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Quadrupole Arrangements in Solid Hydrogen and Nitrogen

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A group-theoretical classification of all possible quadrupole arrangements in a crystal is carried out following the method of Opechowski and Guccione for the classification of spin arrangements in magnetic crystals. The method is applied to find possible quadrupole arrangements in the various phases of solid orthohydrogen and solid nitrogen. It turns out that the quadrupole arrangement in the cubic phase is T_h^6 with axially symmetric quadrupoles. In the hexagonal phase there are two possible arrangements with very low energy. One is C_{6v}^3, where none of the quadrupoles are axially symmetric, and the other is C_{6h}^2, where some are and some are not. The quadrupole arrangement of lowest energy in the tetragonal phase of solid nitrogen is D_{4h}^{14} with non–axial-symmetric quadrupoles.

I. INTRODUCTION

The phase transitions in solid hydrogen and solid nitrogen have been intensively studied during the past few years. They are believed to be mainly due to the quadrupole-quadrupole interaction between the molecules.[1-5] At high orthoconcentrations ($>60\%$) the molecular structure of solid hydrogen changes from hcp above the transition temperature to fcc below it. The transition temperature depends on the orthoconcentration,[3] being about 1.6 °K for normal hydrogen. The change in the crystal structure is accompanied by an onset of ordering of the orthomolecules. A similar situation exists in solid nitrogen,[5] whose molecular structure is hcp (the β phase) above 35.6 °K, and fcc (the α phase) below that temperature. Solid nitrogen is known to have also a high-pressure γ phase. At 20.5 °K and 4015 atm Schuch and Mills[5] found its molecular structure to be body-centered tetragonal (bct).

The knowledge of the ordered structure of the molecules in the ground state in each of the various phases is of particular interest. Experimental evidence exists[5,6] which supports a T_h^6 structure in the cubic phase and a D_{4h}^{14} structure in the tetragonal phase. Assuming each molecule to be represented by an axially symmetric quadrupole, a generalized Luttinger and Tisza method[7] for minimizing the quadrupole-quadrupole interaction energy was able to predict these two structures.[8,9] For the hexagonal phase, however, the experimental situation is not clear.

The purpose of the present work is to predict the ground-state configuration of the molecules in the crystal in each of the various phases. This will be done in two steps:

(a) We shall consider a group-theoretical classification of all possible quadrupole arrangements in a crystal, following the method of Opechowski and Guccione[10] for the classification of spin arrangements in magnetic crystals. A "possible" quadrupole arrangement is an arrangement of quadrupole moments associated with the molecules of a crystal which does not violate any symmetry principles.

(b) We shall calculate the quadrupolar energy of these arrangements in order to find the one with lowest energy. Since in many cases symmetry considerations do not require the quadrupoles to be axially symmetric, we shall explore whether a deviation from axial symmetry may further minimize the quadrupolar energy.

II. INVARIANT QUADRUPOLE ARRANGEMENTS

The problem of classification of all possible quadrupole arrangements is analogous with the problem of classification of possible atom arrangements in a crystal. The latter classification is provided by the theory of space groups, and a catalog of all possible arrangements is given in Ref. 11. The classification of all possible quadrupole arrangements is also similar to the classification of all spin arrangements in a magnetic crystal, a problem which has been solved by Opechowski and Guccione[10] using the theory of magnetic groups. Since quadrupole moments are invariant under time reversal, the theory of space groups is sufficient to classify all possible quadrupole arrangements.

We will not attempt to give a catalog of all possible quadrupole arrangements. In what follows we modify Opechowski and Guccione's classification scheme[10] to derive a method of classification of all possible quadrupole arrangements based on the theory of space groups.

A. Ordered and Disordered States of a Molecular Crystal

The quadrupole moment of a system of charges can be represented by a symmetric second-rank tensor with zero trace.[12] In general, there are five independent components.

We consider a crystal made up of like molecules with nonvanishing quadrupole moments. In analogy with the paramagnetic state of magnetic crystals we define the disordered state of a molecular crystal as one in which the molecular positions are fixed in the crystal, but the molecules are disordered in such a manner that the time-averaged value of their quadrupole moment is zero. The molecules of a crystal in such a state are identical, and one may consider the position of each molecule as a point in the crystal and define the space group of the disordered crystal in the same manner as a crystal made up of identical atoms.

The ordered state of the crystal can be defined as the state in which the molecules are ordered in a specific manner about their positions in the crystal, thereby defining at each molecular position a definite quadrupole moment tensor. Let us consider this ordered state as a spatial array of points, the molecular positions, to each of which we associate a quadrupole moment tensor. By so considering the ordered state we have an analogy with the magnetic state of a magnetic crystal, where the spin vectors are associated with the positions of the magnetic atoms.

B. Definition of Simple Crystals

In order to familiarize the reader with concepts used in Ref. 10, a short summary of them is given in this section. An ordered crystal whose molecular positions are of space-group symmetry F is partitioned into "simple crystals" consisting of molecules whose position vectors can be obtained by applying all elements of the space group F to any one molecular position vector $\vec{r}$. The simple crystal is said to be generated by F from $\vec{r}$. Crystals can be considered as consisting of a certain number of simple crystals. No two simple crystals have molecules in common, and the elements of F permute the molecules of each simple crystal among themselves. We consider now only simple crystals.

If a simple crystal generated by F from $\vec{r}$ has no two position vectors equal, then $\vec{r}$ is called a general position vector; otherwise it is called a special position vector.

A position vector $\vec{r}$ is characterized by its "site space group" $F(\vec{r})$ which consists of all elements of F that generate the set of position vectors $\vec{r}+\vec{t}$, where $\vec{t}$ is a primitive translation. The point group $R(\vec{r})$ of $F(\vec{r})$ is called the site point group.

If F is decomposed into left cosets relative to $F(\vec{r})$, one has

$$F=F(\vec{r})+[g_2|\vec{v}(g_2)]F(\vec{r})+\cdots+[g_n|\vec{v}(g_n)]F(\vec{r}) ,$$

where $\vec{v}(g)$ is the nonprimitive translation associated with the rotation g. Each coset generates a different set of position vectors:

$$\vec{r}+\vec{t};\;\; g_2\vec{r}+\vec{v}(g_2)+\vec{t};\; \ldots;\;\; g_n\vec{r}+\vec{v}(g_n)+\vec{t} .$$

For a fixed $\vec{t}$ we have a set of position vectors whose components for each space group F and $\vec{r}$ are given in Ref. 11. The components of these position vectors are called the coordinates of equivalent positions, and the site point group $R(\vec{r})$ is called the point symmetry. Each set of equivalent positions defines a single simple crystal.

C. Definition of Invariant Quadrupole Arrangements

A quadrupole arrangement in a molecular crystal is given by associating a quadrupole tensor $\overleftrightarrow{Q}$ with each molecule, i.e., $\overleftrightarrow{Q}(\vec{r}_i)$ is defined at all molecular position vectors $\vec{r}_i$ of the crystal. A quadrupole moment tensor is invariant under time reversal and therefore in order to define an invariant quadrupole arrangement we need to specify the transformation properties of $\overleftrightarrow{Q}(\vec{r}_i)$ only under the space-group-symmetry elements.

The symmetry element $f=[g|\vec{v}(g)+\vec{t}\,]$ when applied to $\overleftrightarrow{Q}(\vec{r}_i)$ acts as follows: (i) It transforms $\overleftrightarrow{Q}(\vec{r}_i)$ from $\vec{r}_i$ to $f\vec{r}_i=g\vec{r}_i+\vec{v}(g)+\vec{t}$. (ii) It transforms the components of $\overleftrightarrow{Q}$ according to

$$f\overleftrightarrow{Q}=M(f)\overleftrightarrow{Q}M^{-1}(f) ,$$

where $M(f)$ is a matrix denoting the transformational properties of $\overleftrightarrow{Q}$ under the rotational part g of the space group element f. We then have

$$f\overleftrightarrow{Q}(f\vec{r}_i)=M(f)\overleftrightarrow{Q}(\vec{r}_i)M^{-1}(f)$$

and a quadrupole arrangement is invariant under f if for all i we have

$$f\overleftrightarrow{Q}(\vec{r}_i)=\overleftrightarrow{Q}(\vec{r}_i)$$

and the largest group F which leaves the quadrupole arrangement invariant is called its space group.

D. Construction of All Invariant Quadrupole Arrangements

The method of constructing all invariant quadrupole arrangements is similar to that given for spin arrangements by Opechowski and Guccione.[10] Let F be the space group of the molecular positions in the ordered state. We classify all invariant quadrupole arrangements which can possibly exist in a molecular crystal by showing how to construct for a given crystal all quadrupole arrangements invariant under an arbitrary subgroup L of F. Each arrangement invariant under L can be characterized by specifying the location and value of a certain number of quadrupole tensors. The number, possible location, and value of these quadrupole moment tensors will depend on F, L, and $\vec{r}$.

Let L be the subgroup of F under which the quadrupole arrangement is invariant. It is assumed that in an ordered molecular crystal of space-group symmetry F there are only two cases to be considered: (a) L is identical with F. (b) L is a space group belonging to the same crystal system as F. The number of possible cases is much smaller than in the classification of spin arrangements in magnetic crystals.

It is assumed that the symmetry group L is one of the possible space groups, for it is physically improbable that the atoms of a crystal belong to a Bravais lattice system of higher symmetry than it is required by the crystal point-group symmetry.[13] For example, consider a crystal of molecules composed of two atoms with the molecular positions forming a simple cubic molecular lattice generated by $F = O_h^1$ from $\vec{r} = (0, 0, 0)$. We consider the arrangement with all molecular axes along the z axis. Such an arrangement has as its symmetry group L the semidirect product of the point group D_{4h} and the translations of a simple cubic lattice. This group is a subgroup of O_h^1, but it is not a space group. This arrangement is physically improbable, and one expects that any weak external disturbance, such as heating, would shorten or lengthen the z edge of the cubic cell, consequently changing the molecular lattice from cubic to tetragonal. One can classify the above arrangement as belonging to a crystal system lower than cubic. This is the space group D_{4h}^1 of the tetragonal system, where the unit cell has been doubled in the z direction. We would then have an invariant quadrupole arrangement of symmetry $L = D_{4h}^1$ of the tetragonal system on a molecular lattice generated by $F = O_h^1$ of the cubic system. Such an arrangement, for the reasons stated above, is physically improbable. Within the framework of our model a similar argument rules out the possibility of the orthorhombic C_{2v}^5 arrangement considered recently in the literature[14-17] for hexagonal solid orthohydrogen. In fact, there has been no experimental evidence to date supporting the C_{2v}^5 structure in solid hydrogen.

TABLE I. The number of independent components and matrix form of the quadrupole moment tensor invariant under each of the 32 point groups. The trace is always zero. The case of one independent component corresponds to an axially symmetric quadrupole with its symmetry axis lying along the z axis.

Point group	Number of components	Quadrupole moment tensor
C_1 C_i	5	$\begin{pmatrix} Q_{xx} & Q_{xy} & Q_{xz} \\ Q_{xy} & Q_{yy} & Q_{yz} \\ Q_{xz} & Q_{yz} & Q_{zz} \end{pmatrix}$
C_s C_2 C_{2h}	3	$\begin{pmatrix} Q_{xx} & Q_{xy} & 0 \\ Q_{xy} & Q_{yy} & 0 \\ 0 & 0 & Q_{zz} \end{pmatrix}$
C_{2v} D_2 D_{2h}	2	$\begin{pmatrix} Q_{xx} & 0 & 0 \\ 0 & Q_{yy} & 0 \\ 0 & 0 & Q_{zz} \end{pmatrix}$
C_4 S_4 C_{4h} C_{4v} D_{2d} D_4 D_{4h} C_3 C_{3i} C_{3v} D_3 D_{3d} C_{3h} C_6 C_{6h} D_{3h} C_{6v} D_6 D_{6h}	1	$\begin{pmatrix} -\frac{1}{2}Q_{zz} & 0 & 0 \\ 0 & -\frac{1}{2}Q_{zz} & 0 \\ 0 & 0 & Q_{zz} \end{pmatrix}$
T T_h T_d O O_h	0	

Let us now consider the two cases in detail:

(a) If $\vec{r}$ is a general position vector we assign at $\vec{r}$ an arbitrary quadrupole moment tensor $\overleftrightarrow{Q}(\vec{r})$. To the remaining positions we assign

$$\overleftrightarrow{Q}(f\vec{r}) = M(f)\overleftrightarrow{Q}(\vec{r})M^{-1}(f) ,$$

thereby defining a quadrupole arrangement invariant under the space group F. This method of constructing a quadrupole arrangement is called the standard prescription.[10]

If $\vec{r}$ is a special position vector, then the above standard prescription may lead to contradictions. Let $R(\vec{r})$ be the site point group of $\vec{r}$. The necessary and sufficient condition for the existence of a quadrupole arrangement invariant under the space group F in a simple crystal generated by F from $\vec{r}$ is the existence of a quadrupole moment tensor invariant under $R(\vec{r})$.[10] For each such quadrupole tensor, the standard prescription defines unambiguously a quadrupole arrangement invariant under F.

In Table I we give the matrix form and number of independent components of the quadrupole moment tensors invariant under each of the 32 point groups. The number of independent components of a rank-two symmetric tensor has been given in Ref. 18 and the explicit form of such a tensor has been given in Ref. 19. Table I has been adapted from these references.

From Table I we see that when the site group $R(\vec{r})$ is not one of the point groups T, T_h, T_d, O, and O_h, there exist quadrupole moment tensors invariant under $R(\vec{r})$ with which one can construct invariant quadrupole arrangements using the standard prescription. If $R(\vec{r})$ is one of the above five point groups, we conclude that no invariant quadrupole arrangement exists in the simple crystal generated by F from $\vec{r}$.

(b) Let L be a three-dimensional space group and a subgroup of F. Following Ref. 10 we decompose F into right cosets relative to L:

$$F = L + Lf_2 + \cdots + Lf_n ,$$

where n is the index of the subgroup L of F. We also decompose the position vectors of the simple crystal generated by F from $\vec{r}$ into sets of position vectors relative to L:

$$F\vec{r} = L\vec{r} + Lf_2\vec{r} + \cdots + Lf_n\vec{r} .$$

Sets of position vectors generated by two different

TABLE II. Subgroups of O_h^5 belonging to the cubic system with the same fcc lattice or with a simple cubic lattice (sc) containing one-half of the translations of the original fcc lattice.

Subgroup	Index	Lattice
O_h^5	1	fcc
O^3 T_h^3 T_d^2	2	fcc
O_h^1 O_h^4	4	sc
T^2	4	fcc
O^1 O^2 T_h^1 T_h^2 T_h^6 T_d^1	8	sc
T^1 T^4	16	sc

right cosets from the position vector $\vec{r}$ are either identical or have no position vectors in common.[10] We may write this decomposition as

$$F\vec{r} = L\vec{r} + Lf_2\vec{r} + \cdots + Lf_{n'}\vec{r} \; ,$$

where $n' \leq n$ and no two sets of position vectors have position vectors in common. We can interpret this by saying that the simple crystal generated by F from $\vec{r}$ may be considered as composed of n' interlocking simple crystals generated by L from position vectors $\vec{r}, f_2\vec{r}, \ldots, f_{n'}\vec{r}$.

We now assign quadrupole moment tensors to each of the n' simple crystals independently, using for each the method described in case (a). Each quadrupole arrangement invariant under L in a crystal generated by F from $\vec{r}$ is uniquely characterized by giving the n' quadrupole moment tensors $\overleftrightarrow{Q}(\vec{r}), \overleftrightarrow{Q}(f_2\vec{r}), \ldots, \overleftrightarrow{Q}(f_{n'}\vec{r})$. We derive all invariant quadrupole arrangements by choosing these n' quadrupole moment tensors in all possible ways.

We have given a method of constructing quadrupole arrangements invariant under L in a simple crystal generated by F from $\vec{r}$. The simple crystal is considered as n' interlocking simple crystals generated by L, a subgroup of F, from n' position vectors $\vec{r}, f_2\vec{r}, \ldots, f_{n'}\vec{r}$. If some of the site point groups $R(f_i\vec{r})$ are among the five point groups T, T_h, T_d, O, O_h, then we have a "partial" quadrupole arrangement invariant under L; to the interlocking simple crystals with such site point groups no quadrupole arrangements can be assigned. If all the site point groups are among these five point groups, we conclude that there is no quadrupole arrangement invariant under L in the simple crystal generated by F from $\vec{r}$. As we are interested in the classification of quadrupole arrangements in the ordered state of a molecular crystal, we will not consider any partial arrangement among the possible quadrupole arrangements.

There is also the possibility that the quadrupole arrangement constructed to be invariant under L will in fact be invariant under a higher symmetry group. The symmetry of a quadrupole arrangement is defined as all elements of F that leave the arrangement invariant. The elements of L are of course among such symmetry elements, but there may be additional elements of F, not contained in L, which also leave the arrangement invariant. Quadrupole arrangements constructed from the group L and actually invariant under a higher symmetry group will be classified under the higher symmetry group. If all quadrupole arrangements constructed from L are classified under higher symmetry groups, we will consider that there are no quadrupole arrangements invariant under L in the simple crystal generated by F from $\vec{r}$.

III. SPECIFIC EXAMPLES OF GROUP CLASSIFICATION

In this section we shall use the above procedure to find invariant quadrupole arrangements in crystals whose molecular positions are on fcc, hcp, and bct lattices.

A. fcc Lattice

The symmetry of the molecular positions is O_h^5. We construct all quadrupole arrangements invariant under O_h^5 and all the space groups L belonging to the cubic system which are subgroups of up to index 16 of O_h^5. These subgroups are given in Table II and have been derived using tables of the subgroups of space groups given by Ascher[20] and by Neubüser and Wondratschek.[21]

The molecular positions form a single simple crystal generated by $F = O_h^5$ from the position vector $\vec{r} = (0, 0, 0)$. We first take $L = F$ which corresponds to case (a) above. The site point group $R(\vec{r})$ is O_h, and using Table I we conclude that there is no quadrupole arrangement in the simple crystal generated by O_h^5 from $\vec{r} = (0, 0, 0)$, that is, invariant under O_h^5.

Taking $L = O^3$, T_h^3, T_d^2, or T^2, we again conclude that there is no quadrupole arrangement invariant under L in the molecular crystal under consideration.

Taking $L = O_h^1$ we find that the simple crystal generated by $F = O_h^5$ from $\vec{r} = (0, 0, 0)$ can be considered as two interlocking simple crystals generated by O_h^1 from the position vectors $\vec{r}_1 = (0, 0, 0)$ and $\vec{r}_2 = (0, \frac{1}{2}, \frac{1}{2})$. The site point groups are $R(\vec{r}_1) = O_h$ and $R(\vec{r}_2) = D_{4h}^{(x)}$, where the superscript (x) denotes that the fourfold axis is about the x direction. We conclude that we have a partial quadrupole arrangement with no quadrupole moments on the first of the two interlocking simple crystals. Similarly, taking $L = T_h^1$ we also derive a partial quadrupole arrangement.

Taking $L = T_h^6$, we have a single simple crystal generated by T_h^6 from $\vec{r} = (0, 0, 0)$ with site point group $C_{3i}^{(xyz)} = S_6^{(xyz)}$, the sixfold rotation-reflection axis being along the $[111]$ direction. The axially symmetric quadrupole $\overleftrightarrow{Q}(000)$ is given in Table I in a local coordinate system attached to $\vec{r} = (0, 0, 0)$, where the symmetry axis lies along the [111] direction. The quadrupoles at the remaining equivalent positions are derived by applying the symmetry elements $(C_{2x}|\frac{1}{2}\frac{1}{2}0)$, $(C_{2y}|0\frac{1}{2}\frac{1}{2})$, and $(C_{2z}|\frac{1}{2}0\frac{1}{2})$ to $\overleftrightarrow{Q}(000)$. The quadrupole arrangement, which is axially symmetric in this case and invariant under T_h^6 in a simple crystal generated by O_h^5 from $\vec{r}=(0, 0, 0)$, is shown in Fig. 1. In the same manner, but taking $L=O_h^4$, one derives a second invariant quadrupole arrangement. These results are summarized in Table III.

There are no additional quadrupole arrangements among the groups L considered. Quadrupole arrangements constructed from $L=O^2$, T_h^2, and T^1 are in fact invariant under O_h^4, and those from $L=O^1$ and T_d^1 are invariant under O_h^1.

B. hcp Lattice

A single simple crystal is generated by $F=D_{6h}^4$ from $\vec{r}=(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$. We consider quadrupole arrangements invariant under F and all subgroups of the hexagonal system with the same hexagonal lattice, denoted by $H1$, or with hexagonal lattices $H2$ or $H3$ containing one-third or one-fourth the translations of the original hexagonal lattice. These lattices and the coordinates of the molecular positions in their respective unit cells are shown in Fig. 2. The subgroups considered are listed in Table IV, and the possible invariant quadrupole arrangements derived are listed in Table III. We shall now describe some arrangements which will later prove to be of interest.

For $L=C_{6v}^3(H2)$ we have a single simple crystal generated by L from $\vec{r}=(\frac{1}{3}, 0, \frac{1}{4})$ and site point group $R(\vec{r})=C_s^{(2)}$. The form of the quadrupole tensor $\overleftrightarrow{Q}(\vec{r})$ is given in Table I, where the local coordinate system is that of the two axis and two mutually perpendicular axes in the xz plane. We note that symmetry considerations do not necessitate an axially symmetric quadrupole moment. A possible quadrupole arrangement invariant under L is shown in Fig. 3.

Taking $L=C_{6h}^2(H3)$ we have two interlocking simple crystals generated by L from $\vec{r}_1=(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $\vec{r}_2=(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$ with site point groups $R(\vec{r}_1)=C_{3h}$ and $R(\vec{r}_2)=C_s^{(z)}$. $\overleftrightarrow{Q}(\vec{r}_1)$ is an axially symmetric quadrupole with its major axis in the z direction, and $\overleftrightarrow{Q}(\vec{r}_2)$

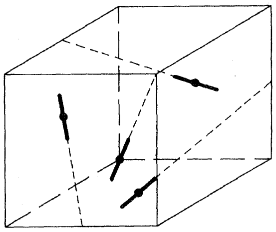

FIG. 1. Axially symmetric quadrupole arrangement invariant under T_h^6 in a simple crystal generated by O_h^5 from $\vec{r}=(0, 0, 0)$. The heavy lines represent the molecular axis, which is also the symmetry axis of the quadrupole. There are four different orientations of the molecular axis, namely, along the [111], [1$\bar{1}$1], [11$\bar{1}$], and [$\bar{1}$11] directions.

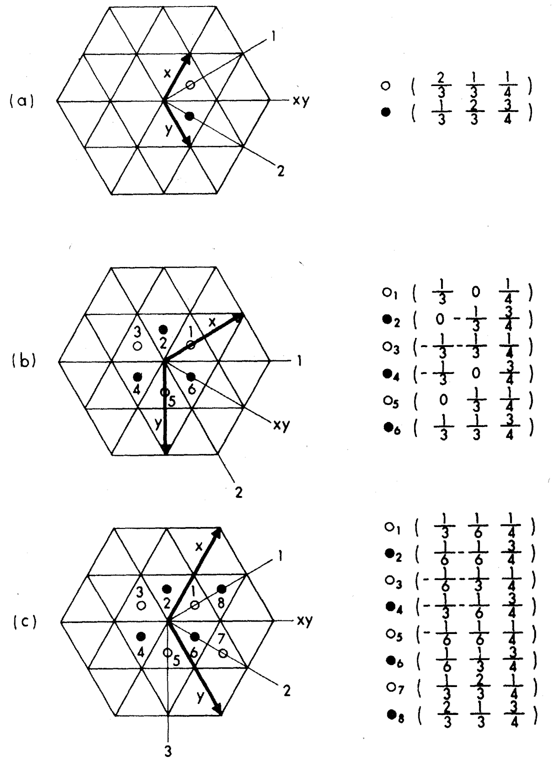

FIG. 2. Positions and primitive translations in the xy plane of (a) the hexagonal $H1$ lattice, which contains two molecular positions per unit cell; (b) the hexagonal $H2$ lattice, which contains six molecular positions per unit cell; (c) the hexagonal $H3$ lattice, which contains eight molecular positions per unit cell.

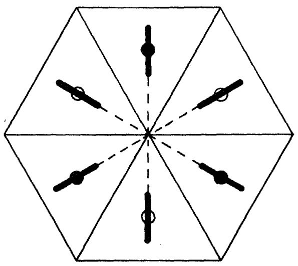

FIG. 3. Quadrupole arrangement invariant under $C_{6v}^3(H2)$ in a simple crystal generated by D_{6h}^4. The heavy lines represent the projection of the molecular axes on the xy plane. The axes are all at an angle θ to the xy plane, being tilted down towards the center of the figure. The quadrupole moments are invariant under a site point group C_s and consequently are not necessarily axially symmetric.

TABLE III. List of the quadrupole arrangements invariant under subgroups L of F in a simple crystal generated by F from $\vec{r}$. The number of interlocking simple crystals, the position vectors $\vec{r}_1$, the site point groups $R(\vec{r}_i)$, and the symmetry elements are included. The orientation of the rotation axis in $R(\vec{r}_i)$ when not in the z direction and the three twofold axes of C_{2v} and D_{2h} are given by superscripts.

F	$\vec{r}$	L	Simple crystals	$\vec{r}_i$	$R(\vec{r}_i)$	Symmetry elements
O_h^5	$(0, 0, 0)$	O_h^4	1	$(0, 0, 0)$	$D_{3d}^{(xyz)}$	$(C_{2x}\,\vert\,0\frac{1}{2}\frac{1}{2})$, $(C_{2y}\,\vert\,\frac{1}{2}0\frac{1}{2})$
		T_h^6	1	$(0, 0, 0)$	$C_{3i}^{(xyz)}$	$(C_{2y}\,\vert\,0\frac{1}{2}\frac{1}{2})$, $(C_{2z}\,\vert\,\frac{1}{2}0\frac{1}{2})$
D_{6h}^4	$(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$	$D_{6h}^4(H1)$	1	$(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$	D_{6h}	
		$D_{6h}^3(H2)$	1	$(\frac{1}{3}, 0, \frac{1}{4})$	$C_{2v}^{(x,z,2)}$	$(C_{6z}\,\vert\,00\frac{1}{2})$
		$D_6^6(H2)$	1	$(\frac{1}{3}, 0, \frac{1}{4})$	$C_2^{(x)}$	$(C_{6z}\,\vert\,00\frac{1}{2})$
		$C_{6h}^2(H2)$	1	$(\frac{1}{3}, 0, \frac{1}{4})$	C_s	S_{6z}
		$C_{6v}^3(H2)$	1	$(\frac{1}{3}, 0, \frac{1}{4})$	$C_s^{(2)}$	$(C_{6z}\,\vert\,00\frac{1}{2})$
		$D_{3h}^3(H2)$	2	$(\frac{1}{3}, 0, \frac{1}{4})$	$C_{2v}^{(x,z,2)}$	C_{3z}
				$(0, -\frac{1}{3}, \frac{3}{4})$	$C_{2v}^{(y,z,1)}$	C_{3z}
		$D_{3h}^2(H2)$	1	$(\frac{1}{3}, 0, \frac{1}{4})$	C_s	C_{3z}, C_{21}
		$C_6^6(H2)$	1	$(\frac{1}{3}, 0, \frac{1}{4})$	C_1	$(C_{6z}\,\vert\,00\frac{1}{2})$
		$C_{3h}^1(H2)$	2	$(\frac{1}{3}, 0, \frac{1}{4})$	C_s	C_{3z}
				$(0, -\frac{1}{3}, \frac{3}{4})$	C_s	C_{3z}
		$D_{6h}^4(H3)$	2	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	D_{3h}	C_{2xy}
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	$C_{2v}^{(y,z,1)}$	S_{6z}
		$D_6^6(H3)$	2	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	D_3	C_{2xy}
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	$C_2^{(1)}$	$(C_{6z}\,\vert\,00\frac{1}{2})$
		$C_{6h}^2(H3)$	2	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	C_{3h}	S_{6z}
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	C_s	S_{6z}
		$C_{6v}^4(H3)$	2	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	C_{3v}	$(C_{6z}\,\vert\,00\frac{1}{2})$
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	$C_s^{(y)}$	$(C_{6z}\,\vert\,00\frac{1}{2})$
		$D_{3h}^4(H3)$	2	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	C_{3h}	C_{2x}
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	C_s	C_{3z}, C_{2x}
		$D_{3h}^1(H3)$	4	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	D_{3h}	
				$(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$	D_{3h}	
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	$C_{2v}^{(y,z,1)}$	C_{3z}
				$(\frac{1}{6}, -\frac{1}{6}, \frac{3}{4})$	$C_{2v}^{(xy,z,3)}$	C_{3z}
		$C_6^6(H3)$	2	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	C_3	$(C_{6z}\,\vert\,00\frac{1}{2})$
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	C_1	$(C_{6z}\,\vert\,00\frac{1}{2})$
		$C_{3h}^1(H3)$	4	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$	C_{3h}	
				$(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$	C_{3h}	
				$(\frac{1}{3}, \frac{1}{6}, \frac{1}{4})$	C_s	C_{3z}
				$(\frac{1}{6}, -\frac{1}{6}, \frac{3}{4})$	C_s	C_{3z}
D_{4h}^{17}	$(0, 0, 0)$	D_{4h}^{17}	1	$(0, 0, 0)$	D_{4h}	
		D_{4h}^9	1	$(0, 0, 0)$	$D_{2h}^{(x,y,z)}$	$(C_{4z}\,\vert\,\frac{1}{2}\frac{1}{2}\frac{1}{2})$
		D_{4h}^{14}	1	$(0, 0, 0)$	$D_{2h}^{(xy,\bar{x}y,z)}$	$(C_{4z}\,\vert\,\frac{1}{2}\frac{1}{2}\frac{1}{2})$
		C_{4h}^2	1	$(0, 0, 0)$	C_{2h}	$(C_{4z}\,\vert\,\frac{1}{2}\frac{1}{2}\frac{1}{2})$

TABLE IV. Subgroups of D_{6h}^4 belonging to the hexagonal system with the same hexagonal $H1$ lattice, to the hexagonal lattice $H2$ containing one-third the translations of the original hexagonal lattice, or to the hexagonal lattice $H3$ containing one-fourth the translations of the original hexagonal lattice.

Subgroup	Index	Lattice
D_{6h}^4	1	$H1$
$D_6^6\ C_{6h}^2\ D_{3h}^{1,4}\ C_{6v}^4$	2	$H1$
D_{6h}^3	3	$H2$
$C_6^6\ C_{3h}^1$	4	$H1$
D_{6h}^4	4	$H3$
$D_6^6\ C_{6h}^2\ D_{3h}^{2,3}\ C_{6v}^3$	6	$H2$
$D_6^6\ C_{6h}^2\ D_{3h}^{1,4}\ C_{6v}^4$	8	$H3$
$C_6^6\ C_{3h}^1$	12	$H2$
$C_6^6\ C_{3h}^1$	16	$H3$

takes the form given in Table I for the point group C_s where the local coordinates consist of the z axis and two mutually perpendicular axes in the xy plane. A possible quadrupole arrangement invariant under L is shown in Fig. 4.

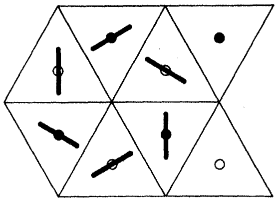

FIG. 4. Quadrupole arrangement invariant under $C_{6h}^2(H3)$ in a simple crystal generated by D_{6h}^4. The heavy lines represent the molecular axes on one of the two interlocking simple crystals and lie on the xy plane. The molecular axis at $\vec{r}_1$ [see Fig. 2(c)] is at an angle ϕ with the xy axis. The quadrupole moments of these molecules are invariant under a site point group C_s and consequently are not necessarily axially symmetric. The quadrupole moments of the second of the simple crystals are axially symmetric about the z direction, and the molecular axes have not been drawn.

C. bct Lattice

A simple crystal is generated by the space group $F = D_{4h}^{17}$ from $\vec{r} = (0, 0, 0)$. We consider all subgroups of F of the tetragonal system with the same body-centered lattice and the simple tetragonal lattice containing one-half the translations of the original lattice. These subgroups are listed in Table V, and the invariant quadrupole arrangements derived are listed in Table III.

Taking $L = D_{4h}^{14}$ we have a single simple crystal generated by L from $\vec{r} = (0, 0, 0)$. The site point group is D_{2h} with the twofold axes along the xy, $\bar{x}y$, and z directions. We note that symmetry considerations do not necessitate an axially symmetric quadrupole moment. The quadrupole arrangement invariant under L is given in Fig. 5.

IV. QUADRUPOLE ARRANGEMENTS OF LOWEST ENERGY

Many of the quadrupole arrangements that are allowed because of symmetry considerations are not energetically possible. Some may even have a positive energy. Our purpose in this section is to look for the quadrupole arrangement of lowest energy. A generalized Luttinger and Tisza method[7] has been used by several authors[8,9,14] to minimize the quadrupole-quadrupole energy in a number of crystal structures. This is done by dividing the crystal into a number of sublattices, with all the quadrupoles on a given sublattice being equal. This method, however, has been applied only to axially symmetric quadrupoles. Nevertheless, we have seen in previous sections that in many cases symmetry considerations do not impose on the quadrupoles the restriction of axial symmetry. Thus it seems reasonable to check whether a deviation from axial symmetry may yield a lower quadrupole-quadrupole energy of the crystal. The interaction energy of two general quadrupoles, which are not axially symmetric, may be written (see Appendix) as the interaction energy of two pairs of axially symmetric quadrupoles, each pair representing one of the two general quadrupoles. In the local coordinate system ξ, η, ζ of a quadrupole, its tensor is diagonal with

$$Q_{\xi\xi} + Q_{\eta\eta} + Q_{\zeta\zeta} = 0 \ .$$

If the quadrupole is axially symmetric with the ζ axis being the symmetry axis, then we have

$$Q_{\xi\xi} = Q_{\eta\eta} = -\tfrac{1}{2} Q_{\zeta\zeta} \ .$$

We then define $Q \equiv Q_{\zeta\zeta}$ as the value of the quadrupole moment of the axially symmetric quadrupole.

TABLE V. Subgroups of D_{4h}^{17} belonging to the tetragonal system with the same bct lattice or with a simple tetragonal lattice (st) containing one-half of the translations of the original bct lattice.

Subgroup	Index	Lattice
D_{4h}^{17}	1	bct
$D_{2d}^{9,11}\ D_4^9\ C_{4h}^5\ C_{4v}^9$	2	bct
$D_{4h}^{1,4,6,7,9,12,14,15}$	2	st
$S_4^2\ C_4^5$	4	bct
$\left.\begin{matrix} D_{2d}^{1,2,3,4,5,8}\ D_4^{1,2,5,6} \\ C_{4h}^{1,2,3,4}\ \ C_{4v}^{1,4,6,7} \end{matrix}\right\}$	4	st
$S_4^1\ C_4^{1,3}$	8	st

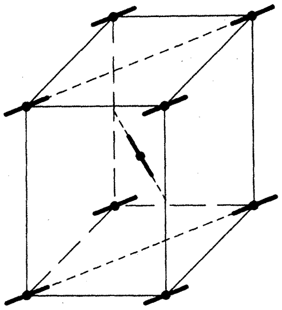

FIG. 5. Quadrupole arrangement invariant under D_{4h}^{14} in a simple crystal generated by D_{4h}^{17} from $\vec{r} = (0, 0, 0)$. The heavy lines represent the molecular axes, which lie along the xy and $\bar{x}y$ directions. The quadrupole moments are invariant under a site point group D_{2h} and consequently are not necessarily axially symmetric.

In order to find how the energy changes when a quadrupole deviates from axial symmetry, we shall assume that $Q_{\xi\xi}$ changes to $-\frac{1}{2}Q + \Delta$ and $Q_{\eta\eta}$ changes to $-\frac{1}{2}Q - \Delta$, where Δ is either positive or negative.

The present calculations of the quadrupolar energy per molecule have been done in the same manner as described in Ref. 9 and include interactions of molecules with separations up to 300 Å. The energies, which will be given in units of °K, have been multiplied by the quantum-mechanical correction factor[14,15] of $\frac{4}{25}$.

A. Ground State of Solid Hydrogen

We shall consider the case of pure orthohydrogen where all the molecules in the crystal have a quadrupole moment. Below the transition temperature the molecular positions form a fcc lattice, while above it they form a hcp lattice. The lattice parameters were taken from known data on solid normal hydrogen[2] as $a = 5.312$ Å for the fcc phase and $a = 3.761$ Å, $c = 6.105$ Å for the hcp phase. The value of the quadrupole moment of the axially symmetric orthohydrogen molecule was taken from Ref. 22 as $Q = 0.1368 \times 10^{-16}$ cm^2.

As is shown in Sec. III A, there are two possible quadrupole arrangements for the fcc lattice, namely, O_h^4 and T_h^6. In both cases symmetry considerations require the quadrupoles to be axially symmetric. The O_h^4 arrangement is excluded because it has a positive energy. The T_h^6 arrangement has an energy per molecule of -7.10 °K and is shown in Fig. 1. There are four sublattices, with the molecular axes in each sublattice lying along a different body diagonal of the unit cell. This arrangement has already been found to be the one with lowest energy when one minimizes the interaction energy of axially symmetric quadrupoles,[8,9] and it is in accord with experimental results.[5,6]

The hcp lattice is divided into either six sublattices, the $H2$ arrangement, or eight sublattices, the $H3$ arrangement (see Sec. III B). The hexagonal arrangement with the lowest energy that could be found for axially symmetric quadrupoles is $C_{6h}^2(H3)$. This arrangement is shown in Fig. 4. Two of the sublattices have quadrupoles along the z direction, while the quadrupoles of the other six sublattices lie on the xy plane with $\phi = -27°$. The energy per molecule of this arrangement is -5.42 °K. Symmetry considerations require the two quadrupoles along the z direction to be axially symmetric, while the six quadrupoles which lie on the xy plane may deviate from axial symmetry. Let us denote as the local η axis the direction on the xy plane perpendicular to the ξ axis of each of these six quadrupoles. Figure 6(c) shows that the energy is lowered from -5.42 to -6.79 °K when $Q_{\eta\eta}/Q$ changes from $-\frac{1}{2}$ to -1. The energy is further lowered to -7.32 °K at $Q_{\eta\eta}/Q = -1$ when ϕ changes from $-27°$ to $-21°$, as is shown in Fig. 6(b).

Another arrangement which seems to have a rather low energy when the quadrupoles are not axially symmetric is $C_{6v}^3(H2)$. This arrangement is shown in Fig. 3. There are six sublattices with the molecular axes tilted at an angle of $\theta = 45°$ above the xy plane. Let us denote as the local η axis of each quadrupole the direction perpendicular to its ξ axis, so that the η axis also makes an angle of 45° with the xy plane. Figure 6(a) shows that the energy is lowered to -7.47 °K when $Q_{\eta\eta}/Q = -1$.

The fact that the transition from the hcp phase

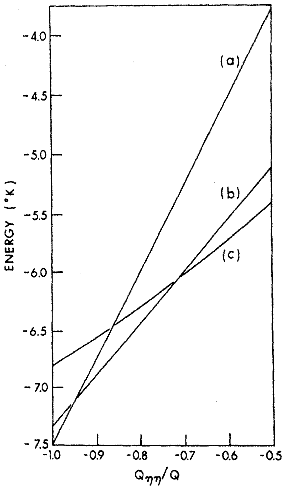

FIG. 6. Energy per molecule as a function of $Q_{\eta\eta}$ in hexagonal solid orthohydrogen for the following arrangements: (a) $C_{6v}^3(H2)$ with $\theta = 45°$; (b) $C_{6h}^2(H3)$ with $\phi = -21°$; (c) $C_{6h}^2(H3)$ with $\phi = -27°$. For comparison, the energy in the cubic T_h^6 arrangement is -7.10 °K.

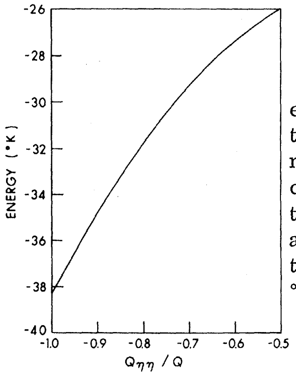

FIG. 7. Energy per molecule as a function of $Q_{\eta\eta}$ in the tetragonal D_{4h}^{14} arrangement of solid nitrogen. For comparison, the energy in the cubic T_h^6 arrangement, at about the same temperature and pressure, is − 33.9 °K.

to the fcc phase when the temperature is lowered is believed to be mainly due to the quadrupole-quadrupole interaction[1] implies that the energy of the hexagonal arrangement must be higher than − 7.10 °K, which is the energy of the cubic arrangement. We can conclude that the deviation of the quadrupoles from axial symmetry cannot be very large in either the $C_{6h}^2(H3)$ or the $C_{6v}^3(H2)$ arrangement, since $Q_{\eta\eta}/Q$ must be greater than about − 0.95, as can be seen in Figs. 6(a) and 6(b).

B. Ground State of Solid Nitrogen

Below 35.6 °K solid nitrogen exists in the fcc α phase. However, at high pressure it transforms into the bct γ phase. From Ref. 5 we obtain the following data: At 3785 atm and 19.6 °K solid nitrogen is still cubic with $a = 5.433$ Å, while at 4015 atm and 20.5 °K it is tetragonal with $a = 3.957$ Å and $c = 5.109$ Å. The value of the quadrupole moment of the axially symmetric nitrogen molecule was taken from Ref. 23 as $Q = -0.3165 \times 10^{-16}$ cm^2.

The quadrupole arrangement at the α phase is T_h^6 as in fcc solid hydrogen. Using the data given above the energy per molecule is calculated to be − 33.9 °K.

The quadrupole arrangement of lowest energy at the γ phase is D_{4h}^{14} for axially symmetric quadrupoles and it remains D_{4h}^{14} even when the quadrupoles deviate from axial symmetry. The D_{4h}^{14} arrangement consists of two sublattices and is shown in Fig. 5. This arrangement was also confirmed experimentally by x-ray diffraction.[5] However, the extent to which the quadrupoles deviate from axial symmetry has not been determined. Using the lattice parameters given above for the γ phase, Fig. 7 shows that the energy is lowered from − 26.0 to − 38.4 °K when $Q_{\eta\eta}/Q$ changes from $-\frac{1}{2}$ to − 1. Here we denote the local η axis as the direction on the xy plane perpendicular to the ζ axis of each quadrupole. We see that the energy of the tetragonal arrangement when the quadrupoles are axially symmetric (− 26.0 °K) is much higher than that of the cubic arrangement (− 33.9 °K). Thus it seems unreasonable that the quadrupoles should remain axially symmetric in the tetragonal phase. It is seen from Fig. 7 that $Q_{\eta\eta}/Q$ must be less than about − 0.87 in order to have the energy of the tetragonal arrangement lower than that of the cubic arrangement.

V. CONCLUSIONS

In this paper we have considered a classification of all possible quadrupole arrangements in a crystal, using the theory of space groups. This has been done by following the method of Opechowski and Guccione[10] which uses the theory of magnetic groups for the classification of spin arrangements in magnetic crystals. The number of possible cases in the quadrupole classification is much smaller than in the analogous spin classification. In addition, many of these arrangements are not possible from an energetic point of view. We have also seen that as far as symmetry is concerned there are many cases where the quadrupoles need not be axially symmetric.

We have applied this method of classification to find the quadrupole arrangement of lowest energy in the various phases of solid orthohydrogen and solid nitrogen. The quadrupole arrangement in the cubic phase is T_h^6 with four sublattices where symmetry considerations require the quadrupoles to be axially symmetric. In the hexagonal phase there are two possible arrangements that have very low quadrupole-quadrupole energy. One is C_{6v}^3, with six sublattices, where none of the quadrupoles are axially symmetric. The other is C_{6h}^2 with eight sublattices, of which six have non-axial-symmetric quadrupoles. From data on solid hydrogen near the hexagonal-to-cubic transition,[2] we have concluded that $Q_{\eta\eta}/Q$ of the non-axial-symmetric quadrupoles must be $\gtrsim -0.95$ for both C_{6v}^3 and C_{6h}^2, where Q is the quadrupole moment of the axially symmetric molecule. In the tetragonal phase of solid nitrogen the lowest-energy arrangement is D_{4h}^{14} with two sublattices, where none of the quadrupoles are axially symmetric. From data on solid nitrogen near the cubic-to-tetragonal transition,[5] we have concluded that $Q_{\eta\eta}/Q$ must be $\lesssim -0.87$.

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One of us (J. F.) would like to thank Professor J. M. Daniels for useful and informative discussions on the problem of the interaction energy between two quadrupoles.

APPENDIX: MUTUAL ENERGY OF TWO QUADRUPOLES

Any arbitrary potential ϕ can be expanded as

$$\phi = \phi_0 + \left(x \frac{\partial \phi_0}{\partial x} + y \frac{\partial \phi_0}{\partial y} + z \frac{\partial \phi_0}{\partial z} \right)$$

$$+\frac{1}{2}\left(x^2\frac{\partial^2\phi_0}{\partial x^2}+\cdots+2xy\frac{\partial^2\phi_0}{\partial x\partial y}+\cdots\right)+\cdots . \tag{A1}$$

The potential energy E of any charge distribution $\rho(x,y,z)$ is

$$E=\int\rho\phi d\tau=\phi_0\int\rho d\tau+\left(\frac{\partial\phi_0}{\partial x}\int\rho x d\tau+\cdots\right)$$
$$+\frac{1}{2}\left(\frac{\partial^2\phi_0}{\partial x^2}\int\rho x^2 d\tau+\cdots\right.$$
$$\left.+2\frac{\partial^2\phi_0}{\partial x\partial y}\int\rho xy d\tau+\cdots\right)+\cdots . \tag{A2}$$

We define the charge distribution tensor as

$$q_{xx}=\int\rho x^2 d\tau,\quad q_{xy}=\int\rho xy\ d\tau\ ,\ \text{etc.} \tag{A3}$$

The first term of Eq. (A2), which is the monopole term, is independent of orientation and vanishes if we assume that the quadrupoles are neutral. The second term also vanishes if we assume that there are no dipole moments. Then we have

$$E=\frac{1}{2}\sum_{ij}q_{ij}\frac{\partial^2\phi_0}{\partial x_i\partial x_j}\ , \tag{A4}$$

where $x_x\equiv x$, $x_y\equiv y$, $x_z\equiv z$, and i, j run over x, y, z. Similarly, the potential ϕ, due to a system of charges ρ', is given by

$$\phi=\frac{1}{2}\sum_{kl}q'_{kl}\frac{\partial^2}{\partial x_k\partial x_l}\left(\frac{1}{r_0}\right), \tag{A5}$$

where k, l run over x, y, z. Hence the potential energy is [from Eqs. (A4) and (A5)]

$$E=\frac{1}{4}\sum_{ijkl}q_{ij}q'_{kl}\frac{\partial^4}{\partial x_i\partial x_j\partial x_k\partial x_l}\left(\frac{1}{r_0}\right) . \tag{A6}$$

The q'_{kl} belong to the quadrupole which produces the potential ϕ, and the q_{ij} belong to the other quadrupole which sits in the field ϕ. E is the mutual energy of the two quadrupoles.

We shall now see how Eq. (A6) is simplified for axially symmetric quadrupoles. Take axes ξ, η, ζ in the quadrupole. These are its principal axes. In this coordinate system the tensor is diagonal. Suppose the quadrupole has axial symmetry about the ζ axis; then we have $q_{\xi\xi}=q_{\eta\eta}\neq q_{\zeta\zeta}$. The conventional definition of a quadrupole moment is based on

$$Q_{\zeta\zeta}=\int\rho(3\zeta^2-r^2)d\tau \tag{A7}$$

with a normalizing factor. Then we have

$$Q\equiv Q_{\zeta\zeta}=2(q_{\zeta\zeta}-q_{\xi\xi}),\quad Q_{\eta\eta}=Q_{\xi\xi}=-\tfrac{1}{2}Q_{\zeta\zeta}. \tag{A8}$$

Thus the charge distribution tensor is

$$\begin{pmatrix}q_{\xi\xi}&0&0\\0&q_{\eta\eta}&0\\0&0&q_{\zeta\zeta}\end{pmatrix}=q_{\xi\xi}I+\frac{1}{2}\begin{pmatrix}0&0&0\\0&0&0\\0&0&Q\end{pmatrix}, \tag{A9}$$

where I is the unit matrix. Transforming to a new coordinate system x, y, z (laboratory system) by means of the orthogonal matrix

$$\begin{array}{c}\\x\\y\\z\end{array}\begin{array}{c}\begin{array}{ccc}\xi&\eta&\zeta\end{array}\\\begin{pmatrix}\lambda_{3x}&\lambda_{2x}&\lambda_{1x}\\\lambda_{3y}&\lambda_{2y}&\lambda_{1y}\\\lambda_{3z}&\lambda_{2z}&\lambda_{1z}\end{pmatrix}\end{array}\ , \tag{A10}$$

where λ_{1x}, λ_{1y}, λ_{1z}, etc., are direction cosines, the tensor then becomes

$$q_{ij}=q_{\xi\xi}\delta_{ij}+\tfrac{1}{2}Q\lambda_{1i}\lambda_{1j}. \tag{A11}$$

Similarly, we have

$$q'_{kl}=q'_{\xi\xi}\delta_{kl}+\tfrac{1}{2}Q'\lambda'_{1k}\lambda'_{1l} \tag{A12}$$

for the other quadrupole. Using the fact that $\nabla^2(1/r_0)=0$ and $\nabla^2\phi_0=0$, Eq. (A6) for axially symmetric quadrupoles becomes

$$E=\tfrac{1}{16}QQ'\sum_{ijkl}\lambda_{1i}\lambda_{1j}\lambda'_{1k}\lambda'_{1l}\frac{\partial^4}{\partial x_i\partial x_j\partial x_k\partial x_l}\left(\frac{1}{r_0}\right), \tag{A13}$$

where the quadrupole which produces the potential ϕ is Q', and the other quadrupole which sits in the field ϕ is Q. In our usual problem $Q=Q'$. Equation (A13) can be shown to be equivalent to the formula for the quadrupolar energy given, for example, in Ref. 9, within a normalizing factor.

Now let us consider a quadrupole which is not axially symmetric. Here

$$q_{\xi\xi}\neq q_{\eta\eta}\neq q_{\zeta\zeta},\ Q_{\xi\xi}\neq Q_{\eta\eta},\ Q_{\xi\xi}+Q_{\eta\eta}+Q_{\zeta\zeta}=0. \tag{A14}$$

Thus the charge distribution tensor [compare with Eq. (A9)] is

$$\begin{pmatrix}q_{\xi\xi}&0&0\\0&q_{\eta\eta}&0\\0&0&q_{\zeta\zeta}\end{pmatrix}=q_{\xi\xi}I+\tfrac{1}{2}\begin{pmatrix}0&0&0\\0&A&0\\0&0&0\end{pmatrix}+\tfrac{1}{2}\begin{pmatrix}0&0&0\\0&0&0\\0&0&B\end{pmatrix}, \tag{A15}$$

where

$$A\equiv-\tfrac{2}{3}(2Q_{\xi\xi}+Q_{\zeta\zeta}),\quad B\equiv-\tfrac{2}{3}(Q_{\xi\xi}-Q_{\zeta\zeta}). \tag{A16}$$

If the quadrupole is axially symmetric, then $A=0$, $B=Q$. Using the transformation (A10), the tensor becomes

$$q_{ij}=q_{\xi\xi}\delta_{ij}+\tfrac{1}{2}A\lambda_{2i}\lambda_{2j}+\tfrac{1}{2}B\lambda_{1i}\lambda_{1j}, \tag{A17}$$

and similarly for the other quadrupole. We thus obtain

$$E=\tfrac{1}{16}AA'\sum_{ijkl}\lambda_{2i}\lambda_{2j}\lambda'_{2k}\lambda'_{2l}\frac{\partial^4}{\partial x_i\partial x_j\partial x_k\partial x_l}\left(\frac{1}{r_0}\right)$$
$$+\tfrac{1}{16}AB'\sum_{ijkl}\lambda_{2i}\lambda_{2j}\lambda'_{1k}\lambda'_{1l}\frac{\partial^4}{\partial x_i\partial x_j\partial x_k\partial x_l}\left(\frac{1}{r_0}\right)$$
$$+\tfrac{1}{16}BA'\sum_{ijkl}\lambda_{1i}\lambda_{1j}\lambda'_{2k}\lambda'_{2l}\frac{\partial^4}{\partial x_i\partial x_j\partial x_k\partial x_l}\left(\frac{1}{r_0}\right)$$

$$+\tfrac{1}{16}BB'\sum_{ijkl}\lambda_{1i}\lambda_{1j}\lambda'_{1k}\lambda'_{1l}\frac{\partial^4}{\partial x_i\partial x_j\partial x_k\partial x_l}\left(\frac{1}{r_0}\right) . \qquad \text{(A18)}$$

For axially symmetric quadrupoles Eq. (A18) reduces to Eq. (A13). We have seen that any non-axial-symmetric quadrupole can be written as a combination of two axially symmetric quadrupoles A and B, with their symmetry axes along two different principal axes of the original quadrupole.

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Properties of Crystalline Argon, Krypton, and Xenon Based upon the Born and Huang Method of Homogeneous Deformations. I. Zero-Pressure Thermal and Elastic Data *

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The thermodynamic properties of solid argon, krypton, and xenon have been calculated for a two-body central force potential. Anharmonic contributions due to thermal expansion have been taken into account via a quasiharmonic calculation based upon the Born and Huang method of homogeneous deformations. The nonarbitrarily adjustable parameters of the Morse potential have been obtained from the solid-state bulk properties in a recursive refinement procedure. For those thermal properties sensitivity dependent upon the dilatation of the lattice the calculations become valid only for temperatures less then $\frac{1}{3}T_M$.

I. INTRODUCTION

Born and Huang[1] (BH), via a perturbation expansion of the partition function, have developed the thermodynamics of a stressed harmonic lattice. The lattice potential energy is expressed as a double expansion in terms of the normal modes of the harmonic Hamiltonian and the parameters of a homogeneous deformation. For strains taken to be homogeneous deformations, the Helmholz free energy is obtained as a series expansion (to second order) in the Lagrangian strain parameters, $\bar{u}_{\alpha\beta}$. The free energy is given by Eq. 43.1 of BH. We have made explicit the formulas of BH applicable to our model of the noble-gas solids.[2]

Our quasiharmonic calculation hence includes the effect of anharmonicity due only to thermal expansion. Truly anharmonic effects due to three- and four-phonon processes have not been considered.

Several workers have developed perturbation theory descriptions of anharmonic phonon interactions.[3-8] More recent advances include the "self-