z_o is closely equal to 1/16. a_H and c_H are lattice constants of the hexagonal ice.

2 Vector Representation in Hexagonal Crystals

Raman scattering involves the optical polarizability which transforms like bilinear forms of Cartesian coordinates, i.e. according to the symmetrized Kronecker square of vector representation $[D^v \otimes D^v]$. In the space group D_{6h}^{4} of the uniaxial crystals of the *hcp* structure the vector representation is the direct sum of the unitary irreducible representations Γ_{6-} (E_{1u}) and Γ_{2-} (A_{2u}), where we write the representation labels of Miller and Love [1] and add those of Herzberg [2] [1]

$$D^v = \Gamma_{6-} \oplus \Gamma_{2-} = E_{1u} \oplus E_{2u}. \tag{1}$$

[1] In Ref. [3] there was written incorrectly $D^v = \Gamma_{6+} \oplus \Gamma_{2+}$, but the other results are correct.

Table 1 gives the characters of these representations.

TABLE 1: Characters of representations of group D_{6h}^{4}

R	$\chi^{D^{v}}(R)$	$\chi^{\Gamma_{6-}}(R)$	$\chi^{\Gamma_{2-}}(R)$
1	3	2	1
3,5	0	-1	1
4	-1	-2	1
2,6	2	1	1
7,9,11	-1	0	-1
8,10,12	-1	0	-1
20,22,24	1	0	1
19,21,23	1	0	1
16	1	2	-1
14,18	-2	-1	-1
13	-3	-2	-1
15,17	0	1	-1

3 Phonons Active in the First-Order Raman Scattering

Raman scattering involves the optical polarizability which transforms as the bilinear components x^2, y^2, z^2, xy, xz and yz. The character $\chi_{RS}(R)$ of the reducible representations of these transformations is related to the character $\chi(R)$ of the 3×3 representation of the group of the rotations R by [4]

$$\chi_{RS}(R) = \chi(R)\,[\chi(R) \pm 1] \tag{2}$$

with + for proper and - for improper rotation. Raman scattering is possible on phonons having unitary irreducible representation with character $\chi^{kl}(R)$ such that

$$n = \frac{1}{N}\sum_{R=1}^{N} \chi_{RS}(R)\chi^{\mathbf{k}l}(R)^{*} \geq 1 \tag{3}$$

where N is the order of the point group of the **k**-wave vector group and l is the number of the irreducible representation of the **k**-wave vector group. In the space group D_{6h}^{4} inspection of the characters of Table 2 enables to find the decomposition

$$[D^{v} \otimes D^{v}] = 2\Gamma_{1+} \oplus \Gamma_{5+} \oplus \Gamma_{6+} \tag{4}$$

In the first-order Raman scattering therefore the Γ_{1+}, Γ_{5+}, Γ_{6+} phonons only are active.

TABLE 2: Characters of representations of group D_{6h}^{4}

R	$\chi_{RS}(R) = \chi^{[D^{\nu} \otimes D^{\nu}]}(R)$	$\chi^{\Gamma_{1+}}(R)$	$\chi^{\Gamma_{5+}}(R)$	$\chi^{\Gamma_{6+}}(R)$
1	6	1	2	2
3,5	0	1	-1	-1
4	2	1	2	-2
2,6	2	1	-1	1
7,9,11	2	1	0	0
8,10,12	2	1	0	0
20,22,24	2	1	0	0
19,21,23	2	1	0	0
16	2	1	2	-2
14,18	2	1	-1	1
13	6	1	2	2
15,17	0	1	-1	-1
	n =	2	1	1

4 Phonons Active in the Second-Order Raman Scattering

The selection rules are simplest to calculate [5,6] for the second-order line spectrum, where both phonons have effectively zero wave vector, and for the part of the second-order continuum due to $\boldsymbol{k}=\mathbf{0}$ phonons. We have two cases: if the two phonons belong to the same branch the two-phonon state is an overtone and if they belong to different branches the two-phonon state is a combination. For the combination states the Raman transition is allowed if the Kronecker product of the irreducible representations of the two phonons contains irreducible representations in common with the polarizability tensor. For the overtone states the symmetrized Kronecker square of the phonon irreducible representation must be formed to determine the selection rules. It should be mentioned that the symmetrized Kronecker square of every $\boldsymbol{k}=\mathbf{0}$ irreducible representation and the components of the polarizability tensor always transform by the identity representation. The overtones of all $\boldsymbol{k}=\mathbf{0}$ phonons are therefore Raman active.

The selection rules for the second-order continuous spectrum due to the phonons with the non-zero wave vector are in principle calculated in exactly the same way as outlined above. However the phonon wave vector $\boldsymbol{k}$ now ranges over the entire Brillouin zone and in calculating the selection rules it is necessary to form the Kronecker products and the symmetrized Kronecker squares of the space group irreducible representations corresponding to all $\boldsymbol{k}$-vectors.

Table 3 gives calculated symmetries of the two-phonon states in the hexagonal ice crystal with notation of Tables XXIV and XXV of ref. 7. Ref. [7-9] include more details concerning symmetries of the Raman active phonon modes, the Raman tensors, the scattering intensity matrices. Also the depolarization of the scattered light in hexagonal ice is discussed.

TABLE 3: Symmetries of the two-phonon states in hexagonal ice

overtones			combinations		
$\Gamma_{1+}\otimes\Gamma_{1+}$	$H_1\otimes H_1$	$L_1\otimes L_1$	$\Gamma_{1+}\otimes\Gamma_{5+}$	$K_4\otimes K_5$	$M_{3-}\otimes M_{4-}$
$\Gamma_{3+}\otimes\Gamma_{3+}$	$H_2\otimes H_2$	$L_2\otimes L_2$	$\Gamma_{1+}\otimes\Gamma_{6+}$	$K_1\otimes K_6$	$M_{1+}\otimes M_{3+}$
$\Gamma_{4-}\otimes\Gamma_{4-}$	$H_3\otimes H_3$	$M_{1+}\otimes M_{1+}$	$\Gamma_{5+}\otimes\Gamma_{6+}$	$K_2\otimes K_5$	$M_{2+}\otimes M_{4+}$
$\Gamma_{5+}\otimes\Gamma_{5+}$	$K_1\otimes K_1$	$M_{2+}\otimes M_{2+}$	$A_1\otimes A_3$	$K_3\otimes K_5$	$M_{1-}\otimes M_{3-}$
$\Gamma_{6+}\otimes\Gamma_{6+}$	$K_2\otimes K_2$	$M_{3+}\otimes M_{3+}$	$H_1\otimes H_2$	$K_4\otimes K_6$	$M_{2-}\otimes M_{4-}$
$\Gamma_{5-}\otimes\Gamma_{5-}$	$K_3\otimes K_3$	$M_{4+}\otimes M_{4+}$	$H_1\otimes H_3$	$K_5\otimes K_6$	$M_{1+}\otimes M_{4+}$
$A_1\otimes A_1$	$K_4\otimes K_4$	$M_{1-}\otimes M_{1-}$	$H_2\otimes H_3$	$L_1\otimes L_2$	$M_{2+}\otimes M_{3+}$
$A_3\otimes A_3$	$K_5\otimes K_5$	$M_{2-}\otimes M_{2-}$	$K_1\otimes K_5$	$M_{1+}\otimes M_{2+}$	$M_{1-}\otimes M_{4-}$
	$K_6\otimes K_6$	$M_{3-}\otimes M_{3-}$	$K_2\otimes K_6$	$M_{3+}\otimes M_{4+}$	$M_{2-}\otimes M_{3-}$
		$M_{4-}\otimes M_{4-}$	$K_3\otimes K_6$	$M_{1-}\otimes M_{2-}$	

5 Depolarization of the scattered light

Depolarization of light in the crystal scattering process has been considered in theoretical analysis of the light scattering by Loudon [8]. The depolarization ratio ρ is the quotient of the intensity of the light polarized in the scattering plane $I_{\parallel}$ and the intensity of the light polarized perpendicularly to this plane $I_{\perp}$

$$\rho = I_{\parallel} / I_{\perp} \tag{5}$$

Table 4 give some examples of the depolarization ratios for the particular modes active in the first and second order scattering. Phonons for the points: Γ, L and M are from the low-energy part of the intensity spectrum. The coordinates of the wave vectors: $\mathbf{k}_\Gamma$, $\mathbf{k}_L$ and $\mathbf{k}_M$ are

$$\mathbf{k}_\Gamma = \pi(\,0, 0, 0), \quad \mathbf{k}_L = \pi(\,1/a_L, 0, 1/c_H\,), \quad \mathbf{k}_M = \pi(\,1/a_L, 0, 0), \tag{6}$$

where $a_L = a_H\sqrt{3}/2$ and a_H, c_H are lattice constants.

TABLE 4: Depolarization ratio

Scattering plane	Symmetry of excitation modes	Depolarization ratio ρ
First order scattering		
xz	$\Gamma_{1+}(1)$	$\lvert a\text{-}b\rvert^2 \mathrm{ctg}^2\alpha \sin^2 2\varphi /[4\lvert a\rvert^2]$
xz	$\Gamma_{5+}(1)$	$\mathrm{tg}^2\alpha\,\mathrm{tg}^2\varphi$
xz	$\Gamma_{5+}(2)$	$(1/4)\mathrm{ctg}^2\alpha \sin^2 2\varphi$
xz	$\Gamma_{6+}(1)$	$\mathrm{tg}^2\alpha\,\mathrm{ctg}^2\varphi$
yx	$\Gamma_{6+}(1)$	$\mathrm{tg}^2\alpha\,\mathrm{tg}^2\varphi$
yx	$\Gamma_{6+}(2)$	$\mathrm{tg}^2\alpha\,\mathrm{ctg}^2\varphi$
Second order scattering		
yx	$L_n(\sigma 1) \otimes L_n(\sigma 1)$ $n = 1,2;\ \sigma = 1,3$ $M_m(\sigma 1) \otimes M_m(\sigma 1)$ [2] $m = 1\pm,2\pm,3\pm,4\pm;\ \sigma = 1,3$	$\mathrm{ctg}^2\alpha\,[1 - (1/2)\sin 4\varphi]\lvert e/h\rvert^2$
yx	$L_n(21) \otimes L_n(22)$ $n = 1,2$ $M_m(21) \otimes M_m(21)$ [3] $m = 1\pm,2\pm,3\pm,4\pm$	$\mathrm{ctg}^2\alpha\,(1 + \sin 4\varphi)\lvert e/h\rvert^2$

In the table α[4] is the angle between the scattering plane and the polarization vector of the incident light and φ is the slide angle of the incident light. The *a, b, e, h* symbols are constants which we can determine from the experimental results *i.e.* from the vibrational spectrum.

Using the Tables XXVI - XXX from [7] and performing summation over all fractional contributions we get in the two-phonon region that the full intensity for the *xy* polarization configuration (*x* for incident and *y* for scattered light) is proportional to $\frac{29}{2}\lvert e\rvert^2$ and for the *zz* polarization configuration is proportional to $19\lvert h\rvert^2$. In the one-phonon region the full intensity for the *xx* or *yy* polarization configuration is proportional to $\lvert a\rvert^2$ and for the *zz* polarization configuration is proportional to $\lvert b\rvert^2$.

The experimental vibrational spectrum for ice in both one-phonon and multiphonon regions is presented for example in reference [10]. Results of the inelastic neutron scattering *i.e.* the intensity spectra in hexagonal ice are given in [11-12]. The depolarization ratio is a quantity of practical importance in the interpretation of lidar observations [13-16].

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[2] In ref. [7] the omission: $M_n(\sigma) \otimes M_n(\sigma)$ is corrected here.

[3] In ref. [7] the omission: $M_n(2) \otimes M_n(2)$ is corrected here.

[4] In ref. [7] we have: $\mathrm{tg}\theta = \mathrm{ctg}\alpha$.

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