Lattice Vibrations in Graphite*

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In both natural and artificial graphites the crystallites are reported to be agglomerates of smaller units, each containing perhaps not more than 12 to 17 well-ordered planes. For atomic displacements perpendicular to a plane the restoring forces are much weaker than for similar displacements in the plane itself. For the latter the restoring forces are so strong that these lattice vibrations will not be excited at low temperatures. In this paper the requisite adaptation of the Debye theory of specific heat is given; it leads to a T^2 law instead of the familiar T^3 law at low temperatures. Unpublished measurements of specific heat between 25° and 60°K by Estermann and Kirkland are cited and compared with the theory; they are found to lead to a value $\theta_D=614°$ for the Debye temperature for the vibrations with weak restoring forces. Combining this with a value $\theta_D=2100°$ for the remaining modes of vibration is found to represent the specific heat over the whole range of temperature.

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 displacements 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, Nernst[2] 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 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

$$g(\nu)d\nu=\alpha\nu^2d\nu=4\pi V(1/c_l^3+2/c_t^3)\nu^2d\nu,$$

$$3N=\int_0^{\nu_D}\alpha\nu^2d\nu=\tfrac{1}{3}\alpha\nu_D^3,$$

where V is the volume of the crystal, and c the velocity of propagation. These expressions would be replaced by

$$\alpha'\nu d\nu=2\pi A(1/c_l^2+2/c_t^2)\nu d\nu, \tag{1}$$

$$2N=\int_0^{\nu_D}\alpha'\nu d\nu=\tfrac{1}{2}\alpha'\nu_D^2, \tag{2}$$

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

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

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

$$C_v=9.6RT^2/\theta^2. \tag{4}$$

Table I shows the average value of C_p measured by Estermann and Kirkland[3] for four specimens of arti-

TABLE I. The specific heat of graphite.

Temp	C_p	θ^2	
25°K	0.032	385,100	
30	0.046	373,700	
35	0.063	371,400	
40	0.0815	375,000	
45	0.103	375,500	
50	0.126	379,000	
55	0.1525	378,800	
60	0.179	384,100	
			Mean 376,900

* This work was done at the Argonne National Laboratory. Application for declassification was made in 1948, but consent was withheld. A new application was granted in January, 1952.

[1] T. Neubert, *Structure and Properties of Artificial and Natural Graphites*, unpublished.

[2] W. Nernst, Ann. Physik **36**, 395 (1911).

[3] Estermann and Kirkland, unpublished.

ficial graphite. 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 614°K for the limit of the frequency of these transverse waves.[4]

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 in this range of temperature is to assign another Debye temperature to all the modes not already included in (3), although this is not strictly correct. Good agreement with the experimental values[5] is obtained with $\theta_2=2100°$. Below 70°K the contribution from this part is negligible, so that the T^2 law of Table I is unaffected.

[4] V. V. Tarassov [Compt. rend. (U.S.S.R.) **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] A. Magnus, Ann. Physik **70**, 303 (1923) and the Landolt Bornstein Tables.

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The Scattering of Slow Neutrons in Polycrystalline Media*

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When a neutron passing through a crystallite has insufficient energy to eject an atom from its site, excitation of a lattice vibration occurs instead. This paper deals mainly with neutrons having energy between 0.5 and 5.0 electron volts, the range where both the cross section for elastic scattering σ_{el}, and that for inelastic scattering σ_{in} vary rapidly with energy. In order to deal with inelastic collisions in which many phonons are exchanged, Finkelstein replaced the Debye model of the crystal by the Einstein model and gave expressions for $J_n(E)$, the probability that a neutron having energy E colliding with an atom of mass M loses at a collision n quanta. Computations of J_n for large and small M show in detail that in the slowing-down process by this mechanism a heavy element is much less efficient than a light element, as in the familiar case of fast neutrons. Since in this range of energy σ_{el} is inversely proportional to E, and since the observed total cross section is independent of energy, this implies that σ_{in} is of the form $\sigma_{in}=\sigma_0(1-A/E)$. Computed values of ΣJ_n are found to lead to this form, irrespective of the particular Einstein temperature assumed for the solid.

WHEN a 100-volt neutron, traveling through a crystal or a crystallite, makes a glancing angle collision with an atom of the lattice, the energy transmitted will be less than the binding energy; in this case, the excitation of a lattice vibration occurs instead of the ejection of the atom from its site. For slower neutrons this becomes increasingly important, until finally the neutron becomes incapable of ejecting an atom, even in a head-on collision. This paper deals mainly with neutrons having energy between 5.0 and 0.5 electron-volts, the range of energy where both the cross section for elastic scattering σ_{el} and the cross section for inelastic scattering σ_{in} are varying rapidly with energy.

In order to deal with inelastic collisions in which many phonons are exchanged, Finkelstein[1] replaced the Debye model of the crystal by the Einstein model. If $\hbar\omega$ is the constant energy difference between successive energy levels of the oscillator, a neutron colliding with an atom of the lattice can lose energy $\hbar\omega$, $2\hbar\omega$, $3\hbar\omega$ $\cdots n\hbar\omega$. If $J_n(E)$ is the probability that a neutron having energy E loses at a collision energy $n\hbar\omega$, the total inelastic cross section is obtained by summing over all values of n not greater than $E/\hbar\omega$:

$$\sigma_{in}=(m/\mu)^2\sigma_f J, \tag{1}$$

$$J=\sum_{n=1}^{n\leq\epsilon} J_n, \tag{2}$$

where m is the mass of the neutron, μ is the reduced mass of the struck nucleus, σ_f is the cross section of the free nucleus, and $\epsilon=E/\hbar\omega$. The expression given by Finkelstein for J_n is the same as that derived by Fermi[2] for the thermalization of neutrons in hydrogenous substances:

$$J_n=(M/4m\epsilon)[f_n(q_1^2)-f_n(q_2^2)], \tag{3}$$

where

$$f_n(x)=e^{-x}(1+x+\cdots+x^n/n!), \tag{4}$$

$$q_1=(m/M)^{\frac{1}{2}}[\epsilon^{\frac{1}{2}}-(\epsilon-n)^{\frac{1}{2}}], \tag{5}$$

$$q_2=(m/M)^{\frac{1}{2}}[\epsilon+(\epsilon-n)^{\frac{1}{2}}], \tag{6}$$

where M is the mass of the struck nucleus.

* This work was done at the Argonne National Laboratory, and the results have been taken from a declassified report by the author.

[1] R. J. Finkelstein, Phys. Rev. **72**, 907 (1947).

[2] E. Fermi, Ricerca sci. **7**, 13 (1936).