THE AMERICAN MINERALOGIST, VOL. 49, MARCH-APRIL, 1964

CRYSTALLOGRAPHIC IMPLICATIONS OF EPR IN NEUTRON-IRRADIATED DIAMOND[1]

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ABSTRACT

Diamonds irradiated with fast neutrons have been studied by electron paramagnetic resonance (EPR). The concentration of free spins and the line width of the signal have been studied as a function of total irradiation, before and after heat treatment. The signal intensity is proportional to total integrated radiation to 10^{18} nvt (fast). Over a thousand free spins are created for each primary neutron collision with a carbon atom. The EPR intensity decreases rapidly after heat treatment. The line widths are independent of radiation up to 10^{17} nvt, and they also decrease markedly after heat treatment. The EPR phenomena in irradiated diamond are quite different from those in graphite. It is suggested that highly irradiated diamond is a mosaic of microcrystals separated by a cement of damaged, amorphous, diamond-like glass. The conclusions of the EPR study support similar conclusions based on cleavage surface optical reflections and differential grinding hardness.

INTRODUCTION

It has been observed that fast neutron irradiation of diamond creates paramagnetic centers (Griffiths *et al.*, 1955). In the present study the concentration of paramagnetic centers and line widths were determined as a function of irradiation in a series of five stones, and the variation of these parameters was investigated after annealing at high temperature. The paramagnetic behavior has been related to changes in the crystallographic properties of the diamonds.

A fast neutron (energy greater than 1MeV) has far more than enough energy to dislodge a carbon atom in the diamond. The effective cross-section of a carbon nucleus to neutrons is 2.5×10^{-24} cm^2. In a cubical stone 1 cm on a side, the total cross-sectional area of the carbon nuclei will be 0.44 cm^2. Irradiation of small stones with a given number n of neutrons will produce roughly (0.44 n) primary collisions per cm^3 of diamond. A particular neutron is not likely to collide again, but the dislodged carbon atom has a large kinetic energy, and the cross-section of other carbons to a moving carbon atom is much larger. A cascade effect follows, which continues until the energy of the many dislodged carbon atoms is exhausted. Keating (1963) has shown that about 100 displaced

[1] Contribution No. 259 from the Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan.

carbon atoms result for each primary collision. The damaged region might be an elongated ellipsoid with major axis along the path of the neutron.

The total disorder in the damaged region is no doubt considerable. There may well be interstitital atoms, vacancies, microcrystalline structure changes, free electrons, holes and several other abnormalities. This paper is not concerned with the detailed nature of the damage site; the paramagnetism will be discussed as if it were essentially all due to unbound electrons.

A part, but not all, of the damage may be repaired by the annealing of the diamonds at high temperature.

Experimental Details

The five stones were irradiated at 300° K. to varying total amounts in a nuclear reactor. The resonance curves were obtained on a standard X-band EPR spectrometer (steady field $H_0 = 3000$ gauss; electron frequency $\nu_e = 9000$ Mc.) with 100 Kc modulation. Spectra were obtained at 300° K., 77° K. and 4° K. The stones were annealed in two stages at 400° C. and 600° C. for one hour at each stage.

The spin concentrations were determined by comparison of signal intensities for the stones with those of known amounts of diphenyl picryl hydrazyl (DPPH) and asphaltene. The peak height of the derivative curve multiplied by the square of the peak-to-peak line width was used as a measure of signal intensity.

Experimental Results

Generally speaking, the EPR spectrum of the irradiated diamonds shows a strong central peak and numerous much weaker satellites. The central line has a g-value of 2.00, but no effort was made to determine g-values to any significant accuracy. Originally, it was observed that the satellites were of symmetrical shape, but the central peaks were of a Dyson shape as in graphite (Wagoner, 1960; Müller, 1961). It was later noted that the spectrometer microwave bridge was thrown off balance by the temporary device used as a specimen holder (the spectrometer was designed for fluid and unconsolidated samples). Proper balance restored symmetry to the signals.

Central Line. The nominal total irradiation, and EPR spin concentrations at 300° K. deduced from the central peak are shown in Table I. The last column shows the apparent number N_c of free spins per collision before annealing

The very large spin concentrations produced by the irradiation are

noteworthy. An average 2000 free spins are produced for each primary collision, or about 20 for each displaced carbon. This indicates considerable secondary damage during the little chain reaction following the primary collision. Apparently many more than 100 carbons are significantly disturbed, although not seriously displaced during the local shower of moving carbon atoms following each collision. The production of free spins is 20 times greater for a given irradiation in diamond than in graphite (Müller, 1961). Perhaps the diamond is in effect more brittle, even on an atomic scale.

The spin concentration is proportional to the total radiation. The

TABLE I. EPR SPIN CONCENTRATIONS IN NEUTRON-IRRADIATED DIAMONDS, 300 ° K

Diamond	Nominal irradiation (nvt)	Observed spin concentration N, spins/cm³			Initial nominal spins per collision site N_c
		Initial	Annealed 400° C.	Annealed 600° C.	
A-1	10^{15}	2.0×10^{18}	3.0×10^{16}	5.0×10^{15}	3500
A-2	10^{16}	1.0×10^{19}	2.0×10^{17}	2.0×10^{16}	1800
A-3	10^{17}	0.4×10^{20}	0.7×10^{18}	1.0×10^{17}	600
A-4	10^{18}	1.0×10^{21}	1.0×10^{19}	1.0×10^{18}	1600
A-5	10^{18}	1.5×10^{21}	1.2×10^{19}	0.6×10^{18}	2500

proportionality carries through all stages of annealing; hence it can be concluded that all the signals observed are due to the damage, and not to the inherent EPR present in many nonirradiated stones (Smith *et al.*, 1959). No EPR curves were run on the stones before irradiation.

It has been suggested by Keating (1960) that the extent of damage in diamond may be used as an indicator of total integrated radiation. Radiation measurements based upon damage in diamond may be more accurate than those based upon other commonly used techniques. If EPR signals are a valid measure of total irradiation, then N_c, the number of free spins per collision, must be constant. The data in Table I show a variation of N_c from 600 to 3500, with an average of 2000. If the EPR signal be assumed as the measure of radiation, all nominal radiation values should be adjusted to agree with a standard value of N_c.

The observed changes in specific gravity (Keating, 1963) for stones A-4 and A-5 indicate that the total irradiation values for these stones are nearly correct. Accordingly, all collision-site concentrations N_{sc} were set at 2000, and the nominal radiation was adjusted to match. The corresponding new collision-site concentration and mean spacing between

TABLE II. ADJUSTED COLLISION-SITE CONCENTRATION N_{pc}, MEAN INTERSITE DISTANCE d_{pc}, AND ADJUSTED NUMBER OF SPINS PER COLLISION SITE N_{sc}, ALL AT 300° K

Diamond	N_{pc}	d_{pc} (Å)	N_{sc}		
			Initial	Annealed 400° C.	Annealed 600° C.
A-1	1.0×10^{15}	1000	2000	35	5
A-2	5×10^{15}	600	2000	40	4
A-3	1.5×10^{16}	400	2000	45	6
A-4	5×10^{17}	120	2000	20	2
A-5	7×10^{17}	100	2000	20	1

collision sites are given in Table II. Also presented is the adjusted number of free spins per collision-site, initially and after each annealing.

The normalization procedure makes all the data more self-consistent. It is seen that the number of spins per damage site is now equal for A-1, A-2, A-3 at any stage of annealing. The smaller number of spins per damage site in A-4 and A-5 suggests that there are more opportunities for deactivation of the electrons in a highly damaged crystal, a suggestion which is a reasonable possibility.

Table III shows the line widths ($2\Delta H$) for the central line after irradiation and after each stage of annealing. The line widths indicate that the individual damage sites in stones A-1, A-2, A-3 do not interact either initially or at either stage of annealing. The line width in each case arises entirely from within the damage site itself. The additional broadening for stones A-4 and A-5 arises from interaction between the electrons of several neighboring damage sites. The line widths for the unannealed diamonds compare fairly well with those observed by Griffiths *et al.* (1955).

It is of interest to calculate the additional line-broadening which would

TABLE III. LINE WIDTH OF EPR SIGNALS IN NEUTRON-IRRADIATED DIAMOND, 300° K.

Diamond	Line width $2\Delta H$ (gauss)		
	Initial	Annealed 400° C.	Annealed 600° C.
A-1	15	1.5	0.30
A-2	15	1.5	0.30
A-3	15	1.5	0.30
A-4	25	2.0	0.60
A-5	30	2.4	0.55

be expected from irregularly distributed dipoles in the observed concentrations. Abragam (1960) has given approximate formulas, valid for dilute concentrations.

$$\Delta H = 5\gamma \frac{h}{2\pi} N.$$

The semi line width, ΔH, is in gauss. The number of electrons per cm^3 is N. The electron gyromagnetic ratio is γ, and Planck's constant is h. For electrons, $\gamma h/2\pi$ is 1.85×10^{-20}. Roughly, then,

$$2\Delta H = 2 \times 10^{-19} N$$

Consider the initial spin concentrations in stones A-4 and A-5. If the electron dipoles were randomly distributed throughout the crystal, then,

$$2\Delta H = (2 \times 10^{-19})(1 \times 10^{21}) = 200 \text{ gauss.}$$

Of course, the paramagnetic dipoles are not randomly distributed but are distinctly clustered in the damaged region. If all the dipoles in one damage site were concentrated at one point, their effects would be added like a random walk, *i.e.*, as the square root of their number:

$$2\Delta H = (2000)^{1/2}(2 \times 10^{-19})(6 \times 10^{17}) = 5 \text{ gauss.}$$

The observed extra broadening above the inherent 15 gauss is 10 to 15 gauss. The dipoles are not in effect concentrated at one point, since the damaged region probably extends over a significant fraction of the intersite distance in these two stones. Keating (1963) calculates that about 10% of the diamond lies in the damaged region at 10^{18} nvt. Thus it would be expected that the line width would be greater, in accord with the completely random model.

For stone A-3, the extra inter-group broadening would be 0.2 gauss, which would not be observed on the 15 gauss line, and for A-1 and A-2 the extra broadening would be entirely negligible.

After the 400° C. annealing, stones A-4 and A-5 would have a calculated broadening of 0.5 gauss, compared to the observed 0.7 gauss; and after 600° C., a calculated extra broadening of 0.2 gauss, compared to the observed value 0.25 gauss. The random and clustered models agree quite closely in this case, because of the very few EPR centers per damaged region. The computed extra broadening for stones A-1, A-2, A-3 in both cases is again negligible, which agrees with the observations. The line width for A-1, A-2, A-3 after the 600° annealing is the same as observed (Smith *et al.*, 1959) for non-irradiated diamonds; this is apparently the lower limit for EPR line width in diamond.

It should be noted in passing that the initial spin concentration within the damaged regions themselves is so high that dipolar broadening would yield an intrinsic line width of the order of a thousand gauss. It appears,

then, that some form of motional or exchange narrowing is operative in the damaged region. This would be expected, since the electrons are only about 4 Å apart within the damaged region.

Hyperfine Structure. No serious attempt was made to characterize in detail the numerous satellite lines observed. All lines were symmetrically paired about $g=2.00$, and spectra with H_0 along the [100] and [110] directions yielded a number of lines which agree in their placement with those observed in non-irradiated stones (Smith *et al.*, 1959). The line widths and "spin concentrations" associated with a representative satellite line are summarized in Table IV.

Stone A-3 shows a markedly stronger hyperfine spectrum intensity

TABLE IV. APPARENT SPIN CONCENTRATION N_H AND LINE WIDTH 2 ΔH FOR A SELECTED HYPERFINE LINE, 300° K.

Diamond	N_H		2 ΔH (gauss)	
	Initial	Annealed 400° C.	Initial	Annealed 400° C.
A-3	1×10^{18}	1×10^{16}	8	2
A-4	1×10^{18}	1×10^{16}	8	2
A-5	4×10^{17}	6×10^{15}	8	2

with respect to the central line; this is no doubt due to a greater concentration of nitrogen and other impurities with magnetic nuclei (Smith *et al.*, 1959).

The hyperfine intensity declines with annealing in proportion to the central line. The correspondence suggests that the same paramagnetic entity is responsible for both the central line and the hyperfine structure.

The initial hyperfine line width is narrower than the central line, and in fact has roughly the line width computed as "extra broadening" for stones A-4 and A-5. This indicates that the EPR centers producing the satellite lines lie outside the main core of the damaged region. Within the core, exchange or motional narrowing would wipe out the hyperfine lines.

After annealing of the stones, the hyperfine line width is essentially the same as the central line, a fact which indicates that all EPR centers throughout damaged and intact parts of the crystal may be contributing. Exchange or motional narrowing effects are probably absent in the diluted system. Since damaged-region centers may now be included, it is seen that no simple quantitative conclusion can be drawn from the

preservation of the 1000:1 ratio of central line to hyperfine intensity before and after annealing. In fact, the maintenance of this correspondence in the face of possible additional hyperfine signals from the damaged region after annealing suggests that the nuclei responsible for the hyperfine lines act as preferred sites for the electron.

RF Saturation Effects. The signal amplitude and the line width of stone A-3 were measured as a function of microwave power after the 600° C. annealing. With maximum available power, the amplitude of the signal could be reduced to about 15% of the value expected if the signal were proportional to H_1. It was also observed that the line broadening to about 1.0 gauss under maximum power, which indicates homogeneous broadening for the central line itself.

No such effects were observed on the stones initially or after annealing at 400° C.

EPR Spectra at Low Temperature. Spectra were run in stone A-5 at 4° K., before annealing. The line width $2\Delta H$ of the central line was reduced to about five gauss, and the intensity was also greatly reduced. Another stone (D-1) irradiated to 10^{18} nvt showed a 5-gauss line at 4° K. A third stone (C-1), also irradiated to 10^{18}nvt, showed a 4-gauss line at 77° K.

No quantitative spin concentration measurements were attempted at low temperatures. It is clear, however, that most of the sources which are paramagnetic at 300° K. become inactive at 77° K. and below. A certain activation energy must be supplied, although, of course, it must not be so great that annealing takes place.

Discussion and Conclusions

It is instructive to compare irradiated diamond with graphite. First, the EPR signal shapes in diamond are symmetrical. Both pure and irradiated graphite show a shape which resembles a mixture of absorption and dispersion curves, resulting from the mixing of resistive and reactive signal components by the electrical skin effect. Graphite is a bulk conductor; diamond is not.

Second, the number of free spins produced by a given dose of neutron radiation is more than an order of magnitude greater in diamond than in graphite. This is probably due to the brittleness of the diamond. Any attempt to explain the change in specific gravity of irradiated diamond by postulating an appropriate amount of undamaged graphite (Wagoner, 1960) yields electron concentrations too low by a factor of 10,000.

Third, the EPR line width in irradiated diamond is independent of irradiation up to a certain level, and then it increases. The line width in

graphite decreases steadily with irradiation, because of increased motional narrowing for the more numerous mobile electrons (Müller, 1961). At no stage of irradiation does diamond show a line even approaching the narrow 1 to 4 gauss line observed in graphite.

Fourth, the line width in irradiated diamond decreases as temperature decreases. In pure graphite, the line width decreases as temperature increases (Wagoner, 1960).

It is concluded, then, that the damaged regions in diamond are not graphitic. The electrons are more firmly bound, and line-narrowing effects are probably of the spin-exchange type, rather than the motional type associated with conduction electrons. A probable structure in the damaged regions is an amorphous, diamond-like glass.

The EPR data support the notion of extensive damaged regions associated with each primary collision, separated by large blocks of undisturbed crystal. As the radiation exposure is increased, the damaged regions become more numerous, and the nearer ones interact magnetically. At 10^{18} nvt, the damage sites occupy an appreciable fraction (10%) of the volume of the crystal. The annealing phenomena suggest that the crystal may actually undergo additional damage in regions between sites, possibly due to stress fractures as the crystal expands to accommodate the damage sites. Further secondary radiation damage, of course, may favor previously weakened regions. These intersite damaged regions offer many additional opportunities for deactivation of paramagnetic electrons upon annealing. The totality of damage sites and intersite damaged regions make up an amorphous diamond-like cement between the mosaic blocks of less disturbed crystal.

The deductions based on paramagnetic resonance are quite consistent with results from studies of optical reflections and grinding hardness (Denning, 1962, 1963). The mosaic blocks could well approach a fraction of a micron in size, which would permit the reflections observed on cleaved surfaces. The introduction of random mosaic blocks and joints would also allow easy fracture of the crystal in directions other than the usual cleavages. The normal great anisotropy of grinding hardness would thus be diminished.

Acknowledgments

The investigation was partially supported by the U. S. Atomic Energy Commission. The diamonds, of excellent quality from Sierra Leone, were donated by the Consolidated African Selection Trust Company. The irradiation was done at Brookhaven National Laboratory. Professor C. Kikuchi obtained the low-temperature EPR spectra. Dr. D. D. Thomp-

son made a number of very helpful suggestions on EPR techniques. The writers express their thanks to all for making this study possible.

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Manuscript received, August 20, 1963; accepted for publication, October 18, 1963.