

The Lattice Vibration of Graphite*

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A frequency spectrum of bending vibration of the graphite crystal lattice is calculated by Hwang-Wang's method on the basis of the Born-Von Kármán theory of lattice vibration. The elastic constants utilized are $S_0/3=2.52 \times 10^8$ dynes/cm for an interaction between atoms of the nearest neighbors in the same plane and $S_1=20.7$ dynes/cm for an interaction between those in the two neighboring different planes. These were determined from the specific heat data. The secular equation solved was determined by Krumhansl and Brooks.

The calculated squared frequency distribution $g(\omega^2)$ is proportional to the square root of ω^2 in an extremely low frequency part. Therefore, in the lowest frequency region the frequency distribution $f(\omega)$ shows ω^2 -dependence like the Debye's continuum and beyond that it becomes ω -dependence like a two-dimensional lattice as predicted by Rosenstock. Our result is in good conformity with that determined from the neutron scattering experiment of Egelstaff and Cocking and is, naturally, consistent with the specific heat data measured by Hoeven and Keesom.

INTRODUCTION

DUE to the layer type structure, the graphite lattice was treated as a two dimensional array. This was justified by an observed T^2 -dependence of the specific heat for temperature between 13°K and 50°K . Later measurement(1) down to 0.4°K , however, revealed that the T^2 -law did not hold at these lower temperatures, and a T^3 -behavior was found. Krumhansl and Brooks(2) predicted theoretically the existence of this transition behavior in an earlier day and attempted to explain it from the theory of lattice vibration. They derived the secular equation for determining the frequencies of the bending vibration of the graphite lattice, and made a semirigorous analysis with a long wavelength approximation.

In this paper, the frequency distribution of the graphite lattice is determined directly from the secular equation derived by Krumhansl and Brooks and the approximation due to the semirigorous analysis is avoided. Only the bending vibrations are considered using the force constants(3) determined from the precise measurements of specific heat at very low temperatures. The stretching vibrations are neglected, because they yield the high frequency part of the frequency distri-

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(1) B. J. C. van der Hoeven, Jr. and P. H. Keesom, Phys. Rev. 130, 1318 (1963).

(2) J. Krumhansl and H. Brooks, J. Chem. Phys. 21, 1663 (1953).

(3) T. C. Lee and J. L. Hwang, Chinese J. Phys. 1, 85 (1963)

bution and their influence on the low temperature specific heat is small. The method used to determine the frequency distribution was developed early by one of the present authors⁽⁴⁾ (J. L. H.).

DETERMINATION OF FREQUENCY SPECTRUM

Confining attention only to the bending vibration and neglecting the next nearest interaction in planes as well as in adjacent planes, the solution of the secular equation was found to be:

$$\begin{aligned} \text{Acoustic branch; } m\omega^2 &= S_0 + S_1(1 \mp \cos\sigma_z \frac{c}{2}) - [S_1^2(1 \mp \cos\sigma_z \frac{c}{2})^2 + S_0^2 |\Gamma|^2]^{\frac{1}{2}} \\ \text{Optical branch; } m\omega^2 &= S_0 + S_1(1 \mp \cos\sigma_z \frac{c}{2}) + [S_1^2(1 \mp \cos\sigma_z \frac{c}{2})^2 + S_0^2 |\Gamma|^2]^{\frac{1}{2}} \end{aligned} \quad (1)$$

$$\text{with } |\Gamma|^2 = \frac{1}{2} \left(\mathbf{1} + 4 \cos \frac{2\sigma_y a}{2} + 4 \cos \frac{\sigma_y a}{2} \cos \frac{\sqrt{3}}{2} \sigma_x a \right),$$

where $S_0/3$ = constant between the nearest neighbors in planes,
 S_1 = constant between the nearest neighbors in adjacent planes,

and $\sigma(\sigma_x, \sigma_y, \sigma_z)$ is a wave vector. $S_0/3$ and S_1 were determined previously⁽³⁾ by us to be 2.52×10^3 dynes/cm and 20.7 dynes/cm respectively. The first Brillouin Zone of a-space is defined by planes normal to vectors

$$\sigma = \pm \pi \mathbf{b}_i,$$

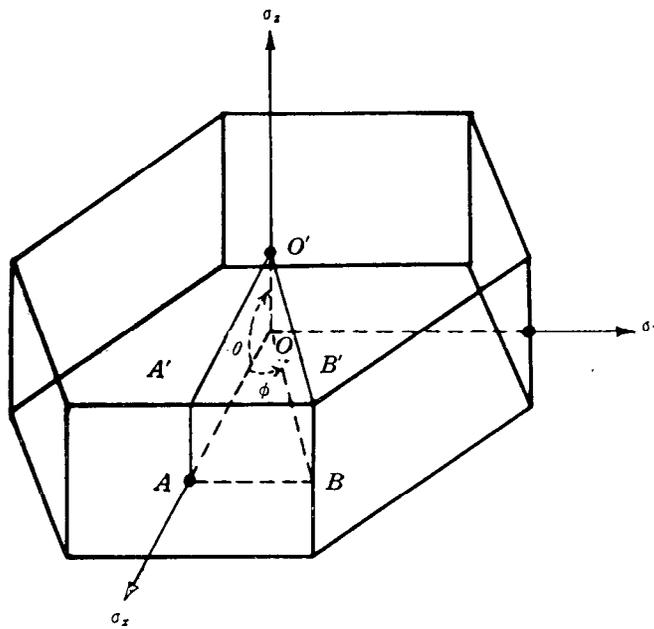


Fig. 1. The Brillouin zone of the graphite lattice

(4) J. L. Hwang, Phys. Rev. **99**, 1098 (1955); J. L. Hwang and C. S. Wang, J. Chem. Phys. **37**, 1655 (1962).

where $b_1 = (2/a\sqrt{3}, 0, 0)$, $b_2 = (1/a\sqrt{3}, -1/a, 0)$, $b_3 = (1/a\sqrt{3}, 1/a, 0)$, $b_4 = (0, 0, 1/c)$ and is illustrated in Fig. 1. Because of symmetry of the secular equation, it is merely required to study 1/24 of the zone.

The solution (1) along nine edges of the 1/24-zone was calculated and contours of constant circular frequency (abbreviated by ω^2 -contours) on its five surfaces

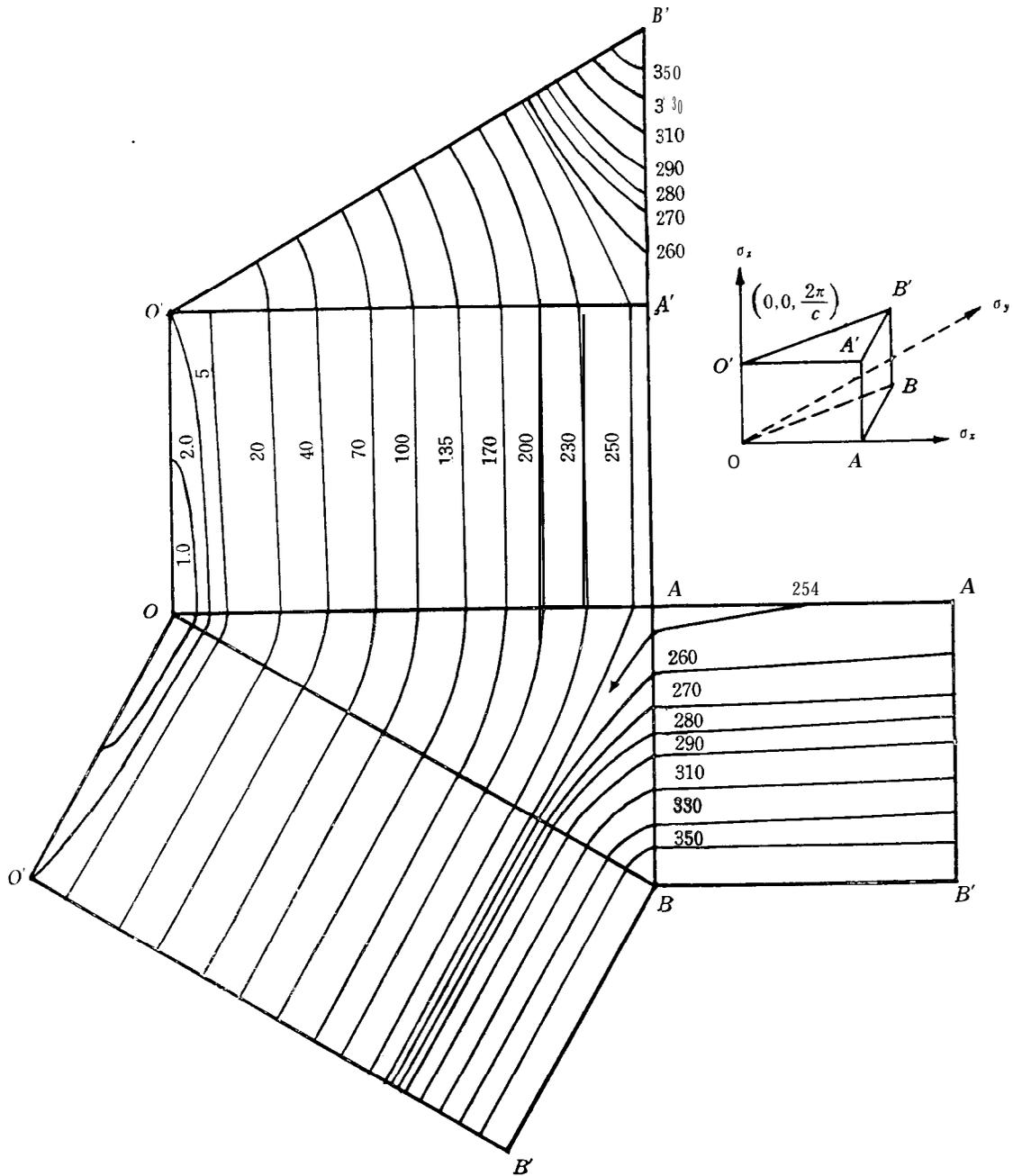


Fig. 2 Contours of constant circular frequency for acoustic branch. O' and A' are points of singularity.

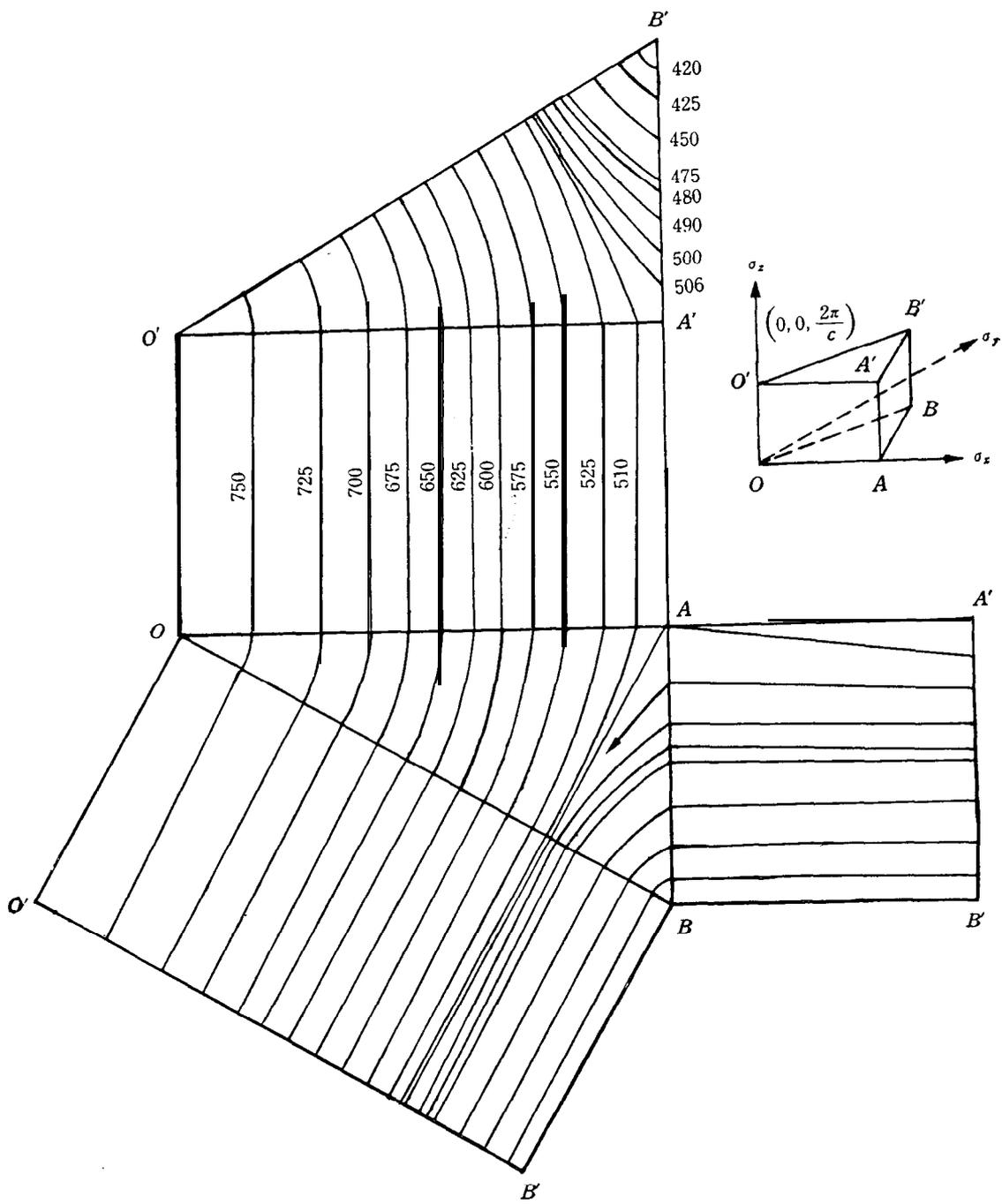


Fig. 3. Contours of constant circular frequency for optical branch.
 O' and A' are points of singularity.

are traced by means of the interpolation scheme proposed in ref. 4 (Fig. 2 and 3). On three additional inner planes passing through σ_z -axis and perpendicular to $\sigma_x\sigma_y$ -plane the ω^2 -contours are then traced in the same manner.

The volume $V(\omega^2)$ enclosed by the surface of constant circular frequency ω^2

(abbreviated by ω^2 -surface) represents the number of modes of vibrations whose frequencies are less than ω^2 . Its magnitude may be computed from the integral

$$V(\omega^2) = \frac{1}{3} \int_0^\pi \int_0^{\frac{\pi}{2}} r^3 \sin \theta d\theta d\phi = \int_0^\pi A(\phi) X(\phi) d\phi, \quad (2)$$

where $A(\phi) = \frac{1}{2} \int_0^{\frac{\pi}{2}} r^2 d\theta$

represents the area enclosed by a ω^2 -contour on any plane of constant ϕ , and

$$X(\phi) = \frac{1}{3} \int_0^{\frac{\pi}{2}} r^2 \sin \theta d\theta - \frac{1}{2} \int_0^{\frac{\pi}{2}} r^2 d\theta$$

means the distance of the center of mass of the area $A(\phi)$ from the σ_z -axis. Applying the Hardy's formula

$$\int_{-3h}^{+3h} f(\phi) d\phi \simeq \frac{h}{100} [28(f_{-3} + f_{+3}) + 162(f_{-2} + f_{+2}) + 220f_0]$$

to Eqn. (2), the volume $V(\omega^2)$ is computed by

$$V(\omega^2) \simeq \frac{\pi}{3600} \left[28 \left(I\left(\frac{\pi}{6}\right) + I(0) \right) + 162 \left(I\left(\frac{5\pi}{36}\right) + I\left(\frac{\pi}{36}\right) \right) + 220 I\left(\frac{\pi}{12}\right) \right],$$

where $I(\phi) = A(\phi)X(\phi)$. $A(\phi)$ and $X(\phi)$ are determined by mechanical means, that is, $A(\phi)$ is obtained by weighing the weight of paper on which area enclosed by ω^2 -contour is drawn, and $X(\phi)$ is obtained by pivoting the area on a needle successively from two points. The volumes $V(\omega^2)$ are then fitted to the form

$$V(\omega^2) = \sum_i a_i [\omega^2 - c_i]^3 + \sum_n b_n \omega^{2n},$$

where the first term is inserted according to the singularity analysis. The frequencies at which the singularities occur can be found from the ω^2 -contours drawn on the outer five surfaces (Fig. 2 and 3). Apart from the corner points of 1/24-zone no other point of singularity can be found in the present study.

The frequency distribution $g(\omega^2)$ is obtained on differentiating $V(\omega^2)$ with respect to ω^2 and the usual definition of frequency distribution $f(\omega)$ is connected with $g(\omega^2)$ by

$$f(\omega) = 2\omega g(\omega^2).$$

$g(\omega^2)$ is illustrated in Fig. 4 and $f(\omega)$ in Fig. 6.

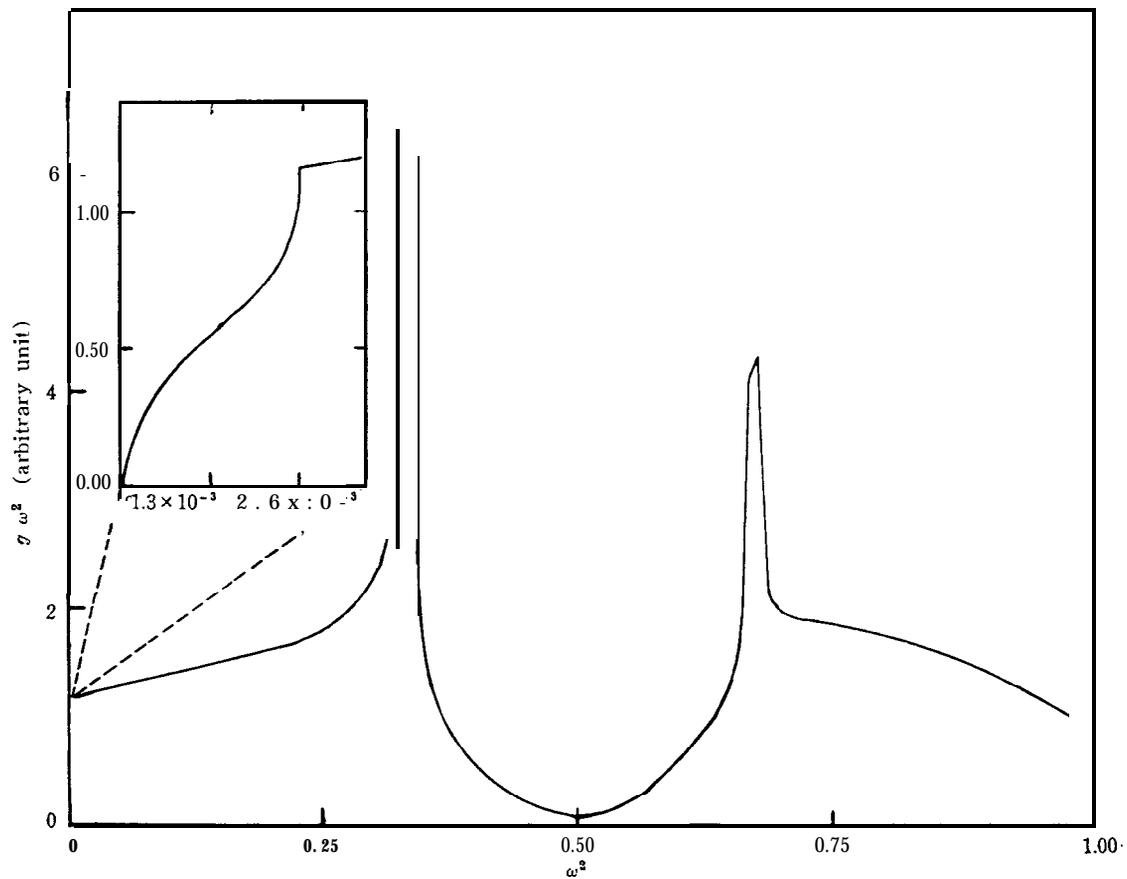


Fig. 4. Frequency distribution $g(\omega^2)$. The lowest frequency part is shown in the inset.

DISCUSSION

An explanation for the transition behavior of low temperature specific heat was given by Krumhansl and Brooks⁽²⁾ as following: For the lowest frequency acoustic modes σ_x and σ_y are small, so that the solution (1) reduces to

$$\omega^2 \approx \frac{S_0 a^2}{12m} (\sigma_x^2 + \sigma_y^2) + \frac{S_1}{m} (1 - \cos \sigma_z \frac{c}{2}),$$

which indicates that the ω^2 -surfaces are surfaces of revolution about the σ_z -axis. For frequencies less than

$$\omega_1^2 = \left(\frac{2S_1}{m} \right) = 2.07 \times 10^{24} (\text{rad/sec})^2$$

the ω^2 -surfaces are complete ellipsoids and yield the Debye frequency distribution for a three dimensional system, that is,

$$g(\omega^2) \propto (\omega^2)^{\frac{1}{2}} \text{ or } f(\omega) \propto \omega^2,$$

For $\omega^2 > \omega_1^2$, they are truncated by the planes $\sigma_z = \pm 2\pi/c$ and becomes gradually like

cylinders. The frequency distribution thus tends to resemble the two dimensional form

$$g(\omega^2) = \text{constant} \quad \text{or} \quad f(\omega) \propto \omega.$$

The correctness of the above- argument may be confirmed again from the Fig. 2 and 3.

It is interesting to compare the present calculation with that of Rosenstock.⁽⁵⁾ He calculated the frequency distribution of bending vibration of two dimensional graphite lattice exactly for certain values of a , β and τ for nearest, 2nd nearest and 3rd nearest neighbours. Fig. 5 illustrates his result for lattices with the nearest interaction only ($\beta/a=0$, $\tau/a=0$). Except for a dissimilarity in the lowest frequency part, two dominant peaks show also a different character: In the two-dimensional case the peak has a cusp of logarithmic infinity, whereas in the three-dimensional case the cusp breaks and the height remains finite.

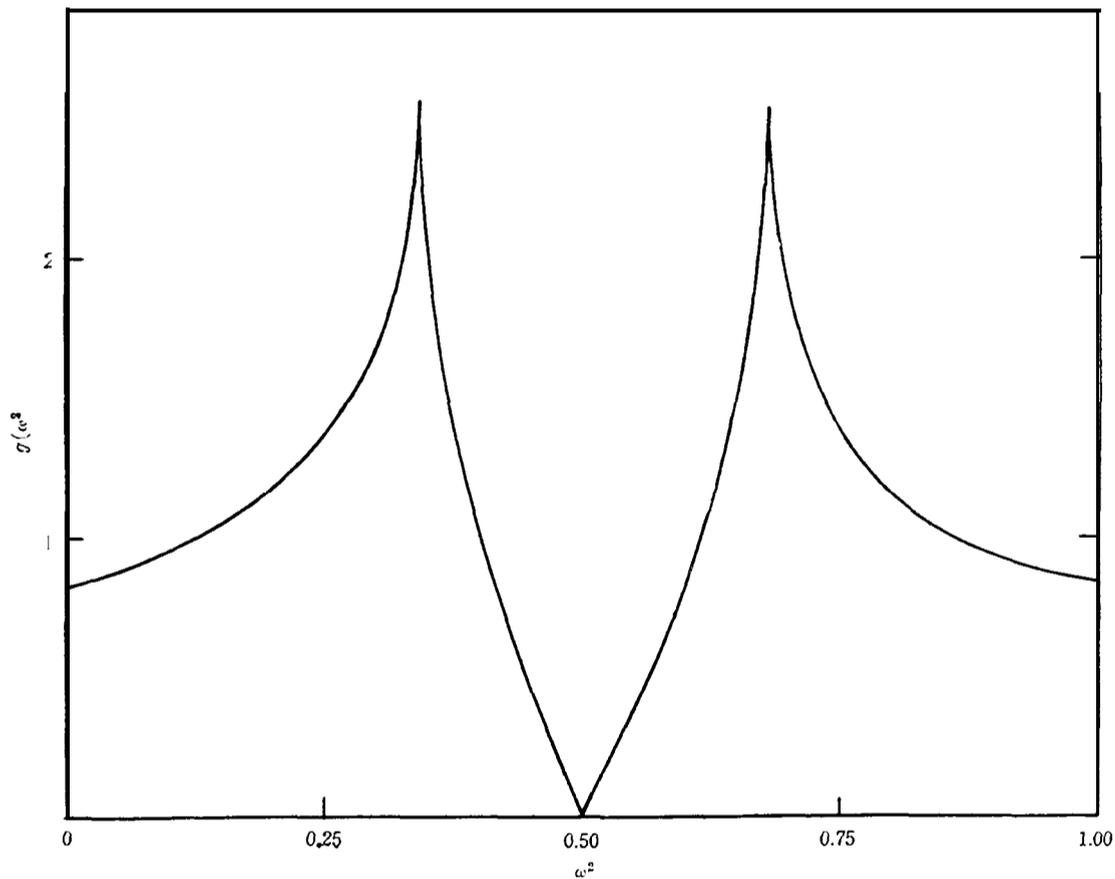


Fig. 5. Frequency distribution $g(\omega^2)$ of the graphite lattice determined by Rosenstock ($\beta/a=\tau/a=0$).

(5) H. B. Rosenstock, J. Chem. Phys. 21, 2064 (1953).

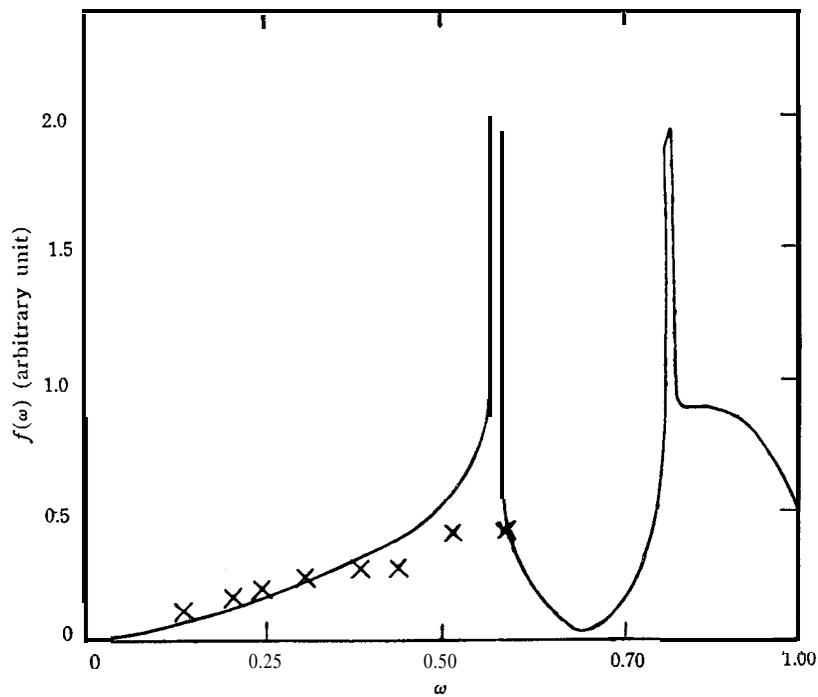


Fig. 6. Frequency distribution $f(\omega^2)$. The points marked by \times are determined by Egelstaff and Cocking with Neutron diffractron technique.

Experimental determination of the frequency distribution by the neutron diffraction was done by Egelstaff and Cocking⁽⁶⁾, and Haywood and Thorson⁽⁷⁾, but the results of both groups disagreed considerably with each other. However, the lower frequency part of the present calculation is in good conformity with the result of Egelstaff and Cocking, except that the existence of the first peak cannot be confirmed from their experiment. The latter is probably due to the fact that their reading points near the location of the first peak were separated too far.

(6) P. A. Egelstaff and S. J. Cocking, *Inelastic Scattering of Neutrons in Solids and Liquids*, (IAEA, Vienna, 1961) p. 569.

(7) B. C. Haywood and I. M. Thorson, *Inelastic Scattering of Neutrons in Solids and Liquids, Vol. 2*, (IAEA, Vienna, 1963) p. 111.