
SECTION C, PHYSICAL SCIENCES

Optical Absorption at 7.8 μ and Spin Resonance in Semiconducting Diamonds[1]

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INTRODUCTION

Semiconducting diamonds are usually found to be transparent to infrared radiation at 7.8 μ although some specimens of these diamonds have shown optical absorption at this wavelength (Clark et al., 1960; Bell, 1964). The electron spin resonance (ESR) spectrum in Type IIb diamonds has been found to consist of a single resonance line at $g = 2.0030 \pm 0.0003$ (Bell, 1964; Bell and Leivo, 1967). It is the purpose of this paper to discuss the nature of the defect in semiconducting diamonds in view of the optical absorption at 7.8 μ and the characteristics of the electron spin resonance absorption line.

EXPERIMENTAL PROCEDURE

Optical transmission and ESR measurements were made on four semiconducting diamonds. A complete description of the diamonds has been given previously (Bell and Leivo, 1967). Infrared transmission measurements were made at room temperature on diamonds DS-1, DS-2, DS-3, and DS-5 using a Beckman IR-7 spectrophotometer. The infrared optical properties of the diamonds are characteristic of Type IIb diamonds, i.e., absorption occurs at 2.43, 3.40, 3.56, and 4.07 μ. In addition, two of the diamonds show absorption at 7.5μ and 7.8 μ. Figure 1 shows the absorption of the diamonds in the 7.8 μ region. Since the diamonds are extremely rare it was considered undesirable to cut the specimens in order to obtain an accurate determination of the absorption coefficient at 7.8 μ; however, the differences in the 7.8 μ region are readily observable. A single ESR line was observed in all the semiconducting diamonds (Bell and Leivo, 1967).

Table I gives a summary of the results obtained on ESR as well as indicating the relative absorption at 7.8 μ. The quantities N_s, g and ΔH refer to the total number of unpaired spins, the g-factor and the line width of the ESR line, respectively. The g-factor was found to be iso-

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tropic and exhibited a positive shift with respect to the free electron value of 2.0023. Likewise, the line width of the resonance line did not change with crystal orientation but was found to vary for each specimen.

TABLE I. LINE WIDTH AND NUMBER OF UNPAIRED SPINS IN SEMICONDUCTING DIAMONDS.

Diamond	Line Width (ΔH) in gauss 298 K	140 K	Total Number of Unpaired Spins (N_s)	g	7.8 μ Absorption
DS-1	8.3	6.9	4.1×10^{14}	2.0028	ND
DS-2	2.7	2.0	5.1×10^{13}	2.0031	ND
DS-3 (a)	1.0	0.2	3.4×10^{13}	2.0030	W
DS-4	1.6	—	—	2.004	—
DS-5	0.3	—	—	2.0027	FS

(a) The line width of DS-3 is 1.8 gauss at 370 K

Notation: ND — not detected; W — weak; FS — fairly strong for semiconducting diamonds

DISCUSSION

The width of the ESR line varies from 0.3 to 8 oersteds at room temperature for five different semiconducting diamonds (See Table I). It was possible to obtain line width measurements at 140 K only on three of the five diamonds. The diamond DS-3 exhibits the largest spin-lattice contribution to the line width for the diamonds on which low-temperature ESR measurements were obtained. The diamond DS-3 also shows a slight infrared absorption at 7.8 μ. Likewise, the diamond DS-5 has a narrow ESR line of 0.3 oersteds and a fairly strong absorption at 7.8 μ. Unfortunately the large size of DS-5 prevented a quantitative measurement of the number of spins and the line width at low temperatures. The diamonds DS-1 and DS-2 have relatively broad ESR lines and no detectable absorption at 7.8 μ. Additional information from Hall measurements (Bell and Leivo, 1967) indicates a reasonably good agreement between the number of acceptors and the number of spins in diamonds DS-1 and DS-2.

Although any model at this time is speculative it is interesting to consider the possibility that the 7.8 μ infrared absorption is a measure of the degree of compensation occurring in these p-type diamonds. Thus, a stronger absorption at 7.8 μ would indicate a larger concentration of donors which could supply electrons for the compensation of acceptor centers. The occurrence of both acceptors and donors in the semiconducting diamond is consistent with Hall data (Leivo et al., 1962). If the ESR signal is associated with acceptors, then it would be expected that the spin resonance signal would decrease as the 7.8 μ absorption increased. Table I shows that this may be true for DS-1 and DS-3. Subsequent ESR and infrared measurements on other Type IIa diamonds show that the above intensity relationship holds for a single resonance line, i.e., as the 7.8 μ absorption increases the ESR signal decreases (very weak ESR signals were observed in the Type IIa diamonds).

If the spins responsible for the ESR absorption are uniformly distributed throughout the specimen, then the width of the resonance line cannot be due to the dipole-dipole interaction ($\Delta H_{d-d} < 0.1$ oersted). However, it is possible that the defects responsible for the acceptor levels in the diamonds lie in thin layers parallel to the (111) plane. Simple considerations of the line width indicate the acceptor density could be as high as 10^{20} - 10^{21} per cc in the impurity layers, with the thickness of a layer being of the order of 100-1000 A.

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