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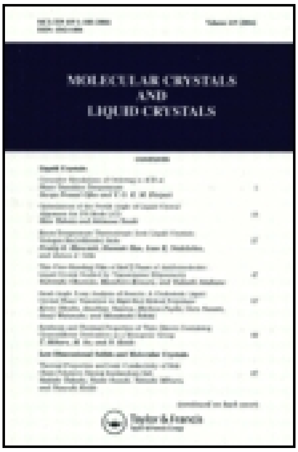

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SPECTROSCOPIC STUDIES OF ORIENTATIONAL DISORDER CRYSTALS USING THE THEORY OF NON-RIGID SYMMETRY

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Abstract Non-rigid symmetry of some molecular crystals having disordered phases has been studied. Classification of librational-rotational movements of molecular group has been carried out. As a result, the selection rules for disordered crystals for IR and Raman spectra of KSCN crystal in disordered phase are investigated and analysed. They are treated mainly according to the selection rules in the factor-group representation.

Keywords: spectroscopic studies, orientational disorder in crystals, non-rigid symmetry, Raman spectra

INTRODUCTION

The discussion of the vibrational spectra of crystals suggests that the crystal represents a completely ordered system having a distinct structure with respect to all internal points. However, simple statistical considerations show that if alternative structures are possible and if they do not differ too much in their free energy and have an appropriate activation energy, the crystal with alternative structures will exist at any temperature. Hence, the disorder can be rather a common phenomenon in crystals at $T\neq0$. An orientational disorder is a specific type of the disorder in a lot of molecular crystals. Such an orientational disordering often results in an order-disorder phase transition. A general peculiarity of disordered phases is the fact that their statistical symmetry is higher than the one in the ordered phase. Some of the authors suppose that in the case an effective symmetry of the Hamiltonian is also higher, which enabled to obtain the selection rules in a regular way. In fact, the character of the vibrational

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spectra and the selection rules can not be obtained simply from the crystallographic symmetry of the disordered phase. Hornig has pointed to that fact as early as in 1949 in a concise treatment of the spectra in the disordered crystals.[1]

The interest in disordered phases gave rise to new theoretical approaches in which an important role is played by symmetry methods.[2] Howewer, a consistent consideration of crystals with elements of the orientational disordering can be carried out to use the theory of non-rigid symmetry introduced by Longuet-Higgins for molecules[3] and applied to crystals by Kiselev et.al.[4,5].

NON-RIGID SYMMETRY AND CRYSTAL STRUCTURE

The term of "non-rigid" crystal is applied to the crystal in which the molecules execute motion such that differ from small vibrations (for example, rotations). In that case it is reasonable to construct the group of non-rigid symmetry which can be defined as a group of the permutation - inversion operations leaving the Hamiltonian invariable. Apart from the identity operation **E** it contains the inversion operations of all atomic coordinates $\mathbf{E}^*$ and the operations of the permutation of the identity atoms **P** (and also the permutation with the following inversion of coordinates $\mathbf{P}^*=\mathbf{P}\times\mathbf{E}^*$). The complete group of the non-rigid symmetry is very bulky. Actually, it has to contain only operations corresponding to the physically available movements (that is for not too high potential activation barrier).

However, application of the non-rigid symmetry group to the classification of excitations often meets difficulties because of lack of the data on irreducible representations of these groups. Certain simplifications arise only in that case when the group of non-rigid symmetry is isomorphic to one of the 230 space groups. Just this is the case with the crystal of potassium

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thiocyanate **KSCN**.

Potassium thiocyanate is an ionic crystal of a comparatively simple structure. At the same time SCN^- ions can be considered as "molecules", their interatomic binding being much stronger than that of the ions in the lattice. The low temperature phase of **KSCN** has a simple orthorhombic Bravais lattice (space group D_{2h}^{11}-Pbcm, Z=4) with the unit cell dimensions of a=6.673, b=6.715, c=7.545 Å [6]. The crystal axes orientations and elements of symmetry shown in Fig.1 was taken as generally accepted (x‖a, y‖b, z‖c). The bc plane coincides with the optic axes plane. The thiocyanate ions lie on a crystallographic c-plane with specified orientations, while potassium ions sandwiched between the thiocyanate layers. The K^+ ion site symmetry is C_2-2 and the anion site symmetry is C_s-m.

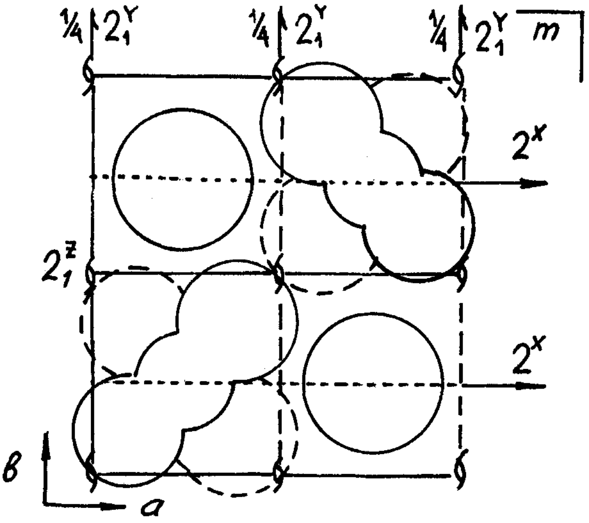

FIGURE 1 Structure of **KSCN-II**.

At 142°C **KSCN** undergoes a λ-transition [7]. The high temperature phase **KSCN-I** is disordered. The SCN^- ions undergo dynamical reorientations between two

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energetically equivalent positions (rotations in the ions plane to 180°). The crystal in phase I belong to statistical space group D_{4h}^{18}-I4/mcm Z=2 with the translations a=b= 6.670, c=7.73 Å.

It is necessary to add the operation of overturn of the SCN^- ions in the low temperature group D_{2h}^{11} to construct a non-rigid group symmetry of the high temperature phase. The following extension of the element set of the symmetry is done to obtain the group having the factor-group on the translation sub-group of group D_{2h}^{11}, which has 32 elements and is not isomorphic to any out of the Fedorov's group.

One can extract an extended set of "non-rigid" translations leading to the change of the Bravais lattice from a primitive to a volumecentred to obtain the isomorphism in that non-rigid group. This allows to present the factor-group on the extended translations group as one which is isomorphic to space group D_{4h}^{18} with two formula units in the primitive cell. These groups are isomorphic but not identical, because these describe the symmetry of different crystal structures.

A statistical structure is due to averaging of all atomic coordinates and can be only employed in the classification of the modes not participating in non-rigid movements with the small amplitudes (translations K^+ and SCN^-). At the same time, for the modes in which non-rigid atoms participate it is necessary to classify by taking into consideration a non-rigid group. Such are the librational rotational movements of the SCN^- groups modes in the KSCN crystal. The difference in these classifications is due to the fact that in non-rigid group the environment symmetry of the individual movements of SCN^- ions must take into account the rotation of the rest of the SCN^- anions. These circumstance change the systematisations in principle.

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RESULTS AND DISCUSSION

The structure of the vibrational representation for the lattice modes of the high temperature phase I can be written by using statistical group D_{4h}^{18} as

$$\Gamma_{vibr}=2A_{2g}+B_{1g}(xx,yy)+3E_g(xz,yz)+A_{2u}(z)+B_{1u}+2E_u(x,y).$$

Thus, the factor-group selection rules for the Raman spectra do not allow the occurrence of the line in the spectra in polarisations **zz**(A_g) and **xx**(B_{2g}). One line may arise in the polarisations **xx**(A_g) and **xy**(B_{1g}) only. The line corresponds to the librational movements of the two unequivalent ionic **SCN**$^-$ groups around the Z axis in the antiphase. The three bands may be found in the polarisations **xz,yz**(E_g). One of them is a translational mode of the **SCN**$^-$ groups and two are librational movements of the anions around X and Y axes.

The application of the non-rigid symmetry group to phase I changes only the classification of the librational modes of the crystal. The systematisations of the librational-rotational states in that phase for the excitations with the wave vector **k**=0 is defined as the classification of the Mathieu functions on the irreducible representations of the non-rigig group which is isomorphic to D_{4h} ^{8}.

A total transformation of the librational states of **KSCN-II** to librational-rotational species of the disordered phase II and then to the rotational states of the isolated **SCN**$^-$ ions are given in Fig.2 which consist several columns. In the right-hand part of the figure the rotational states of free anions for the movement around Z axis are shown. In fact, they represent the run-off levels of the free plane rotator. For the finite potential barrier, hindering the reorientation, the

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librational rotational states are described by the wave functions in the form of the Mathieu functions. The Mathieu functions are indicated in a corresponding column. Along with that, their classification on the irreducible representation of the site group D_{2h} (which is isomorphic to C_{2v} for rotations) are shown. The librational rotational states of the SCN$^-$ anions in a high temperature phase I are given in the next column. They are obtained by taking into account the two translational unequivalent anions in the primitive cell. Therefore, each of the undegenerate states decays in consequence of the interaction into two components corresponding to the inphase and antiphase movements of the SCN$^-$ groups. The dotted lines indicate the same states on the boundary of the Brillouin zone with $K=\pi/c$. They transform to the centre of the zone by the transition I ⇒ II in the ordered phase. Similar scheme of the levels may be applied to the librations l_{xy} of the SCN$^-$ anions with the out-of-plane **xy** movement.

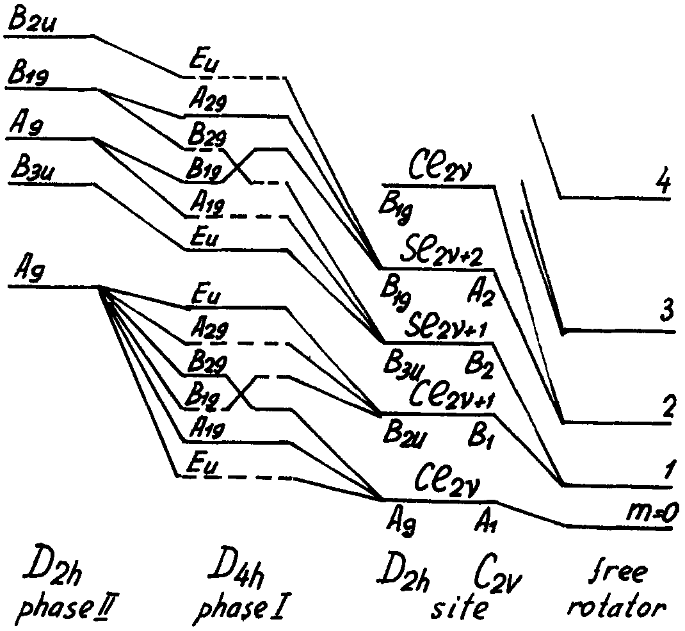

FIGURE 2 Transformation of the librational levels of the SCN$^-$ ions.

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Thus, the consideration of the non-rigid movements lead to both the splitting of the librational states along the lines of inversion doubling and the appearance of the new selection rules for the transitions between the ground and excited states. The variety of the transitions will result in both the emergence of new lines in the librational region of the spectra and the appearance of the low-frequency background associated with the transitions of the tunnel type.

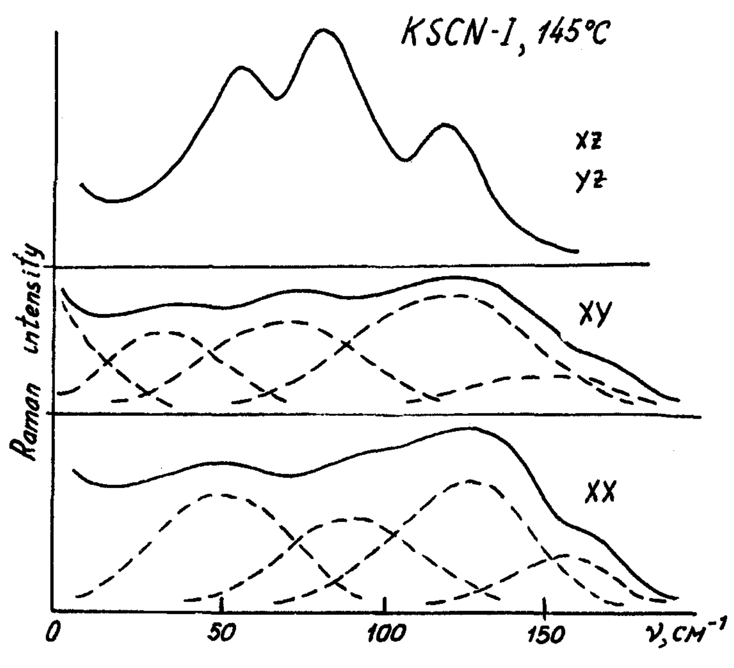

FIGURE 3 Raman spectra of **KSCN** crystal.

The experimental results obtained are given in Fig.3. The origin of the scattering in the polarisation **xy** (curve 2) which is not understood in term of the rigid crystal can be explaind by assuming that the scattering is due to the variety of the transitions in a non-rigid phase. In accord with the selection rules one can expect the appearance of nine bands. Four of them have to get in a comparatively high-frequency region of the spectra

(30-100 cm^{-1}) and five bands would get into a reasonably low-frequency one (1-10 cm^{-1}). There must be present five bands in the polarisation **xx**(A_g+B_{1g}). Four of them must fall into a fairly high-frequency region. Unfortunately, it is difficult to give the exact interpretation for all of the bands in these polarisations but it is clear that the picture observed is in a satisfactory agreement with these predictions. At the same time in accordance with the selection rules there must be observed only two lines of the librational-rotational type in E_g spectra (polarisations **xz** and **yz**). Hence, in addition to the line of the translational type, this prediction agrees with the experiment closely. Therefore, one can conclude that application of the non-rigid symmetry to the disordered phase I allows the interpretation of the Raman spectra of the crystal in the factor-group representation.

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