

CHANGES IN SPECTROSCOPIC PROPERTIES OF CRYSTALS OF THE CLASSES C_{4h} , D_{2d} , D_4 AT THE SECOND-ORDER STRUCTURAL PHASE TRANSITION TEMPERATURE*

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By group-theoretical analysis we determine which of the structural second-order phase transitions, permitted by Landau theory for crystals of C_{4h} , D_{2d} and D_4 symmetry, are accessible to detection by IR absorption and Raman scattering technique.

1. Introduction

Experimental studies of structural second-order phase transitions in ionic crystals can be performed by various spectroscopic techniques [1, 2] including infrared spectroscopy, inelastic light and neutron scattering, EPR, NQR and X-ray analyses. The methods of infrared absorption and Raman scattering [3] can detect a phase transition because the appropriate change in symmetry of the crystal defines the permitted electric dipole and Raman transitions.

Complete information on all possible changes in symmetry of crystals arising in second-order phase transitions was first given by Landau in 1937 [4]. It is well known that of all the transitions, permitted by the thermodynamical conditions, only some can be detected by one of the above-mentioned spectroscopic methods.

In our paper, we shall analyze the possibilities of detection, by infrared absorption

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and Raman scattering, of the structural, second-order phase transitions in ionic crystals with symmetry of the high-temperature phase described by the point groups C_{4h} , D_{2d} and D_4 [5].

2. Thermodynamical and dynamical analysis of structural second-order phase transitions

The properties of the crystal change gradually in the temperature of a second-order phase transition. The distribution of the mass density and electron density $\rho(\mathbf{r})$ varies continuously in this temperature. In the low-symmetry phase, the function of the mass or electron density can be written in the form [4]

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}), \quad (1)$$

where $\rho_0(\mathbf{r})$ is invariant under the operations of the high-symmetry space group, whereas $\delta\rho(\mathbf{r})$ is invariant under the operations of the lower-symmetry space group.

The function $\delta\rho(\mathbf{r})$ which intervenes in Landau's theory describes the real, static and continuous change of the mass or electron density. $\delta\rho(\mathbf{r})$ can be expanded in a complete set of the basis states of irreducible representations of the high-symmetry space group. We see from the Landau theory, however, that only one irreducible representation characterizes the structural change [4]. According to Cochran [6-8], the basis functions of these irreducible representations give the complete set of states for small atomic displacements [9]. These functions are the harmonic phonon eigenfunctions, which describe small displacements of atoms from their high-symmetry equilibrium positions. As it is known from the dynamical theory of phase transitions [6-8], only one normal mode characterizes the symmetry change at T_c . The frequency of this single phonon tends to zero at the transition temperature [3].

If the temperature of the crystal decreases below the critical value of the phase transition, there occur displacements of atoms, which change the symmetry of the crystal. We restrict our discussion to the range of temperatures below but very near T_c beyond the critical region in which the thermally excited time-dependent fluctuations are larger than the mean displacements.

The distortion of the crystal described in terms of the single phonon \mathbf{k}, j is equal to [9]

$$u_\alpha(l, n) = \frac{1}{\sqrt{NM_n}} \delta_\alpha(n|\mathbf{k}j) \langle Q(\mathbf{k}, j) \rangle e^{2\pi i \mathbf{k} \cdot \mathbf{X}(l)}, \quad (2)$$

where N is the number of elementary cells of the crystal, $\mathbf{X}(l)$ — the equilibrium position of an atom n with mass M_n in the l -th elementary cell, $\delta_\alpha(n|\mathbf{k}j)$ — the displacement of the atom n in the direction α with respect to the elementary cell corresponding to the phonon with the quantum numbers \mathbf{k}, j , where j labels the irreducible representation of the reciprocal lattice vector \mathbf{k} of the space group of the crystal, $Q(\mathbf{k}, j)$ is the normal coordinate of the crystal vibrations and, simultaneously, the basis of the irreducible representation j of the vector \mathbf{k} .

The functions of the form (2) form a complete set in terms of which arbitrary distortions in the lower-symmetry phase can be expressed. In particular, the displacements of the

maxima of mass density accompanying the phase transitions considered in the present paper can be written as appropriate combinations of the functions (2).

To the vanishing of the parameter $\langle Q(\mathbf{k}, j) \rangle$ at the temperature T_c corresponds the vanishing of the phonon mode with the quantum numbers \mathbf{k} and j .

Soft acoustical modes give rise to a distortion of the translational lattice and are not of special interest from the point of view of the spectroscopic properties of a crystal. The transversal soft optical modes give rise to atom displacements within the elementary cell and thus can actively cooperate with the electromagnetic radiation. The vanishing of the transversal optical phonon can be studied experimentally with the aid of absorption spectra in the infrared range or by Raman scattering.

3. Infrared absorption and Raman scattering near the Curie point of crystals with high-symmetry phase C_{4h} , D_{2d} and D_4

Among all the permitted changes in crystal symmetry, related with a softening of the appropriate phonons, it is possible to select those which can be detected by Raman scattering or infrared absorption, and those that are not active. This classification of phase transitions can be obtained from the selection rules for the appropriate dipolar transitions which obviously depend on the symmetry of the crystal. The wave lengths used in far-infrared and Raman spectroscopy are larger by several orders of magnitude than the lattice constant. Conservation of the momentum $P = \frac{h}{\lambda}$ requires that the wave vector

of any phonon created or annihilated by such radiation shall be very close to $\mathbf{k} = \mathbf{0}$. Therefore in this paper, we restrict our discussion to the selection rules in the space of normal modes $Q(\mathbf{k}, j)$ with $\mathbf{k} = \mathbf{0}$. The symmetry of the normal mode $Q(\mathbf{k}, j)$ is described by the irreducible representation Γ_j of the space group with the adequate vector $\mathbf{k} = \mathbf{0}$.

As known, the normal mode of a crystal can be active in infrared absorption if at least one of the matrix elements of the induced dipole moment is not equal to zero. This means that the Γ_j representation of a phonon mode must be contained in the representations according to which the induced dipole moment transforms. The condition for this can be formulated as follows [10]

$$\frac{1}{g} \sum_{R \in \mathcal{G}_0} (\pm 1 + 2 \cos \theta_R) \chi_j(R, \tau_R) \neq 0, \quad (R, \tau_R) \in \mathcal{G}_0, \quad (3)$$

where g is the number of elements (R, τ_R) of the group \mathcal{G}_0 , $(\pm 1 + 2 \cos \theta_R)$ — the character of the representation transforming components of an axial vector, and $\chi_j(R, \tau_R)$ the character of the representation Γ_j .

In the case of Raman scattering, the Γ_j representation must be contained in the following representation which transforms the components of the electric polarization tensor. This condition is fulfilled if [10]

$$\frac{1}{g} \sum_{R \in \mathcal{G}_0} 2 \cos \theta_R (\pm 1 + 2 \cos \theta_R) \chi_j(R, \tau_R) \neq 0, \quad (R, \tau_R) \in \mathcal{G}_0, \quad (4)$$

where $2 \cos \theta_R (\pm 1 + 2 \cos \theta_R)$ is the character of the representation according to which the components of the symmetrical tensor of second rank are transformed. The sign “-” is related with reflection rotations by an angle θ . For the fundamental fully-symmetric vibrations, the condition [4] is always fulfilled.

We apply the above selection rules to pinpoint the possibilities of experimental detection by infrared absorption or Raman scattering of the structural phase transitions occurring in crystals of the classes C_{4h} , D_{2d} and D_4 . We consider phase transitions, related with the representations of stars containing the zero vector. Such transitions occur without any change in volume or shape of the elementary cell. This also means that, during the phase transition, the number of atoms in the elementary cell is conserved and the changes in crystal structure take place inside the elementary cells.

On the basis of Landau's theory, we find for crystals of the classes C_{4h} , D_{2d} and D_4 the following possibilities of structural changes (Tables I, II, III). These changes are related to the representations Γ_j of the high-symmetry phase.

TABLE I

	Γ_{1u}	Γ_{2u}	Γ_{2g}	$\Gamma_{3u} + \Gamma_{4u}$	$\Gamma_{3g} + \Gamma_{4g}$
$C_{4h}^1 \rightarrow$	C_4^1	S_4^1	C_{2h}^1	C_s^1	S_2
$C_{4h}^2 \rightarrow$	C_4^3	S_4^1	$C_{2h}^{1'}$	C_s^1	S_2
$C_{4h}^3 \rightarrow$	C_4^1	S_4^1	C_{2h}^4	C_s^2	S_2
$C_{4h}^4 \rightarrow$	C_4^3	S_4^1	C_{2h}^4	C_s^2	S_2
$C_{4h}^5 \rightarrow$	C_4^5	S_4^2	C_{2h}^3	C_s^3	S_2

TABLE II

	Γ_2	Γ_3	Γ_4
$D_{2d}^1 \rightarrow$	S_4^1	C_{2v}^{11}	D_2^1
$D_{2d}^2 \rightarrow$	S_4^1	C_{2v}^{13}	D_2^1
$D_{2d}^3 \rightarrow$	S_4^1	C_{2v}^{11}	D_2^3
$D_{2d}^4 \rightarrow$	S_4^1	C_{2v}^{13}	D_2^3

All the representations active in infrared absorption for the lower- and high-symmetry phases are listed in Table IV. Whereas all the representations active in Raman scattering for both phases are given in Table V.

Tables IV and V give the representations Γ_j of the central point of the Brillouin zone. These representations are related with all the space groups of the symmetry class.

TABLE III

	Γ_2	Γ_3	Γ_4
$D_4^1 \rightarrow$	C_4^1	D_2^1	D_2^1
$D_4^2 \rightarrow$	C_4^1	D_2^1	D_2^3
$D_4^3 \rightarrow$	C_4^2	D_2^2	D_2^2
$D_4^4 \rightarrow$	C_4^2	D_2^2	D_2^4
$D_4^5 \rightarrow$	C_4^3	D_2^1	D_2^1
$D_4^6 \rightarrow$	C_4^3	D_2^1	D_2^3
$D_4^7 \rightarrow$	C_4^4	D_2^2	D_2^3
$D_4^8 \rightarrow$	C_4^4	D_2^2	D_2^4

TABLE IV

Representations active in infrared absorption

High-symmetrical phase	Low-symmetrical phase				
	C_4	S_4	C_{2h}	C_s	C_2
$\Gamma_{1u}; \Gamma_{3u} + \Gamma_{4u}$	$\Gamma_1; \Gamma_3 + \Gamma_4$	$\Gamma_2; \Gamma_3 + \Gamma_4$	$\Gamma_{1u}; \Gamma_{2u}$	$\Gamma_2; \Gamma_1$	Γ_{1u}
D_{2d}	S_4	D_2	C_{2v}	—	—
$\Gamma_4; \Gamma_5$	$\Gamma_2; \Gamma_3 + \Gamma_4$	$\Gamma_2; \Gamma_3; \Gamma_4$	$\Gamma_3; \Gamma_4$	—	—
D_4	C_4	D_2	—	—	—
$\Gamma_2; \Gamma_5$	$\Gamma_1; \Gamma_3 + \Gamma_4$	$\Gamma_2; \Gamma_3; \Gamma_4$	—	—	—

TABLE V

Representations active in Raman scattering

High-symmetrical phase	Low-symmetrical phase				
	C_4	S_4	C_{2h}	C_s	S_2
$\Gamma_{1g}; \Gamma_{2g}; \Gamma_{3g} + \Gamma_{4g}$	$\Gamma_1; \Gamma_2; \Gamma_3 + \Gamma_4$	$\Gamma_1; \Gamma_2; \Gamma_3 + \Gamma_4$	$\Gamma_{1g}; \Gamma_{2g}$	$\Gamma_1; \Gamma_2$	Γ_{1g}
D_{2d}	S_4	D_2	C_{2v}	—	—
$\Gamma_1; \Gamma_3; \Gamma_4; \Gamma_5$	$\Gamma_1; \Gamma_2; \Gamma_3 + \Gamma_4$	$\Gamma_1; \Gamma_2; \Gamma_3; \Gamma_4$	$\Gamma_1; \Gamma_2; \Gamma_3; \Gamma_4$	—	—
D_4	C_4	D_2	—	—	—
$\Gamma_1; \Gamma_3; \Gamma_4; \Gamma_5$	$\Gamma_1; \Gamma_2; \Gamma_3 + \Gamma_4$	$\Gamma_1; \Gamma_2; \Gamma_3; \Gamma_4$	—	—	—

4. Conclusions

From Tables I, II, III, IV and V, the following conclusions can be drawn:

1. The structural phase transitions

$$D_4^{1,5} \rightarrow D_2^1, \quad D_4^{2,6} \rightarrow D_2^3, \quad D_4^{3,7} \rightarrow D_2^2, \quad D_4^{4,8} \rightarrow D_2^4,$$

satisfying the symmetry rules, can be detected in infrared absorption, since the phonon active in the low-symmetrical phase vanishes at the Curie temperature.

2. Similarly, the structural phase transitions

$$D_{2d}^{1,2,3,4} \rightarrow S_4^1 \quad \text{and} \quad C_{4h}^{1,3} \rightarrow C_4^1, \quad C_{4h}^{2,4} \rightarrow C_4^3,$$

$$C_{4h}^5 \rightarrow C_4^5, \quad C_{4h}^{1,2,3,4} \rightarrow S_4^1, \quad C_{4h}^5 \rightarrow S_4^2, \quad C_{4h}^{1,2} \rightarrow C_s^1$$

$$C_{4h}^{3,4} \rightarrow C_s^2, \quad C_{4h}^5 \rightarrow C_s^3,$$

can be detected experimentally in Raman scattering.

The remaining permitted phase transitions cannot be studied by the spectroscopic methods considered.

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