ALCD-3243 Rev.

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CLASSIFICATION CANCELLED

DATE 1-24-52

For The Atomic Energy Commission

William A. Stinson

Chief, Declassification Branch

Lattice Vibrations in Graphite

R. Gurney

Argonne National Laboratory
Chicago 80, Illinois

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When a neutron with energy less than 100 ev is being slowed down in a graphite moderator, the principal mechanism for its loss of energy is the excitation of lattice vibrations. In order to estimate the rate of loss of energy by slow neutrons, a knowledge of the frequency spectrum of the lattice is required.

Graphite has a layer-lattice structure, the atoms within each plane forming a network of hexagons. In both natural and artificial graphites the crystallites are reported to be agglomerates of smaller units. In artificial graphites these units are thin plates, each containing perhaps not more than 12 to 17 parallel well-ordered planes.¹ For atomic displacement perpendicular to a plane, the restoring forces are much weaker than for similar displacements in the plane itself. As early as 1911, when comparing specific heat measurements with the Einstein theory, Nernst² suggested that for graphite it was necessary to use two "Einstein temperatures" instead of the single temperature characteristic of an isotropic substance.

In the lattice waves of Debye there are three directions of propagation, and in each direction a longitudinal wave and two transverse waves (with their displacements at right angles). In graphite the vibrations which have weak restoring forces will be: (a) transverse waves with direction of propagation within the crystal planes and with displacements perpendicular to these planes, and (b) longitudinal waves propagated perpendicular to the planes; if the crystallite units are only from 12 to 17 atoms thick, no waves of long wave

1. T. Neubert, "Structure and Properties of Artificial and Natural Graphites" (unpublished).
2. Nernst, Annalen d. Physik (1911)

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length will be associated with these longitudinal waves. At very low temperatures only the transverse waves (a) will be excited, and the problem reduces to a two-dimensional problem.

The usual Debye expressions defining the frequency spectrum are

$$g(\nu) d\nu = \alpha \nu^2 d\nu = 4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu$$

$$3 = \int_0^{\nu_D} \alpha \nu^2 d\nu = \frac{1}{3} \alpha \nu_D^3$$

where V is the volume of the crystal, and c the velocity of propagation.

These expressions would be replaced by

$$\alpha' \nu d\nu = 2\pi A \left(\frac{1}{c_l^2} + \frac{2}{c_t^2} \right) \nu d\nu \quad (1)$$

$$2 = \int_0^{\nu_D} \alpha' \nu d\nu = \frac{1}{2} \alpha' \nu_D^2 \quad (2)$$

where A is the area of the crystallite plate, if all types of wave propagated in the planes were to be included. Actually the number of modes will be one-third of this value, to include only the particular transverse waves (a). The expression for the partition function becomes

$$\log k(T) = \frac{4}{3} N \frac{N^2}{\Theta^2} \int_0^{\Theta/T} \xi \ln(1 - e^{-\xi}) d\xi \quad (3)$$

and the usual T^3 -law for the specific heat at low temperatures will be replaced by

$$C_v = 9.6 R \frac{T^2}{\Theta^2} \quad (4)$$

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- 3 -
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Table I shows the average value of C_p measured by Astermann and Kirkland³ for four specimens of artificial graphite.

Table I

Temp.	C_p	θ^2
25° K	.032	385,100
30	.046	373,700
35	.063	371,400
40	.0815	375,000
45	.103	375,500
50	.126	379,000
55	.1525	378,800
60	.179	384,100
		Mean 376,900

The last column shows the values of θ^2 derived from (4). The constancy of θ^2 shows that the T^2 -law is closely obeyed over this range of temperature, and leads to a Debye temperature of 6.4° K for the limit of the frequency of these transverse waves.⁴ The contribution to C_v obtained by inserting $\theta = 614^\circ$ into the partition function (3) is shown as Curve (a) in Fig. 15. In discussing any substance at high temperatures, one usually has to take into account the difference between C_p and C_v . The difference ($C_p - C_v$) depends on the value of the square of the coefficient of cubic expansion, which in the case of graphite is abnormally small up to 1000° K, since in two directions the linear expansion is nearly zero. The simplest way of representing the specific heat of graphite in this range of temperature is shown in Fig. 15. Curve (b) is an ordinary Debye curve, drawn for $\theta = 2100^\circ$ K, and normalized to include all modes not already included in (3). The upper curve, obtained by adding the ordinates of Curves (a) and (b) passes rather well through the experimental points⁵. Below 70° K the contribution from Curve (b) is negligible, so that the T^2 -law of Table I is unaffected.

3. Unpublished Project report.

4. V. V. Tarassov (Comptes Rendus Ac. Sci. USSR 46, 111, 1945) arrived at the value 1370° K for this Debye temperature; this seems to be because he used the full number of modes of a three-dimensional lattice.

5. Magnus, Ann. d. Phys. 70, 303 (1923); and Landolt Borstein's tables.

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