the different LO branches do not agree closely with the observations. However, both the model and the experiments indicate that equal coupling of both branches in $Cd(Se_xS_{1-x})$ mixtures occurs for a composition where x is well above its 0.5 value.

Both of the LO phonon branches also couple to the free electrons in the conduction band; this has the effect of shortening the free-electron lifetime since more ways are provided for a fast cascade to the level of the free or bound exciton from which recombination will occur. This interpretation leads to the conclusion that, after excitation into the conduction band has occurred, the cooperation of two different phonons (and their combinations) will populate such recombination levels faster in mixed crystals than in pure crystals, since in the latter the electrons in the conduction band are depleted only by one LO phonon (and its multiples). This higher rate will lead to an increased population density of the recombination center. (The condition that τ_{op} be less than τ_c must obtain.) Thus, we might account for Hurwitz's observation that the threshold for lasing action in some Cd(SeS) mixtures is lower than that of either CdSe or CdS.[31]

ACKNOWLEDGMENTS

We wish to thank D. C. Reynolds for stimulating the work on this topic, D. Naas for growing the platelets we used, and C. W. Litton and T. C. Collins for helpful discussions.

PHYSICAL REVIEW VOLUME 152, NUMBER 2 9 DECEMBER 1966

Low-Temperature Specific Heat and Density of States of Boronated Graphite*

B. J. C. VAN DER HOEVEN, JR.,† AND P. H. KEESOM
Purdue University, Lafayette, Indiana

AND

J. W. MCCLURE
University of Oregon, Eugene, Oregon

AND

G. WAGONER
Carbon Products Division, Union Carbide Corporation, Cleveland, Ohio

(Received 25 July 1966)

The increase in the low-temperature specific heat upon boronation of natural Madagascar flake graphite has been measured. For the pure material below 1.2°K, $C=13.8T+27.7T^3$ μJ/mole deg; for the same graphite boronated to 0.23 at.%, $C=34.5T+29.3T^3$ μJ/mole deg. The change in electronic density of states at the Fermi surface is found to agree well with theoretical expectation. These results allow one to predict the Fermi-level shifts that would be necessary to account for the increased linear specific heat of disordered graphites. However, the Fermi-level shifts so predicted would require much larger changes in other electronic properties than are actually observed. Thus, the excess specific heats cannot be explained as being due to Fermi-level shifts.

INTRODUCTION

CONSIDERABLE experimental[1–3] and theoretical[4,5] work has been done in recent years on the low-temperature heat capacity of graphite. In particular, it is now established that the peculiar temperature dependence of the heat capacity is due to the unusual phonon dispersion relations. Quantitative agreement[5] now exists between theory and experiment for the lattice heat capacity of perfect graphite and for graphites of various degrees of imperfections (especially stacking faults).

The agreement is also good between the theoretical[6] electronic heat capacity of pure single-crystal graphite and the most recent and most accurate experimental

---

* Work supported in part by U. S. Army Research Office (Durham).

† Present address: IBM Watson Research Center, Yorktown Heights, New York.

[1] W. DeSorbo and W. W. Tyler, J. Chem. Phys. **21**, 1660 (1953); U. Bergenlid, R. W. Hill, F. J. Webb, and J. Wilks, Phil. Mag. **45**, 851 (1954); P. H. Keesom and N. Pearlman, Phys. Rev. **99**, 1119 (1955).

[2] W. DeSorbo and G. E. Nichols, J. Phys. Chem. Solids **6**, 352 (1958).

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

[4] K. Komatsu and T. Nagamiya, J. Phys. Soc. Japan **6**, 438 (1951); K. Komatsu, *ibid.* **10**, 346 (1955); K. Komatsu, J. Phys. Chem. Solids **6**, 380 (1958); J. C. Bowman and J. A. Krumhansl, *ibid.* **6**, 367 (1958).

[5] K. Komatsu, J. Phys. Chem. Solids **25**, 707 (1964).

[6] J. W. McClure, IBM J. Res. Develop. **8**, 255 (1964).

determination.[3] However, the experimental investigations[3] have shown that the electronic heat capacities of pure but structurally imperfect graphites are larger than that of pure graphite (about a factor of 2 larger in the case of graphitized lampblack). It has been speculated[3,5] that these differences are due to Fermi-level shifts caused by defect centers acting as electron traps. The object of the present work was to test this speculation by measuring the electronic heat capacity of single-crystal graphite containing boron, which has been established to be an electron acceptor.[7] It should be mentioned that a previous attempt[2] to measure the effect of boron was unsuccessful. However, in the present experiment the sample contains about three times as much boron, the measurements extend to a lower temperature, and the measurements are more accurate.

The electronic heat capacity of the boronated sample is found to be more than twice that of the pure sample, a result which is in good agreement with the theory. From this result and the results of other types of experiments, it is argued that the variations in the electronic heat capacities of the samples containing defects cannot be due to shifts in the position of the Fermi level.

Experimental Results

The experimental method used in this work has already been described.[3] Reported here is a new measurement of the low-temperature specific heat of a carefully prepared boronated natural Madagascar graphite. The increase in specific heat due to the added boron is clearly evident in Table I which also gives the specific heat measured previously[3] on identical material which had not been boronated. The data are plotted in Fig. 1. in the form C/T versus T^2. If the specific heat were of the form $C=\gamma T+\alpha T^3$, the data would lie on a straight line of slope α and intercept γ. Following the usual interpretation, γ is ascribed to electrons and α to lattice vibrations. One can see from Fig. 1 that below 1.2°K the specific heat is well described by only a linear and a cubic term, but that at higher temperatures there is a gentle departure introduced by the T^2 term in the heat capacity.[3] Below 1.2°K, the specific heat of the pure graphite is $C=13.8T+27.7T^3$ μJ/mole deg. Upon boronation to 0.23 at.% the specific heat becomes $C=34.5T+29.3T^3$ μJ/mole deg. The increase by a factor of 2.5 in the value of γ upon boronation is interpreted as a shift of Fermi level in κ space to a region away from the zone corner where the average electronic density of states is increased 2.5 times. The increase in α upon boronation yields a reduction of the Debye parameter Θ_0 from 413°K for pure Madagascar graphite to 405°K for the boronated material. The change in α upon boronation is about 6% whereas the experimental uncertainty is about ±1.5% which results in an uncertainty for the Debye parameter of 2°K. The change in Θ_0 corresponds to a reduction of about 6% in $(c_{44}\sqrt{}c_{33})$, the elastic constant combination most strongly involved in the low-temperature heat capacity

TABLE I. Specific heat of pure and boronated natural Madagascar flake graphite (C is in μJ/mole deg).

T(°K)	C	T(°K)	C
pure		boronated	
0.3816	6.85	0.4783	19.28
0.4090	7.59	0.4817	20.02
0.4275	8.17	0.5055	21.60
0.4613	9.07	0.5466	23.62
0.4250	7.98	0.5824	25.75
0.4475	8.56	0.6212	82.32
0.5011	10.41	0.6435	29.89
0.5404	11.80	0.6799	32.67
0.5905	13.70	0.7569	39.06
0.6352	15.69	0.8431	46.34
0.6686	17.59	0.8976	52.26
0.7214	20.42	0.9588	58.53
0.7571	22.37	1.0306	66.84
0.8089	25.89	1.1140	77.27
0.8419	28.19	1.1818	86.99
0.8879	31.81	1.2586	98.91
0.9429	36.17	1.3140	107.79
1.0095	42.39	1.3631	116.59
1.0899	50.76	1.4066	124.36
1.1563	58.14	1.4561	134.27
1.2507	68.87	1.5222	147.39
1.3516	84.37	1.5801	159.72
1.4644	102.37	1.7184	192.39
1.6637	139.04	1.8250	219.31
1.8722	182.37	1.9540	254.84

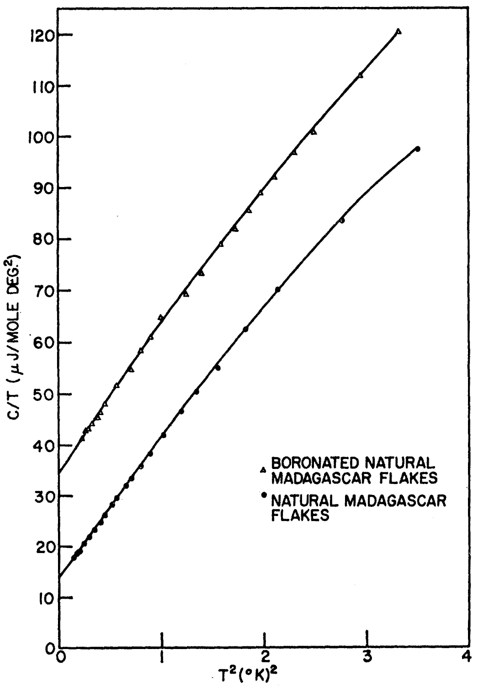

FIG. 1. Plot of C/T versus T^2 for pure and boronated natural Madagascar graphite.

---

[7] D. E. Soule, in *Proceedings of the Fifth Conference on Carbon* (Pergamon Press, Inc., New York, 1962), Vol. I, p. 13.

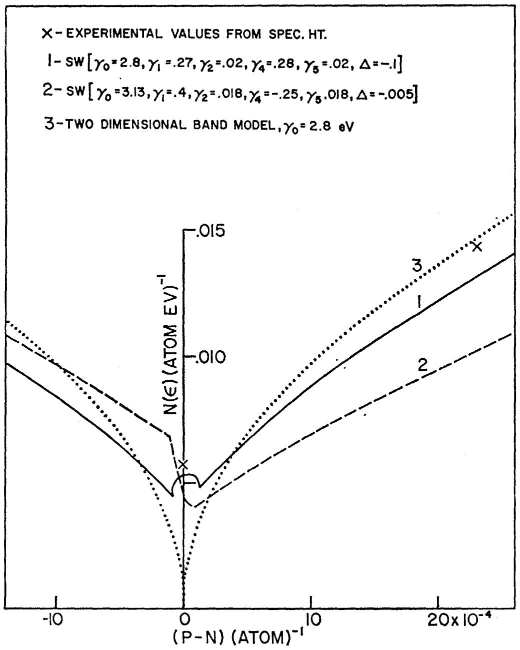

FIG. 2. Density of electronic states versus acceptors/atom for graphite.

graphite.[8] A reduction of c_{44} (which is the elastic constant associated with interplanar shear) and of c_{33} (interplanar compression) is to be expected as boronation reduces the occupation of the π electron orbitals which are most strongly involved in interplanar interaction; however, the large magnitude of the effect is surprising and its explanation should help illuminate the relation between bonding and shear. (It should be noted that the change in α upon boronation is only a little more than twice the uncertainty in the measurements, thus there is a possibility that the change is not so large.)

Sample Preparation

The specimens used in this work were prepared with particular care to avoid chemical contamination and mechanical deformation, either of which could obscure the desired result. The starting material was natural Madagascar flake graphite which had been purified at 3000°C in a chlorine atmosphere. The flakes of graphite were about 1 mm across and about 0.05 mm thick. Most of the flakes are composed of only a few crystallites before pressing. For the pure specimen, a slug one inch in diameter by two inches long was pressed under one ton per square inch and then subjected to a 1 h anneal in a purified tube furnace at 3000°C. A reasonable estimate of the final crystallite size is greater than 100 μ. The boronated specimen was prepared by first boronating the flake graphite at 3000°C for 1 h, then pressing the boronated flakes into a slug and finally annealing the pressed slug at 2600°C for 4 h. Spectroscopic analysis was used after each baking operation to ensure that no appreciable contamination of the specimen had occurred. Impurities of various types ranged in the 1 to 10 ppm range for all specimens. Spectroscopic analysis was also used to determine the level of boronation. The average of five determinations by the National Spectrographic Labs, Inc., was 0.23±0.02 at.%.

Discussion

The electronic heat capacities of pure and boronated single crystals of graphite can be well understood on the basis of our present knowledge of the electron energy-band structure.[9] The energy-band structure near the Fermi level may be represented by the Slonczewski-Weiss (SW) model.[10] Though the exact values of all the parameters in the model are not yet determined, the remaining uncertainty cannot have a strong effect upon the density of states near the Fermi level for pure graphite. This is because all choices of parameters must agree with the results of the de Haas–van Alphen experiments, which fix the volumes of the Fermi surfaces and the effective masses. The experimental results[3] for pure graphite correspond to a density of states of 0.0058/atom eV. As has been pointed out before,[6] assuming a parabolic model for the energy structure and using the de Haas–van Alphen results,[11] one obtains a density of states of 0.0055/atom eV.

We have calculated the densities of states for boronated graphite using the rigid-band model, an approximation which is justified in Appendix A. The calculated density of states at the Fermi level is plotted against excess hole concentration in Fig. 2. The three theoretical curves are for (1) SW parameters[12] which give approximate agreement with the de Haas–van Alphen[11] effect, electron-spin-resonance g shift[12] and diamagnetic susceptibility[13]; (2) SW parameters[14]

---

[8] K. Komatsu (Ref. 5) has shown that the very low temperature lattice heat capacity is due to the out-of-plane modes. His Eq. (2) shows that the frequency distribution f_2 is proportional to the combination of elastic constants $c_{44}^{-1}\,c_{33}^{-1/2}$ for small frequencies, and thus the heat capacity c_2 is proportional to the same quantity at low temperatures.

[9] It has been previously shown (Ref. 6) that the phonon-mediated interaction between electrons has a negligible effect upon the low-temperature heat capacity of graphite. The Coulomb interaction between electrons may be important, in which case the heat capacity is given by the density of quasiparticle states. Similarly the de Haas–van Alphen effect is related to the quasiparticle energy spectrum, so that the only change required in this section to include the Coulomb interaction would be to replace *electron energy* by *quasiparticle energy*.

[10] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958) (see also Ref. 6).

[11] D. E. Soule, J. W. McClure, and L. B. Smith, Phys. Rev. **134**, A453 (1964).

[12] J. W. McClure and Y. Yafet, in *Proceedings of the Fifth Conference on Carbon* (Pergamon Press, Inc., New York, 1962), Vol. I, p. 22.

[13] J. W. McClure, Phys. Rev. **119**, 606 (1960).

[14] S. J. Williamson, S. Foner, and M. S. Dresselhaus, Phys. Rev. **140**, A1429 (1965).

which give agreement with the de Haas–van Alphen effect[11,14] and magnetoreflectivity experiments[15]; and (3) the "two-dimensional" model.[16] It is seen that all three theoretical curves are in fair agreement with the experimental result for the boronated sample, and that the two Slonczewski-Weiss model curves are in good agreement for pure graphite.

Curve No. 1 differs by about 9% from the measured value of $N(\epsilon)$ for pure graphite and by about 14% for the boronated graphite. The discrepancies of curve No. 2 are about twice as much. Although the theoretical curves could be adjusted to obtain exact agreement with the specific-heat results, the resulting band structure would not account as well for other experiments. The general dependence of density of states upon boronation seems to be given by the SW model but it remains to be seen if one set of parameters can yield exact agreement with all the appropriate experiments. It is worthwhile to note that, except for very low boronation levels, the "two-dimensional" band model gives practically the same result as the SW model.

In our use of the rigid-band model we have assumed that each boron atom accepts one electron, producing an excess hole. Previous studies[7] have indicated that only a fraction (about 75%) of the boron atoms behave as acceptors. Such behavior would move the experimental point in Fig. 2 to the left and thereby worsen the agreement with experiment. Thus, the present results indicate that the ionization efficiency of the substitutional boron in single crystals is approximately 100%. The discrepancy can be partly removed by noting that in Ref. 7 the Hall coefficient was taken to be $1/pec$, whereas theoretical calculations[17] indicate that it is $1.2/pec$.

The linear term in the specific heat, γ, has been found[3] to have quite different values for graphites of different degrees of perfection. In his analysis of these different specific heats Komatsu[5] has obtained for γ a value of 13.65 μJ/mole deg^2 for natural Madagascar graphite, 22.4 μJ/mole deg^2 for pile graphite, 25.1 μJ/mole deg^2 for graphitized lampblack (SA 25), and 15.9 μJ/mole deg^2 for pyrographite. Interpreted in the customary way as electronic specific heat, the above values of γ yield densities of states of 0.00577/atom eV, 0.00947/atom eV, 0.01062/atom eV, and 0.00673/atom eV, respectively. It has been suggested that imperfect graphite contains acceptors which shift the Fermi level and modify the heat capacity,[3,5] thus accounting for the above differences. To account for the magnitude of the effect by such a means would require, on the basis of Fig. 2, the addition of some 10^{-3} acceptors per carbon atom. We believe that such an interpretation is inconsistent with other measured electronic properties such as the diamagnetism and the electron-spin-resonance g value.

To illustrate the inconsistency, let us attempt to interpret the deviation of γ of lampblack-base graphite from that of single crystals as due to a Fermi-level shift in the single-crystal graphite band structure. We use the experimentally determined electronic properties of boron-doped single-crystal graphite to demonstrate the influence of acceptors on the Hall coefficient R_H, diamagnetic susceptibility χ_T, and electron-spin-resonance g value. For example, with 1.5×10^{-3} acceptors (boron) per carbon atom (an amount sufficient to double γ) $R_H=0.07$ cm^3/C,[7] $\chi_T=-5\times10^{-6}$ cm^3/g,[7,18] and $\Delta\bar{g}=0.0004$.[19,20] The measured values for chemically pure SA 25 graphitized lampblack are $R_H=-0.007$ cm^3/C,[21] $\chi_T=-20.5\times10^{-6}$ cm^3/g,[22] and $\Delta\bar{g}=0.011$.[20] (For pure single crystals the corresponding values are $R_H=-0.04$ cm^3/C,[7] $\chi_T=-22.1\times10^{-6}$ cm^3/g,[23] and $\Delta\bar{g}=0.014$.[20]) The Hall coefficient of -0.007 can be obtained either by doping with donors to about 9×10^{-3} donors/carbon atom or by such small doping that the contribution to the Hall effect of holes continues to nearly cancel that due to electrons as in pure single crystals. (The two-carrier Hall effect has two values of $(n\text{-}p)$ for each value of R_H.) The large values of both χ_T and $\Delta\bar{g}$ are only consistent with the latter case. Similar arguments show that the amount of Fermi-level shift from the pure single-crystal value is too small to affect the electronic specific heat of any of the disordered types of graphite mentioned above.

We now consider the question of whether the band structure of disordered graphite is the same as that of single crystals, If it is not, the above comparison of the electronic properties of disordered graphite with those of doped single crystals might be of dubious validity. It is our opinion that the band structure of disordered graphite is indeed modified by stacking faults such as those which produce turbostratic graphite but that the modification is such that the allowable variation of the Fermi level among disordered graphites is even more restricted than for the single-crystal band structure. The principal effect of turbostratic stacking is to reduce the interaction between the planes of graphite and to result in electronic properties more closely describable by the two-dimensional model.[24] In such a case the electronic properties change even more rapidly as a

---

[15] M. S. Dresselhaus and J. G. Mavroides, IBM J. Res. Develop. **8**, 262 (1964).

[16] P. R. Wallace, Phys. Rev. **71**, 622 (1947); C. A. Coulson, Nature **159**, 265 (1947).

[17] J. W. McClure and L. B. Smith, in *Proceedings of the Fifth Conference on Carbon* (Pergamon Press, Inc., New York, 1963), Vol. II, p. 3.

[18] For the units of specific susceptibility we use cm^3/g and employ unrationalized Maxwell equations. These units are also termed emu/g by some authors and cgs emu by others.

[19] G. Wagoner (unpublished data). See Ref. 20 for the definition of $\Delta\bar{g}$.

[20] L. S. Singer and G. Wagoner, J. Chem. Phys. **37**, 1812 (1962). The L113SP reported in this reference has the same electronic properties as does purified SA 25 graphite.

[21] See the last paper listed under Ref. 4.

[22] G. Wagoner (unpublished data).

[23] D. E. Soule, Wright Air Development Division Tech. Rept. 61-72 Vol. 39 Contract AF33(616)-6915 (1963).

[24] J. W. McClure, in Symposium on Carbon, Tokyo, Japan, 1964 (extended abstracts, p. I-4) (unpublished).

function of acceptor concentration than for the three-dimensional band structure.[25] We thus conclude that the increased linear term in the specific heat of disordered graphite cannot be explained as a Fermi-level shift with the single-crystal band structure; further, it does not appear likely that any plausible modification of graphite band theory to better describe disordered graphite will allow for any appreciable variation of the Fermi level among graphite samples of different degrees of disorder. Thus, there is currently no explanation of the excess linear heat capacity of disordered types of graphite.

APPENDIX

A calculation of the change in the density of states of a single layer of graphite with addition of attractive or repulsive potentials on lattice sites has been published by Fukuda.[26] We use his calculation to show that the change in the density of states at the Fermi level is small for the impurity concentration in the present sample. The same result should hold for three-dimensional graphite.

Fukuda uses the Coulson free-electron-network model.[27] In the unperturbed lattice the energy near the top of the valence band (measured from the bottom of the band) is given by

$$E=\hbar^2q^2/2m\,, \tag{A1}$$

where

$$\cos ql\cong\pm\alpha_0\kappa/2\sqrt{3}\,. \tag{A2}$$

In the above α_0 is the lattice parameter, $l=\alpha_0/\sqrt{3}$ is the distance between nearest-neighbor carbons, and κ is the small distance from the corner of the hexagonal Brillouin zone (which is the top of the valence band). Thus

$$E\cong\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{2l}\right)^2+\frac{\pi\alpha_0\kappa}{2\sqrt{3}l^2}\right]=E_0+\tfrac{1}{2}\sqrt{3}\alpha_0\kappa\gamma_0\,, \tag{A3}$$

where $E_0=4.7$ eV and $\gamma_0=2.0$ eV. The value of E_0 given by this model is too small, but that for γ_0 is the correct order of magnitude.

Fukuda gives the change in density of states in terms of a phase shift Γ, which near the top of the valence band may be written as

$$\Gamma\cong 9\Delta l\pi\Omega\eta(\cos ql\,\sin ql)/ql\,, \tag{A4}$$

where

$$\Delta=2mV_0\epsilon/\hbar^2\,, \tag{A5}$$

and

$$\Omega\eta=\frac{N'(E)}{3\alpha_0^2}\frac{dE}{d(\kappa^2)}\,. \tag{A6}$$

In the above ϵ is the range and $-V_0$ is the average value of the perturbing potential (the limit $\epsilon\longrightarrow 0$ has been taken with $\epsilon\ V_0$ held constant) and $N'(E)$ is the unperturbed density of states per atom for one spin orientation, $N'(E)=|E-E_0|/\sqrt{3}\pi\gamma_0^2$. Thus we find $\pi\Omega\eta$ becomes $1/(8\sqrt{3})$ and

$$\Gamma\cong-(3\sqrt{3}/4\pi\gamma_0)\Delta l|E-E_0|\,. \tag{A7}$$

The change in density of states for this case is given by $-(n_I/\pi)d\Gamma/dE$, where n_I is the number of impurities per carbon atom. We find for the total density of states of both spins

$$N_{\text{tot}}(E)=2[|E-E_0|-(9/4\pi)n_I\gamma_0\Delta l]/\sqrt{3}\pi\gamma_0^2\,. \tag{A8}$$

We now set the density of holes equal to the density of impurities to find the density of states at the Fermi level at low temperatures. Neglecting the small perturbation in the density of states, we have $n_I=(E-E_0)^2/\sqrt{3}\pi\gamma_0^2$. The fractional change in the density of states at the Fermi level is then

$$\begin{aligned}\Delta N_{\text{tot}}(E)/N_{\text{tot}}(E)&=-(9/4\pi^{3/2}3^{1/4})\Delta l n_I^{1/2}\\&=-0.31\Delta l n_I^{1/2}\,.\end{aligned} \tag{A9}$$

We must now estimate the value of the parameter Δl. In a simpler case we could use Friedel's criterion[28] that the screening of the potential is just enough to keep the Fermi level unchanged. However, the Friedel criterion does not lead to a reasonable result in the present case. If the perturbing potential is represented by a screened Coulomb potential, the quantity ϵV_0 would be $-Re^2$, where R is a numerical factor. Alternatively we could choose V_0 to be the difference between the boron and carbon ionization energies (about 3 eV) and ϵ to be half the carbon-carbon distance, which yields $R=0.15$. Fukuda calculated for $\Delta l=-1$, which corresponds to $R=0.19$. Therefore $\Delta l=-1$ seems a reasonable estimate. We then find for $n_I=2\times10^{-3}$ (the doping level used in this work) that $\Delta N/N=0.014$. Thus we see that the change in the density of states due to the perturbing potential is small in this case, so that the rigid-band approximation is justified.

---

[25] G. Wagoner, Sixth Conference on Carbon, Pittsburgh, Pennsylvania, 1963 (unpublished).

[26] Y. Fukuda, J. Phys. Soc. Japan **20**, 353 (1965).

[27] C. A. Coulson, Proc. Phys. Soc. (London) **A67**, 608 (1954).

[28] J. Friedel, Advan. Phys. **3**, 446 (1954).