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*COUPLING BETWEEN INTERMOLECULAR AND INTRAMOLECULAR VIBRATIONS
 IN A CRYSTAL*

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A model of a molecular crystal with "semi-rigid" molecules is examined. The conditions for separation of intermolecular and intramolecular vibrations are investigated. By way of example a two-dimensional lattice with C_{4v} symmetry is examined.

BORN'S theory of crystal lattices gives the most general solution of the problem of propagation of elastic waves in a crystal. In the case of complex molecular crystals, however, direct application of the theory leads merely to several very general deductions; hence it is natural to seek approximate models that would make it possible to move forward in utilizing the Born theory of crystal lattices. One such model for molecular crystals consists of separating the molecules as a whole from the lattice; in the first approximation the molecules are considered as solids with six degrees of freedom.¹ Solution of the problem formulated in this way made it possible to investigate the propagation of orientational-translational waves in the crystal and to determine the conditions for separation of the translational and orientational oscillations. In the following approximation the molecules are regarded as "semi-rigid" systems, that is, systems for which the magnitude of the intramolecular interactions is much greater than that of the intermolecular ones. In this case the interaction between molecules can be treated as a perturbation.

The solution should result in free-molecule vibrations that are modulated by lattice vibrations. A problem of this kind has been examined by Davydov,² but was solved only in the general form and primarily from the standpoint of energy transfer from the intramolecular vibrations to the lattice vibrations, a transfer leading to attenuation of the vibrations and broadening of the absorption bands.

A more detailed solution of this problem permits an investigation of the interaction between intermolecular and intramolecular vibrations.

The present study is devoted to an examination of the coupling between intermolecular and intramolecular vibrations and the conditions for their separation. We solve only the classical problem through the application of group theory.

1. Let us examine a three-dimensional crystal containing N molecules of S atoms each. The unit cell contains ν molecules; n is the ordinal number of the cell and n_ν is the index of the molecule. The

potential energy of the interaction of the atoms in the crystal are given by

$$U = \frac{1}{2} \sum_{n_\nu, n'_\nu, \alpha, \alpha'} \lambda_{n_\nu n'_\nu}^{\alpha\alpha'} (r_{n_\nu}^\alpha - r_{n'_\nu}^{\alpha'})^2 \cos^2 \gamma_{n_\nu n'_\nu}^{\alpha\alpha'} + \sum_{n_\nu, \alpha, \beta} k_{n_\nu}^{\alpha\beta} (r_{n_\nu}^\alpha - r_{n_\nu}^\beta)^2 \cos^2 \gamma_{n_\nu}^{\alpha\beta}, \quad (1)$$

where $r_{n_\nu}^\alpha$ is the displacement vector of the α th atom of the n_ν th molecule, $k_{n_\nu}^{\alpha\beta}$ and $\lambda_{n_\nu n'_\nu}^{\alpha\alpha'}$ are the coefficients of elastic interaction of two atoms belonging and not belonging to one and the same molecule, respectively, and $\gamma_{n_\nu n'_\nu}^{\alpha\alpha'}$ is the angle between the vector $r_{n_\nu}^\alpha - r_{n'_\nu}^{\alpha'}$ and the line connecting the centers of gravity of both atoms in the equilibrium position. This line has an invariable orientation in space; we denote its direction cosines relative to the coordinate axes through a, b and c with appropriate indices.

Let us separate the displacements of the molecule as a whole; to this end we write

$$r_{n_\nu}^\alpha = r_{n_\nu} + l_{n_\nu}^\alpha \times \theta_{n_\nu} + \sum_{\beta} \eta_{n_\nu}^{\alpha\beta}, \quad (2)$$

where r_{n_ν} is displacement of the center of gravity of the n th molecule, θ_{n_ν} is the angle of rotation of the n_ν th molecule about its instantaneous axis, $l_{n_\nu}^\alpha$ is the distance of the α atom from the instantaneous axis, $\eta_{n_\nu}^{\alpha\beta}$ is the relative displacement of atoms α and β in the molecule, satisfying the condition

$$m_{n_\nu, \alpha} \eta_{n_\nu}^{\alpha\beta} + m_{n_\nu, \beta} \eta_{n_\nu}^{\beta\alpha} = 0$$

and expressed in the system rigidly connected with the principal axes of the ellipsoid of inertia of the molecule. Here $m_{n_\nu, \alpha}$ and $m_{n_\nu, \beta}$ are the masses of the α and β atoms in the n th molecule.

For small angular oscillations

$$\theta_{n_\nu} = \vartheta_{n_\nu} + \varphi_{n_\nu} + \psi_{n_\nu},$$

where ϑ_{n_ν} , φ_{n_ν} and ψ_{n_ν} are the angles of rotation about the principal axes of the inertia ellipsoid.

In the new coordinates the total energy of the crystal is given by

$$\begin{aligned} U &= \frac{1}{2} \sum_{n_\nu, n'_\nu, \alpha, \alpha'} \lambda_{n_\nu n'_\nu}^{\alpha\alpha'} \left\{ (r_{n_\nu}^\alpha - r_{n'_\nu}^{\alpha'}) + l_{n_\nu}^\alpha \times (\vartheta_{n_\nu} + \varphi_{n_\nu} + \psi_{n_\nu}) \right. \\ &\quad \left. - l_{n'_\nu}^{\alpha'} \times (\vartheta_{n'_\nu} + \varphi_{n'_\nu} + \psi_{n'_\nu}) + \sum_{\beta} \eta_{n_\nu}^{\alpha\beta} - \sum_{\beta'} \eta_{n'_\nu}^{\alpha'\beta'} \right\}^2 \cos^2 \gamma_{n_\nu n'_\nu}^{\alpha\alpha'} + \sum_{n_\nu, \alpha, \beta} k_{n_\nu}^{\alpha\beta} (\eta_{n_\nu}^{\alpha\beta})^2, \\ T &= \frac{1}{2} \sum_{n_\nu} \left\{ M_{n_\nu} \dot{r}_{n_\nu}^2 + J_{n_\nu, \vartheta} \dot{\vartheta}_{n_\nu}^2 + J_{n_\nu, \varphi} \dot{\varphi}_{n_\nu}^2 + J_{n_\nu, \psi} \dot{\psi}_{n_\nu}^2 + \sum_{\alpha, \beta} \mu_{n_\nu}^{\alpha\beta} (\dot{\eta}_{n_\nu}^{\alpha\beta})^2 \right\}, \end{aligned} \quad (3)$$

where M_{n_ν} is the mass of the molecule and $\mu_{n_\nu}^{\alpha\beta}$ is the reduced mass of the α and β atoms of the n th molecule.

Writing the Lagrangian and seeking the solution in the form of plane waves

$$x_{n_\nu} = X_\nu \exp \{i(\omega t - a_x n \tau)\}, \quad \vartheta_{n_\nu, x} = \Theta_{\nu, x} \exp \{i(\omega t - a_x n \tau)\}, \quad \eta_{n_\nu, x}^{\alpha\beta} = H_{\nu, x}^{\alpha\beta} \exp \{i(\omega t - a_x n \tau)\}, \quad (4)$$

where a is the distance between molecules belonging to one simple lattice, we obtain the determinant:

$$\begin{vmatrix} -M_{n_\nu} \omega^2 + A & \dots & R_1 & \dots & K & \dots & P & \dots \\ \dots & R_2 & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots \\ \dots & \dots & K & \dots & -J_{n_\nu, \beta} \omega^2 + B & \dots & N & \dots \\ \dots & \dots \\ \dots & \dots & P & \dots & M & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & -\mu \omega^2 + C & \dots \\ \dots & L & \dots \end{vmatrix}$$

where

$$\begin{aligned}
 A &= \sum_{\alpha\alpha'} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} (a_{n\nu n'\nu'}^{\alpha\alpha'})^2, & R_1 &= \sum_{\alpha\alpha'} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} a_{n\nu n'\nu'}^{\alpha\alpha'} b_{n\nu n'\nu'}^{\alpha\alpha'} e^{i(na_x - n'a_y)\tau}, & R_2 &= \sum_{\alpha\alpha'} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} (a_{n\nu n'\nu'}^{\alpha\alpha'})^2 e^{i(n-n')a_x\tau}, \\
 K &= \sum_{\alpha\alpha'} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} a_{n\nu n'\nu'}^{\alpha\alpha'} (c_{n\nu n'\nu'}^{\alpha\alpha'} l_{n\nu y}^{\alpha\alpha'} - b_{n\nu n'\nu'}^{\alpha\alpha'} l_{n\nu z}^{\alpha\alpha'}) e^{i(n-n')a_x\tau}, & B &= \sum_{\alpha\alpha'} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} [(b_{n\nu n'\nu'}^{\alpha\alpha'} l_{n\nu z}^{\alpha\alpha'})^2 - (c_{n\nu n'\nu'}^{\alpha\alpha'} l_{n\nu y}^{\alpha\alpha'})^2], \\
 N &= - \sum_{\alpha\alpha'} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} [(b_{n\nu n'\nu'}^{\alpha\alpha'})^2 l_{n\nu z}^{\alpha\alpha'} l_{n\nu z}^{\alpha\alpha'} + (c_{n\nu n'\nu'}^{\alpha\alpha'})^2 l_{n\nu y}^{\alpha\alpha'} l_{n\nu y}^{\alpha\alpha'}] e^{i(n-n')a_x\tau}, & P &= \sum_{\alpha} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} (a_{n\nu n'\nu'}^{\alpha\alpha'})^2 e^{i(n-n')a_x\tau}, \\
 M &= \sum_{\alpha} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} (b_{n\nu n'\nu'}^{\alpha\alpha'} l_{n\nu z}^{\alpha\alpha'} - c_{n\nu n'\nu'}^{\alpha\alpha'} l_{n\nu y}^{\alpha\alpha'}) a_{n\nu n'\nu'}^{\alpha\alpha'} e^{i(n-n')a_x\tau}, & C &= k_{n\nu}^{\alpha\beta} + \sum_{n'\alpha'} \lambda_{n\nu n'\nu'}^{\alpha\alpha'} (a_{n\nu n'\nu'}^{\alpha\alpha'})^2, & L &= \lambda_{n\nu n'\nu'}^{\alpha\alpha'} e^{i(n-n')a_x\tau}.
 \end{aligned} \tag{5}$$

From expressions (3) and (5) we see that the variables do not separate along the dispersion curve; consequently, all types of vibrations are coupled with each other.

The motion of absolutely rigid molecules is determined by the condition

$$\eta_{n\nu n'\nu'}^{\alpha\alpha'} = 0,$$

i. e., is described by the determinant in the upper left-hand corner (this case was examined earlier in Ref. 3).

The movement of atoms inside a fixed molecule, obtained when the motion of the molecule as a whole is eliminated is described by the determinant in the lower right hand corner. We see that the intramolecular frequencies in the crystal are displaced by an amount on the order of the natural frequencies of the crystal. Each frequency of the isolated molecule splits and gives rise to ν dispersion modes.

In both intermolecular and intramolecular vibrations there is obtained a determinant of the $3s\nu$ th order in which the nondiagonal terms between the blocks contain linear functions of the coefficients λ , i. e., quantities of the next lower order compared with terms pertaining to the intramolecular oscillations. Solution of the determinant in general form is impossible. However, the presence of different orders of the coefficients indicates that an approximate solution is possible in principle.

The most direct, although cumbersome, method consists of reducing the secular equation to a polynomial form, for example, by the method of A. N. Krylov, and then finding the roots by Newton's method of successive approximations.

The presence of symmetry in the crystal makes it possible to utilize the method of group theory to quasi-linearize the determinant that corresponds to the limiting frequencies by introducing geometrically symmetrical coordinates. The blocks in the determinant thus obtained correspond to the coordinates of the non-separating oscillations. The frequencies associated with the determinant blocks can also be found by Newton's method.

Separation of the lattice and intermolecular vibrations is possible only for the limiting frequencies in special cases of symmetry. It will be seen from the expression for the potential energy that the intramolecular displacement vectors $\eta_{n\nu}^{\alpha\beta}$ enter into the vector $r_{n\nu}^{\alpha}$ with different signs relative to the coordinates of the displacement of the center of gravity of the molecules for each atomic pair α and β . The same thing applies to the rotation vectors $l_n \times \theta_n$. This means that these vectors are characterized by identical symmetry relative to the coordinates of displacement of the center of gravity and that therefore the separation of the translational and intermolecular oscillations for the limiting frequencies occurs for the same types of symmetry as the separation of the translational and orientational oscillations. The conditions for separation of the last have been analyzed in Refs. 1 and 3.

2. By way of illustrative example let us examine a two-dimensional square lattice containing two diatomic molecules per unit cell (see figure). For it to be possible to determine the limiting frequencies corresponding not only to the wave vector $\tau = 0$ but also to the vector $\tau = \pi/a$, let us double the number of molecules in the cell.

According to expression (2), the coordinates of the atoms will be

$$\begin{aligned}
 x_{2k-1}^{\alpha} &= x_{2k-1} + 1/2 (-1)^k l\vartheta_{2k-1}; & x_{2k}^{\alpha} &= x_{2k} + 1/2 (-1)^{\alpha} \eta_{2k}; \\
 y_{2k-1}^{\alpha} &= y_{2k-1} + 1/2 (-1)^{\alpha} \eta_{2k-1}; & y_{2k}^{\alpha} &= y_{2k} - 1/2 (-1)^{\alpha} l\vartheta_{2k}
 \end{aligned} \tag{6}$$

($\alpha = 1, 2$ and $k = 1, 2$). We shall neglect second-order quantities in the projections of the displacements.

Let us agree to limit our examination to interaction with nearest neighbors: then each molecule will

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ANGULAR DISTRIBUTIONS OF PHOTOFISSION FRAGMENTS FROM URANIUM

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The angular distributions of photofission fragments from uranium at x-ray energies of 9.4, 12 and 26.5 Mev were determined using a 30 Mev synchrotron. The anisotropy was found to increase sharply with decreasing x-ray energy. The ratios of the anisotropic to the isotropic fission yields at the above energies 0.55 ± 0.09 , 0.13 ± 0.05 , and 0.05 ± 0.04 respectively.

THE angular distributions of photofission fragments from uranium were determined with nuclear emulsions. The source of the x-rays was the 30 Mev synchrotron of the Physics Institute of the Academy of Sciences.

Ilford D-1 plates of 100 and 200 μ thickness were impregnated with a saturated solution of uranyl acetate and were placed in the x-ray beam at a distance of 1 m from the synchrotron target. The method of Belovitskii and Romanova¹ of impregnation and final development of the emulsions was utilized. By a careful timing of the different steps in the processing of the emulsions we succeeded in obtaining clearly legible tracks of the fission fragments while the α -tracks were scarcely noticeable. The plates were irradiated at the following three synchrotron energies: 9.4, 12, and 26.5 Mev.

The scanning was performed with MBI-2 microscopes with a 60 \times objective and 5 \times ocular. In scanning, all tracks with dip angles greater than 15 $^\circ$ were rejected. For the retained tracks the angles between the direction of motion of the fragments and the x-ray beam were measured. Since the origin of the tracks could not be determined the angles ϑ and $\pi - \vartheta$ were indistinguishable and the obtained angular distribution is actually $[I(\vartheta) + I(\pi - \vartheta)]$.

In order to determine the fraction of fissions due to background neutrons some of the uranium-impregnated plates were placed at the time of the irradiation outside of the x-ray beam. The fissions in these plates could be due to the background neutrons which are approximately uniformly distributed around the synchrotron, and to scattered γ -rays. The scanning of these plates revealed that for all x-ray energies the

TABLE I. Angular distribution of photofission fragments from U²³⁸

| Maximum x-ray energy, E_{\max} Mev | Number of tracks | Distribution of tracks (per steradian) | | |
|--------------------------------------|------------------|----------------------------------------|------------------------------------|-----------------------------------|
| | | 0-30 $^\circ$ 180-150 $^\circ$ | 30-60 $^\circ$ 150-120 $^\circ$ | 60-90 $^\circ$ 120-90 $^\circ$ |
| 9.4 | 3901 | 1 \mp 0.03 | 1.35 \mp 0.04 | 1.36 \mp 0.04 |
| 12 | 2053 | 1 \mp 0.04 | 1.09 \mp 0.04 | 1.16 \mp 0.04 |
| 26.5 | 2507 | 1 \mp 0.04 | 1.10 \mp 0.04 | 1.06 \mp 0.04 |