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QUADRUPOLE ARRANGEMENTS IN SOLID GADOLINIUM MOLYBDATE

Jasmine Rita.M and Uma Devi.S
DEPARTEMENT OF ENGINEERING MATHEMATICS, COLLEGE OF ENGINEERING, ANDHRA UNIVERSITY, VISAKHAPATNAM – 530 003

Abstract: Quadrupole arrangements in Gadolinium Molybdate $Gd_2\ (MoO_4)_3$ crystal are carried out by using group theoretical method of Opechowski and Guccione for the classification of magnetic spin arrangements in the various phase transitions. It turns out that the quadrupole arrangement of Gadolinium Molybdate in the tetragonal phase is D_{2d}^{3} with non-axial symmetric quadrupoles. In orthorhombic phase there are two possible quadrupole arrangements with low energy in which one is C^8_{2v} and the other is D^1_2 both are axially symmetric quadrupoles.

Key Words: Space group, symmetry elements, orthorhombic phase, tetragonal phase and quadrupole arrangements

Introduction:

$Gd_2(MoO_4)_3$ had been prepared first B.Y. Borchardt (3) and this material was found to be ferroelectric by Borchanrdt and Bierstedt (4,5) these authors (4) also gave preliminary result of a space-group determination carried out by Prewitt who found orthorhombic symmetry, space group C_{2v}^{8}, for the ferroelectric room-temperature modification of $Gd_2(Mo0_4)_3$ the structure of the tetragonal subcell was solved by Abrahams and Bernstein (1). The present communication reports the full structure of the ferroelectric room-temperature modification of $Gd_2\ (Mo0_4)_3$ as determined from three-dimensional single crystal x-ray counter data. There are four formula units in the orthorhombic unit cell of dimensions: a=10.388, b=10.419,c=10.701Å.

The atomic co-ordinations are as follows (all atoms in position 4c of Pba2):

The Gd atoms have seven nearest oxygen neighbors at tetrahedral oxygen neighbors at distances ranging from 2.27 to 2.44Å. All Mo atoms have a tetrahedral oxygen environment with distances varying between 1.73 and 1.80Å. These nearest neighbor environment differences between the two ferroelectric orientations result through movements of several oxygen atoms by as much as 0.7Å mainly in the plane normal to the z-axis (the direction of spontaneous polarization). The changes in interatomic distance of nearest neighbors however, are all under 0.05 Å. The structure of the tetragonal subcell as found by Abrahams and Bernstein (1), corresponding to the average structure of the two ferroelectric orientations, comes very close to the high-temperature (above 160^0 C) structure (space group D_{2d}^{3})

The phase transitions of solid Gadolinium Molybdate are studied during past few years. They are mainly due to quadrupole – quadrupole interaction between the molecules. A group analysis is made of external lattice vibrations in $Gd_2(MoO_4)_3$ for k = (1, 1, 0) in the high-symmetry D phase and for the point in the low-symmetry C phase. It is shown that the phase transition is induced by instability of one double degenerate T1-phonon at the M-point of the Brillouin zone which changes into two A1-phonons, infrared and Raman active below the phase transition. The far-infrared reflectivity and transmission measurements show that these critical modes are extremely weak and lie at 45cm and 56 cm at 150 °C. When rising the temperature they become indistinct and probably disappear above the phase transition. This behaviour together with known dielectric and Raman scattering is discussed in terms of the recent theory of the soft-mode behaviour in improper ferroelectrics. The solid Gadolinium molybdate is known to have a high pressure β – phase. In this paper symmetry considerations are used to show that it is possible for solid Gadolinium molybdate to have structure similar to the tetragonal D_{4h}^{14} arrangement in solid N_2 if indeed quadrupole interactions dominate the intermolecular potential.

Classification of Quadrupole Arrangements:

The classification of all possible quadrupole arrangements is analogous with the problem of classification of possible arrangements in a crystal. The classifications of all possible atom arrangements in a crystal are provided by the theory of space groups. All possible quadrupole arrangements are also similar to the classification of all spin arrangements in a magnetic crystal, a problem which has been solved by Opechowski and Guccione using theory of magnetic groups. Here we derive a method of classification of all possible quadrupole arrangements based on theory of space groups.

The method of classifying all possible quadrupole arrangements in a crystal by using the theory of space groups was described in detail(7). This was done by following the method of Opechowski and Guccione (10) for the classification of spin arrangements in magnetic crystal. Let F be the space group of the molecular position in the ordered state. All invariant quadrupole arrangements which can possibly be exist in a molecular crystal by showing how to construct for 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 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 systems as F. It is assumed that the symmetry group L is one of the possible space group, 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. 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 from $\vec{r} = (0, 0, 0)$. We consider the arrangement with all molecular axes along the z- axis. Such an arrangement has its symmetry group L the semi direct 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 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 space group D_{4h}^1 of the tetragonal systems, 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^8_{2v}, arrangement considered recently in the literature (6-8) for hexagonal solid orthohydrogen. In fact, there has been no experimental evidence to supporting the C^8_{2v} structure in solid hydrogen

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

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

There by defining a quadrapole 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 $\vec{r}$. Then the necessary and sufficient condition for the existing 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 $R(\vec{r})$. For each such quadrupole tensor, the standard prescription defines unambiguously a quadrupole arrangement invariant under F.

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

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

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

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

Sets of position vectors generated by two different right cosets from position vector $\vec{r}$ are either identical or have no position vectors in common.

We may write this decomposition as

$$F\vec{r} = L\vec{r} + Lf_2\vec{r} + \ldots. + Lf_{n'}\vec{r}$$

Where n'≤ n and no two sets of position vectors have position vectors in common.

Now assign quadrupole moment tensors to each of the n' simple crystal 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 n' quadrupole moment tensors $\overleftrightarrow{Q}(\vec{r})$, $\overleftrightarrow{Q}(f_2\vec{r})$,.... $\overleftrightarrow{Q}(f_{n'}\vec{r})$. We derived all in variant quadrupole arrangements by choosing these n' quadrupole moment tensors in all possible ways.

Now let us consider the Gadolinium Molybdate crystal where all molecules will have the quadrupole moments. It will have the orthorhombic symmetry C_{2v} at room temperature and will the tetragonal symmetry D_{2d} above 160° c. In this space group D_{2d} of the tetragonal system the unit cell has double in the z- direction. We would have an invariant quadrupole arrangement on a molecular lattice generated by F= O_h^1 of the cubic systems. But such an arrangement is physically improbable. In table1 we have given the matrix form and number of independent components of quadrupole moment tensors invariant under each of the point group in Gadolinium Molybdate crystal (8,9). If the site group R($\vec{r}$) is not one of the point groups T, T_h, T_4, O, and O_h there exists no quadrupole moment tensors invariant under R($\vec{r}$) with which we can construct invariant quadrupole arrangements using standard prescription(10). While H_2 or N_2 molecule is invariant under inversion and under reflection and two fold rotations perpendicular to the molecular axis, so as in Gadolinium Molybdate molecule. So as a consequence, a site point group that permits a quadrupole arrangement in H_2 will permit such an arrangement in Gadolinium Molybdate, for the site point group C_{2v} the molecular axis of H_2 or N_2 can be along the rotation axis or perpendicular to either of the two reflection planes, while the molecular axis of Gadolinium Molybdate can be only along rotation axis.

Table 1: The number of independent components and matrix form of the quadrupole moment tensors invariant under each of the point groups. In case of one independent component corresponds to an axially symmetric quadrupole with its symmetry axis lying along the z- axis.

Point Group	No. of Components	Quadrupole Moment Tensors
D_{2d}	1	$\begin{pmatrix} \frac{-1}{2}Q_{xx} & 0 & 0 \\ 0 & \frac{1}{2}Q_{xx} & 0 \\ 0 & 0 & Q_{zz} \end{pmatrix}$
C_{2v}	2	$\begin{pmatrix} Q_{xx} & 0 & 0 \\ 0 & Q_{yy} & 0 \\ 0 & 0 & Q_{zz} \end{pmatrix}$
D_2	2	$\begin{pmatrix} Q_{xx} & 0 & 0 \\ 0 & Q_{yy} & 0 \\ 0 & 0 & Q_{zz} \end{pmatrix}$

In tetragonal lattice the molecular moments from a simple crystal generated by D_{2d}^3 form the position vector $\vec{r}$ =(0,0,0). The possible quadrupole arrangements for this solid Gadolinium Molybdate are invariant under these subgroups given in table 2.

Table2: List of the quadrupole arrangements of Gadolinium Molybdate invariant under subgroups L of F. The site point groups R($\vec{r}$) and symmetry elements are given in the table. The site point groups R($\vec{r}$) and the symmetry elements are included. The orientation of rotation axis in R and the two fold axes of C_{2v} are given by superscripts.

F	L	R($\vec{r}$)	Symmetry Elements
D_{2d}^{3}	D_{2d}^{3}	$C_{2v}^{(x,xy,\overline{xy})}$	$\left(C_{2x}/-\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right)$
	D_{2d}^{1}	$D_{2}^{(x,y,z)}$	$\left(C_{4z}/-\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right)$
C_{2V}^{8}	C_{2v}^{8}	$C_{2v}^{(x,x,y)}$	$\left(C_{4z}/-\frac{1}{2}\ \frac{1}{2}\ 0\ \right)$
	C_{2}^{2}	$C_{2}^{(x,x,z)}$	$(C_{2z}/0\ \ 0\ \ \frac{1}{2})$
D_{2}^{1}	C_{2}^{1}	$C_{2}^{(1)}$	$(C_{6z}/0\ \ 0\ \ \frac{1}{2})$

Conclusion:

In this paper we have found all possible quadrupole arrangements in a crystal Gadolinium Molybdate using the theory of space groups. This has been done by the method of Opechowski and Guccione (10) which uses the theory of magnetic groups for the classification of spin arrangements in magnetic crystals. The quadrupole arrangement of lowest energy in the β-phase of solid Gadolinium Molybdate is found. Table2 shows that in tetragonal lattice there are no possible quadrupole arrangements in which molecular axes can lie on the xy-plane as in the D_{4h}^{14} arrangement in solid nitrogen. In orthorhombic phase they will have two qudrupole arrangements in xy- plane.

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