4. Although a short-range model gives an adequate qualitative picture, there is little doubt that forces out to fourth or fifth neighbors and possibly beyond, play a significant role in the determining of the details of the lattice dynamics of sodium.

5. There are still several aspects of the problem to be considered: (i) the abnormal behavior of the $[00\zeta]\,L$ branch, (ii) extension of the analysis to more distant neighbors, (iii) the possibility of deriving an interatomic potential, and (iv) the temperature behavior of the phonons.

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Lattice Vibrations in Pyrolitic Graphite

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The dispersion relation for the longitudinal acoustic lattice waves propagating in the direction of the hexad axis in (pyrolitic) graphite, at room temperature, has been determined by neutron spectrometry. The dispersion curve has very closely the form of a sine curve, with a maximum frequency of $(3.84\pm0.06)\times10^{12}$ cps, for the zone-boundary phonon of wavelength $c=6.70$ Å. The transverse acoustic lattice waves were less well determined, but show roughly similar behavior with a maximum frequency at the zone boundary of $(1.3\pm0.3)\times10^{12}$ cps. Values for certain elastic constants have been deduced from the measurements: in units of 10^{11} dyn/cm^2, $C_{33}=3.9\pm0.4$, and $C_{44}=0.42\pm0.2$.

INTRODUCTION

THE lattice dynamics of graphite has been discussed theoretically by a number of authors.[1–9] The consensus of these discussions is that the lattice modes can be approximately divided into vibrations (a) with atomic motions in the hexagonal planes of atoms and (b) with motions normal to the planes. Because the binding of the planes to each other is very much weaker than the binding of the atoms in the planes, motions of the planes with respect to one another have little influence upon the frequencies except for those relatively few modes in which the planes move substantially as rigid units. Thus, only at very low temperatures does the specific heat of graphite[8–11] have the familiar T^3 dependence; at intermediate temperatures it tends to display the T^2 dependence characteristic of a plane lattice. The transition between these two types of behavior is determined by the modes for which the hexagonal planes move as units; in this paper we present an experimental study of the dispersion relation for these modes at room temperature, by neutron spectrometry.

The dispersion relation between the frequency (ν) and the wave vector ($\mathbf{q}$) for the normal modes of vibration of a crystal lattice may be obtained by a study of the coherent one-phonon scattering of slow neutrons from a single-crystal specimen.[12] These scattering processes are governed by equations expressing conservation of energy and "crystal momentum":

$$E_0-E'=\pm h\nu, \tag{1a}$$

$$\mathbf{Q}=\mathbf{k}_0-\mathbf{k}'=2\pi\boldsymbol{\tau}-\mathbf{q}, \tag{1b}$$

where E_0, E' are the energies, and $\mathbf{k}_0$, $\mathbf{k}'$ the wave vectors, of the incident and scattered neutrons, respectively; $\mathbf{Q}$ is the momentum transfer vector, $\boldsymbol{\tau}$ is a reciprocal lattice vector, and h is Planck's constant.

The study of the lattice vibrations of graphite by means of slow neutron scattering has so far been prevented by the lack of sufficiently large single-crystal specimens. Recently, however, the production has been

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achieved[13] of large specimens of pyrolitic graphite, a material which displays certain single-crystal characteristics. In this material the hexagonal planes of carbon atoms have a common hexad axis, the [001] axis, but are otherwise randomly oriented. Unambiguous information concerning longitudinal acoustic lattice vibrations propagating along the [001] direction can be obtained from the neutron-scattering experiments. In addition, the transverse acoustic vibrations can be studied in a limited way.

Previous neutron scattering experiments on graphite[14,15] have been concerned with other aspects of the problem.

EXPERIMENTS

The experiments were performed on the triple-axis crystal spectrometer at the NRU reactor, using the constant momentum transfer (constant **Q**) mode of operation[16] with fixed outgoing energy. In this mode, the analyzing spectrometer is set at a fixed energy (E')

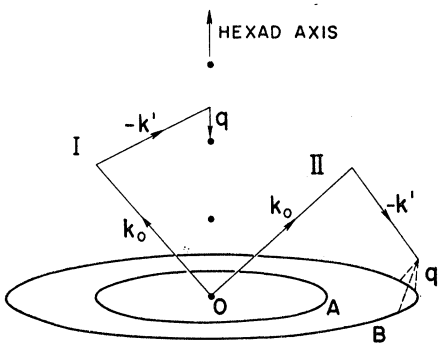

FIG. 1. Reciprocal space diagram for pyrolitic graphite, showing two possible experimental arrangements for studying lattice waves propagating along the [001] axis direction.

and the energy (E_0) of the incident neutrons is varied. The spectrometer is programmed so that the angle of scattering (ϕ) and the specimen orientation (ψ) change with E_0 in such a way that the wave vector transfer **Q** is kept constant. Thus, energy distributions are measured at a fixed point in reciprocal space. The centers of neutron groups observed in the energy distribution yield the frequencies, ν, of lattice vibrations of wave vector **Q** in the extended zone (i.e., of **q** in the reduced zone).

The pyrolitic graphite specimen[17] consisted of a stack

[13] See C. A. Klein, W. D. Straub, and R. J. Diefendorf, Phys. Rev. **125**, 468 (1962).

[14] P. A. Egelstaff and S. J. Cocking, in *International Atomic Energy Agency Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, October*, 1960 (International Atomic Energy Agency, Vienna, 1961), p. 569.

[15] A single energy distribution given by A. D. B. Woods, B. N. Brockhouse, M. Sakamoto, and R. N. Sinclair (reference 14, p. 487) is now thought to be spurious because of contamination by Debye–Scherrer lines. (The results reported for substances other than graphite are believed correct.)

[16] B. N. Brockhouse, reference 14, p. 113.

[17] The specimen was kindly supplied by Dr. R. J. Diefendorf of the General Electric Company, Schenectady, N. Y.

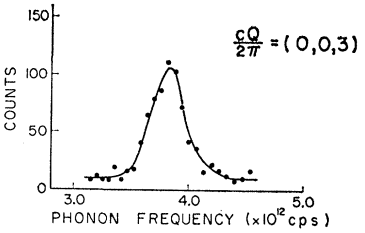

FIG. 2. Neutron group observed by means of arrangement I, at the point $cQ/2\pi = (0,0,3)$.

of four square sheets, each approximately 5 cm on edge and 0.5 cm thick. The reciprocal lattice of pyrolitic graphite is illustrated in Fig. 1. It consists of the reciprocal lattice of the ideal graphite structure, rotated about the [001] direction (the hexad axis) to produce smeared-out "rings" of reciprocal lattice points, except, of course, along the [001] direction itself. The rings A and B, represent the (100) and (110) type reciprocal lattice points after such a rotation. Only experimental arrangements of type I allow unambiguous measurements of phonon frequency and wave vector. In these arrangements the vectors **Q**, **q**, and τ all lie along the [001] direction. In arrangements such as that labeled II, the phonon wave vector is not well defined in either magnitude or direction; this is indicated by the dashed lines.

Longitudinal acoustic modes which propagate in the [001] direction can be studied by means of arrangement I. (Transverse modes do not contribute because the

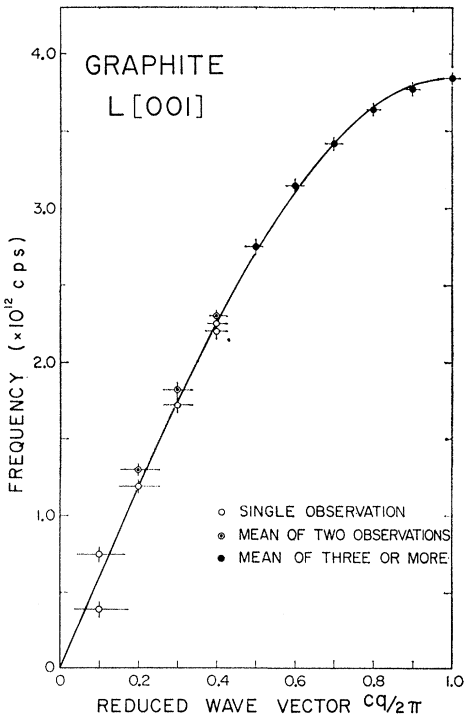

FIG. 3. Dispersion curve for the L[001] modes in which the planes move as rigid units. The solid line is the best fitting (simple) sine wave to the experimental points. The assignment of errors is discussed in the text.

TABLE I. Elastic constants of graphite.

Elastic constant (units 10^{11} dyn/cm^2)	C_{33}	C_{44}
Reference 8	$\geqslant 1.8$	0.23
Reference 9	3.56	0.405[a]
		0.292[b]
Present work	3.9 ± 0.4[c]	0.42 ± 0.2

[a] Canadian natural graphite (CNG) sample.
[b] Pile graphite sample, with smaller crystallite size than CNG.
[c] This value for the error on C_{33} is assigned from a consideration of the low-q phonon data only; if it is assumed that all the observed frequencies may be utilized via Eq. (2), this error is reduced to about $\pm0.2\times10^{11}$ dyn/cm^2.

direction of motion of the atoms is normal to the momentum transfer.) Values of $L[001]$ phonon frequencies were obtained at several regularly spaced $\mathbf{Q}$ values along the [001] axis over the range $c|\mathbf{Q}|/2\pi=2.2$ to 4.4, where c (6.70 Å) is the lattice constant along the hexagonal direction. Figure 2 shows a typical neutron group observed in an experiment for which $c|\mathbf{Q}|/2\pi=3.0$. The center of the peak gives the frequency of the phonon, in this case 3.84×10^{12} cps. The complete results are shown in Fig. 3, in which phonon frequency is plotted against reduced wave vector. For the modes studied in this paper it is appropriate to use a Brillouin zone twice as large as the usual one in the [001] direction. Thus, at the zone boundary the wavelength of the phonons is equal to the lattice constant c.

The pyrolitic graphite samples used have a mosaic spread about the hexad axis of approximately 5°; this leads to rather large errors in $\mathbf{q}$, particularly at small $\mathbf{q}$ values, as is indicated in Fig. 3. Indeed, at small $\mathbf{q}$, individual observations of phonon frequency at the same nominal reduced wave vector are more widely scattered than would be expected from instrumental errors (shown by vertical error bars in Fig. 3). At higher $\mathbf{q}$, however, independent frequency measurements at the same $\mathbf{q}$ fall within the instrumental energy resolution, and mean values have been plotted (the filled circles) in the interests of clarity. This improved experimental precision suggests that the $L[001]$ mode frequencies do not increase very rapidly as the angle between the wave vector and the [001] axis increases,

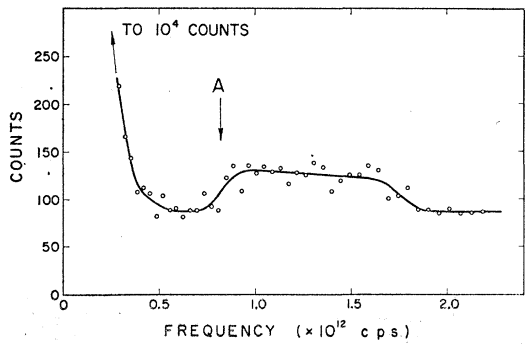

FIG. 4. Energy distribution observed by means of arrangement II, at the point $c\mathbf{Q}/2\pi=(1,0,0.5)$.

except for small values of $\mathbf{q}$. This explanation is confirmed by direct observation of well-defined neutron groups involving such inclined phonon wave evectors.

The slope of the curve near the origin is related to the elastic constant C_{33}; the value given by the present experiments is $(3.9\pm0.4)\times10^{11}$ dyn/cm^2 (see the following section). Estimates of elastic constants have been made by Bowman and Krumhansl,[8] and by Komatsu,[9] who deduced values of C_{33} (and C_{44}) from consideration of the compressibility and of the low-temperature specific heat. Their values are listed in Table I, together with the values obtained in this work.

We now consider the possibility of obtaining useful data from observations of the type labeled II in Fig. 1. In particular, it is of interest to discover ways of observing the transverse modes of vibration with wave vectors parallel to the [001] axis, which cannot be studied with arrangement I. Certain of these transverse modes will involve purely sliding motions of the hexagonal planes of atoms with respect to each other, while the individual planes remain undistorted. Normal modes with wave vectors inclined to the [001] axis involve varying degrees of distortion of the planes, especially extension and compression of the short carbon-carbon bonds. It is generally believed that the forces between carbon atoms in the same plane are very much larger than those between atoms in different planes. Thus we would expect modes which distort the individual planes to have considerably higher frequencies than those which do not. [Note: The same qualitative arguments apply to the longitudinal modes with wave vectors inclined to the [001] axis; but these modes chiefly involve bending the planes, with very little distortion of the carbon-carbon bond lengths or angles. Furthermore, the forces involved in the $L[001]$ vibrations are an order of magnitude larger than those involved in the $T[001]$ vibrations (see Discussion section); the latter vibration frequencies are thus much more sensitive than the former to the "admixture" of in-plane forces consequent upon inclination of the wave vector to the [001] direction.]

We have made observations at various places in reciprocal space such as points vertically above the rings A and B. The neutron-scattering processes observed may be associated with a range of phonon wave vectors as indicated by the dashed lines. However, we may expect the frequency of the transverse phonon, whose wave vector is parallel to the [001] axis, to be lower than any other observable phonon frequency. The situation is complicated by resolution effects, and by the large mosaic spread about the hexad axis. Figure 4 shows the result of one such experiment, in which the mode of lowest frequency would have a reduced wave vector half way to the zone boundary in the [001] direction. The sharp rise to a very high peak around the zero-frequency region is probably due partly to defect scattering, and partly to multiple elastic scattering of

the incident neutron beam in the graphite. The interesting feature of Fig. 4 is the significant rise in scattered intensity at the point A, which is well resolved from the pseudo-elastic peak. It seems reasonable to identify the increased scattered intensity as being associated with low-frequency transverse modes propagated along or nearly along the [001] axis, and to assign them frequencies of the order of 1.0×10^{12} cps. Other, similar experiments which we have performed support this explanation, but do not fully confirm it.

Assuming our interpretation is correct, then a consideration of the data obtained leads to a frequency at the zone boundary of $(1.3\pm0.3)\times10^{12}$ cps for the transverse mode with wave vector parallel to the [001] axis. On the further assumption that the dispersion curve is a simple sine curve, as in the L[001] case, we can deduce a rough value for the elastic constant C_{44}. This is listed in Table I together with previous estimates of this quantity.

DISCUSSION

In the previous section measurements were presented of those vibrations of the graphite lattice in which undistorted hexagonal planes of carbon atoms moved relative to each other in two distinct modes, longitudinal and transverse. The dispersion relation for the longitudinal, L[001], modes (involving variation of the interplanar spacing) has been completely and unambiguously measured. The dispersion curve is very well fitted by a two-term Fourier series of the form[18,19]

$$4\pi^2M\nu^2=A_1(1-\cos\tfrac{1}{2}cq)+A_2(1-\cos cq), \qquad (2)$$

where M is the mass of the carbon atom, and the coefficient (or force constant) A_2 is 1.6% of A_1. Additional Fourier terms do not significantly improve the fit to the experimental results. The least-squares Fourier analysis was performed using the Datatron computer. The solid line in Fig. 3 is the best fit to the results if only one Fourier component is employed. In this L[001] mode of vibration, the individual sheets of carbon atoms remain undistorted while the interplanar distance is varying. The forces involved are thus purely interplanar, and the excellent fit displayed in Fig. 3, indicates that these interplanar forces are almost entirely between nearest-neighbor planes.

The observation of the transverse modes (involving sliding motions of the plans of atoms) is necessarily more tentative, but we feel the interpretation given in the previous section is probably correct. The first-neighbor interplanar force constant relating to these transverse modes is about 10% of the analogous L[001] force constant. This is substantially higher than would be expected on the basis of a model of the graphite lattice involving simple r^{-n} short-range repulsive, and Van der Waals r^{-6} attractive, interatomic forces.

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Escape Mechanism of Secondary Electrons in Polar Crystals*

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A simplified theory for the motion of secondary electrons produced inside a solid by electron bombardment is proposed. The Boltzmann transport equation is solved for scattering due to electron-phonon collisions. Forward scattering is found to be very predominant, and accordingly the scattering integral is greatly simplified if, further, a constant energy loss per collision can be assumed. Postulating also a form for the internal excitation function, the solution is obtained and applied to calculate the energy distribution, the angular dependence, and the dependence of the total external current on the electron affinity. Despite the oversimplified assumptions the model clearly shows the difference with the theories given for metals by Wolff and others. Several experimental features as observed on MgO are compatible with the theory.

1. INTRODUCTION

IN the theory of secondary emission of electrons from a solid usually two steps are distinguished. The first one is concerned with the production of secondary electrons inside the material resulting from the bombardment by the primary electron source. Basically a computation of this nature requires a knowledge of the electron wave functions in the solid, its band structure, and the matrix elements for the interacting potential. Such theories have been given by several authors and have been summarized in papers by Dekker and van

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