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Annealing Behavior of the 7070 Å Color Center and ESR Spectrum in Irradiated Naphthalene Crystals†

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Abstract—The annealing characteristics of the optical absorption at 7070 Å and the ESR spectrum in X-ray irradiated naphthalene crystals have been studied. The color center decays exponentially during isothermal annealing while the ESR spectrum exhibits a second order bimolecular decay. Thermal activation energies for the two decays are 1.1 ± 0.2 eV and 0.9 ± 0.2 eV, respectively.

1. Introduction

Recent reports by Akasaka *et al.*(1,2) show that certain optical absorption peaks in the spectra of irradiated organic crystals can be assigned to optical transitions of the radical responsible for the ESR spectrum, as previously suggested by Itoh and Okubo(3). For naphthalene crystals Akasaka *et al.*(2) report that the optical bands at 3800 Å and 5400 Å and the ESR spectrum have similar annealing behavior—exponential decay with an activation energy of 0.87 ± 0.06 eV. Furthermore, theoretical calculations by Hanazaki(3) of the energy levels of the hydronaphthyl radical which produces the ESR signal also support this interpretation.

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In addition to the absorption lines measured by Akasaka *et al.*, however, irradiated naphthalene has a prominent absorption line at 7070 Å.(4) Ringel *et al.*(4) reported that this absorption line also decayed exponentially during isothermal annealing with an activation energy of 1.0 ± 0.2 eV. Because of the similarity of this annealing behavior to that reported by Akasaka *et al.*,(2) a simultaneous study of the annealing kinetics of the 7070 Å center and the ESR spectrum in irradiated naphthalene crystals was undertaken. Although the ESR spectrum initially decayed approximately exponentially as reported by Akasaka *et al.*,(2) at long times a second-order decay process dominated, characteristic of bimolecular recombination. The 7070 Å absorption peak decayed exponentially with no evidence for second-order decay. Also, even though the activation energies for the decay of the ESR spectrum and the 7070 Å absorption line were similar, the actual rate constants differed by more than a factor of two in the temperature range employed. It can therefore be concluded that the 7070 Å absorption line and the ESR spectrum result from different defects.

2. Experiment

High purity naphthalene crystals were wrapped in Mylar foil to prevent sublimation and irradiated for 75 hr in the ports of a Phillips X-ray unit. A tungsten target was used with a 45 keV and a 20 mA beam. Samples for the ESR and optical measurements were annealed together so they would have almost identical thermal histories. The ESR measurements were made in an X-band spectrometer with a 100 kHz magnetic field modulation of 40 G to average out much of the hyperfine structure and give a large signal. Absolute spin concentrations were estimated from comparison with measurements of DPPH recrystallized from benzene. The optical absorption measurements were made with a Bausch and Lomb 0.5 m monochromator, tungsten lamp, and a silicon photodiode detector.

Three isothermal annealing experiments were made with pairs of samples annealed at 325, 335, and 344 °K. The annealing characteristics of the optical absorption line at 7070 Å and the ESR spectrum were quite different as shown in Fig. 1. In the right-hand graph in Fig. 1, the logarithm of the optical and ESR absorptions is plotted

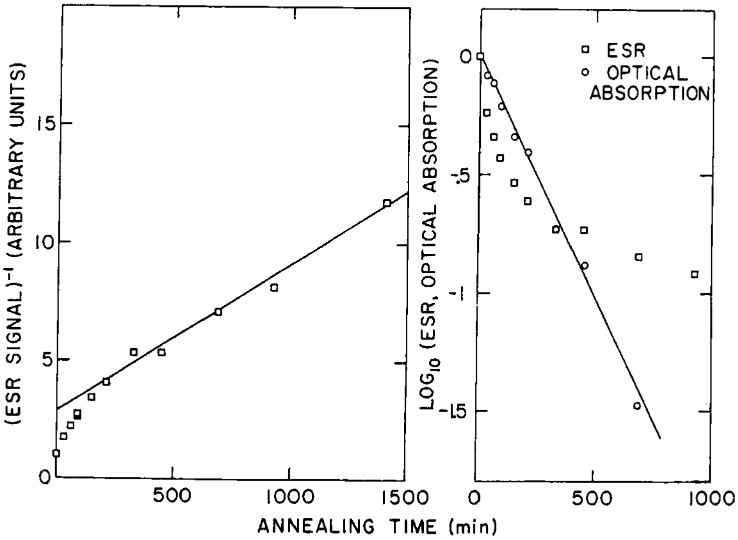

Figure 1. Isothermal annealing at 335 °K. The right-hand graph shows the logarithm of both the optical absorption at 7070 Å and the ESR signal versus annealing time. The left-hand graph shows the reciprocal of the ESR signal versus annealing time. The data in both graphs are normalized to their initial values.

as a function of annealing time at 335 °K. It is evident that the optical absorption line decays exponentially with annealing time while the ESR decay is more complicated. At first, the ESR decay is approximately exponential, as reported by Akasaka *et al.*(2) After the ESR signal has decayed to about one fifth of the original value, a second-order decay process is observed, with the reciprocal of the signal linear with annealing time. This second-order behavior is shown in the left-hand graph of Fig. 1, where the annealing results are plotted on a reciprocal scale versus time. During the decay the ESR spectrum did not appear to change other than in magnitude at the low resolution used so only one type of radical seems to contribute to the signal.

The annealing behavior at the other two temperatures was similar but with different rate constants. The rate constants for the first-order decay of the ESR signal and their thermal activation energies are given in Table 1. The behavior of the optical absorption line at 7070 Å is in good agreement with that reported previously by Ringel

TABLE 1 Rate Constants and Activation Energies for the 7070 Å Color Center and ESR Spectrum in Irradiated Naphthalene Crystals

Annealing temperature	Initial spin concentration	Second-order rate constant ESR spectrum	First-order rate constant 7070 Å color center
325 °K	9.8×10^{17} cm^{-3}	3.2×10^{-21} cm^{3}min^{-1}	1.3×10^{-3} min^{-1}
335 °K	7.2×10^{17} cm^{-3}	8.4×10^{-21} cm^{3}min^{-1}	4.7×10^{-3} min^{-1}
344 °K	1.4×10^{18} cm^{-3}	1.9×10^{-20} cm^{3}min^{-1}	1.2×10^{-2} min^{-1}
Activation energy		0.9 ± 0.2 eV	1.1 ± 0.2 eV

et al.(4) The activation energy for the decay of the ESR signal, 0.9 ± 0.2 eV, also is in agreement with that reported by Akasaka *et al.*(2) but the second-order decay at long annealing times was not observed by these authors. It is possible that their measurements did not extend to sufficiently small spin concentration for the second-order decay to be observed.

3. Discussion

Because the isothermal decay of the ESR spectrum at long times was of second-order while the absorption peak decayed exponentially, the spectra must have different origins. While the ESR spectrum has been shown to be due to the hydronaphthyl radical(2,3) the defect responsible for the 7070 Å line remains unidentified.

Since the form of the ESR spectrum was not observed to change with annealing, it is presumed that only one kind of radical contributes to the signal. The change in decay of the ESR spectrum from first-order to second-order at long times could be due to radicals generated in a non-uniform distribution—in pairs for example. Bimolecular recombination in such a case could produce an approximately first-order decay.(5) After these radicals have decayed, the remainder, presumably more uniformly distributed in the crystal, would recombine bimolecularly giving rise to the second-order decay observed at long annealing times.

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