Spin Resonance in Neutron-Irradiated Graphite*

K. A. MÜLLER
Battelle Memorial Institute, Geneva, Switzerland
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The carrier spin-resonance line of neutron-irradiated single crystals of graphite at 300°K has been observed as a function of the thermal neutron flux up to a dose of 9.6×10^{18} *nvt*. From the intensity increase and the g shift for H parallel to the c axis, it is concluded that on the average 30 holes become mobile per *nvt* per cm^3. This is in agreement with earlier work of Hennig and Hove which was based on electrical measurements. It is shown that the line they reported in spin-resonance experiments on polycrystalline graphite was due to mobile charge carriers and not to paramagnetic carbon centers as they assumed. The number of holes created is compared to a recent electron transmission microscopy investigation of Bollmann where the damage has been observed directly. It is estimated that about one hole per displaced carbon atom is freed.

For the unirradiated graphite the linewidth was found to be anisotropic, being 4.6 gauss for H parallel and 3.0 gauss for H perpendicular to the c axis. This shows for the first time an incomplete "motional" narrowing for mobile carrier spin resonance. The anisotropy as well as the width decreases monotonically with irradiation, and at the highest dose investigated the linewidth is isotropic and equal to 1.3 gauss. The change in linewidth with irradiation and temperature is interpreted as due to a change in spin lattice relaxation time T_1 which is caused by carrier scattering via spin-orbit interaction.

I. INTRODUCTION

A MODEL of radiation damage in graphite based on neutron-irradiated polycrystalline material has been proposed by Hennig and Hove.[1] Bollmann[2] has recently reported the observation of radiation damage in graphite with electron-transmission microscopy. Wagoner[3] investigated the spin resonance line due to charge carriers in purified single crystals of graphite. We thought that observation of this line as a function of the irradiation dose might give additional information on the kind and number of created charge carriers as given by HH, a correlation to the structural work, and some verification of Wagoner's conclusions for pure graphite.

II. EXPERIMENTAL

Ten single crystals of natural graphite with base areas between 0.056 and 0.183 cm^2 and thicknesses from about 0.1 to 0.2 mm were irradiated in steps to a dose of 9.6×10^{18} *nvt* (thermal flux) at temperatures of 20° to 30°C.[4] Four of these crystals were kept loose, and the others were cemented on supports. The spectrometer used worked at a wavelength of 3.2 cm. The intensity of the resonance was compared to calibrated samples of DPPH or ZnS powder containing known concentrations of Mn^{2+} ions. The g values, linewidths, and asymmetry parameters were determined as indicated by Feher and Kip.[5] Figure 1 shows a record from a single crystal of 0.125 cm^2 base area, for $H\|c$ orientation at room temperature, irradiated to a dose of 9.6×10^{18} *nvt*. The line shows the characteristic Dysonian shape. It has shifted from the unirradiated position by 68.5 gauss to a higher magnetic field, its intensity has increased by a factor of 15, and the line has narrowed to 1.3 gauss.

III. g VALUES

The g values of the unirradiated crystals at 300°K for H parallel and perpendicular to the c axis were found to be $g_{\|}=2.0495\pm0.0003$, $g_{\perp}=2.0032\pm0.0002$ in agreement with those reported[3] and prove that the carrier concentration is intrinsic. The high anisotropy is caused by the mainly two-dimensional motion of the carriers in the lattice. For $H\|c$ there is therefore a much greater orbital contribution $\Delta g_{\|}$ than for $H\perp c$. The collision time τ_R of holes and electrons with the lattice is about 3×10^{-13} sec,[6] or a factor 10^5 shorter than the time T_2 after which a spin loses its memory. Therefore $\Delta g_{\|}$ represents an average of the g shift of the electrons and holes present.

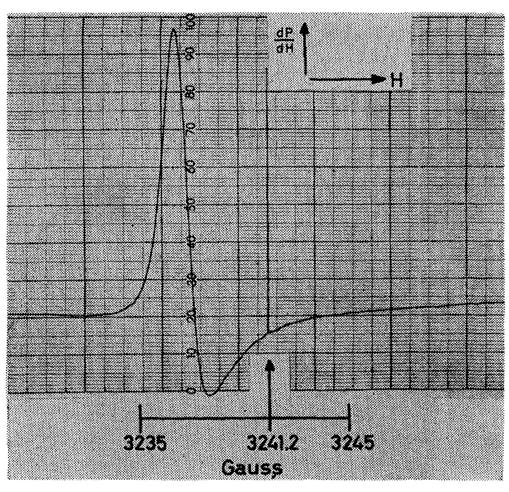

FIG. 1. The carrier spin-resonance line of a single crystal of graphite irradiated to 9.6×10^{18} *nvt* at 300°K for $H\|c$ and 9091 Mc/sec.

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[1] G. R. Hennig and J. E. Hove, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955*, (United Nations, New York, 1956), Vol. 7, pp. 666. Hereafter referred to as HH.

[2] W. Bollmann, J. Appl. Phys. **32**, 869 (1961).

[3] G. Wagoner, Phys. Rev. **118**, 647 (1960).

[4] Carried out at the Swimming Pool Reactor Saphir Würenlingen (Switzerland).

[5] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

[6] J. W. McClure, Phys. Rev. **112**, 715 (1958).

Elliott[7] pointed out that Δg is approximately given by

$$\Delta g \sim \lambda/\Delta, \qquad (1)$$

where λ is the spin-orbit coupling constant; and for $E_F \gg kT$ in (1), $\Delta = E_F$, where E_F has to be measured from the band edge for each type of carrier. Wagoner introduced in (1) for pure graphite $E_F^e = 200°K$ for electrons and compared this with his experimental values at 77°K. He did not consider the contributions of the two types of carriers which are opposite in sign. The number of holes is about equal to the number of electrons at 77°K and above.[6] The distance of the Fermi level from the top of the valence band E_F^h is comparable to the distance from the bottom of the conduction band E_F^e.[8] This should lead to a small g shift at low temperatures. At the higher temperature where E_F^e, $E_F^h \ll kT$, according to reference 7 one has to introduce into (1) $\Delta = kT$ for both types of carriers. This should again lead to no g shift if the electrons would contribute as much as the holes. Therefore, the mean hole contribution is greater than that of the electrons.

With irradiation, $\Delta g_{\parallel}$ decreases [Fig. 2(a)]. At 10^{19} *nvt* the number of carriers created (see Sec. V) exceeds the intrinsic value of holes or electrons by a factor of over 40. If donors were created even with the greater hole contribution to $\Delta g_{\parallel}$, a change of sign of the g shift at that dose might be expected. The asymptotic approach of $\Delta g_{\parallel}$ to zero can be easily explained by a lowering of the Fermi level into the valence band (growing of E_F^h). As we observed further a decrease of $\Delta g_{\parallel}$ by introducing $(HSO_4)^-$ acceptors electrolytically between the graphite layers, we conclude that acceptors are created by the neutron bombardment, in agreement with what HH[1] deduced from thermoelectric and Hall effect data on polycrystalline graphite.

IV. LINEWIDTH

The linewidth for pure graphite was found to be anisotropic and, for $H \perp c$, smaller than the isotropic one Wagoner reported for his chlorine-treated crystals. We therefore decided not to treat ours at all, since according to the g factor they must be as clean as his. We find, at 300°K, $\Delta H_{\parallel} = 4.6 \pm 0.2$ and $\Delta H_{\perp} = 3.0 \pm 0.2$ gauss. From this we conclude that the line at 300°K in pure graphite is not completely motionally narrowed, and one has to distinguish between the relaxation time T_1 and T_2. Probably T_1 is near the time one calculates from $\Delta H_{\perp}$, i.e., $T_1 \sim 2 \times 10^{-8}$ sec. With irradiation the asymmetry in the width decreases, probably the mean spread in g values gets smaller, and, at a dose of 10^{19} *nvt*, $\Delta H_{\perp} = \Delta H_{\parallel} = 1.3$ gauss [see Fig. 2(b)]. Now complete motional narrowing is present and $T_1 = T_2$.

We do not believe that the spin lattice relaxation time T_1 is determined by impurity content, as assumed by Wagoner. Rather, we find that a simple application of Elliott's[7] formula for T_1 due to carrier scattering via spin-orbit interaction,

$$T_1 \sim \tau_R / (\Delta g)^2, \qquad (2)$$

accounts for all observations. It might be thought that formula (2), deduced for the diamond lattice, can have at most a qualitative meaning in our case. As T_1 can be assumed to be isotropic, Δg has to be regarded as a mean

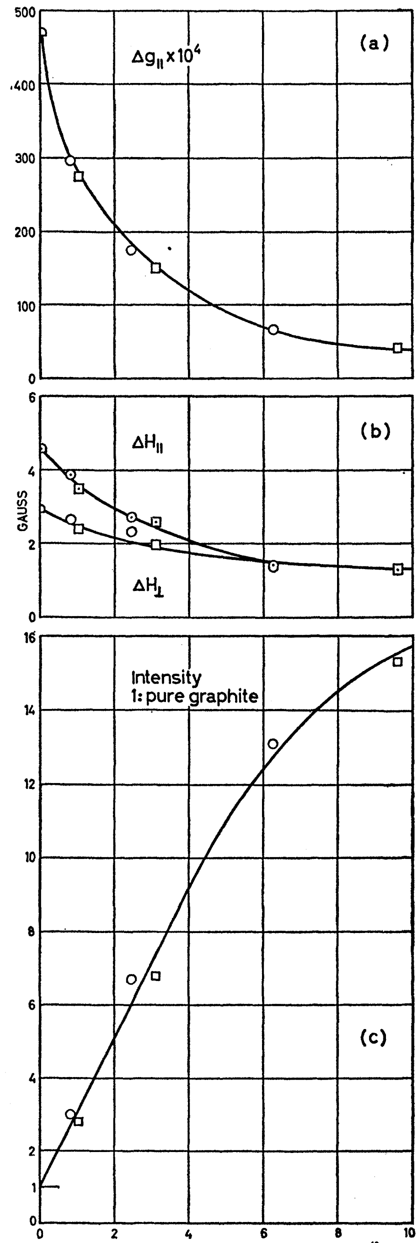

FIG. 2. (a) The g shift for $H \| c$, (b) the linewidths, and (c) the intensity of the spin-resonance line of graphite as a function of irradiation dose at 300°K.

[7] R. J. Elliott, Phys. Rev. **96**, 266 (1954).
[8] D. E. Soule and J. W. McClure, J. Phys. Chem. Solids **8**, 29 (1959), and Ph. Nozières, Phys. Rev. **109**, 1510 (1958).

value lying between $\Delta g_{\parallel}$ and $\Delta g_{\perp}$. We introduced as a first check $\Delta g_{\parallel}$ and $\Delta g_{\perp}$ for 300°K into (2) and found that T_1 should lie between 3×10^{-7} and 10^{-9}. This compares favorably with our previous estimate of T_1.[9] Secondly, for pure graphite, formula (2) accounts qualitatively for the line narrowing with increasing temperature. τ_R gets shorter, but $\Delta g_{\parallel}\propto 1/T$, and therefore T_1 gets longer as reported.[3] Thirdly, with irradiation at 300°K, $\Delta g_{\parallel}$ and $\Delta g_{\perp}$ decrease,[10] and again T_1 should increase, in agreement with our observation that *both* $\Delta H_{\perp}$ and $\Delta H_{\parallel}$ decrease. That T_1 is caused by the Elliott mechanism is once more supported by the narrowing of the isotropic line on cooling crystals irradiated to more than 5×10^{18} *nvt*, where $\Delta g_{\parallel}$ decreases slightly—a width of 0.9 gauss was observed at 90°K.

V. INTENSITY

As a measure of intensity, we used the amplitude of the derivative per unit base area times the square of the linewidth. The values for $H\|c$ and $H\perp c$ were the same within the experimental error. The mean value of both is plotted in Fig. 2(c) as a function of the irradiation. The unit is 1 for pure graphite. For the given doses the number of created carriers should be proportional to the dose. The departures from linearity for doses higher than 6×10^{18} *nvt* can be interpreted as a change in the skin depth δ_c and a shift in Fermi level.

From the slope and magnitude of the intensity at zero dose, where the change in skin depth and shift in Fermi level can be neglected, knowing the total number n_t for pure graphite to be $1.45\times10^{19}/\text{cm}^3$,[7,11] we obtain the mean number of holes created per cm³ by each *nvt* to be 30.[12] This compares well with the value of 23 (10^{-4} per C atom at 5×10^{17} *nvt*) obtained by HH[1] in comparing the electronic properties of irradiated polycrystalline graphite with graphite anodically oxidized in H_2SO_4. As the mean free path of a high-energy neutron in graphite is 3–4 cm, this gives us a mean value of 100–120 charge carriers created by each hitting neutron at 300°K.

[9] Wagoner followed a typographical error in reference 6, where (2) is printed as $T_1\sim\tau_R(\Delta g)^2$, and obtained a disagreement by a factor of 10^7.

[10] The change of $\Delta g_{\perp}$ with irradiation is found to be proportional to $\Delta g_{\parallel}$.

[11] Confirmed by spin resonance (see reference 3).

[12] After the present paper was completed, we found in Bull. Am. Phys. Soc. **6**, 129 (1961) that G. Wagoner has carried out a similar investigation. He obtained a value of 2.5×10^{18} acceptors per cm³ for 6×10^{16} *nvt* with energies higher than 1 Mev. It is reasonable to assume that the thermal neutron flux is higher. This yields for his samples less than 30 created acceptors per thermal *nvt* per cm³ and suggests that his irradiation was carried out at a higher temperature where stronger annealing takes place.

VI. COMPARISON WITH STRUCTURAL WORK

Bollmann,[2] in his recent dark-field transmission electron microscopy investigation, found black and white dots in graphite flakes irradiated to 10^{20} *nvt*. He advanced strong arguments that the black ones are "holes" (Brinkman spikes) burned in the layers by the high-energy release of primary or secondary carbon atoms, and the white dots are crystallized clusters between them. The spikes show diameters ranging from 60 A down to 10 A (the lower limit of resolution). Taking into account that the smaller events are slightly more frequent, a mean size of 25 A seems reasonable, which leads to an average of 200 displaced C atoms per event. HH[1] estimate from energy considerations that 50–100 carbon atoms are displaced per hitting neutron, which is somewhat lower than our estimate from Bollmann's work. As at 300°K half of the damage anneals out,[13] we are led to the conclusion that about as many acceptors are created as carbon atoms are displaced.

The model of HH was founded to some extent on a paramagnetic resonance investigation on neutron-irradiated polycrystalline graphite. The line found, of width $\sim$1 gauss, was interpreted as due to single interstitial carbon atoms. We have detected *no* other line than the conduction carrier resonance line. For high irradiation doses, the *g* value and the width of our line becomes isotropic and ΔH approaches 1 gauss. It seems likely that the line reported by HH is due to carrier resonance. The line narrowing they report on warming slightly irradiated samples from 77°K to 300°K might be understood as a change in anisotropic broadening by the temperature-dependent $\Delta g_{\parallel}$ value. In comparing their estimated number of displaced carbon atoms with their resonance line intensity, they came to the conclusion that only a small fraction of the displaced C atoms gave rise to paramagnetism in contrast to the present investigation. Because of the polycrystalline samples, the diffusion, and the skin effect, an underestimate seems to have been made.

ACKNOWLEDGMENTS

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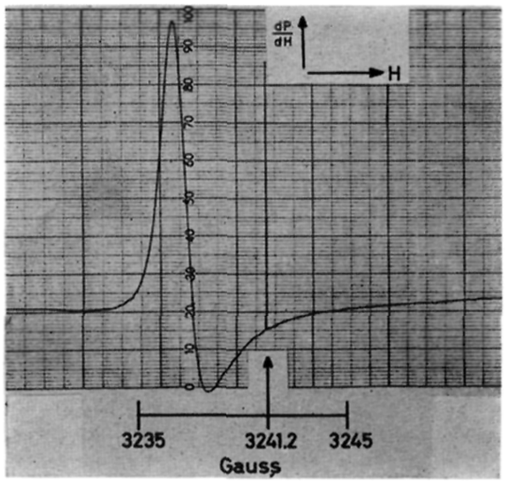
[13] D. T. Keating, Phys. Rev. **98**, 1859 (1955).



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