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Magnetic Susceptibility of Neutron-Damaged Graphite*

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Previous work on the magnetic susceptibility of graphite as it is affected by temperature and bromination is extended to include effects of neutron irradiation at about room temperature. Data taken at both room temperature and liquid nitrogen temperature are analyzed and yield consistent values for the number of electrons trapped out by damage defects, thus further establishing the validity of the theory. The trapping rate of electrons, with neutron exposure, is found to be slightly nonlinear and a fair fit of the empirical curve is

$$\text{number of trapped electrons per carbon atom} = 1.4\times10^{-4}t^{2/3},$$

where t is the flux in mwd/ct. This two-thirds power dependence cannot be taken too literally, since neither the quantity nor quality of the data is sufficiently good. Data are also given for the buildup of paramagnetic centers as damage increases.

I. INTRODUCTION

WHEN graphite is subject to small amounts of fast neutron irradiation, there result two general effects on its electronic properties. One of these is the change (decrease) in the scattering relaxation time of the electrons and the other is the change in the number of conduction electrons due to trapping by the damage defects. In studying the mechanism of radiation damage, it is frequently necessary to separate these effects; thus measurements of the magnetic susceptibility are of major importance since this property is only sensitive to the number of effective electrons. In a previous paper,[1] the theory of the susceptibility in graphite was discussed as applied to its dependence on temperature and on bromination (the formation of dilute brom-graphite residue compounds, which do not materially alter the band structure of the graphite but do trap out small numbers of electrons). The present paper will discuss the neutron damage effects, for reasonably light exposures (less than 150 mwd/ct [2]), as they apply to the validation of the susceptibility theory. The damage mechanism itself has been interpreted elsewhere[3] and will not be considered here.

II. DATA AND DISCUSSION

Figure 1 gives the observed susceptibility of type AGOT-KC graphite as a function of integrated flux,

* Based on studies conducted for the U. S. Atomic Energy Commission.

[1] J. E. Hove, Phys. Rev. **100**, 645 (1955).

[2] For the present case, one mwd/ct is equivalent to 1.7×10^{17} nvt for neutrons over one-half Mev.

[3] G. R. Hennig and J. E. Hove, "Interpretation of radiation damage to graphite," Proceedings of the Conference on Peaceful Uses of Atomic Energy, Geneva, August 8–20, 1955.

expressed as mwd/ct.[2] The core diamagnetism has already been subtracted, so that these data represent the Peierls type of diamagnetic susceptibility as discussed in reference 1. The values are all normalized to the unirradiated value at the respective temperature of measurement. Most of the data were taken at this laboratory, although the three low damage measurements at 78°K were made by Goldsmith.[4] The room temperature data were obtained by three measurements in mutually perpendicular directions[5] using a Faraday method[6] and are considerably more accurate than the low temperature data, which were found by a Gouy technique.

Reference 1 gives the theoretical variation of the normalized susceptibility with the lowering of the Fermi level ($\Delta\zeta$) at these two temperatures. By cross-plotting this against Fig. 1, the empirical variation of Fermi level with amount of neutron damage is obtained, and is shown in Fig. 2. A curve of the two-thirds power of the neutron exposures is shown fitted to these data

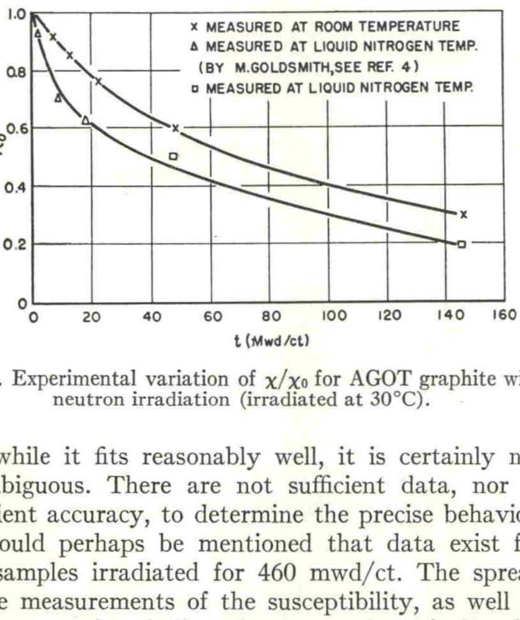

FIG. 1. Experimental variation of χ/χ_0 for AGOT graphite with neutron irradiation (irradiated at 30°C).

and while it fits reasonably well, it is certainly not unambiguous. There are not sufficient data, nor of sufficient accuracy, to determine the precise behavior. It should perhaps be mentioned that data exist for two samples irradiated for 460 mwd/ct. The spread in the measurements of the susceptibility, as well as other properties, indicated some serious fault with these specimens and the data are considered too poor to include here. However, the general implication of these 460 mwd measurements is that the curve of Fig. 2 tends to straighten out at about 100 mwd/ct instead of continuing the two-thirds power trend.

For the sake of comparison, Fig. 3 shows the low damage data superimposed on the bromination data of reference 1, using a correlation of 25 mwd/ct to one atomic % of bromine. The agreement is good, in accord

[4] M. Goldsmith, Argonne National Laboratory (in the classified AEC literature).

[5] W. P. Eatherly and J. D. McClelland, Phys. Rev. 89, 661–662 (1953).

[6] J. J. Donoghue, "Apparatus for the precise measurement of magnetic susceptibilities by the Faraday method" (unclassified), NAA-SR-117, May 25, 1953.

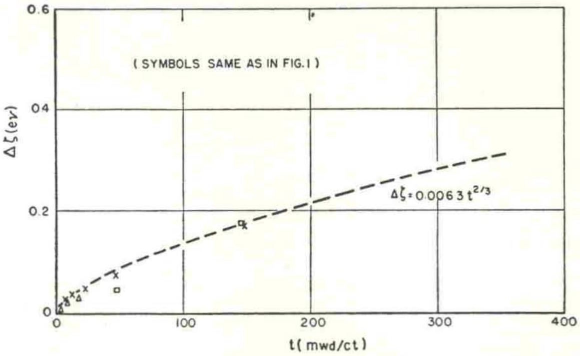

FIG. 2. Variation of $\Delta\zeta$ for AGOT graphite with neutron irradiation (irradiated at 30°C).

with the previously noted correspondence in the Hall coefficient behavior.[7] It should be noted from Fig. 3 that even though the low-temperature points do not agree accurately with the room temperature data, the error is less than about 25%. The sensitivity of the cross-plotting procedure used to obtain Fig. 3 is such that about a 10% error in either the calculations or data could account for this discrepancy. The numerical constants used in the theory[1] do not quite account for the observed unirradiated graphite temperature dependence and, in fact, give an error of about 5% in the right direction to decrease the discrepancy. In view of this, the agreement between the measurements at 78°K and 300°K can be considered as good, further strengthening the validity of the theory.† By using the relation between the change in the Fermi level and the number of trapped electrons given in reference 1, the trapping rate is

$$\frac{dn_e}{dt} = 10^{-4} t^{-\frac{1}{3}} \text{ per carbon atom per mwd/ct.}$$

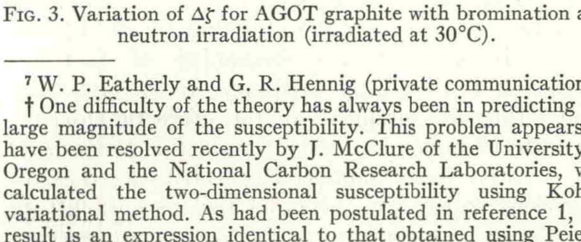

FIG. 3. Variation of $\Delta\zeta$ for AGOT graphite with bromination and neutron irradiation (irradiated at 30°C).

[7] W. P. Eatherly and G. R. Hennig (private communication).

† One difficulty of the theory has always been in predicting the large magnitude of the susceptibility. This problem appears to have been resolved recently by J. McClure of the University of Oregon and the National Carbon Research Laboratories, who calculated the two-dimensional susceptibility using Kohn's variational method. As had been postulated in reference 1, the result is an expression identical to that obtained using Peierl's development except for a much larger constant coefficient, so that the theoretical value checks the experimental value in a very reasonable manner. This work was reported by Dr. McClure at the Pittsburgh APS meeting in March, 1956.

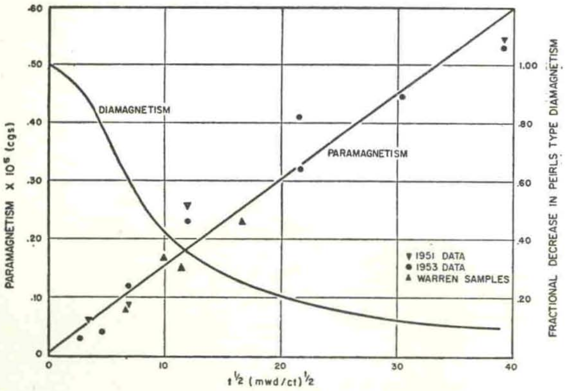

FIG. 4. Increase in paramagnetism for AGOT graphite with neutron irradiation (irradiated at 30°C).

Thus the trapping rate decreases weakly with increasing damage until about 100 mwd/ct, where it probably levels off at about 2×10^{-5}.

As neutron bombardment proceeds, there will be a buildup of trapping defect centers having an associated spin and hence a paramagnetism, which is very small for neutron exposures of the order discussed in this paper. This has been observed by resonance techniques[3] and the interpretation is that these spin centers are single, negatively ionized, interstitial carbon atoms. The paramagnetic susceptibility due to these defects can also be measured by the static Faraday method used to obtain our present data,[8] although with some difficulty because of the small magnitudes involved. The technique depends on the anisotropy of the Peierls-type diamagnetism as compared to the isotropy of the paramagnetic centers and, of course, is the more accurate the greater the degree of orientation of the graphite crystallites. The data obtained in this way for AGOT graphite are shown on Fig. 4, which also shows the changes in the diamagnetism for purposes of comparison. Several of the lower damage points are on more highly oriented specimens obtained from B. E. Warren of MIT. Within the relatively large errors shown, the paramagnetic susceptibility may be represented as

$$\chi_P \simeq 1.5\times10^{-8}\,(\mathrm{mwd})^{\frac{1}{2}}$$

in cgsm units. It is interesting to compare this with the increase in the resonant spin centers observed in the carefully calibrated experiments of Hennig and Smaller.[3] Their data also show an approximate proportionality to the square root of the integrated flux, such that the number of paramagnetic defects per carbon atom is about $0.4\times10^{-4}\,(\mathrm{mwd})^{\frac{1}{2}}$. Assuming that this is also the number of static paramagnetic centers, it is readily deduced that the averaged static magnetic moment of a single such defect is 3.2β, where β is the Bohr magneton. The observed g factor from the resonance work is nearly 2, implying an electronic configuration with no orbital angular momentum. The static average magnetic moment is then

$$\mu = 2\beta[S(S+1)]^{\frac{1}{2}},$$

where S is the total spin quantum number. The value $S=\frac{3}{2}$ gives a moment of 3.9β which is in reasonable agreement with the experimental value of 3.2β, especially considering the crudity of the static data and the difficulties of comparing neutron exposures in two separate irradiations. This value of the total spin implies that the interstitial carbon has three unpaired electrons, although it is generally not possible to specify the actual spectroscopic state without knowing the effect of the lattice electric field. If the latter is small, one would expect a $^4S_{\frac{3}{2}}$ state. It can be noticed (as pointed out in reference 3) that more electrons are trapped (by perhaps a factor of 3 or 4) than are paramagnetic centers formed. This may be interpreted as meaning that vacancies (and close vacancy-interstitial pairs) can trap two electrons to form diamagnetic centers. Such a picture can be shown[3] to be consistent with various low-temperature annealing data of damaged graphite.

We wish to acknowledge the very great influence of W. P. Eatherly in furthering the understanding of these problems in graphite, both concerning the susceptibility and other properties as well.

Note added in proof.—Since this was written, J. W. McClure has published his work in Phys. Rev. **104**, 661 (1956). This and more recent work throw considerable doubt on the high value of γ_1 which the present author finds necessary on the basis of the single model assumed. Despite the admitted weaknesses of the present theory, it is nonetheless still true that it leads to a relative susceptibility which is apparently consistent with a wide range of data.

[8] "Solid state and irradiation physics quarterly progress report," April–June 1953; North American Report, NAA-SR-268 (unclassified), December 1, 1953.

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