closure are large compared with his own dimensions. The phonons are in an analogous situation.

To obtain a formal proof, consider a cylinder inscribed into the slab as shown from the side and from the top in Fig. 1. The vectors $\vec{k}_1$ and $\vec{k}_2$ represent the quasi-momenta of a phonon incident and specularly reflected from the wall. As shown in Ref. 1, the phonon distribution function $f(\vec{k}, \vec{x})$ of the stationary, but because of the heat flow, nonequilibrium system has axial symmetry with respect to any line perpendicular to the slab faces. This means that at the point "$A$" we have

$$f(\vec{k}_1, \vec{x}) = f(k, \theta, \vec{x}) = f(\vec{k}_2, \vec{x})$$

because $f$ is independent of $\varphi$, and $k$ and $\theta$ do not change in specular reflection.

Consequently, the distribution function found for the infinite slab fulfills the boundary conditions of specular reflection on the walls of the cylinder or prism, as well as the Boltzmann equation. Hence, it is the solution of the problem in question. It is further evident that the distribution function is invariant with respect to the introduction of any kind of specularly reflecting walls as long as they are perpendicular to the slab boundaries.

It should be noted that the distribution function, and therefore the conductivity, is independent of the cross-sectional dimensions of the sample. This is not true if the reflection is diffuse rather than specular, or if there is radiative or conductive loss of heat through the walls. We expect therefore, the theory to hold best for highly polished samples.

Our thanks are due to J. M. Robinson, Dr. J. Mennig, and Dr. T. Auerbach for discussions on the subject and to the Sektion Physik, Universität München, for its hospitality.

*On leave from the Department of Physics, The Florida State University, Tallahassee, Fla. 32306.

[1] P. Erdös and S. B. Haley, Phys. Rev. 184, 951 (1969).

PHYSICAL REVIEW B VOLUME 4, NUMBER 2 15 JULY 1971

# Comment on Generalized Forces in Solids

P. D. DeCicco
*Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139
(Received 15 March 1971)

A simple model for the application of the Hellmann-Feynman theorem to the equilibrium condition for a solid is discussed.

Some concern over the accuracy of charge densities of solids calculated from Bloch functions has been raised by an article of Wannier *et al.*[1] Using the Hellmann-Feynman theorem, they found a relationship between the charge distribution in a unit cell of a periodic crystal and the equilibrium condition for the crystal, which had explosive consequences for "nearly free-electron" metals. However, Kleinman[2] has considered in detail the electrostatics involved in determining the force acting on a nucleus in a large finite crystal and has concluded that one must take into account the electronic charge density and the nuclei near the surface. The plausibility of Kleinman's conclusion has been questioned on the grounds that it is unusual to expect surface effects to play an important role in the determination of a bulk quantity such as the equilibrium lattice constant.[3] The purpose of this paper is to show explicitly for a simple model that the equilibrium condition is determined by a surface effect.

Let us consider a classical system of $N+1$ bodies at positions $x_n = an$, $n = 0, 1, 2, \ldots, N$, each joined to its nearest neighbors by springs with spring constant $K$ and rest length $a_0$. The potential energy of the system is then $U(a) = \frac{1}{2}NK(a - a_0)^2$, so that $dU/da = NK(a - a_0)$. The analog of the Hellmann-Feynman theorem for this system is $dU = -\sum_n F_n dx_n$ where $F_n$ is the force on the $n$th body produced by the rest of the system. Considering the case of uniform strain, $dx_n = n\,da$, we see that $dx_0 = 0$ and $F_n = 0$ for $1 \leq n \leq N-1$ since these bodies experience equal and opposite forces from the identically strained springs on either side. Therefore, we have from the Hellmann-Feynman theorem (D'Alembert's principle[4]) $dU = -F_N dx_N = k(a - a_0) \times N\,da$ so that $dU/da$ is obtained exactly in this case from the force on the body at the end of the chain. This argument is easily generalized to three dimensions, establishing the role of the surface in the equilibrium condition.

By introducing springs joining second neighbors in the chain, we can easily produce a model for the variation of the lattice constant close to the surface, analogous to that described in Kleinman's paper.[2]

[1]G. H. Wannier, C. Misner, and G. Schay, Jr., Phys. Rev. 185, 983 (1969).
[2]Leonard Kleinman, Phys. Rev. B 1, 4189 (1970).
[3]Gregory H. Wannier and Gunther Meissner, Phys. Rev. B 3, 1240 (1971).
[4]Herbert Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1959), p. 14.

PHYSICAL REVIEW B VOLUME 4, NUMBER 2 15 JULY 1971

# Quadrupole Arrangements in Solid CO

J. Felsteiner and D. B. Litvin
*Department of Physics, Technion–Israel Institute of Technology, Haifa, Israel*
(Received 24 February 1971)

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 $\gamma$ nitrogen cannot be formed in solid CO, in accord with recent experimental results.

## I. INTRODUCTION

In a previous paper[1] 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 $\alpha$ 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 $\gamma$ phase. At 20.5 °K and 4015 atm Schuch and Mills[6] 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 Guccione[8] 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

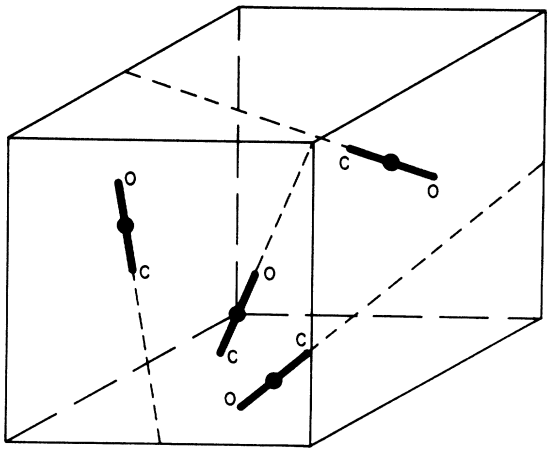


FIG. 1. Quadrupole arrangement of CO invariant under $T^4$ in a simple crystal generated by $O_h^5$. There are four different orientations of the molecular axis, namely, along the [111], [1$\bar{1}$1], [11$\bar{1}$], and [$\bar{1}$11] directions.