

**Zeitschrift:** Helvetica Physica Acta  
**Band:** 41 (1968)  
**Heft:** 6-7  
  
**Artikel:** The low-temperature specific heat of graphite  
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**DOI:** <https://doi.org/10.5169/seals-113930>

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## The Low-Temperature Specific Heat of Graphite

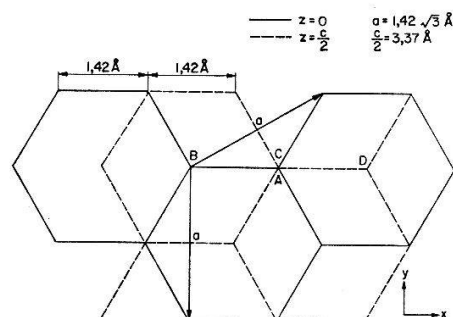
by **I. Estermann**

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(23. IV. 68)

Having been separated from active research in Solid State Physics for almost twenty years, I can contribute to this issue honoring Georg Busch only by recalling heretofore unpublished work on a problem which attracted my interest in the early 1940's and which, although some important contributions have been made to its solution in the meantime, still leaves some questions unanswered.

As is well known today, graphite was used as a neutron moderator in the early nuclear reactors and was found to undergo drastic changes of its physical properties under prolonged exposure to neutron irradiation. I then belonged to the large group of scientists who were participating in the U.S. Atomic Energy Project (then called the Manhattan Project) and to the smaller group who were specifically concerned with the graphite problem. According to a hypothesis proposed by Eugene Wigner, the changes in mechanical, electrical and thermal properties of the graphite under neutron irradiation were assumed to be due to the displacement of C-atoms from their lattice sites into interstitial positions by the impact of high-energy neutrons, a phenomenon which was called the Wigner effect.



The lattice structure of graphite.

Solid lines indicate one plane, dotted lines indicate a neighboring plane.

The crystal structure of graphite (Fig. 1) is very anisotropic, consisting of a stack of atomic planes with interatomic distances of  $1.42 \text{ \AA}$  separated from one-another by a distance of  $3.37 \text{ \AA}$ . As a result, an atom displaced from its original site can easily be accommodated in an interstitial position. We assumed that these interstitial atoms would make the lattice more rigid in the  $c$ -direction and, therefore, increase the Debye temperature  $\theta_D$  of the crystal. Such a change should influence the specific heat at low temperatures, particularly in the region of the validity of the  $T^3$  law, where

$$C_V = \frac{12}{5} \frac{\pi^4 R}{\theta_D^3} T^3 \quad (1)$$

i.e. inversely proportional to  $\theta_D^3$ .

In collaboration with G. Kirkland, I tried to test this idea by measuring the specific heats of virgin and irradiated graphite of the same origin (designated AGOT by the manufacturer) and comparing the  $C_V$  vs  $T^3$  curves for samples which had been exposed to various intensities of neutron flux. As our whole cryogenic facility consisted of a small, home-made hydrogen liquefier [1] operating from gas cylinders without the use of a compressor, we were only able to reach temperatures of slightly below 20°K, and we could not achieve a very high degree of accuracy because we had only very small samples of 'pedigreed' graphite at our disposal. Our results were somewhat disappointing: although we observed a small difference in the specific heat between the virgin and the strongly irradiated samples, it was barely outside the limits of error and in the opposite sense of our expectations. We observed, however, that we had apparently not reached the  $T^3$  region; in fact our measured values of the specific heat agreed much better with a  $T^2$  dependence than with the expected dependence on  $T^3$ .

Because of the pressure of other work and because the project was classified – it only became declassified more than ten years later – we did not pursue this problem any further and the results were never published by us. Some years later, however, GUERNEY [2], then working at the Argonne National Laboratory, obtained access to our results and in 1952 the authorization to publish a summary of our data referring to virgin graphite (our reports were then still classified). He also recognized the proportionality of the specific heat to  $T^2$  between 25 and 60°K and obtained from our data a mean value of 376,000 for  $\theta_D^2$  or  $\theta_D = 614^\circ\text{K}$ . In his paper, he developed a theory of the specific heat of graphite, taking into account the anisotropy of the crystal lattice together with the assumption that in artificial graphite the crystallites are agglomerates of small units, each of them containing only approximately 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 the corresponding lattice vibrations are not excited at low temperatures. Contributions to the specific heat at low temperatures, are therefore, provided only by the vibrations with weak restoring forces. These consist of (a) transverse waves with direction of propagation within the lattice planes and (b) longitudinal waves propagated perpendicular to the planes. Because of the small size of the agglomerates, waves of long wave length will not be associated with the longitudinal vibrations and no contribution to the specific heat at low temperatures will result. This modified, two-dimensional theory yields an equation for the low temperature specific heat of the form

$$C_V = \frac{9.6 R}{\theta_D^2} T^2 \quad (2)$$

in agreement with our measurements of  $C_P$ , neglecting the difference  $C_P - C_V$  in the temperature range under consideration. For high temperatures, the vibrations with strong restoring forces must also be considered; these yield good agreement with theory under the assumption of a second Debye temperature  $\theta_{D2} = 2100^\circ\text{K}$ , but below  $T = 70^\circ\text{K}$  the contribution from this part of the energy spectrum to the specific heat is negligible and the  $T^2$  dependence remains unchanged.

The problem was taken up again in 1953 by DE SORBO and TYLER [3] who made more accurate measurements of the specific heat on large samples of high-purity

Acheson graphite in the temperature range from 13 to 300°K. Their measurements confirm the  $T^2$  dependence of  $C_V$  (or  $C_P$ ) over the range from 13 to 54°K even better than our previous results. At the same time KRUMHANSL and BROOKS [4] reexamined the theoretical aspects of Guerneys work and developed a more detailed theory of the vibrational modes of the graphite lattice which also leads to the  $T^2$  dependence of the specific heat of graphite at low temperatures. In contrast to Guerneys theory, this behavior does not appear as a size effect but as an intrinsic property of the elastic anisotropy of the graphite lattice. On this basis, the experimental data from 15–1000°K can be fitted to a theoretical curve by dividing the lattice vibrations into two types: modes with atom displacements normal to the layer planes with a Debye temperature  $\theta_{D1} = 900^\circ\text{K}$ , and modes with atom displacements within the planes with  $\theta_{D2} = 2500^\circ\text{K}$ .

The story, however, does not end here. The experimental data seem to indicate deviations from the  $T^2$  dependence appearing below 15°K, and the theory leaves the possibility open that at much lower temperatures a  $T^3$  law may finally be reached. Since present-day computer facilities permit the exact numerical calculation of the vibrational spectrum of the graphite lattice, it would be very interesting to compare the results of such computations with those of new measurements at liquid helium temperatures. I am also inclined to believe that the small irradiation effect observed by us in the early measurements was due to a contribution of the relatively weakly bound interstitial atoms to the vibrational spectrum and not to a stiffening of the lattice as we assumed at that time.

### References

- [1] J. E. AHLBERG, I. ESTERMANN and N. O. LUNDBERG, R.S.I. 8, 422 (1937).
- [2] R. W. GUERNEY, Phys. Rev. 88, 465 (1952).
- [3] W. DE SORBO and W. W. TYLER, J. Phys. 27, 1660 (1953).
- [4] J. KRUMHANSL and H. BROOKS, J. Chem. Phys. 27, 1663 (1952).

## Some Recent Experimental Studies of the Gray-Tin Band Structure<sup>1)</sup>

by A. W. Ewald

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(29. IV. 68)

*Abstract.* Recent studies of Shubnikov-de Haas oscillations, conventional transport, the piezo-Hall effect, magnetoflection and free-carrier absorption in gray tin are reviewed. The Shubnikov-de Haas oscillations have yielded detailed information about the  $F_g^+$  conduction band including the nonparabolicity, nonsphericity and effective  $g$ -factor. The oscillations are strongly affected by the

<sup>1)</sup> Preparation of this review was assisted by support from the Advanced Research Projects Agency through the Northwestern Materials Research Center and from the National Science Foundation.