FORCE CONSTANTS FOR THE GRAPHITE LATTICE

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1. Introduction

Early force-constant models of graphite [1,2] assumed that lattice vibrations parallel and perpendicular to the basal plane are independent, and, although such decoupling is computationally convenient for the calculation of some crystal properties, these models have only a limited application. They describe a lattice which is unstable, since the shear modulus C_{44} is zero, and are inappropriate for defect-structure calculations for example. Thus, in an earlier study [3,4] which used the method of lattice statics to obtain the atomic displacements around a vacancy, we were restricted to a two-dimensional model of a layer.

The purpose of the present work was to develop a stable, three-dimensional model so that further defect calculations can be made. We required the model to predict the experimental elastic constants and give a good fit to the available phonon-dispersion data [5]. In earlier developments of three-dimensional models to fit this data, Nicklow et al. [5] and Mani and Ramani [6] determined force constants based on pair-wise interactions and valence constants respectively. In both sets, a non-zero value of C_{44} was assigned, but, for these models, this has the consequence of requiring an external pressure to be imposed to maintain equilibrium, and thus C_{44} would become zero under the application of stress-free equilibrium. The model used here avoids this difficulty.

2. The Model and Force Constants

A full discussion of the problems involved in fitting the constants involved in interactions between up to third neighbours in a plane and up to second neighbours on adjacent planes is the subject of a forthcoming paper [7]. We give there the relations which must be obeyed for stress-free equilibrium, and, in addition, it is noted that since the Cauchy relation $C_{13}=C_{44}$ is not satisfied by the elastic constants, at least one three-body interaction between adjacent layers is required. The available experimental data are insufficient to enable the constants of the most-general model to be determined, and it is necessary to set some constants to zero and to limit by physical reasoning the range of values of others. Full details are given in [7], and it is sufficient to merely present here values for the model which was finally found to best meet the requirements outlined in section 1.

Some constants were those which can be considered to arise from a pair-wise, interatomic potential function V(r), and others were of the valence type. The former give rise to forces on atoms which are either parallel or perpendicular to the line joining two atom centres, and are given by

$$R_n = d^2V/dr^2 \text{ and } T_n = r^{-1}\, dV/dr \quad (\text{at } r = r_n)$$

respectively, where r_n is the perfect-lattice spacing between nth nearest neighbours. For the model considered here, n = 1,2,3,4,5, as shown schematically in Fig.1, where the atoms neighbouring the atom at the origin (atom O) are labelled 1 to 5. We have assumed that the 5th-neighbour interaction between, say, atoms O and 5 is the same as that between atoms 1 and 5. In addition to these 10 parameters, three valence constants were used. They are (a) an interplanar constant λ giving energy changes due to changes in angle ϕ shown in Fig.1 as $\frac{1}{2}\lambda r_1^2 \sin^4\phi\,(\Delta\phi)^2$; (b) an in-plane, adjacent-bond-angle constant μ, as used in earlier, simple models [1,2]; and (c) an in-plane, adjacent-bond-length constant ν, equivalent to k_{rr} used in [6].

The values found for these various parameters are given in Table 1 in units of Nm^{-1}. As discussed in [7], they can be expressed in terms of the more conventional force-constant matrix for interactions between nth neighbours, which has the form (referred to $\hat{x}_1$, $\hat{x}_2$, $\hat{x}_3$):

$$\begin{pmatrix} A_n & D_n & E_n \\ -D_n & B_n & 0 \\ F_n & 0 & C_n \end{pmatrix}$$

where $B_4 = A_4$; D_n is non-zero only for n=2; E_n and F_n are non-zero only for n=5 (interaction O-5, for example) and n=5' (interaction 1-5, for example); and $F_5' = E_5'$.

The numerical values (in Nm^{-1}) of the remaining constants are given in Table 2, as are those calculated from the constants given by Nicklow et al. [5] and Mani and Ramani [6].

3. Discussion

The elastic constants (in $10^{10}Nm^{-2}$) given by the new model are compared with experimental values and those obtained in [5] and [6] in Table 3. The predicted dispersion curves along the Γ-Δ-A and Γ-Σ-M axes of the zone are shown in Fig.2. It can be seen that the new model gives an excellent fit to the experimental data, and, furthermore, it describes a lattice in stress-free equilibrium. The latter condition was not met in the models of Nicklow et al. [5] and Mani and Ramani [6]. (Additional inconsistencies in the latter work are discussed in [7].)

The present model uses a combination of pair-wise and valence potentials, and this has a distinct advantage for defect-structure calculations. The forces required to simulate defects can be derived very easily from the force constants; these forces are zero in a pure valence-potential model, and would have to be obtained from an independent calculation [4]. For a single vacancy in the present model,

for example, the force acting on the nth nearest-neighbour atom in an unrelaxed position is simply $-r_n T_n$. For n=1, this equals -20 eV/Å. The application of this model to the structure of vacancy clusters is in progress.

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References

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Table 2

Force Constant	New Model	Ref. 5 +	Ref. 6 +
A_1	323.362	362.00	4.977
B_1	279.950	199.00	625.941
C_1	231.950	199.00	46.863
A_2	-33.533	-52.00	48.933
B_2	91.440	133.00	60.260
C_2	-38.533	-52.00	7.423
D_2	22.517	0	31.758
A_3	-18.830	- 3.70	-22.779
B_3	0	28.80	-22.779
C_3	0	28.80	0
A_4	0.529	0.77	0.626
C_4	0.997	5.80	5.724
A_5	0.433	0	0
$B_5 = B_5'$	- 0.250	0	0
C_5	0.362	0	0
E_5	- 0.259	0	0
F_5	- 1.612	0	0
A_5'	- 0.053	0	0
C_5'	0.848	0	0
E_5'	0.465	0	0

+ Finite Pressure values

Table 1

T_1	231.950	R_1	241.746	λ	-0.486
T_2	-38.533	R_2	122.440	μ	8.000
T_3	0	R_3	-18.830	ν	-4.400
T_4	0.250				
T_5	- 0.250				

Table 3

	New Model	Expt. 8,9	Ref. 5	Ref. 6
C_{11}	106*	106	144	43
C_{66}	44*	44	46*	91
C_{33}	3.65*	3.65	3.71	3.65*
C_{13}	1.50*	1.50	$=C_{44}$	$=C_{44}$
C_{44}	0.40*	0.40	0.46	0.40*

* Experimental value used to fit force constants.

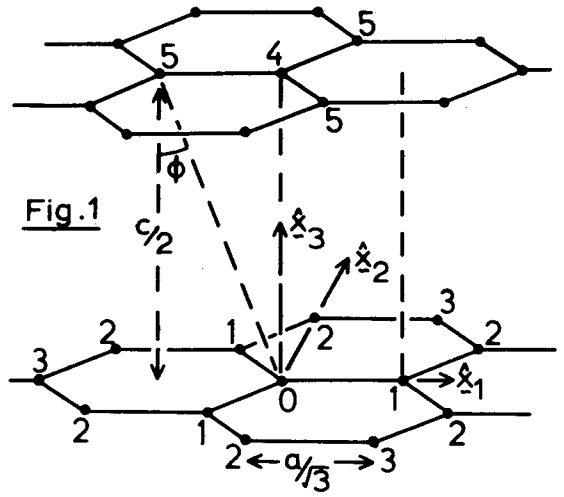

Fig.1

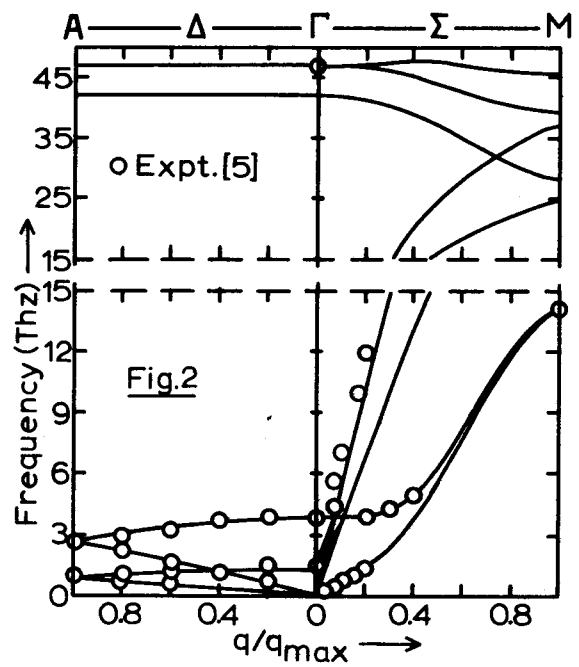

Fig.2