Theory of the Magnetic Susceptibility of Graphite

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The theory of the magnetic susceptibility of graphite is presented in terms of a three-dimensional Wallace electron energy band structure. The experimentally observed variation with temperature is explained in a satisfactory manner, provided the interplane resonance integral occurring in the band approximation is given a value of about 0.5 ev. This is about five times larger than the previously used estimate and implies that a two-dimensional band approximation may be invalid in many cases. The in-plane resonance integral is obtained by fitting the variation, with electron concentration, of the electrical resistivity of a graphite-bisulphate residue compound. In this way a value of 1.63 ev for this integral is obtained. It might be noted that these values enabled a better fit of the resistivity over the entire range of bisulphatization than could be obtained by a two-dimensional theory. On the other hand, the value thus obtained for the actual

magnitude of the susceptibility is lower than that observed by a factor of about 40. The (room temperature) variation of the susceptibility of bromine graphite is then analyzed on the basis of the above theory, using the indicated values of the constants. In this way, a value is obtained for the percentage of the bromine which is ionized. This is found to be weakly dependent on the amount of bromine, varying between 18% at 0.3 atomic percent bromine to 13% at 0.8 atomic percent bromine. The experimental value has been found to vary slightly around 18%. This agreement is very good and indicates that the theory is valid in explaining relative variations of the susceptibility, even though there is difficulty in predicting the absolute magnitude. The latter is the only serious discrepancy found in the present work and has not yet been explained.

I. INTRODUCTION

GRAPHITE shows a very high diamagnetic susceptibility which is, in addition, extremely anisotropic.[1] These properties have been explained by

Eatherly[2] and Smoluchowski[3] as due to the highly anisotropic Brillouin zone structure of the conduction band.[4] It was originally shown by Peierls,[5] and later

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[1] N. Ganguli and K. S. Krishman, Proc. Roy. Soc. (London) **177**, 168 (1940).

[2] W. P. Eatherly, see comments in discussion following reference 3.

[3] R. Smoluchowski, Revs. Modern Phys. **25**, 178 (1953).

[4] P. R. Wallace, Phys. Rev. **71**, 622 (1947).

[5] R. Peierls, Z. Physik **80**, 763 (1933).

extended by Wilson,[6] that there are terms in the magnetic susceptibility of crystalline conductors which depend on the curvature of the energy surfaces near the Fermi level and which can become large (and negative), especially if the band is nearly filled or nearly empty. These effects arise from changes in the level density rather than spin interactions and, for free electrons, reduce to the well-known Landau diamagnetism.[7] The earlier applications of this to graphite[2,3] utilized a two-dimensional approximation to the band structure[4] and were able to explain, in a qualitative way, the rapid changes in the susceptibility with such factors as bromination.[8] However, difficulties arose in making quantitative comparisons with experiment, particularly those relating to temperature effects. For this reason, a more detailed study was made using a three-dimensional band structure; the present paper gives the results of this study. In general, these results have been successful in explaining relative changes of the susceptibility. In addition, it has been possible to evaluate some of the constants inherent in the band structure by correlation of the theoretical and experimental susceptibility. The values of these constants thus obtained are of the order of magnitude of previous estimates (all of which are very approximate), but differ sufficiently to have a significant effect on the theoretical interpretation of the electrical properties of graphite.

There is one discrepancy between theory and experiment which the present work reduces, but does not remove. This concerns the absolute magnitude of the susceptibility. Previous attempts[3] to calculate this yielded a value which was lower than the observed by a factor of several hundred. The present calculation is still low by a factor of about forty. While this may be merely an error, either in the derivation or in the numerical work, all attempts to find such an error have failed. It should be emphasized that the theory of the magnetic susceptibility of electronic conductors presents some of the most difficult problems in solid-state physics and, at present, cannot be considered as generally satisfactory. This is especially true when the bands are degenerate (or nearly degenerate), as in the case of graphite, in which case terms which are usually considered negligible may become important.[6] Adams[9] has made some calculations for bismuth, where he shows that such terms are important, although it is very difficult to use his results for graphite. As will be seen, the use of the simpler (single band) theory of Peierls[5] for graphite is apparently satisfactory in explaining all relative variations of the susceptibility and fails only in predicting the magnitude. This would seem to imply that, if the trouble lies in neglecting terms of possible importance, these terms can be put into the form of the Peierls expression times a slowly varying function. The

latter would then approximately cancel for the relative susceptibility.

II. TEMPERATURE DEPENDENCE

Using the nondegenerate theory of Wilson,[6] the conduction electron contribution to the magnetic susceptibility per unit volume is

$$\chi = \frac{\mu_0^2}{12\pi^2}\left(\frac{m}{h^2}\right)^2 \int \left[\frac{\partial^2 E}{\partial k_x^2}\frac{\partial^2 E}{\partial k_y^2} - \left(\frac{\partial^2 E}{\partial k_x \partial k_y}\right)^2\right]\frac{\partial f_0}{\partial E}d^3\mathbf{k}, \quad (1)$$

for a constant magnetic field in the Z-direction. The integration is over all $\mathbf{k}$ space, f_0 is the Fermi-Dirac distribution function, and μ_0 is the Bohr magneton. The Wallace[4] model for the conduction band structure of graphite gives two touching bands, the lower one completely filled (at zero temperature) and the upper completely empty. If the origin of $\mathbf{k}$ is translated to one of the corners of the hexagonal Brillouin zone,[1] the Wallace energy values (near the corner) are

$$\epsilon = -\gamma_1 \cos\frac{c}{2}k_z \pm \left[\gamma_1^2 \cos^2\frac{c}{2}k_z + \tfrac{3}{4}\gamma_0^2 a^2 \kappa_{xy}^2\right]^{\frac{1}{2}}, \quad (2)$$

where ϵ is measured from the energy of band touching and the $(\pm)$ refers to the upper (empty) and lower bands. Here $\kappa_{xy}^2 = \kappa_x^2 + \kappa_y^2$ where $\kappa_x = k_x - k_y$ (corner), etc., and a and c are the magnitudes of the lattice translation vectors. The constants γ_0 and γ_1 are resonance integrals between coplanar and interplane nearest neighbors, respectively, and have been roughly estimated by Coulson[10] as being 0.9 ev and 0.09 ev. For the purposes of the present work, these will be regarded as disposable constants to be determined by experiment.

Using Eq. (2), it is a straightforward, although laborious, procedure to reduce Eq. (1) to the form

$$\chi = \frac{\mu_0^2}{\pi^2}\left(\frac{m}{h^2}\right)^2 \frac{a^2\gamma_0^2}{c\gamma_1(4kT)}\int_{-\infty}^{\infty}\text{sech}^2\left(\frac{\epsilon-\Delta\zeta}{2kT}\right)h\left(\frac{\epsilon}{\gamma_1}\right)d\epsilon, \quad (3)$$

where $\Delta\zeta$ is the Fermi energy measured from the top of the filled band. The function $h(x)$ is symmetrical and has the following form for $x > 0$:

$$h(x) = \frac{(2+x^2)}{2(1-x^2)^{5/2}}\left\{\ln\left[\frac{x}{2-x^2-[(1-x^2)(4-x^2)]^{1/4}}\right]\right.$$
$$\left. -[(1-x^2)(4-x^2)]^{1/2}\right\} \text{ for } 0 < x < 1$$

$$= \frac{(2+x^2)}{2(x^2-1)^{5/2}}\left\{\frac{\pi}{2} - \tan^{-1}\left[\frac{(2-x^2)}{[(x^2-1)(4-x^2)]^{1/2}}\right]\right.$$
$$\left. -[(x^2-1)(4-x^2)]^{1/2}\right\} \text{ for } 1 < x < 2$$

$$= \frac{\pi(x^2+2)}{2(x^2-1)^{5/2}} \text{ for } x > 2.$$

[6] A. H. Wilson, Proc. Cambridge Phil. Soc. 49, 292 (1953).
[7] L. Landau, Z. Physik 64, 629 (1930).
[8] G. Hennig, J. Chem. Phys. 19, 922 (1951); J. Chem. Phys. 20, 1438, 1443 (1952).
[9] E. N. Adams II, Phys. Rev. 89, 633 (1953).
[10] C. A. Coulson and R. Taylor, Proc. Phys. Soc. (London) A65, 815 (1952).

Thus for small x, $h(x)$ diverges logarithmically, while it has a slight peak at $x=2$ and approaches $\frac{1}{2}\pi x^{-3}$ for large x. The expansion of $h(x)$ for small x is

$$h(x) \simeq -\ln x - 0.614 + O(x^2);$$

it is valid to introduce this into Eq. (3) if $\gamma_1 > 4kT$. At room temperature, $4kT = 0.1$ ev and the *a priori* assumption will be made that γ_1 is greater than this. Note that the approximation becomes better for lower temperatures.

For an untreated graphite single crystal, the quantity $\Delta\zeta$ is zero. Under this condition, and evaluating the constants of Eq. (3), there is found

$$-\chi_0 \simeq (0.375 \times 10^{-7}) \frac{\gamma_0^2}{\gamma_1} \left(\ln\frac{\gamma_1}{2kT} + 0.27 \right) \qquad (4)$$

in cgs mass units (ergs g^{-1} gauss^{-2}). This is correct up to an order of $(kT/\gamma_1)^2$. The variation of χ_0 with temperature has been measured by Ganguli and Krishnan,[1] Goldsmith,[11] McClelland,[12] and Owen.[13] In using these data, the core diamagnetism of the carbon atoms must be subtracted in order to obtain a value corresponding to the susceptibility considered here. The corrected experimental results are plotted in Fig. 1, normalized to 300°K. Superimposed on this plot are curves of Eq. (4) (normalized similarly) for several values of γ_1. It is apparent from this that the best fit is obtained when γ_1 is between 0.5 and 0.8 ev, with 0.5 ev appearing preferable. The commonly used value of 0.1 ev gives worse agreement with the observed results than can be accounted for on the basis that one is approaching the limit of validity inherent in Eq. (4) at room temperature. Thus, in the work to follow, a value of 0.5 ev will be used for γ_1. If χ_0 is plotted against $\ln T$, a straight line results at low temperatures (less than about room temperature) with a slope proportional to $(\gamma_0^2\gamma_1^{-1})$. This slope, with a γ_1 of 0.5 ev, gives a value of 10.5 ev for γ_0. The same value of γ_0 is obtained from fitting the experimental magnitude of the susceptibility (about 22.1×10^{-6} cgs units). Previously estimated values[10,14] of γ_0 lie between 1.0 and 3.0 ev and it is not likely that the order of magnitude of these former values is wrong. Furthermore, as will be shown later, a γ_0 of 10 ev gives serious discrepancies with the brom-graphite data, which require a value of about 1.6 ev. Thus, as mentioned in the previous section, it must be concluded that the coefficient in Eq. (1) is low by a factor of about forty. At present this cannot be explained. Since all of the relative changes of χ appear to be explained by Eq. (1), however, it is reasonable to assume that whatever causes this discrepancy does not greatly alter the form of the energy integral; similarly, it probably does not depend on a serious alteration of the assumed energy band structure [Eq. (2)].

[11] M. Goldsmith, J. Chem. Phys. **18**, 523 (1950).
[12] J. D. McClelland (private communication).
[13] M. Owen, Ann. Physik **37**, 657 (1912).
[14] K. Komatsu and T. Nagamiya, J. Phys. Soc. Japan **6**, 438 (1951).
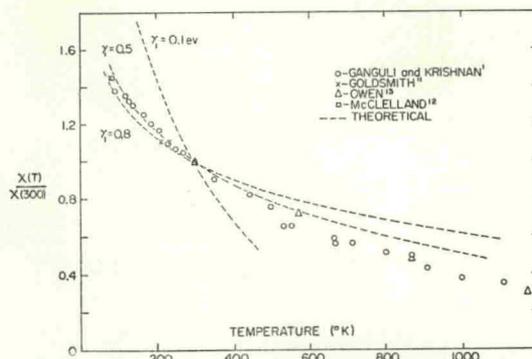
FIG. 1. The relative variation with temperature of the conduction electron diamagnetic susceptibility of normal graphite.

III. BROM-GRAPHITE RESIDUE COMPOUNDS

The electronic properties of many of the interstitial compounds of graphite have been extensively studied by Hennig.[8] The compound of particular interest to the present report is that with bromine. The brom-graphite residue compounds are useful in studying the properties of graphite because a fraction of the bromine is always ionized, which thus removes electrons from the graphite band. Since the bromine is presumably at crystal boundaries,[8] it has little effect on the band structure itself. The fraction of the residual bromine which is ionized is fairly constant (at about 18%) for ion concentrations of from 0.01 to 0.09 atomic percent. This ionized fraction was obtained by Hennig by comparing the electrical resistivity with that for graphite-bisulphate compounds, for which the ion concentration can be found with a reasonable accuracy by electrolytic methods. Since the ion concentration also represents the number of electrons which are removed from the band, the brom-graphite residue compounds permit a study of various electronic properties of graphite as a function of various known electron concentrations. In the present paper, the experimental susceptibility of brom-graphite, measured by Hennig and McClelland,[15] will be compared with the theory.

The effect of depleting electrons from the graphite conduction band will be to alter $\Delta\zeta$, the Fermi energy measured from the top of the band, in Eq. (3) for the magnetic susceptibility. Although $\Delta\zeta$ will actually be negative, χ is a symmetrical function of $\Delta\zeta$ [because of the use of Eq. (2) for the energy spectrum] and $\Delta\zeta$ may be taken as a positive quantity only. If $\Delta\zeta$ is small (considerably less than γ_1), the function $h(\epsilon/\gamma_1)$ in the integrand may be expanded as was done in the last section. Then the susceptibility (in cgs mass units) becomes

$$-\chi \simeq (0.375 \times 10^{-7}) \frac{\gamma_0^2}{\gamma_1} \left\{ \ln\frac{\gamma_1}{2kT} - 0.614 \right.$$
$$\left. + \frac{1}{2}F\left(\frac{\Delta\zeta}{2kT}\right) \right\}, \qquad (5)$$

[15] G. Hennig and J. D. McClelland, J. Chem. Phys. (to be published).
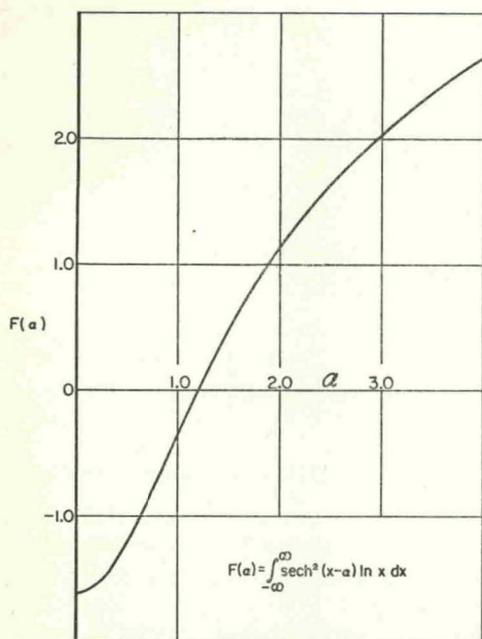
FIG. 2. A plot of the function $F(\alpha)$.

where

$$F(\alpha) = -\int_{-\infty}^{\infty} \mathrm{sech}^2(x-\alpha)\, \ln x\, dx.$$

The function F must be found by numerical integration but, once obtained, it is known for any temperature. It is given in Fig. 2 as a function of its argument.

If $\Delta\zeta$ is much larger than $4kT$, the integrand in Eq. (3) has an appreciable value only at $\epsilon=0$ and $\epsilon=\Delta\zeta$. Then the susceptibility is

$$-\chi \simeq (0.375\times10^{-7})\frac{\gamma_0^2}{\gamma}$$

$$\times\left\{\frac{\gamma_1}{32kT}\exp\left[-\tfrac{1}{4}\exp\frac{\Delta\zeta}{kT}\right]+h\left(\frac{\Delta\zeta}{\gamma_1}\right)\right\}. \quad (6)$$

The first term corresponds to the integration around $\epsilon=0$ and is negligible. The remaining term is temperature independent and is the analog of the Landau susceptibility of a degenerate free electron gas. It is,
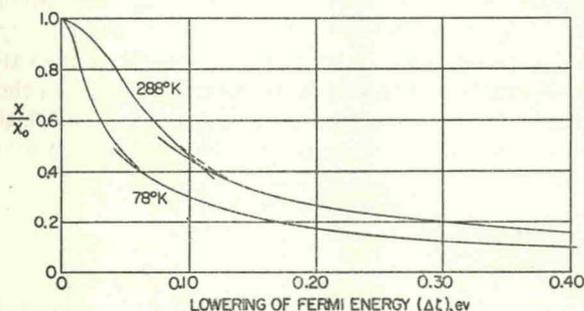
of course, evident that if enough electrons are trapped out of the energy band, graphite must look nearly metallic.

Since, from the last section, γ_1 has a value of about 0.5 ev, the ranges of validity of Eqs. (5) and (6) overlap at low temperatures and nearly do so even at room temperature. Thus, a satisfactory picture of Eq. (3) may be obtained by plotting Eqs. (5) and (6) and connecting them smoothly. This is done in Fig. 3, which actually plots χ/χ_0, where χ_0 is the value for $\Delta\zeta=0$. Two temperatures, 78° and 288°K, are shown. The experimental points of Hennig and McClelland[15] for type AGOT-KC graphite are given in Fig. 4 as a function of q, the atomic percent of bromine in the residue compound. A cross plot of Figs. 3 and 4 yields the variation of $\Delta\zeta$ with bromine concentration, which is shown in Fig. 5. As can be seen from Fig. 5, one may very nearly put

$$\Delta\zeta = 0.054q^{\frac{2}{3}}, \quad (7)$$

where q is atomic percent of bromine and $\Delta\zeta$ is in ev.

It is necessary to know the relationship between the number of electrons trapped (n_e) and $\Delta\zeta$. First of all, it can be shown that, at room temperature and below, the temperature dependence of $\Delta\zeta$ is negligible for graphite (the variation is not more than about 10%). Then, one can relate

$$n_e = \int_0^{\Delta\zeta} N(\epsilon)d\epsilon,$$

where $N(\epsilon)$ is the density of states per carbon atom if n_e is the number of trapped electrons per atom. Using the energy spectrum of Eq. (2), it is easily shown that

$$n_e \simeq \frac{2\gamma_1(\Delta\zeta)}{\sqrt{3}\pi^2\gamma_0^2} \quad \text{for} \quad \Delta\zeta \ll \frac{4}{\pi}\gamma_1. \quad (8)$$

For a γ_1 of 0.5 ev, this is a valid approximation insofar as the present work is concerned. The value of γ_0 can be independently obtained from the variation of the electrical resistivity with the residue graphite-bisulphate compound. This has also been studied by Hennig,[8] and, by electrolytic methods, the number of trapped elec-

FIG. 3. Theoretical variation of the relative susceptibility of graphite with Fermi energy [from Eqs. (5) and (6)].
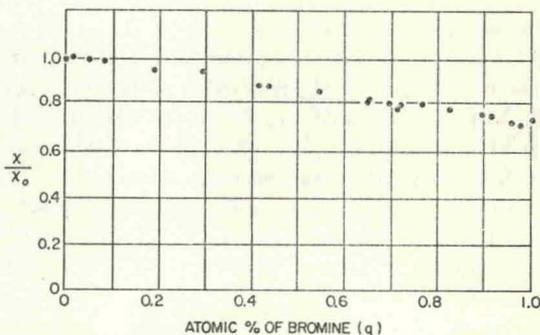
FIG. 4. Experimental variation of the relative susceptibility of brom-graphite with amount of bromine (from reference 15).

trons has been directly determined. Using the band structure of Eq. (2), the resistivity, normalized to the untreated resistivity, can be written[8]

$$\frac{\rho}{\rho_0} = (\ln 2) \Big/ \ln\left(2\cosh\frac{\Delta\zeta}{2kT}\right). \qquad (9)$$

It has been assumed here that $\Delta\zeta$ is considerably less than γ_1 and that the electron relaxation time is energy independent; the latter would be expected if boundary or defect scattering were predominant. Using Eq. (8), Eq. (9) may be written in terms of the number of electrons trapped per atom, with γ_0 as a parameter. On Fig. 6 is reproduced the resistivity variation found by Hennig[8] for room temperature and 144°K, together with a plot of Eq. (9) for $\gamma_1 = 0.5$ ev and $\gamma_0 = 1.63$ ev. The room temperature fit is good but it becomes worse for the low temperature. The latter may be because the scattering is not strictly energy independent or that the band structure is not sufficiently accurate. It should be mentioned that as long as γ_1 is much larger than both $\Delta\zeta$ and kT, the theoretical two- and three-dimensional resistivities are identical in terms of $\Delta\zeta$, but a two-dimensional energy band model gives n_e proportional to $(\Delta\zeta)^2$. A two-dimensional fit[8] is also shown in Fig. 6, and it can be seen that this is less satisfactory than the three-dimensional result.

Using the values 0.5 ev and 1.63 ev thus obtained for γ_1 and γ_0, the relation between the number of trapped electrons (per C atom) and the Fermi energy lowering (in ev) becomes

$$n_e \simeq 2.2 \times 10^{-2}\Delta\zeta. \qquad (10)$$

If p is the atomic percent of the bromine which is ionized, then n_e may be written as $(10^{-4}p)q$. Introducing Eq. (10) into Eq. (7) (the relation between $\Delta\zeta$ and q as found from the susceptibility), there is found

$$p \simeq 12q^{-\frac{1}{3}}\%. \qquad (11)$$

Thus, p varies from 18% ionization for $q = 0.3$ atomic percent of bromine to 13% ionization at $q = 0.8$ atomic percent of bromine. This is in good agreement with the estimates which Hennig obtained independently (which varied slightly around a value of 18%). It is
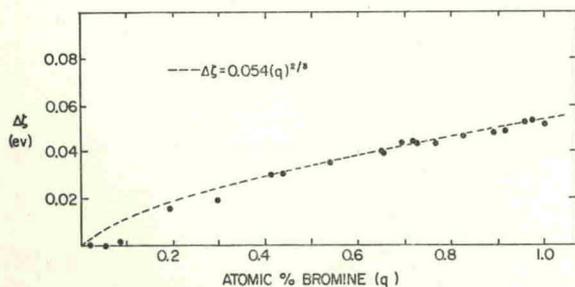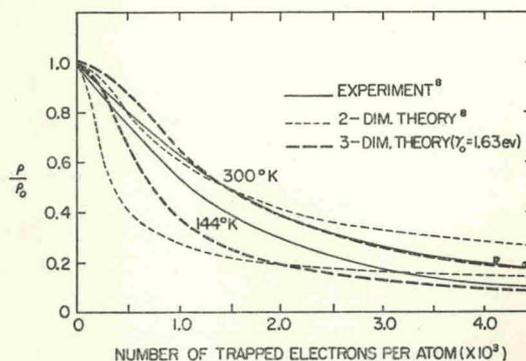
FIG. 6. Relative variation of the electrical resistivity of brom-graphite with electron concentration.

especially gratifying to note that the values found from the magnetic susceptibility data involve no arbitrary parameters, i.e., the constants γ_1 and γ_0 were obtained by completely independent methods.

IV. CONCLUSIONS

The major conclusion arising from the present work is that the relative changes of the magnetic susceptibility of graphite with temperature and with electron concentration can be quantitatively explained by a simple single-band theory if a three-dimensional energy band spectrum is used. This requires an in-plane resonance integral of 1.63 ev and an interplane integral of about 0.5 ev. The latter is considerably higher than the estimate made by Coulson[10] and this implies that a two-dimensional graphite model may be an invalid approximation for many of the electronic properties. It does not, however, appear that this simple theory can predict the actual magnitude of the observed susceptibility. It is not yet clear whether this discrepancy (a factor of about forty) can be removed by a multiband theory[9] or whether it is due to a serious fault in the graphite band structure. For example, Johnston[16] has pointed out that there is a slight band overlap inside the zone; it is conceivable that this could contribute a sizeable diamagnetism, although it would seem highly fortuitous if this effect showed the same relative behavior as found in the present paper. Because of the success of the present treatment of the relative variation, however, it is a reasonable presumption that any neglected effects of importance can be put into the form of a term like Eq. (1) multiplied by a slowly varying function of temperature and electron concentration. The latter term would then approximately cancel in a relative expression.

[16] D. S. Johnston, Atomic Energy Research Establishment, Harwell Report AERE-855, 1952 (unpublished).

FIG. 5. Variation of the Fermi energy ($\Delta\zeta$) of brom-graphite with amount of bromine as determined from the susceptibility variation.