Inadvertent symmetries in a lattice-dynamical model of graphite

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The lattice-dynamical model for graphite by Nicklow, Wakabayashi, and Smith (NWS) [Phys. Rev. B 5, 4951 (1972)] has been found to contain subtle inadvertent additional symmetries. These lead to the unexpected *qualitative* consequences of (1) nonexistence of Rayleigh surface waves and (2) a high-order degeneracy on the Brillouin-zone boundary—neither of which is justified on general principles. We discuss how these consequences arise, and we present our extension of the NWS model which removes them. We give a brief survey of several more elaborate models of graphite subsequent to the NWS model, indicating which also contain the inadvertent additional symmetries discussed here. The parameter set presented here for this extension is an improvement over that given earlier by us [Phys. Rev. B 23, 4208 (1981)].

INTRODUCTION

The rather extensive neutron scattering measurements of the lattice dynamics of graphite and the force-constant model fitted to them, published by Nicklow, Wakabayashi, and Smith (NWS),[1] have been quite influential in subsequent investigations involving the dynamics of systems containing graphite. Our own studies of the dynamics of bare and adsorbate-covered graphite surfaces[2–4] are examples of such later work. However, we discovered that there are somewhat subtle defects in the NWS force-constant model which can be characterized as inadvertent extra symmetries. Although in Refs. 2–4 we have alluded to these defects and our extensions to remove their undesirable effects, there has not been a satisfactory discussion of them. It is the purpose of this Comment to provide such a discussion. We conclude with a brief survey of the major graphite models published since NWS, and indicate which contain the inadvertent additional symmetries discussed here. In addition, the force-constant values for our extension of the NWS model which were published in Ref. 3 (and used for the results of Refs. 2 and 4) differ slightly from what we had intended, because of a computer program error;[5] here we will present a set of corrected values and an assessment of the discrepancies between the earlier and present sets.

To focus the discussion, Fig. 1 exhibits a convenient labeling of the atoms in a reference unit cell (cell a) of the graphite structure; the basis is taken to be atoms $1a$, $2a$, $3a$, and $4a$. While this is not the conventional basis, the fact that all basis atoms lie on a reflection plane simplifies the form of the prototypical general atomic force-constant (AFC) matrices, which are presented in Table I for the first three shells of in-plane neighbors [1NN(∥), 2NN(∥), 3NN(∥)] and the first two shells of out-of-plane neighbors [1NN(⊥) and 2NN(⊥)]. As a convenient teminology we refer to the geometrical relation of two atoms as a "bond" (e.g., the "3NN(∥) bond").

The NWS model includes bonds through 3NN(∥) and 1NN(⊥), with axially symmetric (AS) contraints and an additional equivalencing of the two sets of 2NN(∥) bonds, $(1a,1c)$ and $(2a,2c)$, which are not strictly related by symmetry. The restriction to this set of interactions was obviously motivated in large measure by a desire not to try to force an overly elaborated model on measurements that were very restricted above the frequencies accessible to thermal neutron scattering and which were also subject to uncertainties arising from the orientational disorder in pyrolytic graphite.[1] This restriction inadvertently contains additional symmetries which lead subtly to two nonphysical results: (1) Rayleigh surface waves do not exist on the (0001) surface, and (2) there is a threefold degeneracy at

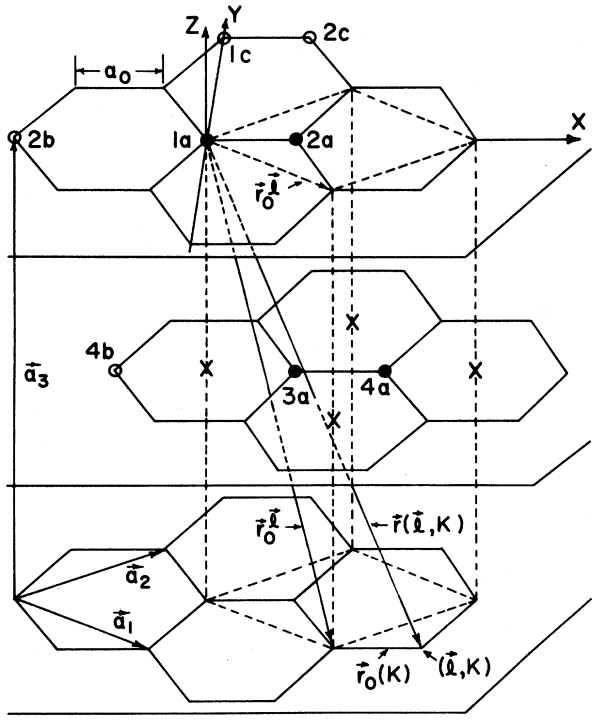

FIG. 1. Reference geometry for the graphite crystal structure. Basis atoms for the reference unit cell a are shown as filled circles, and prototypical atoms in neighboring unit cells b and c which interact with cell a are shown as open circles. a_0 is the nearest-neighbor distance, and $r_c = c/2$ is the interplanar distance.

For a general wave vector with $k_z=0$, by *general* symmetry there is a rigorous decoupling of $(x,y)(\parallel)$ motions from $z(\perp)$ motions, and the unexpected threefold degeneracy in the NWS model appears in the z motion. Hence, we will consider only the (zz) block of the dynamical matrix; at the K point, this block is further block diagonalized as follows:

$$\begin{pmatrix} D(1,1) & D(1,2) & D(1,3) & D(1,4) \\ D(2,1) & D(2,2) & D(2,3) & D(2,4) \\ D(3,1) & D(3,2) & D(3,3) & D(3,4) \\ D(4,1) & D(4,2) & D(4,3) & D(4,4) \end{pmatrix} = \begin{pmatrix} A & 0 & 0 & 0 \\ 0 & B & C & 0 \\ 0 & C & B & 0 \\ 0 & 0 & 0 & A \end{pmatrix} , \quad (1)$$

where A, B, and C in Eq. (1) are the K-point (zz)-matrix elements which are not identically zero by *general* symmetry at this wave vector.[9] The expected double degeneracy $\omega^2=A$ corresponds to motion of either the 1-atoms alone or the 4-atoms alone. The remaining eigenvalues $\omega^2_{\pm}=B\pm C$ correspond to the 2- and 3-atoms moving with equal amplitude either together (ω^2_+) or in opposition (ω^2_-).

In the NWS model, ω^2_+ becomes degenerate with the $\omega^2=A$ doublet as follows: First, $\gamma_5'=\gamma_5$ [the assumed equivalence of $(1a,1c)$ and $(2a,2c)$ 2NN$(\parallel)$ coupling]. Thus, $D(1,1)$ and $D(2,2)$ differ only in the self-interaction terms that are contributed by *inter*planar couplings to 1- and 2-atoms. Second, in the NWS model 1-atoms have *no* interplanar coupling, while 2-atoms couple *only* to 3-atoms; thus,

$$MD(2,3) = -2\gamma_4\cos(ck_z/2) \ . \quad (2)$$

Hence, at the K point the (2,3) coupling contributes $-MC=2\gamma_4$ to the (2,2) self-interaction:

$$D(2,2)=D(1,1)+2\gamma_4/M$$

or (3)

$$B=A-C \ ,$$

so that $\omega^2_+\equiv B+C=A$, giving the third member of the observed degeneracy.

EXTENSION TO THE NWS MODEL TO REMOVE INADVERTENT SYMMETRY

While the removal of the assumed equivalence between the $(1a,1c)$ and $(2a,2c)$ 2NN$(\parallel)$ interactions would suffice to remove the spurious third degeneracy at the K point, the more important extension appears to be that of including the 2NN$(\perp)$ class of interplanar couplings. Accordingly, we have followed NWS by retaining the AS constraints and the $(1a,1c)$-$(2a,2c)$ equivalence; we also have assumed $(1a,3a)$-$(1a,4b)$ equivalence. This latter equivalence would seem to be even more valid than the former, because the interplanar interactions are more nearly pairwise ones and van der Waals–like. In our extension, we aimed to fit the frequencies of NWS. The high-frequency bands are insensitive to the addition of the 2NN$(\perp)$ interactions, and since they are largely governed by the in-plane interactions, we take the NWS parameters for the 1NN$(\parallel)$, 2NN$(\parallel)$, and 3NN$(\parallel)$ bonds. The lowest TO (E_{2g1}) and LO (B_{1g1}) zone-center frequencies are most sensitive to the 1NN$(\perp)$ and 2NN$(\perp)$ interactions, so we fitted the parameters of these interactions to reproduce the NWS values of these frequencies as follows. First, parameters ϵ_N, σ_N of a (6,12) potential were determined from the NWS values for α_4, γ_4. Then, holding the range parameter fixed at σ_N, we varied the energy parameter ϵ while both the 1NN$(\perp)$ set of parameters (α_4,γ_4) and the 2NN$(\perp)$ set $(\alpha_5,\beta_5,\gamma_5,\epsilon_5)$ were determined by this common (12,6) potential via the AS formulas [Eq. (13) of Ref. 3]; this variation proceeded until the resulting E_{2g1} and B_{1g1} eigenvalues lay between those of NWS, with the B_{1g1} eigenvalues being somewhat closer than those of E_{2g1} to account for the compressional stiffness contributed by the repulsive component of the 1NN$(\perp)$ interaction. At this stage, $\epsilon=0.04\epsilon_N$ and $\sigma=\sigma_N$; these values were used to fix α_4 and γ_4. Then, our model eigenvalues for E_{1g1} and B_{1g1} were fine tuned to match the NWS eigenvalues by independent adjustment of the 2NN$(\perp)$ radial and tangential AS force constants ϕ_r^5 and ϕ_t^5. Table II gives the force-constant values for the NWS model,[1] our original attempt at extension (model I),[2-4] and our set (model II) corrected for the error of Ref. 5. The fitting procedure described above is not entirely unique, and the model III results in Table II are an alternative set obtained by the best fit to E_{2g1} and B_{1g1} while using a common (12,6) potential for both 1NN$(\perp)$ and 2NN$(\perp)$ interactions and varying *both* the energy ϵ and range σ parameters.

We may assess the range of discrepancy among models I, II, and III by reference to the modes of a thirteen-layer graphite slab for $\bar{\Gamma}$, the origin, and $\bar{K}$, the corner of the bare graphite surface BZ; we focus our attention on key modes

TABLE II. Axially symmetric interplanar force constants for bulk graphite. Values in any column, which are identical to those of the column immediately to the left of it, are left blank (this convention emphasizes the differences between the models). Intraplanar force constants are identical with NWS. (Unit $=10^5$ dyn cm^{-1}.)

	NWS (Ref. 1)	Model I (Ref. 3)	Model II (Present work)	Model III (Present work)
α_4	-7.7×10^{-3}	5.99×10^{-4}		4.08×10^{-4}
γ_4	-5.8×10^{-2}	-1.947×10^{-2}		-2.93×10^{-2}
α_5	0	-1.076×10^{-3}	-1.247×10^{-3}	-1.120×10^{-3}
β_5	0	-7.67×10^{-4}	-5.95×10^{-4}	-6.79×10^{-4}
γ_5	0	-4.23×10^{-3}	-4.22×10^{-3}	-3.14×10^{-3}
ϵ_5	0	-1.033×10^{-3}	-1.537×10^{-3}	-1.041×10^{-3}

TABLE I. Graphite atomic force-constant matrices and axially symmetric constraints. The 2NN($\perp$) AFC obey additional, more complex AS constraints; e.g., $C^2(\alpha_5-\beta_5)=S^2(\gamma_5-\beta_5)$ and $S\epsilon_5=C(\alpha_5-\beta_5)$, where $C^2=r_c^2/(a_0^2+r_c^2)$, $S^2=a_0^2/(a_0^2+r_c^2)$, and $r_c=\frac{1}{2}c=\frac{1}{2}|\vec{a}_3|$

Neighbor class	AFCM	AS constraints
1NN($\parallel$)	$\underline{\phi}(1a,2a)=\begin{pmatrix}\alpha_1 & 0 & 0\\ 0 & \beta_1 & 0\\ 0 & 0 & \gamma_1\end{pmatrix}$	$\gamma_1=\beta_1$
2NN($\parallel$)	$\underline{\phi}(1a,1c)=\begin{pmatrix}\alpha_2 & \epsilon_2 & 0\\ -\epsilon_2 & \beta_2 & 0\\ 0 & 0 & \gamma_2\end{pmatrix}$	$\gamma_2=\alpha_2,\ \epsilon_2=0$
	$\underline{\phi}(2a,2c)=\begin{pmatrix}\alpha_2' & \epsilon_2' & 0\\ -\epsilon_2' & \beta_2' & 0\\ 0 & 0 & \gamma_2'\end{pmatrix}$	$\gamma_2'=\alpha_2',\ \epsilon_2'=0$ (NWS: $\alpha_2'=\alpha_2$, also)
3NN($\parallel$)	$\underline{\phi}(1a,2b)=\begin{pmatrix}\alpha_3 & 0 & 0\\ 0 & \beta_3 & 0\\ 0 & 0 & \gamma_3\end{pmatrix}$	$\gamma_3=\beta_3$
1NN($\perp$)	$\underline{\phi}(2a,3a)=\begin{pmatrix}\alpha_4 & 0 & 0\\ 0 & \alpha_4 & 0\\ 0 & 0 & \gamma_4\end{pmatrix}$	none
2NN($\perp$)	$\underline{\phi}(1a,3a)=\begin{pmatrix}\alpha_5 & 0 & -\epsilon_5\\ 0 & \beta_5 & 0\\ -\delta_5 & 0 & \gamma_5\end{pmatrix}$	$\delta_5=\epsilon_5$
	$\underline{\phi}(1a,4b)=\begin{pmatrix}\alpha_5' & 0 & -\epsilon_5'\\ 0 & \beta_5' & 0\\ -\delta_5' & 0 & \gamma_5'\end{pmatrix}$	$\delta_5'=\epsilon_5'$

the bulk Brillouin-zone (BZ) boundary, whereas a twofold degeneracy is the highest phonon degeneracy to be expected for nonzero wave vector.

NONEXISTENCE OF RAYLEIGH SURFACE WAVES

An examination of Table I reveals that, even without the AS constraints, there are no couplings between particle motions perpendicular to the (0001) planes (z) and motions parallel to these planes (x,y) up through the bonds included in the NWS model. Hence, there cannot be in such a model the elliptical particle motion that is so characteristic of Rayleigh surface waves. On the other hand, general considerations of hexagonally symmetric elastic continua have demonstrated that Rayleigh surface waves *should* exist on such surfaces as the (0001) surface of graphite.[6] Thus, it is necessary to have a lattice-dynamical model which contains the z-to-(x,y) couplings required to relieve the surface stress and give the elliptical polarization of a Rayleigh wave.[7] The two sets of 2NN($\perp$) bonds in Table I manifestly provide such coupling. In retrospect, there are also some geometrical arguments for the inclusion of 2NN($\perp$) couplings: The 2NN($\perp$) bonds are only slightly longer than the 1NN($\perp$) bond (ratio $=3.64$ Å/3.35 Å$=1.087$), and there are substantially more of them [e.g., in Fig. 1, the $(1a,2a)$ plane is coupled to the $(3a,4a)$ plane by only one 1NN($\perp$) bond per unit cell, while there are three $(1a,3a)$, three $(1a,4b)$, and three $(2a,4a)$ 2NN($\perp$) couplings].

EXTRA DEGENERACY AT THE BULK BZ BOUNDARY

When we first applied the NWS model in a calculation of the (0001)-surface projected bulk phonon bands, we observed a threefold degeneracy at the bulk K point (midpoint of the BZ edge paralleling the c axis), whereas a twofold degeneracy is the highest to be expected by symmetry.[8]

consisting of the tops of the bulk bands and the surface modes associated with each bulk band. With the exceptions to be noted below, these key mode frequencies agree among the three models to within 2 GHz. The surface-layer sums of squared amplitudes (SSA) for surface modes in this group agree to within 3.5%; there are some larger discrepancies between the surface-layer SSA for the top-of-bulkband modes in this group (up to 10% variation), but because these modes are bulk modes with small amplitude in the surface layer (i.e., two or more orders of magnitude smaller than an amplitude uniform across the slab), these discrepancies in amplitude are not significant. All the key modes for models I and II fall into this group of close agreement.

The exceptions to close agreement in the key modes are two. (1) For the $\bar{\Gamma}$ bulkband whose top in model II is at 41.7697 THz and whose associated surface mode in model II is at 41.7163 THz, the model III frequencies are, respectively, 41.7874 and 41.7117 THz. Thus, the surface mode frequency is almost within the group of close agreement; however, its surface-layer SSA is only 90% that of models I and II. The top-of-bulkband mode in model III (at 18 GHz higher than models I and II) has a surface-layer SSA that is 5.6 times that of models I and II, but it is still over one order of magnitude smaller than a uniform amplitude. (2) For the $\bar{K}$ bulkband whose top and surface state in model II are, respectively, at 16.9178 and 16.6215 THz, the model III frequencies are 17.0323 and 16.6080 THz, respectively. As in (1), the model III surface mode is in closer agreement (than the bulkband top) but here it is 13 GHz lower, and its surface-layer SSA is only 75% that of models I and II. The model III bulkband top is 114 GHz higher than models I and II, and its surface-layer SSA is 127% that of models I and II (but still over an order of magnitude smaller than a uniform amplitude).

We may conclude from this range of discrepancy between models I, II, and III that, although model III does produce some results that differ noticeably from models I and II, nevertheless the discrepancies are so small that they are unlikely to be resolvable in practical comparisons. Furthermore, we may conclude that the models I and II produce results close enough that the results obtained with model I earlier should be as reliable as those obtained with model II; this reinforces the point emphasized in Ref. 5. (It will also bear emphasizing, however, that one must keep to the *same* model in such applications as the calculation of bulk and of high-surface-area sample vibrational spectra to be differenced in the calculation of surface specific heat.)

Although in this paper we have concentrated on the inadvertent symmetries in the original NWS model and our extensions to remove them we can make contact with several more recent, more elaborate graphite models. The models of Ahmadieh and Rafizadeh include neighbor classes up through 4NN($\parallel$) and 2NN($\perp$), using central-potential models.[10] Mani and Ramani give a valence-force field model which includes neighbor classes through 3NN($\parallel$) and 1NN($\perp$).[11] Nicholson and Bacon give both a general tensor-force model and an axially symmetric model supplemented with some valence-force field interactions; both include neighbor classes 3NN($\parallel$) and 2NN($\perp$).[12] Maeda, Kuramoto, and Horie give an axially symmetric model extended such that, for in-plane interactions, the tangential force constant can be different for out-of-plane and in-plane displacements; neighbor classes 2NN($\parallel$) and 1NN($\perp$) are included.[13] Finally, in a paper that appeared while this paper was in preparation, Al-Jishi and Dresselhaus give an extension of the model of Maeda *et al.* that includes 4NN($\parallel$) and 4NN($\perp$) neighbors and fits most known data relating to the vibrations of graphite.[14] Of these models, those of Refs. 11 and 13 include 1NN($\perp$) neighbors only, and hence cannot yield Rayleigh surface waves; in addition, they do not distinguish between the two different classes of 2NN($\parallel$) neighbors, and hence will give rise to the spurious threefold degeneracy at the bulk K point. The models of Refs. 10, 12, and 14 are free of the defect of inadvertent symmetries discussed in the present paper.

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[5]The error is that a_0, the in-plane nearest-neighbor distance, was inadvertently given the value 1 Å instead of 1.41 Å on the right-hand side of the $i=5$ equations of Eq. (13) in Ref. 3. It must be emphasized, however, that our fitting procedure fitted the *frequencies* (and hence the AFC) and not the underlying ϕ_r, ϕ_t parameters; consequently, the results in Refs. 2–4 are not as greatly in error as it might seem at first. Of course, values of ϕ_r^5, ϕ_t^5 reconstructed from the 2NN($\perp$) AFC of Ref. 3 would be completely spurious (and even internally inconsistent) because of this error. Note also that, in the present paper, we have reverted to the more standard use of c for the length of $\vec{a}_3$, whereas in Refs. 2–4, c denoted the interplanar spacing.

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[8]Our initial calculations were carried out in single precision on a Control Data Corporation 6600 computer which yields about 14 significant decimal digits; the threefold degeneracy observed in ω^2 at the K point for the NWS model was exact to this precision. On the other hand, NWS apparently did not observe this extra degeneracy because their calculations were carried out in single precision on an IBM S/360 computer, and the 6 to 7 significant digit precision did not reveal the third degeneracy [R. M. Nicklow (private communication)].

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