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Quadrupole Arrangements in Solid CO

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The group-theoretical classification of all possible quadrupole arrangements which was carried out in a previous paper for crystals such as H_2 and N_2 is extended here to include CO, the molecules of which lack a center of symmetry. It turns out that the quadrupole arrangement in the cubic phase is T^4 with axially symmetric quadrupoles. From symmetry considerations of the quadrupoles only, it is shown that a structure similar to the tetragonal D_{4h}^{14} arrangement in γ nitrogen cannot be formed in solid CO, in accord with recent experimental results.

I. INTRODUCTION

In a previous paper¹ a group-theoretical classification of all possible quadrupole arrangements was carried out for crystals such as H_2 and N_2 . In this paper the method is extended to include the CO crystal, the molecules of which lack a center of symmetry. Below 61.5 °K, CO is stable in the so-called α phase, in which the centers of the molecules are fixed on a fcc lattice.² The CO molecules are ordered in a manner similar to that of N_2 except that the symmetry of the former is reduced and the appropriate space group is T^4 instead of T_h^6 . The intermolecular quadrupole-quadrupole interaction is believed to play a primary role in the ordering of the molecules.³⁻⁵

Solid N_2 is known to have also a high pressure γ phase. At 20.5 °K and 4015 atm Schuch and Mills⁶ found its molecular structure to be body-centered tetragonal with the space group being D_{4h}^{14} . However, in CO, which has a larger quadrupole moment,⁷ they did not observe a similar structure at high pressure. In this paper symmetry considerations are used in order to show that it is impossible for solid CO to have a structure similar to the tetragonal D_{4h}^{14} arrangement in solid N_2 if indeed quadrupole interactions dominate the intermolecular potential.

II. CLASSIFICATION OF QUADRUPOLE ARRANGEMENTS

The method of classifying all possible quadrupole arrangements in a crystal by using the theory of space groups was described in detail in Ref. 1. This was done by following the method of Opechowski and Guccione⁸ for the classification of spin arrangements in magnetic crystals. As applied to CO, the classification of quadrupole arrangements

is identical with that given in Ref. 1, except for the following difference. While a H_2 or N_2 molecule is invariant under inversion and under reflection and twofold rotations perpendicular to the molecular axis, a CO molecule is not. As a consequence, a site point group that permits a quadrupole arrangement for H_2 or N_2 may not permit such an arrangement in the case of CO, or it may lead to additional restrictions in determining the orientation of the CO molecular axis. Thus, there is no quadrupole arrangement in CO if the site point group is, for example, C_{3i} , for this group contains inversion symmetry. For the site point group C_{2v} , for example, the molecular axis of H_2 or N_2 can be along the rotation axis or perpendicular to either

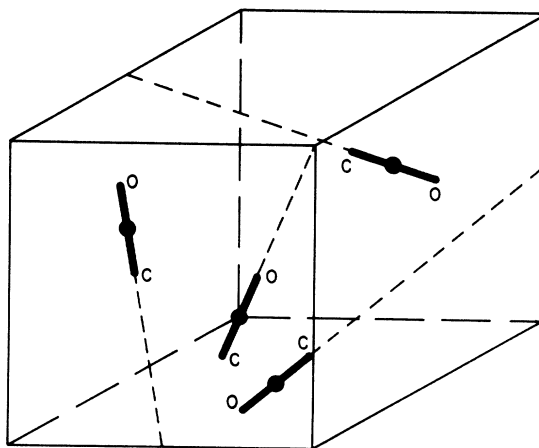


FIG. 1. Quadrupole arrangement of CO invariant under T^4 in a simple crystal generated by O_h^3 . There are four different orientations of the molecular axis, namely, along the $[111]$, $[1\bar{1}\bar{1}]$, $[1\bar{1}1]$, and $[\bar{1}\bar{1}1]$ directions.

TABLE I. List of the quadrupole arrangements of CO invariant under subgroups L of F . The site point groups R and the symmetry elements are included. The orientation of the rotation axis in R when not in the z direction and the three twofold axes of C_{2v} are given by superscripts.

F	L	R	Symmetry elements
O_h^5	T^4	$C_3^{(xyz)}$	$(C_{2y} 0\frac{1}{2}\frac{1}{2}), (C_{2x} \frac{1}{2}0\frac{1}{2})$
D_{4h}^{17}	D_{4h}^7	C_{4v}	$(I \frac{1}{2}\frac{1}{2}\frac{1}{2})$
	C_4^5	C_4	
	D_{2d}^3	$C_{2v}^{(x,xy,\bar{x}y)}$	$(C_{2x} \frac{1}{2}\frac{1}{2}\frac{1}{2})$
	C_{4v}^4	$C_{2v}^{(x,xy,\bar{x}y)}$	$(C_{4x} \frac{1}{2}\frac{1}{2}\frac{1}{2})$
	C_{4v}^7	$C_{2v}^{(x,x,y)}$	$(C_{4x} \frac{1}{2}\frac{1}{2}\frac{1}{2})$
	C_4^3	C_2	$(C_{4x} \frac{1}{2}\frac{1}{2}\frac{1}{2})$

of the two reflection planes, while the molecular axis of a CO molecule can be only along the rotation axis. Table I of Ref. 1, which gives the matrix form of the quadrupole-moment tensor invariant under each of the 32 point groups, must be altered to be applicable to CO. In addition to the five point groups T , T_h , T_d , O , and O_h which do not permit invariant quadrupole tensors in solid H_2 and N_2 , one must add the following point groups: C_i , C_{2h} , D_{2h} , S_4 , C_{4h} , D_{2d} , D_4 , D_{4h} , C_{3i} , D_3 , D_{3d} , C_{3h} , C_{6h} , D_{3h} , D_6 , and D_{6h} .

In the cubic and the tetragonal lattices the molecular positions form a simple crystal generated by O_h^5 and D_{4h}^{17} , respectively, from the position vec-

tor $\vec{r} = (0, 0, 0)$. We refer to Tables II and V of Ref. 1 for the lists of subgroups of O_h^5 and D_{4h}^{17} taken into consideration. The possible quadrupole arrangements for solid CO, invariant under these subgroups, are given in Table I. This table is analogous with Table III of Ref. 1.

III. DISCUSSION

As is seen in Table I, there is only one possible quadrupole arrangement in cubic CO, which is T^4 with axially symmetric quadrupoles. This arrangement, which is in agreement with Ref. 2, is shown in Fig. 1. It is similar to the T_h^6 arrangement in cubic H_2 and N_2 (see Fig. 1 of Ref. 1), which is known^{8,9} to have the lowest quadrupole-quadrupole interaction energy.¹⁰

The quadrupole arrangement of lowest energy which is possible in the γ phase of solid N_2 was found in Ref. 1 to be D_{4h}^{14} in agreement with experimental results.⁶ The molecular axes lie on the xy and $\bar{x}y$ directions as shown in Fig. 5 of Ref. 1. Inspection of Table I shows that in a tetragonal lattice there is no possible quadrupole arrangement in which the molecular axes can lie on the xy plane as in the D_{4h}^{14} arrangement in γ nitrogen. This is in accord with the experimental results of Schuch and Mills,⁶ who observed such a structure only in N_2 .

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