

- ⁷S. H. Glarum, *J. Phys. Chem. Solids*, **24**, 1577 (1963).
⁸O. H. LeBlanc, Jr., *J. Chem. Phys.* **39**, 2395 (1963).
⁹L. Friedman, *Phys. Rev.* **133**, A1668 (1964).
¹⁰A. I. Korn, R. A. Arndt, and A. C. Damask, *Phys. Rev.* **186**, 938 (1969).
¹¹H. Jones and C. Zener, *Proc. Roy. Soc. (London)* **145A**, 268 (1934).
¹²J. B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins Press, Baltimore, Md., 1958).

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Atomic Vibrations in the (00.1) Graphite Surface: Observation with Low-Energy Electron Diffraction and Lattice-Dynamic Calculations

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Low-energy electron diffraction has been used to measure the variation of the surface Debye temperature Θ_1 in the [00,1] direction of graphite as a function of the energy of incident electrons. A change (hexagonal-trigonal) in the symmetry of the diffraction diagram, depending on the penetration of electrons, was observed. This change in symmetry has been made use of in selecting, from the many other values of Θ_1 we had measured, the one associated with the first layer of the (00.1) surface of graphite, namely $(690 \pm 70)^\circ\text{K}$. Furthermore, the dynamics of the Born lattice has been applied to compute the Debye temperature of the first layer of the surface associated with the normal (Θ_1) and parallel ($\Theta_{||}$) directions of the (00.1) face. The computed value of Θ_1 is in fairly good agreement with the one determined experimentally. The computed value of $\Theta_{||}$ is close to that previously obtained by other authors using different methods of calculation.

I. INTRODUCTION

The measurement technique of mean-square displacement for surface atoms by low-energy electron diffraction (LEED) is now a well-established technique¹; nearly all the cubic metals have been studied in this way. The interpretation of the results, however, remains problematical owing to the lack of a precise definition of the surface. Experimentally, $\langle u^2 \rangle$ is determined by using a beam of progressively decreasing energies of the incident electrons, thereby, obtaining smaller and smaller penetration of the surface layers. Hitherto, it has been assumed that the pattern obtained with the smallest energy of incident electrons is representative of the surface structure. This bold hypothesis is a consequence of the absence of any precise LEED theory.

A pseudokinetic theory linking the diffracted intensity to $\langle u^2 \rangle$ was proposed by Jones, McKinney, and Webb,² but recently Baudoing *et al.*,³ taking Ni as an example, showed that the above theory is not elaborate enough to explain the experimental observations. It can be said that, at present, it is not possible to ascertain which pattern - among those obtained with very low-energy electrons - corresponds to the vibrations in the first layer of the surface.⁴

In this paper, we shall first report the measure-

ment of the mean-square displacement $\langle u^2 \rangle_1$ perpendicular to the (00.1) surface of graphite as a function of the electron energy. Then a means of obtaining the precise value of $\langle u^2 \rangle_1$ associated with the first atomic layer of the surface is suggested. Finally, a calculation based on Born lattice dynamics⁵ is provided to check the experimental results.

II. EXPERIMENTAL

If the incident electrons strike the surface normally and observation is made on the reflected electrons in the same direction (or in one very close to that), the intensity I of the specular spot is given by the expression⁶

$$I = K \exp(-16\pi^2/\lambda^2) \langle u^2 \rangle_1, \quad (1)$$

where λ is the wavelength associated with the electrons. Here the term K stands for the contribution due to the diffraction and the exponential corresponds to the diffusion due to the thermal vibrations.

The mean-square displacement $\langle u^2 \rangle$ depends on the temperature T . Usually¹ another parameter, the Debye temperature Θ , is introduced to describe $\langle u^2 \rangle$; this parameter is independent of T in the harmonic approximation except at low temperatures. $\langle u^2 \rangle$ and Θ are linked by the relation

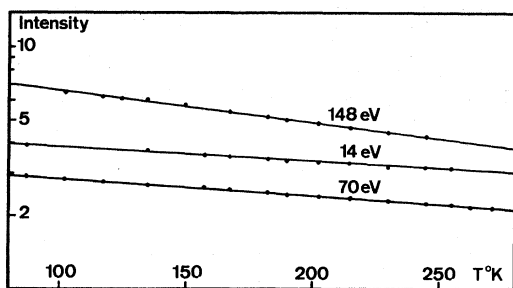


FIG. 1. Intensity of (00) spot vs temperature for various electron energies (arbitrary units).

$$\langle u^2 \rangle = 3\hbar^2 T / 4\pi^2 m k \Theta^2, \quad (2)$$

where the symbols have their usual meaning.

Equations (1) and (2) give a linear relation between $\ln I$ and T , from which it is possible to calculate the Debye temperature Θ_1 of the surface vibration in graphite normal to the (00.1) face.

Measurements were made on Ceylon graphite that had been cleaved, then baked at 900 °C in an ultra-high vacuum. The remaining pressure was about 10^{-10} Torr. We observed the intensity variation of the specular spot (00) as a function of temperature. Observations were made as the temperature was decreasing from 300 to 100 °K in about 30 min. The sample of graphite ($3 \times 3 \times 0.2$ mm³) was fixed on a metallic holder through which cooled gaseous helium was passed.

The temperature was measured by a thin-foil resistance-temperature sensor stuck to this holder.⁶ The intensities were measured by means of photometry and were corrected for the background.

For all electron energies (14–400 eV), we always found a linear relation between $\ln I$ and T . Some of these experimental lines are shown in Fig. 1. The slopes of these lines enabled us to determine the corresponding Debye temperature. The results obtained for various electron energies can be found in Fig. 2. There are about 50 experimental points. The scatter of the experimental points never exceeds 10%.

A. Debye Temperature of Bulk

In Fig. 2 [for high-energy electrons (> 150 eV)] the existence of an asymptote parallel to the energy axis can be noticed. This indicates that the Debye temperature of the bulk in the [00.1] direction is about 800 °K, which is in agreement with an estimation (760 °K) of Magnus.⁷

B. Debye Temperature of Surface

In the absence of LEED theory it is impossible to pick out the correct value of Θ for the surface

atoms in graphite from the various values obtained by low-energy diffraction. In what follows, an indirect method of solving this problem is presented. We have observed that the symmetry of the diagrams varied with the electron energy. For an energy greater than 200 eV, the symmetry is hexagonal. At medium energy it becomes trigonal, reverting back to hexagonal again at lower energies (below 70 eV). This behavior is depicted in Fig. 3 where the ratio $[I_{(01)} + I_{(\bar{1}0)}] / [I_{(10)} + I_{(0\bar{1})}]$ is shown. This curve is only approximate as far as the absolute magnitudes of the extrema are concerned, but it gives a tolerably good description of the variation of $[I_{(01)} + I_{(\bar{1}0)}] / [I_{(10)} + I_{(0\bar{1})}]$. When $[I_{(01)} + I_{(\bar{1}0)}] / [I_{(10)} + I_{(0\bar{1})}] = 1$, the symmetry is hexagonal; otherwise it is trigonal. We agree with David *et al.*⁸ that this behavior is related to the symmetry of graphite. (In some cases the trigonal symmetry may be replaced by a hexagonal symmetry resulting from the existence of different parity steps at the surface of the crystal.⁸)

The symmetry of the graphite in bulk is hexagonal as observed from the diffraction at high energies (deep penetration). On the other hand, if we consider a crystal made up of only two layers, the symmetry turns trigonal, becoming hexagonal again for monolayer crystal.

We think that at high energies the bulk symmetry imposes on the pattern a hexagonal symmetry. At about 100 eV, the contribution is mainly due to the first two layers. This might explain the trigonal diagram obtained here. Below 70 eV, the diffraction would be due to the first layer or to a fraction thereof.

On the basis of the above arguments we have chosen the Debye temperature measured at 70 eV, as the one associated with the first layer atoms, namely,

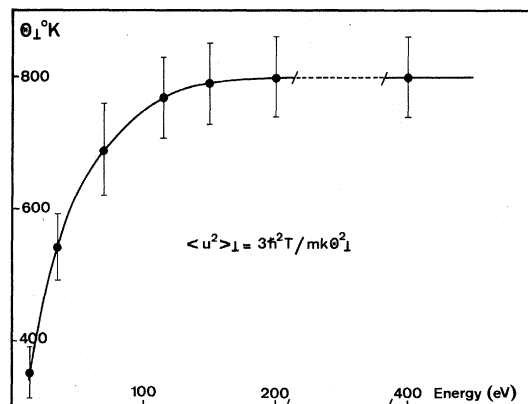


FIG. 2. Debye temperature of surface atoms perpendicular to the (00,1) plane as a function of electron energy.

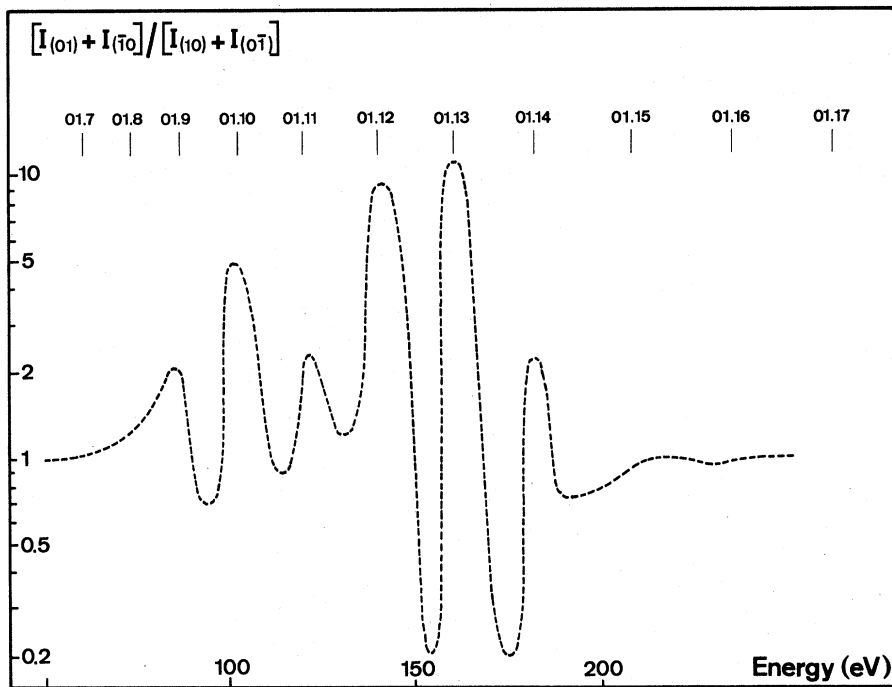


FIG. 3. Symmetry of the diffraction pattern is hexagonal below 70 eV; it becomes trigonal at medium energy, reverting back to hexagonal again at high energy (see text).

$$\Theta = (690 \pm 70)^\circ \text{K},$$

a value which is in good agreement with a measurement made by Laschkarew and Kuzmin⁹ in 1934 using LEED.

This choice involves an important implication, viz., below 70 eV, the effective Debye temperature decreases very quickly. We think it represents the "Debye temperature" of the electrons of the outside areas of the surface atoms. The low values may arise from three sources. (a) The electrons of the outer shells of the surface atoms are far from the nucleus and as they tend to spread out¹⁰ near the surface, one may think that their vibration amplitude is greater than that of the nucleus. (b) There may be local overheating due to the impact of the electrons, and therefore a change in the distribution of the surface phonons. (c) At very low electron energies, dynamical effects (multiple diffraction) are not negligible.

We also have endeavored to measure the surface Debye temperature $\Theta_{||}$ in a direction parallel to the (00.1) plane. According to MacRae¹ the incident and reflected beams must make an angle close to $\frac{1}{2}\pi$ with the normal of the crystal.

This experiment could not be carried out on graphite for it was impossible to observe a diffraction spot of high order in order to obtain a grazing reflection.

III. CALCULATION OF $\langle u^2 \rangle$

The theoretical determination of Θ by means of $\langle u^2 \rangle$ is done by using the lattice dynamics of Born.⁵

Until now, such calculations¹¹ have been applied only to few substances of the cubic system. We thought it interesting to generalize this method to the hexagonal system, and to try and check our experimental results. This is the reason why we have calculated the mean-square displacements of the vibrations to the (00.1) surface of graphite.

According to Born⁵ and Wallis *et al.*,¹¹ $\langle u^2 \rangle$ satisfies the equation

$$\langle u^2 \rangle_{i,k} \approx \frac{kT}{m} [D^{-1}]_{i,k} \quad (3)$$

in the high-temperature limit, where $i = 1, 2, 3$ corresponds to the vibration direction, $k = 1, 2, 3$ describes the atom, and $[D^{-1}]_{i,k}$ is the diagonal coefficient corresponding to the atom k for the direction i . The normal direction to the (00.1) surface is chosen such that $i = 3$.

Besides the harmonic approximation, the hypotheses used for the calculation are (a) noncentral forces; (b) first-neighbor interaction in the layer and out of the layer; (c) a crystal in the shape of a parallelepiped including N -mn cells, N representing the number of cells normal to (00.1); (d) free vibrations in both the (00.1) and (00. $\bar{1}$) faces fulfilling the cyclic condition of Born for the four other faces.

The graphite cell includes four atoms (see Appendix). They are numbered 1, 2, 3, 4, having the respective coordinates $0, 0, 0; \frac{1}{3}, \frac{2}{3}, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$. We have expressed the dynamical matrix by following the classical method.⁵ For graphite it is a $12N \times 12N$ matrix, rotationally invariant.

(See the Appendix for details.)

In the present case, the atoms 1 and 2 are on the free (00.1) surface. The solution of (3) with the help of the dynamical matrix $[D]$ enables us to obtain, using Eq. (2), the Debye temperature of the atoms 1 and 2 on the (00.1) surfaces.

A. Computation of Θ_1

Computation for the atoms 1 and 2 is made by using (3) with $k=1, 2, i=j=1$ and $k=1, 3, i=j=2$, respectively.

Thus, having obtained $\langle u^2 \rangle_{11}$ and $\langle u^2 \rangle_{12}$, we deduce the Debye temperature in the direction normal to the surface, i. e., Θ_{11} and Θ_{12} . The corresponding equations have already been expressed in a previous paper.¹²

In the form (4) of Ref. 12 giving Θ_{11} and Θ_{12} , the Hooke's force constants γ and γ' appear. γ is the force applied to atom 1 in the [00.1] direction when atom 2 moves a unit length in the same direction. γ' is a similar coefficient (see dynamical matrix) concerning the atoms 2 and 3.

The tables¹³ give the elastic constants of graphite. Using Ref. 14 we may deduce the Hooke's force constants. We obtain γ' with a low scatter, whereas γ varies from 1 to 100 in range. To carry out the calculation we have used the magnitude of γ' given by Ref. 13, i. e., $\gamma' = 5.67 \times 10^3$ dyn cm⁻¹, but we did not use any of these values for γ on account of their extreme scatter.

In order to determine γ , we have fitted its value so that the Debye temperature of the bulk, computed by Eqs. (2) and (3), was 800 °K for atom 2. We found $\gamma = 53 \times 10^3$ dyn cm⁻¹.

We have chosen atom 2 for the fitting of γ for, in our model, this atom is directly linked to the adjacent layer, whereas for atom 1 this is not so. As such, atom 2 is nearer to reality than atom 1. As a matter of fact, this choice is not very important because with the value of γ computed as above, we find the bulk Debye temperature of atom 1 to be 780 °K, a value quite close to 800 °K, the Debye temperature of atom 2.

The computation carried out under these conditions gives the following results for the surface Debye temperatures:

$$\Theta_{11} = 720 \text{ }^\circ\text{K}, \quad \Theta_{12} = 730 \text{ }^\circ\text{K}.$$

We have used a computer and taken a crystal with $N=7$ (14 layers) and $n=200$. So we obtain Debye temperatures close to those of a semi-infinite crystal to within about 1%.

The fitting with the experimental determination [$\Theta_1 = (690 \pm 70)$ °K] can be considered as fairly satisfactory in spite of the roughness of the model chosen.

We have also computed Θ_{13} and Θ_{14} , the Debye temperatures of the atoms located in the second

layer under the surface, and the values obtained are

$$\Theta_{13} = 780 \text{ }^\circ\text{K}, \quad \Theta_{14} = 760 \text{ }^\circ\text{K}.$$

The theoretical mean-square displacements of the vibrations of the second-layer atoms are, therefore, not far from those of the bulk atoms. This shows that the motion of the atoms is mainly governed by the forces operating in the layer.

B. Computation of Θ_{\parallel}

The same values as those previously computed, but associated with the directions parallel to (00.1) ($k=1$ or $k=2$), i. e., Θ_{11} and Θ_{12} were determined from (2) and (3).

The parameters occurring in the calculation are the Hooke's force constants α , β , and α' (see the Appendix), taken from Refs. 12 and 13: $\alpha = 194 \times 10^3$, $\beta = 913 \times 10^3$, $\alpha' = 10 \times 10^3$ dyn cm⁻¹.

Note the very low value of α' , a parameter explaining the interaction between the layers. To make the computations easier, one neglects α' in favor of α and β . It is as if one considered a crystal made up of only one layer for the computation of Θ_{\parallel} . This implies for our model that the surface Debye temperature is the same as that of the bulk for the directions parallel to (00.1).

The hypothesis of the high-temperature limit is no longer valid here. This is why we use a more general expression¹¹ to compute $\langle u^2 \rangle_{i,k} = \langle u^2 \rangle_{i,k}$ with $i=1, 2$ and $k=1, 2$,

$$\langle u^2 \rangle_{i,k} = (\hbar/2m)[D^{-1/2} \coth(\hbar D^{1/2}/2kT)]_{i,k}. \quad (4)$$

The expression (4) makes it possible to find (3) again by expanding the hyperbolic cotangent function and retaining only the first term. Thus we get an error for Θ_1 which can be neglected if compared with the one due to the uncertainty already existing on γ and γ' . It is quite different for the vibrations parallel to (00.1). The computation using (2) and (4) gives

$$\Theta_{11} = \Theta_{12} = 2300 \text{ }^\circ\text{K} \text{ for } T = 400 \text{ }^\circ\text{K}.$$

This quantity was determined previously with the help of two other methods: Application of the Debye theory of the heat capacity to graphite⁷ yields $\Theta_{\parallel} \approx 2300$ °K; whereas a similar calculation for low temperature and for the long-waves approximation¹⁵ gives $\Theta_{\parallel} \approx 2500$ °K. Our computation is therefore in agreement with the above results.

IV. DISCUSSION

In this study the variation of the symmetry of the diffraction patterns, when considering their intensity, provided us with a method of choosing a precise value of the Debye temperature associated with first-layer surface atoms from a range of values obtained with low-energy diffraction of electrons.

It should be emphasized, however, that this method is slightly imprecise, since the transition from trigonal-hexagonal symmetry is not clear-cut. However, in the absence of a satisfactory LEED theory it is the only method at our disposal.

We must also say that, unfortunately, it is not a general method, since the crystal observed must have a symmetry of surface different from that of bulk.

Another point which we did not emphasize is the linear variation observed experimentally between the logarithm of the intensity diffracted in (00) and the temperature (Fig. 1). This shows that the Debye temperature normal to the surface is constant with temperature ($T > \frac{1}{3}\Theta$). This fact is not comparable with the theoretical^{16,17} and experimental¹⁸ results showing that Θ varies with temperature when $T < \frac{1}{3}\Theta$ and $T < \frac{1}{2}\Theta$, respectively. Calculations^{16,17} have been carried out on fcc crystals and observations¹⁸ have been made on chromium (bcc) whereas graphite is hexagonal.

Finally, it must be pointed out that in our computation we have used the same Hooke's-law coefficients for bulk and surface. It was not necessary to proceed like Wallis *et al.*,¹¹ i.e., to fit the force coefficients in the first layer, to obtain a satisfactory agreement between the computation and the experiment.

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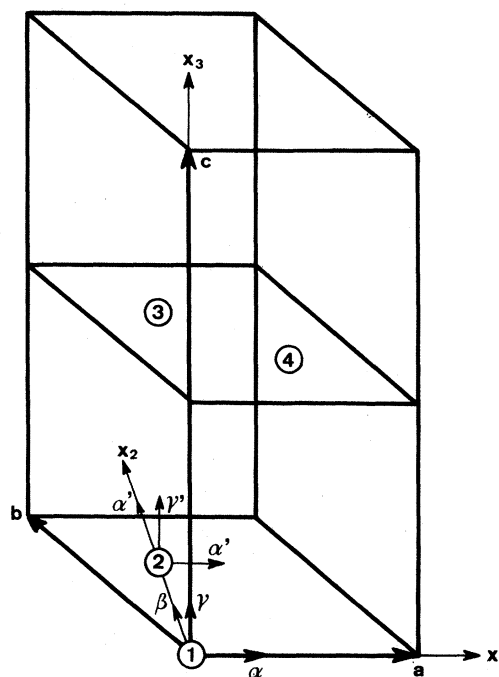


FIG. 4. Graphite cell and Hooke's force constants.

R. B. Roy for helping us to translate this paper, and to M. Oberlin who provided us with graphite crystals.

APPENDIX

The dynamical matrix for N cells in the [00.1] direction ($2N$ layers) is

$$D = \frac{1}{m} \begin{vmatrix} X_0 & Y_1 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 \\ Y_2 & X & Y_1 & 0 & \cdots & 0 & 0 & 0 & 0 \\ 0 & Y_2 & X & Y_1 & \cdots & 0 & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & \cdots & Y_2 & X & Y_1 & 0 \\ 0 & 0 & 0 & 0 & \cdots & 0 & Y_2 & X & Y_1 \\ 0 & 0 & 0 & 0 & \cdots & 0 & 0 & Y_2 & X'_0 \end{vmatrix}$$

D is a $12N \times 12N$ matrix where X, X_0, X'_0, Y_1, Y_2 , are 12×12 matrices. These 12×12 matrices stand for the interaction between the i twofold layer and the j twofold layer,

$$X = \begin{vmatrix} A & B & 0 & 0 \\ B^* & C & D & 0 \\ 0 & D & C & B \\ 0 & 0 & B^* & A \end{vmatrix}, \quad X_0 = \begin{vmatrix} A & B & 0 & 0 \\ B^* & C_0 & D & 0 \\ 0 & D & C & B \\ 0 & 0 & B^* & A \end{vmatrix}, \quad X'_0 = \begin{vmatrix} A & B & 0 & 0 \\ B^* & C & D & 0 \\ 0 & D & C_0 & B \\ 0 & 0 & B^* & A \end{vmatrix},$$

$$Y_1 = \begin{vmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & D & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix}, \quad Y_2 = \begin{vmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & D & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix},$$

where A , B , C , C_0 , and D are 3×3 matrices which describe the interaction between the atoms of a cell

$$A = \begin{vmatrix} \frac{3}{2}(\alpha + \beta) & 0 & 0 \\ 0 & \frac{3}{2}(\alpha + \beta) & 0 \\ 0 & 0 & 3\gamma \end{vmatrix}, \quad B = \begin{vmatrix} a & b & 0 \\ b & c & 0 \\ 0 & 0 & d \end{vmatrix}, \quad C = \begin{vmatrix} \frac{3}{2}(\alpha + \beta) + 2\alpha' & 0 & 0 \\ 0 & \frac{3}{2}(\alpha + \beta) + 2\alpha' & 0 \\ 0 & 0 & 3\gamma + 2\gamma' \end{vmatrix},$$

$$C_0 = \begin{vmatrix} \frac{3}{2}(\alpha + \beta) + \alpha' & 0 & 0 \\ 0 & \frac{3}{2}(\alpha + \beta) + \alpha' & 0 \\ 0 & 0 & 3\gamma + \gamma' \end{vmatrix}, \quad D = \begin{vmatrix} -\alpha' & 0 & 0 \\ 0 & -\alpha' & 0 \\ 0 & 0 & -\gamma' \end{vmatrix},$$

with

$$a = -\alpha \exp i\left(\frac{1}{3}u_1 + \frac{2}{3}u_2\right) - \frac{1}{4}(\alpha + 3\beta) \{ \exp[-i(\frac{2}{3}u_1 + \frac{1}{3}u_2)] + \exp i(\frac{1}{3}u_1 - \frac{1}{3}u_2) \},$$

$$b = -\frac{1}{4}\sqrt{3}(\alpha - \beta) \{ \exp[-i(\frac{2}{3}u_1 + \frac{1}{3}u_2)] - \exp i(\frac{1}{3}u_1 - \frac{1}{3}u_2) \},$$

$$c = -\beta \exp i\left(\frac{1}{3}u_1 + \frac{2}{3}u_2\right) - \frac{1}{4}(3\alpha + \beta) \{ \exp[-i(\frac{2}{3}u_1 + \frac{1}{3}u_2)] + \exp i(\frac{1}{3}u_1 - \frac{1}{3}u_2) \},$$

$$d = -\gamma \{ \exp i\left(\frac{1}{3}u_1 + \frac{2}{3}u_2\right) + \exp[-i(\frac{2}{3}u_1 + \frac{1}{3}u_2)] + \exp i(\frac{1}{3}u_1 - \frac{1}{3}u_2) \},$$

where u_1 and u_2 are the components of the "wave vector" in the first Brillouin zone, and where

$$\begin{vmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \gamma \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} \alpha' & 0 & 0 \\ 0 & \alpha' & 0 \\ 0 & 0 & \gamma' \end{vmatrix},$$

respectively, stand for the Hooke's-law constants between the 1-2 and 2-3 atoms (see Fig. 4). β and γ' are central forces; α , γ , and α' are noncentral forces.

A. Debye Temperature Perpendicular to (00.1) Surface

We have

$$\Theta_{\perp 1} = \frac{\hbar}{k} \left(\frac{3}{mE} \right)^{1/2}, \quad \Theta_{\perp 2} = \frac{\hbar}{k} \left(\frac{3}{mF} \right)^{1/2},$$

where

$$E = n^{-2} \sum_{u_1, u_2} M_{1,N}, \quad F = n^{-2} \sum_{u_1, u_2} M_{2,N}.$$

$M_{1,N}$ and $M_{2,N}$ are given by the N following iterations:

$$M_{1,i} = \{ P - Q [R - \gamma'^2 (S - QP^{-1})^{-1}]^{-1} \}^{-1},$$

$$M_{2,i} = [R - QP^{-1} - \gamma'^2 (S - QP^{-1})^{-1}]^{-1},$$

with

$$P = 3\gamma,$$

$$Q = \gamma^2 [3 + 2\cos u_1 + 2\cos u_2 + 2\cos(u_1 + u_2)],$$

$$R = 3\gamma + \gamma'(2 - \delta_{i,N}),$$

$$S = 3\gamma + \gamma'(2 - \delta_{i,1}) - \gamma'^2 M_{2,i-1}, \quad M_{1,0} = 0, \quad M_{2,0} = 0.$$

B. Debye Temperature Parallel to (00.1) Surface

We have

$$\Theta_{\parallel} = \frac{\hbar}{k} \left(\frac{3}{mG} \right)^{1/2},$$

where

$$G = n^{-2} \sum_{u_1, u_2} M_3,$$

and where

$$M_3 = \frac{\mathfrak{N}}{\mathfrak{D}} + \frac{1}{2} \left(\frac{\hbar}{kT} \right)^2 - \frac{1}{5} \frac{1}{(12)^2} \left(\frac{\hbar}{kT} \right)^4 \frac{3}{2} (\alpha + \beta) + \frac{2}{35} \frac{1}{(12)^3} \left(\frac{\hbar}{kT} \right)^6 \left[\frac{3}{4} (\alpha + \beta)^2 + bb^* + cc^* \right],$$

with

$$\mathfrak{N} = \frac{3}{2} (\alpha + \beta) \left[\frac{3}{4} (\alpha + \beta)^2 - bb^* - cc^* \right]$$

and

$$\mathfrak{D} = \left[\frac{3}{4} (\alpha + \beta)^2 - aa^* - bb^* \right] \left[\frac{3}{4} (\alpha + \beta)^2 - bb^* - cc^* \right] - [ab^* + bc^*] [a^*b + b^*c].$$

¹A. U. MacRae, *Surface Sci.* **2**, 522 (1964); H. B. Lyon and G. A. Somorjai, *J. Chem. Phys.* **44**, 3707 (1966); R. M. Goodman, H. H. Farrell, and G. A. Somorjai, *ibid.* **48**, 1046 (1968); C. Corotte, P. Ducros, and A. Mascall, *Compt. Rend.* **267**, 544 (1968).

²E. R. Jones, J. T. McKinney, and M. B. Webb, *Phys. Rev.* **151**, 476 (1966).

³R. Baudoing, C. Corotte, and A. Mascall, *J. Phys. C* **31**, 1 (1970).

⁴However after the last studies by Duke and Laramore (private communication), we may think that a theoretical improvement was performed, but it is rather difficult to apply this theory to the experiment.

⁵M. Born, *Rept. Progr. Phys.* **9**, 294 (1942); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1966); A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1963).

⁶G. Albinet, J. Suzanne, J. P. Biberian, and M. Bienfait, *Rev. Phys. Appl. (Paris)* (to be published).

⁷A. Magnus, *Ann. Physik* **70**, 203 (1923).

⁸G. David, J. Escard, and S. Goldsztaub, *Colloq. Intern. Centre Natl. Rech. Sci. (Paris)* **187**, 179 (1969); G. David, *Comm. Energie At. (France)*, *Rappt. No.* R. 3891 (1969).

⁹W. E. Laschkarew and E. W. Kuzmin, *Nature* **134**, 62 (1934).

¹⁰H. J. Juretschke, *The Surface Chemistry of Metals and Semi-conductors*, edited by H. C. Gatos (Wiley, New York, 1959); J. Bardeen, *Phys. Rev.* **44**, 653 (1936); R. Smoluchowski, *ibid.* **60**, 661 (1941).

¹¹B. C. Clark, R. Herman, and R. F. Wallis, *Phys. Rev.* **139**, A860 (1965); A. A. Maradudin, D. L. Mills, and S. Y. Tond, *The Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (Wiley, New York, 1969), p. 16; R. F. Wallis, B. C. Clark, and R. Herman, *ibid.*, p. 17; F. W. de Wette and R. E. Allen, *ibid.*, p. 18.

¹²J. P. Biberian and M. Bienfait, *Compt. Rend.* **270**, 1301 (1970).

¹³W. N. Reynolds, *Physical Properties of Graphite* (Elsevier, Amsterdam, 1968), p. 35.

¹⁴G. Champier, J. M. Genin, and C. Janot, *Compt. Rend.* **257**, 1843 (1963).

¹⁵K. Komatsu, *J. Phys. Soc. Japan* **10**, 346 (1955).

¹⁶R. E. Allen and F. W. Wette, *Phys. Rev.* **188**, 1320 (1969).

¹⁷R. F. Wallis, *Phys. Rev.* **167**, 652 (1968).

¹⁸R. Kaplan and G. A. Somorjai (private communication).