Elastic constants and anisotropic pair correlations in solid hydrogen and deuterium[1]

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The anisotropic displacement–displacement correlation function for the two types of pairs of nearest neighbours in solid hcp hydrogen and deuterium is studied. Two mechanisms contributing to the deviation of the pair distribution function from axial symmetry around the pair axis are identified. The one is due to the anisotropy of the phonon dispersion relations and is treated in a generalized Debye model parameterized in terms of the elastic constants. The elasticity tensor is decomposed into rotationally irreducible parts, and certain new relations between the elastic constants of hcp crystals with central forces are derived. The other mechanism arises from the immediate, anisotropic environment of a pair and is treated using a generalized Einstein model. The relevance of these results for the interpretation of the microwave spectrum of pairs of orthohydrogen molecules in parahydrogen is also discussed.

On étudie la fonction de corrélation anisotrope déplacement–déplacement pour les deux types de paires de plus proches voisins dans les cristaux hc de l'hydrogène et du deutérium solides. On identifie deux mécanismes qui contribuent à faire dévier la fonction de distribution des paires de la symétrie axiale autour de l'axe des paires. Le premier mécanisme est dû à l'anisotropie des relations de dispersion des phonons, et on le traite dans le cadre d'un modèle de Debye généralisé dont les paramètres sont exprimés en termes des constantes d'élasticité. Le tenseur d'élasticité est décomposé en parties rotationnellement irréductibles, et certaines relations nouvelles entre les constantes d'élasticité des cristaux hc avec forces centrales sont établies. Le second mécanisme provient de l'environnement immédiat anisotrope d'une paire, et on le traite en utilisant un modèle d'Einstein généralisé. On discute aussi la portée de ces résultats sur l'interprétation du spectre de micro-ondes de paires de molécules d'orthohydrogène dans le parahydrogène.

[Traduit par le journal]

1. Introduction

The recent observation (1, 2) at high resolution of the microwave absorption spectrum of pairs of orthohydrogen molecules in parahydrogen crystals has provided extremely accurate data about the intermolecular interactions in the solid. A key element in the theory of the rotational level structure of the solid is the replacement of the intermolecular interactions by the 'renormalized' interactions which, in first approximation, are given by the average values of the instantaneous interactions over the vibrational motion of the centres-of-mass of the molecules (3–6). In solid hydrogen at low temperatures only the motion due to the zero-point lattice vibrations need be considered.

According to neutron scattering experiments (7), the single-particle distribution of the molecular displacements around the lattice sites is spherically symmetric, as is natural in view of the close-packed structure of the solid. In first approximation, the pair distribution functions describing the correlations in the relative motions of the two molecules in nearest neighbour, and more distant, pairs are also

spherically symmetric. The renormalization of anisotropic interactions of definite tensorial form then does not change this form but only the magnitude of the coupling constants. For multipolar interactions, such as the electric quadrupole–quadrupole (EQQ) interaction, the coupling constants actually remain unchanged (8).

In higher approximation, the pair distribution functions show an axially symmetric anisotropy due to a smaller amplitude of the relative motion of the two molecules along the line joining them than perpendicular to it (3, 4, 6). The resulting renormalized pair interactions are still axially symmetric in this approximation, and in particular the form of the EQQ interaction is not changed but the EQQ coupling constant for nearest neighbours in solid hydrogen is reduced by about 10–20%. In the next stage of refinement one must expect that due to the dependence of the phonon frequencies and polarizations on the direction of propagation, and due to the crystalline environment of a pair, the axial symmetry of the pair distribution function will be broken. Averaged over such a distribution, the EQQ interaction yields a component which contributes to the splitting of the ground rotational level of an orthohydrogen pair in a parahydrogen matrix.

The inclusion of this effect has been found indispensable for arriving at a consistent analysis of the microwave results. The magnitude of the effect is described by the nonaxiality parameter η defined as

[1] $$\eta = \langle u_x^2 - u_y^2 \rangle / R_0^2$$

where $u = u_1 - u_2$ is the relative displacement of molecules 1 and 2 with equilibrium separation R_0, the z axis is along the equilibrium intermolecular line, and the x and y axes are chosen in a suitable way relative to the surroundings of the pair, cf. [5] and [6]. The order of magnitude of the absolute value of η obtained (5) from an analysis of the microwave spectra is 2×10^{-3} which should be compared with the value 1.1×10^{-2} of $\langle u_{1x}^2 \rangle / R_0^2$, cf. [7]. One of the purposes of the present paper is to present a calculation of η for in-plane (ip) and out-of-plane (op) pairs based on the lattice dynamical properties of the solid.

In the self-consistent phonon theory (9), the ground state wave function is assumed to be the product of a Gaussian and a Jastrow function. The latter describes the short-range correlations in the hard-core region of the intermolecular potential, whereas the former gives meaning to the phonon concept in quantum crystals. As pointed out by Horner (10), the internal consistency of this procedure requires that the Jastrow function should affect explicitly only the moments of the pair distribution function higher than the second. Since η depends only on the second moments

[2] $$\langle u_\alpha u_\beta \rangle = \int g(u) u_\alpha u_\beta \, du$$

of the pair distribution function, $g(u)$, we may replace $g(u)$ in the calculation of η by its Gaussian part which corresponds to the ground state of a model harmonic Hamiltonian. The force constants appearing in the latter can be obtained from the true intermolecular potential by the usual methods of the theory of quantum crystals (9), and these force constants, and hence the Gaussian part of $g(u)$, will of course depend implicitly on the assumed Jastrow function. Such a calculation requires a large computational effort, and will not be attempted here. Instead we approximate the above harmonic Hamiltonian by simple models requiring only a small number of parameters.

Two contributions to η of a rather different nature can be distinguished and will be calculated in this paper. The one arises from the dependence of the phonon frequencies and polarizations on the direction of propagation relative to the c axis. This effect is present also in an anisotropic continuous medium where the pair 1, 2 can be any two points. A

natural model for the calculation of this effect is a generalized Debye model in which the anisotropy of the phonon propagation is taken into account. This model is parameterized in terms of the long-wavelength modes which in turn depend on the elastic constants of the medium, for which the experimental values can be used, obtained from neutron scattering, Brillouin scattering, or speed-of-sound experiments. To carry out this program it is convenient to decompose the elasticity tensor into parts transforming irreducibly under rotations, as discussed in Sect. 3. Certain new relations between the elastic constants of hcp structures obtained along these lines as a by-product, and of interest in connection with the compressibility of these crystals, are also discussed in Sect. 3. The calculation of the pair correlation matrix [2] on the basis of the anisotropic Debye model is presented in Sect. 4. The Debye model cannot be expected to be accurate for the short-wavelength modes for which the molecular displacements in the real crystal, as contrasted to the continuum, will depend on the precise arrangement of the immediately surrounding molecules of the pair. This effect and in particular the influence of the difference in the surroundings of the two types of pair, is investigated in Sect. 5 on the basis of a generalized Einstein model in which the coupling between neighbouring, originally isotropic Einstein oscillators, is taken into account by perturbation theory. In Sect. 6 our results are compared with those in ref. 6, and the consequences for the analysis of the microwave spectrum are discussed.

2. Definition of the Different Coordinate Frames

It is convenient to list together the three frames used in the calculations. The local frames introduced here are the same as in ref. 4, but slightly different from those used in ref. 6.

(a) The Crystal Frame

The crystal frame is $(\hat{\imath}, \hat{\jmath}, \hat{k})$, where $\hat{k}$ is directed along the c axis of the crystal, and the $\hat{\imath}\hat{k}$ plane contains the vector τ connecting the two molecules in the unit cell. The primitive translation vectors are

[3] $$t_1 = \tfrac{1}{2}a(3^{1/2}\hat{\imath} - \hat{\jmath})$$
$$t_2 = \tfrac{1}{2}a(3^{1/2}\hat{\imath} + \hat{\jmath})$$
$$t_3 = c\hat{k} = (8/3)^{1/2} a\hat{k}$$

and

[4] $$\tau = \tfrac{1}{3}(t_1 + t_2) + \tfrac{1}{2}t_3$$

The local frames for the ip and op pairs are cho-

sen such that the two molecules lie on the local z axis which points from molecule 1 to 2, and such that the local xz plane is a plane of reflection symmetry of the lattice.

(b) The In-plane Frame

The unit vectors $\hat{x}$, $\hat{y}$, $\hat{z}$ of this frame are defined by

$$a\hat{x} = 3^{-1/2}(2t_1 - t_2)$$
$$[5] \qquad a\hat{y} = -(3/8)^{1/2}t_3$$
$$a\hat{z} = t_2$$

and the two molecules are at $R_1 = 0$ and $R_2 = t_2$. The ip frame is obtained from the crystal frame by a rotation with Euler angles $(\alpha\beta\gamma) = (\frac{1}{2}\pi, \frac{1}{2}\pi, -\frac{1}{2}\pi)$.

(c) The Out-of-plane Frame

The op frame with unit vectors $\hat{x}$, $\hat{y}$, $\hat{z}$ defined by

$$a\hat{x} = 2^{1/2}(\frac{1}{4}t_3 - \frac{1}{3}t_1 - \frac{1}{3}t_2)$$
$$[6a] \qquad a\hat{y} = t_1 - t_2$$
$$a\hat{z} = \tau$$

The two molecules are at $R_1 = 0$ and $R_2 = \tau$ and belong to the same unit cell. The Euler angles of the op frame relative to the crystal frame are $(0, \beta_0, 0)$ where $\cos^2\beta_0 = \frac{2}{3}$.

In the present context a more natural choice of the op frame is to rotate the frame [6] through 90° around the z axis, giving

$$[6b] \qquad \hat{x}' = \hat{y}, \quad \hat{y}' = -\hat{x}, \quad \hat{z}' = \hat{z}$$

For both pairs the x axes are then perpendicular to the c axis. We note that since $\eta'(\text{op}) = -\eta(\text{op})$, the relative sign of η for the two pairs depends on the choice of frame.

3. The Elastic Constants and the Anisotropy of the Long-wavelength Modes in Hexagonal Crystals

The frequencies, $\omega(q)$, and polarization vectors, $e(q)$, of the long-wavelength modes ($qa \ll 1$) in a crystal satisfy a wave equation of the form

$$[7] \qquad \rho\omega^2 e_\alpha = C^{\alpha\beta\gamma\delta} q_\beta q_\delta e_\gamma$$

where the indices refer to Cartesian components, and the summation convention is used. For a composite lattice, the elasticity tensor C consists of two parts (11, 12)

$$[8] \qquad C = C_{\text{ext}} + C_{\text{int}}$$

where in the notation of ref. 11, p. 239,

$$[9] \qquad C_{\text{ext}}^{\alpha\beta\gamma\delta} = [\alpha\gamma, \beta\delta] + [\gamma\beta, \alpha\delta] - [\gamma\delta, \alpha\beta]$$

and

$$[10] \qquad C_{\text{int}}^{\alpha\beta\gamma\delta} = (\alpha\beta, \gamma\delta)$$

the brackets being definite expressions involving the force constants of the lattice. The quantity [10] is the contribution from the so-called internal strain which is the microscopic displacement of the sublattices relative to each other induced by an externally imposed macroscopic deformation.

The elasticity tensor $C^{\alpha\beta\gamma\delta}$ possesses the point group symmetry of the lattice and the additional symmetry relations (11)

$$[11] \qquad C^{\alpha\beta\gamma\delta} = C^{\beta\alpha\gamma\delta} = C^{\alpha\beta\delta\gamma} = C^{\delta\gamma\alpha\beta}$$

To take advantage of these symmetry properties it is convenient to use spherical tensors. Under rotations of the coordinate system the fourth rank tensor C transforms contragrediently to a direct product of two symmetrical, second rank, Cartesian tensors, since for an eigenmode of [7] the quantity

$$[12] \qquad C^{\alpha\beta\gamma\delta} q_\beta q_\delta e_\alpha e_\gamma = \rho\omega^2$$

is invariant. The tensor C is reducible and out of its components one can form five irreducible tensors, either according to the coupling scheme $(qq)(ee)$ or $(qe)(qe)$. Using the former, we obtain the set

$$C_{4M}^{(22)} \sim \{(qq)^2; (ee)^2\}^{4M}$$
$$C_{2M}^{(22)} \sim \{(qq)^2; (ee)^2\}^{2M}$$
$$[13] \qquad C_{2M}^{(20)} \sim \{(qq)^2; (ee)^0\}^{2M}$$
$$C_{00}^{(22)} \sim \{(qq)^2; (ee)^2\}^{00}$$
$$C_{00}^{(00)} \sim \{(qq)^0; (ee)^0\}^{00}$$

with a total of $9+5+5+1+1=21$ components. In [13] the $\sim$ mean "contravariant to," $\{A^j; B^{j'}\}^{JM}$ denotes the M component of a spherical tensor of rank J formed from the irreducible tensors A^j and $B^{j'}$,

$$[14] \quad \{A^j; B^{j'}\}^{JM} = \sum_{m,m'} C(jj'J; mm'M)A^{jm}B^{j'm'}$$

and

$$[15] \qquad (qq)^{jm} = C(11j; 000)q^2 C_{jm}(\theta, \phi)$$
$$[16] \qquad (ee)^{jm} = C(11j; 000) C_{jm}(\beta, \alpha)$$

where (q, θ, ϕ) and $(1, \beta, \alpha)$ are the polar coordinates of q and e, respectively, and

$$[17] \qquad C_{jm}(\theta, \phi) = (4\pi/2j + 1)^{1/2} Y_{jm}(\theta, \phi)$$

Tensors of odd rank and those containing odd-rank tensors in the intermediate stage of the coupling, vanish in virtue of the relations [11]. The set of

irreducible tensors obtained by using the coupling scheme $(qe)(qe)$ in [13] will be denoted by $\bar{C}_{LM}^{(ll')}$. The sets $C_{LM}^{(ll')}$ and $\bar{C}_{LM}^{(ll')}$ are equivalent in the sense that they are related by a unitary transformation.

The number of independent components of C is reduced further by the point symmetry of the lattice. For an isotropic medium only the two scalars $C_{00}^{(00)}$ and $C_{00}^{(22)}$ remain, the Lamé coefficients. Under cubic symmetry the combination C_{40} + $(5/14)^{1/2} (C_{44} + C_{4\bar{4}})$ is invariant and hence may be nonvanishing, resulting in a total of three independent elastic parameters. For a hexagonal system there are five nonvanishing components, $C_{00}^{(00)}$, $C_{00}^{(22)}$, $C_{20}^{(20)}$, $C_{20}^{(22)}$, and $C_{40}^{(22)}$, which are invariant under rotations around the c axis. Expressions for the irreducible components of C in terms of the Cartesian components are given in the Appendix.

For a close-packed hexagonal lattice no further reduction of the number of independent components is possible on the basis of symmetry, since the symmetry elements are the same for all values of c/a. However, for $c/a = (8/3)^{1/2}$ an "accidental degeneracy" arises (13). Consider a lattice sum of the form

[18] $$S = \sum_{j \neq 1} f(\mathbf{R}_{1j})$$

where $f(\mathbf{R})$ falls off faster than R^{-3}, so that the sum converges absolutely. If $f(\mathbf{R})$ is decomposed into components transforming as spherical tensors under rotations, the contributions from the first two shells of neighbours to the second-rank components vanish identically for any $f(\mathbf{R})$. As an illustration of this property consider an arrangement of charges on the lattice where each of the 12 sites nearest to the central site is assigned a charge q_1, and each of the 6 next nearest sites a charge q_2. The quadrupole moment of this arrangement as a function of c/a goes through zero at the point $(8/3)^{1/2}$. The contributions from the more distant shells to the second-rank part of [18] alternate in sign and as a result this part is usually negligibly small.

The above property of the hcp lattice leads to an additional reduction of the number of independent elastic parameters if one assumes pairwise, central effective interactions. The external part of the elasticity tensor can then be expressed (ref. 11, p. 248) in the form [18], and in an hcp lattice the two second-rank components of C_{ext} therefore vanish for all practical purposes,

[19] $$C_{20}^{(20)}{}_{ext} = C_{20}^{(22)}{}_{ext} = 0$$

On the other hand, C_{int} is not of the form [18] even for central forces, and its second-rank components therefore need not vanish.[2] However, $C_{20}^{(20)}{}_{int}$ and $C_{20}^{(22)}{}_{int}$ are not independent. One can show from the hexagonal symmetry that for central forces

[20] $$\bar{C}_{20}^{(20)}{}_{int} = 0$$

where the definition of $\bar{C}$ differs from [13] by the order of the coupling,

[21] $$\bar{C}_{20}^{(20)} \sim \{(qe)^2 : (qe)^0\}^{20}$$

Since $\bar{C}_{20}^{(20)}{}_{ext}$ is a linear combination of $C_{20}^{(20)}{}_{ext}$ and $C_{20}^{(22)}{}_{ext}$, [19] and [20] together imply that

[22] $$\bar{C}_{20}^{(20)} = 0$$

for hcp crystals and central forces. Transcribed into the conventional matrix notation (cf. the Appendix), [22] reads

[23] $$C_{33} + C_{13} - C_{12} - C_{11} = 0$$

This relation has been known empirically for several years. Franck and Wanner (15) derived it for hcp helium from the compressibility data for hydrostatic pressure, which show that the c/a ratio does not change with pressure. Since the anisotropy of the compressibility of hexagonal crystals is determined by the single coefficient (16)

[24] $$\beta = C_{33} + C_{13} - C_{12} - C_{11}$$

this coefficient must vanish for helium, thus implying [23]. Wanner and Meyer (17) noted that various hcp crystals have a similar elastic behaviour, in contrast to crystals for which c/a is not equal to $(8/3)^{1/2}$. This led them to postulate the validity of [23] for solid parahydrogen for which the pressure dependence of c/a had not been investigated, but for which c/a was known to be very close to $(8/3)^{1/2}$ at normal pressure. This argument can now be reversed. The validity of [23] for hcp crystals with central forces leads to their isotropic compressibility.

We now return to the wave equation [7], and we note that it is equivalent to the variational problem of finding the extrema of the invariant form

[25] $$I_q(e) = C^{\alpha\beta\gamma\delta} q_\beta q_\delta e_\alpha e_\gamma$$

for a fixed q and varying e subject to the normalization condition

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[2]It was claimed recently (14) that the central potential model predicts zero internal strain in the hcp lattice, but this conclusion is incorrect. Contrary to the author's assertion, his expression (9.30), p. 101, does not vanish even for the simplest nearest neighbour central force model.

[26] $e^{\alpha}e_{\alpha} = 1$

The vectors $e(q)$ for which $I_q(e)$ is stationary satisfy [7] and hence are the polarization vectors of the modes with wave vector q. The stationary values of $I_q(e)$ determine the frequencies through the relation

[27] $\rho\omega^2(q) = I_q[e(q)]$

We rewrite [25] in terms of the irreducible tensors [13],

[28] $I_q(e) = \sum\limits_{l,l'} \sum\limits_{L,M} C_{LM}^{(ll')}\{(qq)^l, (ee)^{l'}\}^{LM}$

Using [14]–[16], the explicit expression for $I_q(e)$ in terms of the polar angles of q and e in the crystal frame is readily found to be

[29] $q^{-2}I_q(e) = (1/3)C_{00}^{(00)} - (1/6\sqrt{2})C_{20}^{(20)}(2 + 3\cos 2\theta + 3\cos 2\beta) + (1/24)A_0^{22}(1 + 3\cos 2\beta)$
$\times (1 + 3\cos 2\theta) - \tfrac{1}{2}A_1^{22}\sin 2\beta \sin 2\theta \cos(\alpha - \phi) + (1/8)A_2^{22}(1 - \cos 2\beta)(1 - \cos 2\theta)\cos[2(\alpha - \phi)]$

where the coefficients A_m^{22} are linear combinations of the elastic constants given by

[30] $A_m^{22} = \sum\limits_L C(22L; m\bar{m}0)C_{L0}^{(22)}$

or by [A5]. Minimization of [29] with respect to α and β yields three orthogonal directions of polarization for each $\hat{q} = (\theta, \phi)$, viz.,

$\alpha_1 = \phi + \tfrac{1}{2}\pi,$ $\beta_1 = \tfrac{1}{2}\pi$ (e_1)

[31] $\alpha_2 = \phi,$ $\tan 2\beta_2 = B(\theta)$ (e_2)

$\alpha_3 = \phi + \pi,$ $\tan 2\beta_3 = -B(\theta)$ (e_3)

where

[32] $B(\theta) = \dfrac{2(C_{44} + C_{13})\sin 2\theta}{C_{33} - C_{11} + (C_{11} + C_{33} - 2C_{44})\cos 2\theta}$

The vector e_1 lies in the basal plane perpendicular to q and specifies the truly transverse mode (T_1). The other two modes, with displacement vectors lying in the plane containing q and the z-axis, are called quasilongitudinal (L) and quasitransverse (T_2). It is always possible to choose the values of the arc tangent in [31] so that the L mode corresponds to e_2 and the T_2 mode to e_3.

We note that the result [31] has been established for a general hexagonal lattice without assuming the validity of [23]. It shows that the polarization vectors of the sound waves in an arbitrary hexagonal crystal depend on only four of the five elastic constants and are independent of C_{12}. Moreover, C_{12} is involved only in the expression for the frequency of the T_1 mode and not in those for the other two modes. The three speeds of sound, $v_j = \omega_j/q$, in the direction of $\hat{q} = (\theta, \phi)$ are found from [27] and [29]. Substituting [31] into [29], we obtain the result

[33] $\rho v_1^2(\theta) = f_1 + f_2 \cos 2\theta$

[34] $\rho v_{2,3}^2(\theta) = g_1 + g_2(\cos 2\theta + \cos 2\beta_{2,3})$

$+ g_3 \cos 2\theta \cos 2\beta_{2,3} + \exp[i(\phi - \alpha_{2,3})]$
$\times g_4 \sin 2\theta \sin 2\beta_{2,3}$

where

[35] $4f_1 = 2C_{44} + C_{11} - C_{12}$
$4f_2 = 2C_{44} - C_{11} + C_{12}$

and

[36] $4g_1 = C_{33} + C_{11} + 2C_{44},$ $4g_2 = C_{33} - C_{11}$
$4g_3 = C_{33} + C_{11} - 2C_{44},$ $2g_4 = C_{13} + C_{44}$

We see that C_{12} appears only in [33]. If we rewrite this equation in the form

[37] $\rho v_1^2(\theta) = \tfrac{1}{2}(C_{11} - C_{12})\sin^2\theta + C_{44}\cos^2\theta$

it becomes apparent that a speed-of-sound measurement of C_{12}, which would allow a test of the validity of the relation [23], requires a measurement of the speed of the T_1 mode propagating at a sufficiently large inclination to the c axis.

The dispersion relations [33], [34] for elastic waves in hexagonal crystals have been known for a long time (18). However, we believe that the method of derivation proposed here, as well as the simple analytic form [31] for the polarization directions, are new. The most important result for our present purpose is the anisotropy of the long-wave-length modes described by [31], [33], [34], which will be applied in the next section to the calculation of the nonaxiality parameter.

4. Calculation of the Pair Correlation Function and Nonaxiality Parameter in the Anisotropic Debye Model

Solid parahydrogen has an hcp structure with two identical molecules per unit cell. In the Debye model of the lattice vibrations, the three optic modes corresponding to each wave vector in the first Brillouin zone (BZ) are treated as acoustic modes extrapolated to wave vectors in the second BZ. In terms of the normal modes of the corresponding harmonic lattice Hamiltonian, the displacement correlation matrix for a pair of molecules at a separation R_{12},

[38] $\Lambda_{\alpha\beta} = \langle 0|(u_{2\alpha} - u_{1\alpha})(u_{2\beta} - u_{1\beta})|0\rangle$

is then given by

[39] $\Lambda_{\alpha\beta} = (\hbar/MN) \sum_{q,j} \omega_j^{-1}(q)e_{j\alpha}(q)e_{j\beta}(q)$
$$\times (1 - \cos q \cdot R_{12})$$

where MN is the total mass of the crystal.

The main approximation involved in the Debye model is that the true dispersion relations are replaced for all q by the long-wavelength limit,

[40] $$\omega_j(q) = v_j(\hat{q})q$$

where $v_j(\hat{q})$ is the speed of sound of polarization j in the direction $\hat{q}$. In the generalized, or anisotropic, Debye model adopted here, the velocities of sound are assumed to be given by [33], [34], and the polarization vectors by [31]. Substituting [40] into [39], and replacing the sum over $\hat{q}$ over the first and second BZ by an integral over a Debye sphere with radius q_D given by

[41] $$q_D R_0 = (6\pi^2\sqrt{2})^{1/3}$$

we obtain

[42] $\Lambda_{\alpha\beta} = (\hbar/8\pi^3\rho) \int \sum_{j=1}^{3} [v_j^{-1}(\hat{q})e_{j\alpha}(\hat{q})e_{j\beta}(\hat{q})]$
$$\times f(\hat{q}, R_{12}) \, d\hat{q}$$

where

[43] $$f(\hat{q}, R_{12}) = \int_0^{q_D} q(1 - \cos q \cdot R_{12}) \, dq$$

This radial integral can be performed exactly, giving

[44] $$f(\hat{q}, R_{12}) = q_D^2[n_1(\gamma_{12}) + \gamma_{12}^{-2} + \tfrac{1}{2}]$$

where

[45] $$\gamma_{12} = (q_D R_{12})\hat{q} \cdot \hat{R}_{12}$$

and

[46] $$n_1(x) = -(\cos x + x \sin x)/x^2$$

The remaining angular integral in [42] was evaluated numerically for various sets of elastic constants parameterizing $v_j(\hat{q})$ and $e_j(\hat{q})$ as given by [31]–[36]. In Table 1 we list the different sets of elastic constants used in the calculations. These include the experimental sets of Nielsen (7), Wanner and Meyer (17), and Thomas (19), as well as the theoretical set calculated by Goldman (20) on the basis of the self-consistent phonon theory. The results of calculations of the dimensionless displacement correlation matrix, $\Lambda_{\alpha\beta}/R_0^2$, are shown in Table 2 where the superscripts refer to the local frames [5] and [6b].

As seen from Table 2, the results for the different sets of elastic constants are reasonably consistent, except for the Wanner and Meyer (17) set. Moreover, the Wanner and Meyer elastic constants lead to another difficulty. We have also calculated the matrix $\Lambda_{\alpha\beta}$ for hcp deuterium using the elastic constants and lattice parameters quoted in Nielsen (7) and Wanner and Meyer (17). Using the Nielsen data, we find that the resultant matrix for D_2 is very nearly proportional to that for H_2,

[47] $$[\Lambda_{\alpha\beta}/R_0^2]_{D_2} = 0.54[\Lambda_{\alpha\beta}/R_0^2]_{H_2}$$

As a result, the ratio of η for the two solids is the same for ip and op pairs. This result is very plausible in view of the similarity of the two solids. On the other hand, using the Wanner and Meyer (17) elastic constants, a relation similar to [47] is not obtained and the ratio $\eta(D_2)/\eta(H_2)$ we calculate is quite different for the two pairs. viz., 1.59 for ip and 0.54 for op pairs. From this unreasonable result we conclude that the Wanner and Meyer set of elastic constants is not internally consistent.

From Table 2 it may appear that the results for η are not very sensitive to the precise values of the elastic constants used in the calculation, since there is a rather wide variation in the elastic constants shown in Table 1. However, we wish to point out that η is quite sensitive to the internal consistency of the elastic constants within a set. This point is illustrated by the following. Goldman (21) has separately calculated the external contribution [9] to the elasticity tensor in solid H_2 and D_2. As discussed in Sect. 3, this tensor has only three independent parameters because of the 'accidental' vanishing in a close-packed lattice of its two second rank components. It is convenient to take C_{13}, C_{33}, and C_{44} as the independent parameters, since in a hexagonal lattice these receive no contribution from the internal strain and must therefore be equal to the corresponding parameters of C_{ext}. The remaining two parameters, C_{11}^{ext} and C_{12}^{ext}, can be obtained from [19] and are given by

[48] $4C_{11}^{ext} = 3C_{33} + 2C_{44} + C_{13}$
$4C_{12}^{ext} = C_{33} - 2C_{44} + 3C_{13}$

Taking the values of C_{13}, C_{33}, and C_{44} from Table 1, the Goldman (20) set, we find $C_{11}^{ext} = 4.10$ kbar and $C_{12}^{ext} = 0.98$ kbar, which agree with the values quoted in ref. 21. Comparing these values with the Goldman set, we see that neglect of the internal strain contribution to C results in an error of about 10% for C_{11} and 30% for C_{12}. On the other hand, we find that these relatively small changes in C lead to a dramatic change in the values of η, viz.,

TABLE 1. Various sets of elastic constants (in kbar) for solid hydrogen and deuterium

Reference		C_{11}	C_{12}	C_{33}	C_{13}	C_{44}	V (cm^3/mol)
Nielsen (7)[a]	H$_2$	4.2	1.8	5.1	0.5	1.1	22.8
	D$_2$	8.2	2.9	10.2	0.9	2.3	19.94
Wanner and	H$_2$	3.62	1.19	4.40	0.41	0.83	22.87
Meyer (17)[b]	D$_2$	6.68	2.32	7.88	1.11	1.64	20.19
Thomas (19)[c]	H$_2$	3.32	1.30	4.08	0.56	1.04	23.20
Goldman (20)[d]	H$_2$	3.72	1.37	4.51	0.57	1.15	22.73

[a]Neutron scattering in p-H$_2$ at 5.4 K and o-D$_2$ at 5 K.
[b]Velocity of sound measurements on n-H$_2$ and o-D$_2$ at 4.2 K.
[c]Brillouin scattering in p-H$_2$ at 13.2 K.
[d]Theoretical calculations for p-H$_2$ at 0 K.

TABLE 2. Displacement correlation matrix and nonaxiality parameter in the anisotropic Debye model. Based on various sets of elastic constants designated as in Table 1

(a) In-plane pairs, frame [5]

Reference		$10^2 R_0^{-2} \times$				η ($\times 10^3$)
		Λ_{xx}	Λ_{yy}	Λ_{zz}	Λ_{yz}	
Wanner and Meyer (17)	H$_2$	2.048	2.040	1.921	0	0.08
Nielsen (7)	H$_2$	1.955	1.835	1.819	0	1.20
Thomas (19)	H$_2$	2.092	1.943	1.957	0	1.49
Goldman (20)	H$_2$	1.994	1.877	1.869	0	1.17
Wanner and Meyer (17)	D$_2$	1.185	1.172	1.111	0	0.13
Nielsen (7)	D$_2$	1.064	1.013	0.998	0	0.51

(b) Out-of-plane pairs, frame [6b]

Reference		$10^2 R_0^{-2} \times$				η' ($\times 10^3$)
		$\Lambda_{x'x'}$	$\Lambda_{y'y'}$	$\Lambda_{z'z'}$	$\Lambda_{y'z'}$	
Wanner and Meyer (17)	H$_2$	2.093	2.025	1.931	0.041	0.68
Nielsen (7)	H$_2$	1.975	1.880	1.767	0.070	0.95
Thomas (19)	H$_2$	2.107	2.015	1.877	0.074	0.92
Goldman (20)	H$_2$	2.012	1.931	1.808	0.063	0.81
Wanner and Meyer (17)	D$_2$	1.207	1.171	1.110	0.022	0.36
Nielsen (7)	D$_2$	1.078	1.033	0.974	0.034	0.45

[49]
$$10^3\,\eta(\text{ip}) = -0.49 \quad (1.17)$$
$$10^3\,\eta'(\text{op}) = 0.24 \quad (0.81)$$

where the correct values obtained with the Goldman set (20), in which the internal strain contribution is included, are shown in parentheses.

In connection with the results shown in Table 2, we make the following remarks. The distribution in the relative displacements, $u = u_2 - u_1$, can be represented by an ellipsoid M, $M^{\alpha\beta} u_\alpha u_\beta = 1$, where $M^{\alpha\beta}$ is the inverse of the correlation matrix $\Lambda_{\alpha\beta}$ defined by [38]. According to Table 2, the principal axes of M for ip pairs coincide with the axes [5], as demanded by the crystal symmetry, and M is flattened along the y axis, i.e., along the crystal c axis, giving a positive η. For op pairs, the third principal axis of M makes a small angle of the order of 1° with the local z' axis, and the flattening along the y' axis is less than for ip pairs, resulting in a smaller but still positive η'. These results are as expected for a

model describing a continuous, uniaxial medium in which the shape of the correlation ellipsoid for two points of given separation can depend only on the angle, θ_{12}, between the c axis and the line joining the two points. For $\theta_{12} = 0$, M must be axially symmetric, for $\theta_{12} = \frac{1}{2}\pi$, the asymmetry must be a maximum, and for a reasonably smooth anisotropy of the sound propagation, the asymmetry of M can be expected to vary smoothly between these two limits. In particular, the sign of η should be the same for all θ_{12}, provided the x axis of the local frame is always chosen parallel to the basal plane. These properties are all borne out by the results in Table 2.

5. Calculation of the Nonaxiality Parameter in a Perturbed Einstein Model

As explained in Sect. 1, the effect of the immediate crystalline environment on the pair correlation function of a pair of nearest neighbouring molecules cannot be expected to be given correctly in the Debye model introduced in Sect. 4, since in that model the motion of the molecules is assumed to be equal to that of the corresponding points in a continuous medium. We investigate this 'crystalline' effect here on the basis of an Einstein model perturbed by the intermolecular interaction which provides a coupling between neighbouring Einstein oscillators, which leads to a nonvanishing η depending on the spatial arrangement of the four common nearest neighbours of the pair.

The Hamiltonian for the lattice is

[50] $H = K + V$

where K is the kinetic energy of the translational motion of the molecules and V the total potential energy of interaction. In the Einstein model the Hamiltonian [50] is replaced by

[51] $H_0 = K + \sum_i \frac{1}{2} m \omega_E u_i^2 \equiv K + V_0$

where ω_E can be obtained by minimizing the expectation value of H over the ground state, $|0\rangle$, of H_0. We obtain instead a value of ω_E from the measured width of the single-particle distribution function,

[52] $u_i^2 = (3\hbar/2m\omega_E)$

According to inelastic neutron scattering data (7), this quantity in solid hydrogen at $T = 5.4$ K has the value 0.48 Å^2, giving $\omega_E = 9.8 \times 10^{12}$ rad/s, or $T_E = \hbar\omega_E/k = 75$ K.

In the Einstein model, the pair correlation function is axially symmetric and η vanishes. We now introduce

[53] $V_1 = V - V_0$

as a perturbation which in second order produces correlations leading to a nonvanishing value of η. The perturbed ground state correct to second order in V_1 is given by $|\psi_0\rangle = T|0\rangle$, where T is the operator (22)

[54] $T = 1 - \sum_N' \alpha_N p_N V_1 + \sum_N' \sum_M' \alpha_N \alpha_M p_N V_1 p_M V_1$
$- \sum_N' \alpha_N^2 (p_N V_1 p_0 V_1 + \frac{1}{2} p_0 V_1 p_N V_1)$

The primes indicate exclusion of the ground state, p_N is the projection operator onto the degenerate manifold of states with energy

$$E_N = \sum_i (N_i + 3/2)\hbar\omega_E$$

$$N = \sum_i N_i = 0, 1, 2, \ldots,$$

and

$$\alpha_N = (E_N - E_0)^{-1}$$

We assume for V a quadratic expression in the displacements u_i of the form

[55] $V = \frac{1}{2} \sum_{i,j} u_i \cdot \Phi_{ij} \cdot u_j$

where the constants Φ_{ij} are regarded as the effective force constants in the model harmonic Hamiltonian in the spirit of quantum crystal theory. We parametrize these force constants in terms of a model of pairwise, nearest neighbour, central effective interactions.

[56] $V = \sum_{i<j} \psi(R_{ij}^2)$

giving

[57] $\Phi_{ij}^{\alpha\beta} = -4R_{ij}^\alpha R_{ij}^\beta \psi'' - 2\delta_{\alpha\beta}\psi'$

where $R_{ij} = R_j - R_i$, α and β denote Cartesian components, and

[58] $\psi' = (d\psi/d(R^2))_{R_0}$, $\psi'' = (d^2\psi/d(R^2)^2)_{R_0}$

are the two parameters characterizing the model. The perturbation [53] is then given by

[59] $V_1 = \sum_{i<j} \sum_{\alpha\beta} \Phi_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta} + \sum_{i,\alpha} a_{i\alpha} u_{i\alpha}^2$

The last term turns out to give no contribution to η and may be discarded.

In the perturbed ground state η is given by

[60] $\eta = \langle\psi_0|\Omega|\psi_0\rangle/R_0^2$

where Ω is the operator

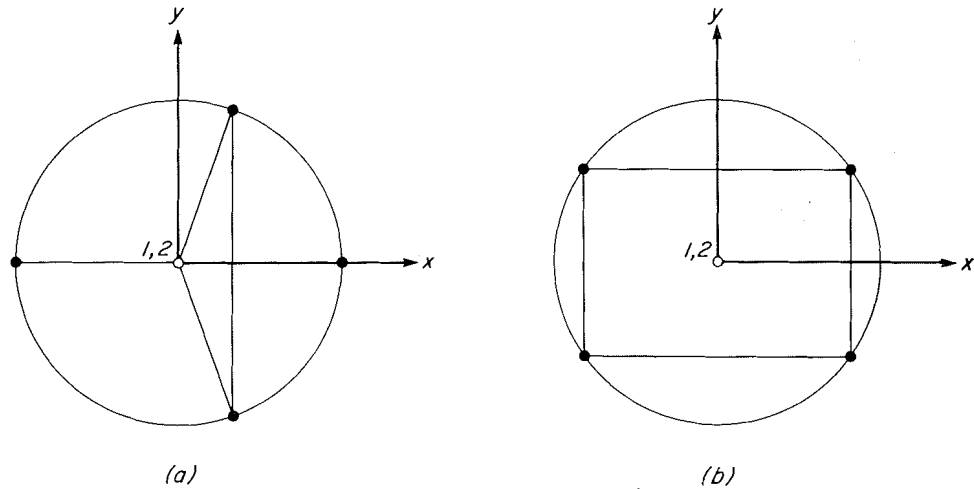[61] $\Omega = (u_{2x} - u_{1x})^2 - (u_{2y} - u_{1y})^2$

FIG. 1. Nearest-neighbour environment of ip pairs (*a*) and op pairs (*b*) in an hcp lattice. For both pairs the vector $\boldsymbol{R}_{12}$ points out of the page. The four common nearest neighbours of each pair shown by the black dots lie on a circle of radius $\frac{1}{2}\sqrt{3}R_0$ in the plane perpendicular to and bisecting $\boldsymbol{R}_{12}$.

which can be written as a sum of a single-particle and a two-particle operator, $\Omega = \Omega_1 + \Omega_2$, where

[62] $\qquad \Omega_1 = (u_{1x}^2 - u_{1y}^2) + (u_{2x}^2 - u_{2y}^2)$

[63] $\qquad \Omega_2 = 2(u_{1y}u_{2y} - u_{1x}u_{2x})$

In the central-force model, Ω_1 gives no contribution to [60],

[64] $\qquad \langle \psi_0 | \Omega_1 | \psi_0 \rangle = 0$

because for central forces the perturbed single-particle distribution function remains spherically symmetric in second order.

Using [54], [57], [59], and [64], we obtain

[65] $\quad \langle \psi_0 | \Omega | \psi_0 \rangle = [\langle 0 | V_1 p_2 \Omega_2 p_2 V_1 | 0 \rangle$

$\qquad\qquad + 2 \operatorname{Re} \langle 0 | \Omega_2 p_2 V_1 p_2 V_1 | 0 \rangle]/(2\hbar\omega_E)^2$

The only nonvanishing terms are of the form

$\qquad \langle 0 | \Omega_2 | 1_1 1_2 0_3 \rangle \langle 1_1 1_2 0_3 | V_1 | 1_1 0_2 1_3 \rangle \langle 1_1 0_2 1_3 | V_1 | 0 \rangle$

and

$\qquad \langle 0 | V_1 | 0_1 1_2 1_3 \rangle \langle 0_1 1_2 1_3 | \Omega_2 | 1_1 0_2 1_3 \rangle \langle 1_1 0_2 1_3 | V_1 | 0 \rangle$

where 3 refers to one of the four nearest neighbours common to molecules 1 and 2. This shows the nature of the processes contributing to η in this model. The term $\boldsymbol{u}_1 \cdot \boldsymbol{\Phi}_{12} \cdot \boldsymbol{u}_2$ in V_1 gives rise to an axially symmetric distortion and does not contribute to η, and the same remark applies to the purely quadratic terms in [59]. From [65] we obtain

[66] $\quad \langle \psi_0 | \Omega | \psi_0 \rangle = -(24\hbar\psi''^2/m^3\omega_E{}^5)$

$\qquad\qquad \times \sum_n (R_{1n}{}^x R_{2n}{}^x - R_{1n}{}^y R_{2n}{}^y) R_{1n} \cdot R_{2n}$

where the sum over *n* extends over the four

neighbours of the pair 1, 2, cf. Fig. 1. The angle between $\boldsymbol{R}_{1n}$ and $\boldsymbol{R}_{2n}$ is 60° for all four neighbours and both types of pair, and $\boldsymbol{R}_{1n} \cdot \boldsymbol{R}_{2n} = \frac{1}{2}R_0{}^2$, but the sum in [66] is different for the two types corresponding to p = ip and p = op, and is given by

[67] $\quad \sum_n (R_{1n}{}^x R_{2n}{}^x - R_{1n}{}^y R_{2n}{}^y) = \gamma(p)R_0{}^2$

where $\gamma(\mathrm{ip}) = \frac{1}{3}$ and $\gamma(\mathrm{op}) = 1$, and *x* and *y* refer to the pair frames defined in Sect. 2. Combining [60], [66], and [67], we get

[68] $\qquad \eta(p) = -\gamma(p)(12\hbar R_0{}^2/m^3\omega_E{}^5)\psi''^2$

For the effective potential ψ we use the Lennard-Jones potential of Raich and Kanney (23), with $\varepsilon = 1.25 \times 10^{-15}$ erg and $\sigma = 3.46$ Å, which was obtained by fitting the measured $k = 0$ optical phonon frequencies in parahydrogen to a harmonic lattice model. This is clearly the most appropriate potential to use in an Einstein model. The value of R_0 used in ref. 23 was 3.756 Å, giving $\psi'' = 2.1 \times 10^{16}$ erg/cm⁴, and hence

[69] $\quad \eta(\mathrm{ip}) = \frac{1}{3}\eta(\mathrm{op}) = -\frac{1}{3}\eta'(\mathrm{op}) = -0.77 \times 10^{-3}$

Thus in the Einstein model the magnitude of η for ip pairs is smaller than for op pairs, reflecting the fact that the immediate environment of ip pairs is more symmetric than for op pairs, cf. Fig. 1 and [67]. This result is in contrast to that for the Debye model where $\eta(\mathrm{ip})$ is larger than $\eta'(\mathrm{op})$. The two results are not contradictory, however, since the variation in η in the Debye model is largely determined by the angle, θ_{12}, between the pair axis and the *c* axis, whereas in the Einstein model the value of θ_{12} is irrelevant and the immediate environment plays the

determining role. We assume the two contributions to be additive and we regard the Einstein contribution as a correction of the short-wavelength contribution in the Debye model. This tends to decrease $\eta(ip)$ and to increase $\eta'(op)$, and hence to reduce the difference between the two pairs predicted by the Debye model.

The Einstein model predicts a definite ratio, $\eta(op)/\eta(ip) = 3$, and a definite sign of η, which can be expected to be realistic. On the other hand, the magnitude of the Einstein contribution is quite uncertain, since it depends on $\psi''(R_0)^2$ which is doubtless not given correctly by the Lennard-Jones model. At present, the magnitude of the Einstein contribution is therefore best regarded as an adjustable parameter, to be determined if possible from the experimental data, as discussed in the next section.

6. Concluding Remarks

Assuming that the contributions calculated in the Debye and Einstein models are additive, the final expression for η for the two types of pair, p, are

[70] $$\eta(p) = \eta_D(p) + \eta_E(p)$$

where with respect to the local frames [5] and [6] we have

[71] $$\eta_D(ip) = 1.20 \times 10^{-3},$$
$$\eta_D(op) = -0.95 \times 10^{-3}$$

and

[72] $$\eta_E(ip) = \tfrac{1}{3}\eta_E(op) \equiv \Delta$$

where according to [68] we have $\Delta < 0$. The values [71] correspond to the set of elastic constants from Nielsen (7) (H_2), and Δ is regarded as an adjustable parameter. Using [70], [71], [72], we find[3] from an analysis of the microwave data given in ref. 2 that $|\Delta| \lesssim 10^{-4}$ and that $\Delta < 0$ in agreement with the prediction [68].

Our results for η are quite different from those obtained in ref. 6, and in this connection we wish to make the following remarks. In ref. 6, η was obtained as a sum of two contributions, viz.,

[73] $$\eta(p) = \eta_1(p) + \eta_2(p)$$

where η_1 appears as a parameter in the self-consistent harmonic phonon wave function calculated by V. V. Goldman (unpublished) and quoted in ref. 6, with the values

[74] $$\eta_1(ip) = -0.1 \times 10^{-4}, \quad \eta_1(op) = -0.7 \times 10^{-4}$$

whereas η_2 is calculated numerically with the help

[3]S. Luryi and J. Van Kranendonk. To be published.

of a three-particle distribution function in the form of a product of three Jastrow functions, the result being

[75] $$\eta_2(ip) = \tfrac{1}{3}\eta_2(op) = -0.53 \times 10^{-3}$$

The latter calculation is essentially equivalent to our Einstein model, and the values [75] are in reasonable agreement with [69]. However, the numerical values are very uncertain, since the parameter $\psi''(R_0)^2$ in [69] and a similar parameter involved in [75] may easily be in error by one or two orders of magnitude.

The discrepancy between [74] and our corresponding Debye model result is not understood. Our result appears more reasonable since, as discussed in Sect. 4, in an elastically uniaxial medium one expects $\eta(ip)$ and $\eta(op)$ to be of the same order of magnitude, and $|\eta(op)| < |\eta(ip)|$, whereas [74] predicts the opposite relation and almost an order of magnitude difference. On the basis of [73]–[75] it was assumed in ref. 6 that $\eta(op) = 4\eta(ip)$. In our opinion, this assumption is incorrect and is the origin of the difficulties remaining in the analysis of the microwave spectrum carried out in ref. 6, as will be discussed in a separate paper.

Another conclusion can be drawn from our generalized Debye model relevant to the interpretation of the microwave results. Consider the 'oblateness' parameter

[76] $$\zeta = \langle u_x^2 + u_y^2 - 2u_z^2 \rangle / R_0^2$$

which measures the axially symmetric flattening of the pair distribution function, or of the ellipsoid M defined in Sect. 4, along the local z axis, which is responsible for the reduction of the multipolar coupling constants. As seen from Table 2, ζ is larger for op than for ip pairs, and the multipolar reduction factors, $\xi_{j+1,j}$, which decrease with increasing ζ, must hence be larger for ip than for op pairs. For the EQQ interaction we find, using the set of elastic constants of ref. 7 and assuming $c/a = (8/3)^{1/2}$,

[77] $$\xi_{54}(ip) - \xi_{54}(op) \cong 0.01$$

Therefore, a nonvanishing empirical value of the difference [77] of this order of magnitude or smaller cannot be interpreted as due to a deviation of the c/a ratio from the close-packed value, as suggested in ref. 2.

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Appendix: The Irreducible Components of the Elasticity Tensor

The explicit expression for the irreducible components [13] of the elasticity tensor C with Cartesian components C^{abcd}, corresponding to the coupling scheme $(qq)(ee)$ is

$$[A1] \quad C_{LM}^{(ll')} = \sum_{\mu...b'} C(11l; \mu\nu m)C(11l'; \mu'\nu'n)$$
$$\times C(ll'L; mnM)U^{\mu}{}_a U^{\nu}{}_b U^{\mu'}{}_{a'} U^{\nu'}{}_{b'} C^{aa'bb'}$$

where $U^{\mu}{}_a$ is the matrix of the transformation from Cartesian to spherical components, which has the nonvanishing elements

$$[A2] \quad U^1{}_x = -U^{-1}{}_x = iU^1{}_y = iU^{-1}{}_y = 2^{-1/2},$$
$$U^0{}_z = 1$$

The transformation [A1] is unitary in the sense that

$$[A3] \quad \sum_{a...d} C^{abcd}C_{abcd} = \sum_{l,l'} \sum_{L,M} (-1)^M C_{LM}^{(ll')} C_{L\bar{M}}^{(ll')}$$

In evaluating [A1] it is convenient to use the Voigt notation in which the six pairs of Cartesian indices are replaced by single numerical indices according to the scheme $xx = 1$, $yy = 2$, $zz = 3$, $yz = 4$, $xz = 5$, $xy = 6$, e.g., $C^{xxyy} = C^{yyxx} = C_{12}$, $C^{zzzz} = C_{33}$, etc.

Using [A1] for the independent components for hexagonal symmetry, we obtain

$$[A4] \quad C_{L0}^{(ll')} = \sum_m C(ll'L; m\bar{m}0)A_m^{ll'}$$

where

$$A_0^{00} = (1/3)(C_{33} + 4C_{44} + 3C_{11} - C_{12})$$
$$A_0^{20} = -(\sqrt{2}/6)(2C_{33} + 2C_{44} - 3C_{11} + C_{12})$$
$$[A5] \quad A_0^{22} = (1/6)(4C_{33} - 8C_{44} + 3C_{11} - C_{12})$$
$$A_1^{22} = -(C_{13} + C_{44})$$
$$A_2^{22} = \tfrac{1}{2}(C_{11} + C_{12})$$

The final expressions for the irreducible components in terms of the elastic constants are

$$C_{00}^{(00)} = (1/3)(C_{33} + 4C_{44} + 3C_{11} - C_{12})$$
$$C_{20}^{(20)} = -(\sqrt{2}/6)(2C_{33} + 2C_{44} - 3C_{11} + C_{12})$$
$$[A6] \quad C_{00}^{(22)} = (\sqrt{5}/30)(4C_{33}4C_{44} + 9C_{11}$$
$$+ 5C_{12} + 12C_{13})$$
$$C_{00}^{(22)} = -(\sqrt{14}/42)(4C_{33} - 2C_{44} - 3C_{11}$$
$$- 7C_{12} + 6C_{13})$$
$$C_{40}^{(22)} = (2\sqrt{70}/35)(C_{33} - 4C_{44} + C_{11} - 2C_{13})$$

The set of irreducible components corresponding to the alternative coupling scheme $(qe)(qe)$ can be obtained by replacing $C^{aa'bb'}$ in [A1] by $\tilde{C}^{aa'bb'} = C^{aba'b'}$. In particular, one finds in this way

$$[A7] \quad \tilde{C}_{20}^{(20)} = -(\sqrt{2}/3)(C_{33} + C_{13} - C_{11} - C_{12})$$

Since in an hcp lattice with central forces $\tilde{C}_{20}^{(20)} = 0$, we have that

$$[A8] \quad \beta = C_{33} + C_{13} - C_{11} - C_{12}$$

vanishes in such a lattice. Finally, from [A6] and [A7], or directly from the definitions, it follows that

$$[A9] \quad 3\tilde{C}_{20}^{(20)} = C_{20}^{(20)} + \sqrt{7}C_{20}^{(22)}$$

Hence if $\beta = 0$, we also have $C_{20}^{(20)} = -\sqrt{7}C_{20}^{(22)}$.