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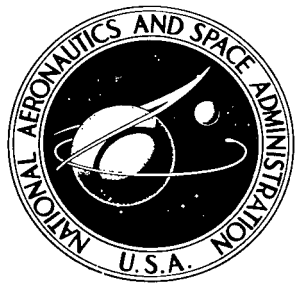

GROWTH KINETICS OF THE S_H CENTER ON MAGNESIUM OXIDE USING ELECTRON PARAMAGNETIC RESONANCE

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16. Abstract

Electron paramagnetic resonance spectroscopy was used to study the growth of S_H centers on magnesium oxide powder which had hydrogen adsorbed on its surface. The centers were produced by ultraviolet radiation (2537×10^{-10} m; 2537 Å). The effects of both radiation intensity and hydrogen pressure were also studied. At constant hydrogen pressure and radiation dose, the initial S_H center growth rate was found to be zero order. Beyond the initial region the growth rate deviated from zero order and finally approached saturation. The results are interpreted in terms of a model which assumes that the S_H center is a hydrogen atom associated with a surface vacancy. Saturation appears to result from a limited supply of surface vacancies.

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SUMMARY

Electron paramagnetic resonance spectroscopy was used to study the growth of S_H centers on magnesium oxide powder which had hydrogen adsorbed on its surface. The centers were produced by ultraviolet radiation (2537×10^{-10} m; 2537 Å). The effects of both radiation intensity and hydrogen pressure were also studied. At constant hydrogen pressure and radiation dose, the initial S_H center growth rate was found to be zero order. Beyond the initial region the growth rate deviated from zero order and finally approached saturation. The results are interpreted in terms of a model which assumes that the S_H center is a hydrogen atom associated with a surface vacancy. Saturation appears to result from a limited supply of surface vacancies.

INTRODUCTION

The electron paramagnetic resonance (EPR) technique has been used to study a wide variety of paramagnetic species on the surface of metal oxides (refs. 1 to 3). Such studies contribute to our understanding of important processes such as catalysis, chemisorption, and dissolution. Many of the paramagnetic species are produced by irradiation, by gas adsorption, or by a combination of the two.

One species that had attracted our attention (ref. 4) is the S' center formed by ultraviolet irradiation of magnesium oxide (MgO). It has been more recently named the S_H center by Tench and Nelson (ref. 5). They produced S_H centers by γ irradiation of MgO which had hydrogen gas adsorbed on its surfaces. They were also able to produce the S_D center by using deuterium gas instead of hydrogen. Tench and Nelson postulate that the S_H center is a proton associated with a surface F center. To explain the narrow EPR line width, they contend that the proton must be no closer than 4×10^{-10} meter (4 Å) to the unpaired electron.

This report presents our results on the growth kinetics of the S_H centers produced by ultraviolet radiation (2537×10^{-10} m; 2537 Å). The effects of intensity as well as hydrogen pressure were investigated. The data are interpreted in terms of the Tench and Nelson model, and a mechanism for the production of the S_H center is postulated.

EXPERIMENTAL APPARATUS AND PROCEDURE

Materials

The MgO was prepared from reagent grade powder. The powder was first boiled in distilled water for several hours and converted magnesium hydroxide ($Mg(OH)_2$). It was then evaporated to a paste, extruded into pellets (1-mm diam) with a hypodermic syringe, and dried. Subsequent operations were carried out in a quartz tube (2-mm i.d., 4-mm o.d., and 160-mm length). The top end was blown into a spherical reservoir (1.7 cm^3 volume) for containing the hydrogen gas. The pellets of MgO (0.12 g) were placed in the lower portion of the tube to a height of 5 centimeters. Only the lower centimeter was actually measured in the EPR apparatus, but the excess sample was deemed useful in scavenging traces of oxygen (present in the cover gas) which would act as a poison. The pellets in the tube were then degassed at 850° C under a vacuum of 10^{-5} torr for several hours. After the sample was cooled to room temperature, high-purity hydrogen at a known pressure was added and the sample tube sealed. The hydrogen pressures used ranged from 150 torr (10^{19} molecules) to 0.05 torr.

Irradiation

The MgO sample was irradiated with a low-pressure mercury-vapor lamp which produces a strong 2537×10^{-10}-meter (2537-Å) line of 62 microwatts per square centimeter at 45.7 centimeters. The sample tube was rotated at 200 rpm to achieve as nearly as possible uniform ultraviolet penetration. The quartz tube and atmosphere had negligible attenuation on the 2537×10^{-10}-meter (2537-Å) line. Preliminary runs were made to determine the range of exposure and distances required.

To study the growth kinetics, the number of S_H centers (as measured by EPR) was recorded as a function of irradiation time. For the sample with 150 torr of hydrogen, studies were made at four radiation intensities: 1.6×10^{13}, 10.5×10^{13}, 3.24×10^{14}, and 5.77×10^{14} photons per second for the 1-centimeter length of sample. The different intensities correspond to different distances between the sample and the radiation source: 45.7, 17.8, 10.16, and 7.6 centimeters, respectively. Prior to the start of

each different intensity study, the sample was heated to 400° C for a time sufficient to reduce the S_H center concentration to below the limit detectable in the EPR spectrometer.

Electron Paramagnetic Resonance Measurements

The EPR spectra were obtained for each irradiated sample using a conventional spectrometer operating at about 9.3 gigahertz and with a dual sample cavity of TE_{104} mode. A first derivative spectrum of the S_H center with good resolution is shown in figure 1. The shape and g value verify the spectrum to be that for the Tench and Nelson S_H center. For convenience, all our measurements were made with greatly "overmodulated amplification" to enclose all the spins in a curve shape more closely resembling the calibration standard, pitch in potassium chloride. The overmodulation also allowed measurements over a wider range of spin concentrations. The number of spins was calculated from the formula $I = KWH$, where I is the intensity, K is the curve correction, W is the width (peak to peak), and H is the height. The standard pitch curve was very similar to the S_H curve except that it contains an additional 20 percent of the spins in the wings. Thus K_{sample} was taken as 0.8 K. The pitch sample contained 3×10^{15} spins per 1-centimeter length. We estimated that the absolute error in the number of spins (number of S_H centers) in our sample was about ±30 percent.

RESULTS AND DISCUSSION

Preliminary Experiments

In preliminary experiments we found that some S_H centers initially have a fast decay rate. For example, in a freshly prepared sample the centers produced by an initial radiation of a few seconds decayed by about 20 percent after 15 minutes, 30 percent after 4 hours, and 34 percent after 12 hours. When this sample was annealed at 400° C, the remaining centers were destroyed. A subsequent second irradiation produced a smaller fraction of fast decaying S_H centers; only 10 percent decayed after 15 minutes. An additional anneal followed by another irradiation resulted in a further reduction in the number of fast decaying centers; only 2 percent decayed in 15 minutes. An explanation for the changing decay rate results was not obvious from the experiments performed, but we speculate that a nonequilibrium condition of the surface initially existed and this was eventually equilibrated by sufficient annealing. At any rate, the

preliminary experiments served as a conditioning treatment for the sample, and this made it unnecessary to correct the growth curves for simultaneous decay of the centers.

Growth Curves Interpreted in Terms of a Mechanism

The spin growth curves at 150 torr are plotted in figure 2 as a function of time. Their general appearance is typical of other growth curves with a rapid buildup finally approaching saturation. In figure 3, the initial portion of one of the curves (45.2-cm distance between lamp and sample) is plotted. The linear dependence of the number of S_H centers on time indicates zero-order kinetics. This zero-order kinetics is also indicated by the initial slope of unity on all the log-log plots in figure 2.

We believe the initiating reaction is the dissociation of a hydrogen molecule by a photon:

$$H_2(gas) + h\nu \rightarrow 2H\cdot(gas) \tag{1}$$

It should be noted that the energy of the photon (2537×10^{-10} m; 2537 Å) is not sufficient to cause ionization, or vacancy formation. If reaction (1) were the initial rate-controlling step, the rate would be proportional to the hydrogen pressure. However, in our experimental setup the hydrogen gas was in large excess, and thus the hydrogen pressure remained essentially constant during the reaction and gave rise to the pseudo-zero-order kinetics which we found.

The initial growth rate for the curve in figure 3 can be calculated to be 3.2×10^{11} spins (S_H centers) per second for a 1-centimeter length of sample. The radiation dose rate used to obtain this curve (45.7 cm between lamp and sample) was 1.6×10^{13} photons per second for the 1-centimeter length. Because two S_H centers can be produced for each photon, the radiation efficiency was thus about 1 percent in the initial portion. The efficiencies for all the curves in figure 2 are similar in magnitude. The low efficiency can be due to incomplete photon absorption by the hydrogen, the short lifetime of the hydrogen atoms, or a combination of the two. If there is incomplete absorption of the photons, one would expect the initial rate (and thus photon efficiency) to vary with the hydrogen pressure. Experimentally this was found to be true, as is discussed in the section Effect of Hydrogen Pressure.

The effect of the short lifetime of the hydrogen atoms would be that only those hydrogen atoms formed immediately adjacent to a MgO surface would be expected to be adsorbed. The reaction is represented by

$$H\cdot(gas) \rightarrow H\cdot(adsorbed) \tag{2}$$

The actual formation of the S_H center arises from the surface diffusion of the adsorbed hydrogen atom to a surface anion vacancy:

$$H\cdot\text{(adsorbed)} + \text{surface anion vacancy} \rightarrow S_H \qquad (3)$$

As time proceeds in the growth process (fig. 2), it appears that the initiating reaction is no longer the rate-controlling step because the kinetics deviate from zero order. This is reasonable because the surface vacancies are being used up and cause reaction (3) to slow down and affect the overall rate of the reaction. If this is a true picture, the number of spins (S_H centers) at saturation may be equal to the original number of surface anion vacancies. From figure 2, this number is about 3.5×10^{15} for the 1-centimeter length of sample (0.024 g). The surface area of the sample as determined by the Brunauer-Emmett-Teller method is about 170 square meters per gram (ref. 4) or 4 square meters (4×10^{20} Å^2) for the sample measured. This corresponds to about 5×10^{19} anion sites on the surface of MgO. The ratio of surface anion vacancies to surface sites would then be about 1 to 14 000; we believe this is not an unreasonable value.

Effect of Dose Rate

In figure 4, the growth curves have been normalized by plotting the number of S_H centers as a function of radiation dose rather than of time. To calculate the radiation doses for the various distances between the sample and the lamp, we made use of the inverse square law. The data for the various distances are essentially superimposable. The reproducibility of the curve indicates that no significant irreversible changes occur on the surface of the MgO sample; for example, an important point is that our ultraviolet radiation obviously does not generate new surface vacancies. Furthermore, the fact that the four curves in figure 2 can be superimposed in figure 4 indicates that the growth rate is proportional to the dose rate.

Effect of Hydrogen Pressure

Figure 5 presents growth rate curves at two hydrogen pressures, 15 and 150 torr, with equal irradiation rates. The general appearance of both curves is the same. As expected, the initial slope of the 15-torr curve is essentially 1 (on the log-log plot), which indicates again zero-order kinetics. However, the initial rate at 15 torr is approximately only 1/10 of that at 150 torr. Thus, it appears that the rate of reaction (1) is indeed roughly proportional to the hydrogen pressure. This indicates (as mentioned previously) incomplete absorption of the photons by the hydrogen gas, which gives rise

to low photon efficiency. Note that the photoefficiency for our system is 0.1 percent at 15 torr as compared with 1.0 percent at 150 torr.

The final feature to observe in figure 5 is the saturation values of S_H centers. It is essentially the same for both pressures, that is, about 3.5×10^{15} spins. This lends credence to our belief that the saturation value at high pressures is limited by the number of surface anion vacancies and not by available hydrogen. In contrast, a third sample where we used a hydrogen pressure of 0.05 torr gave a saturation value of 1×10^{15} for the number of S_H centers. At this low pressure, only about 1.4×10^{15} atoms of hydrogen were available. Thus, it appears that at relatively low pressures, the hydrogen can limit the number of S_H centers.

SUMMARY OF RESULTS

We have shown by electron paramagnetic resonance that ultraviolet radiation can produce S_H centers on magnesium oxide (MgO) containing adsorbed hydrogen (H_2). The growth curves show an initial linear buildup of S_H centers; at longer periods of time saturation is approached. The initial rate is pseudo-zero-order; it is, however, proportional to the radiation flux and roughly proportional to the hydrogen pressure. The saturation value of S_H centers is independent of radiation flux and hydrogen pressure (when in excess). The ratio of the number of S_H centers to anion sites is 1 to 14 000 at saturation.

The mechanism we propose for the formation of S_H centers consists of three reactions:

$$H_2(\text{gas}) + h\nu \rightarrow 2H\cdot(\text{gas})$$

$$2H\cdot(\text{gas}) \rightarrow 2H\cdot(\text{adsorbed})$$

$$H\cdot(\text{adsorbed}) + \text{surface anion vacancy} \rightarrow S_H$$

The initial rate-controlling step appears to be the first reaction.

Our study supports the model for the S_H center proposed by Tench and Nelson: a proton associated with a surface F center. However, our mechanism for its formation was likely quite different from theirs. The γ radiation they used would have given rise to vacancy production as well as ionization of the hydrogen.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 1, 1971,
114-03.

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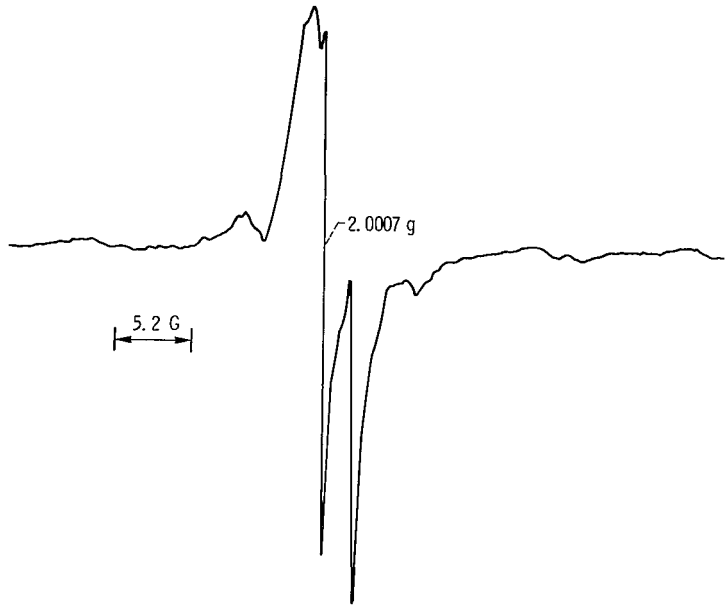

Figure 1. - High-resolution EPR spectron of S_H center. Modulation amplitude equivalent to 2-gauss width.

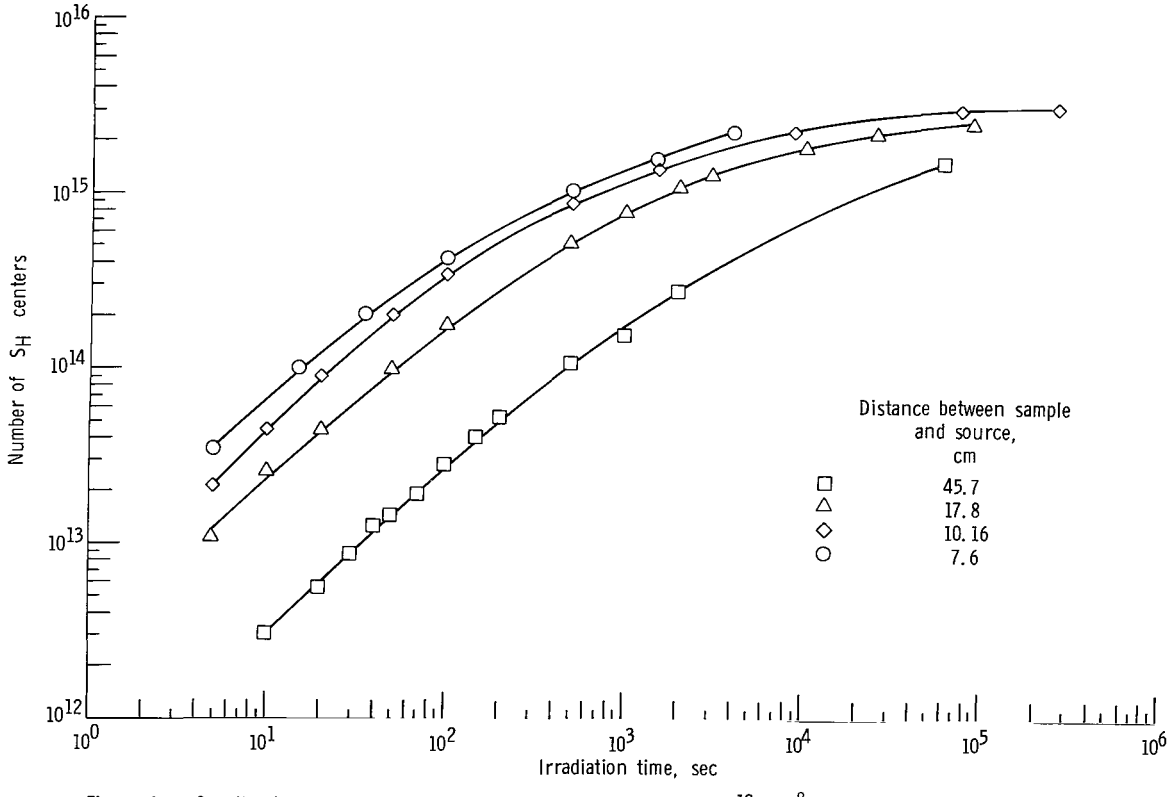

Figure 2. - Growth of S_H centers on MgO under ultraviolet (2537×10^{-10} m; Å) irradiation. Hydrogen pressure, 150 torr; number of S_H centers based on 1-centimeter length of sample.

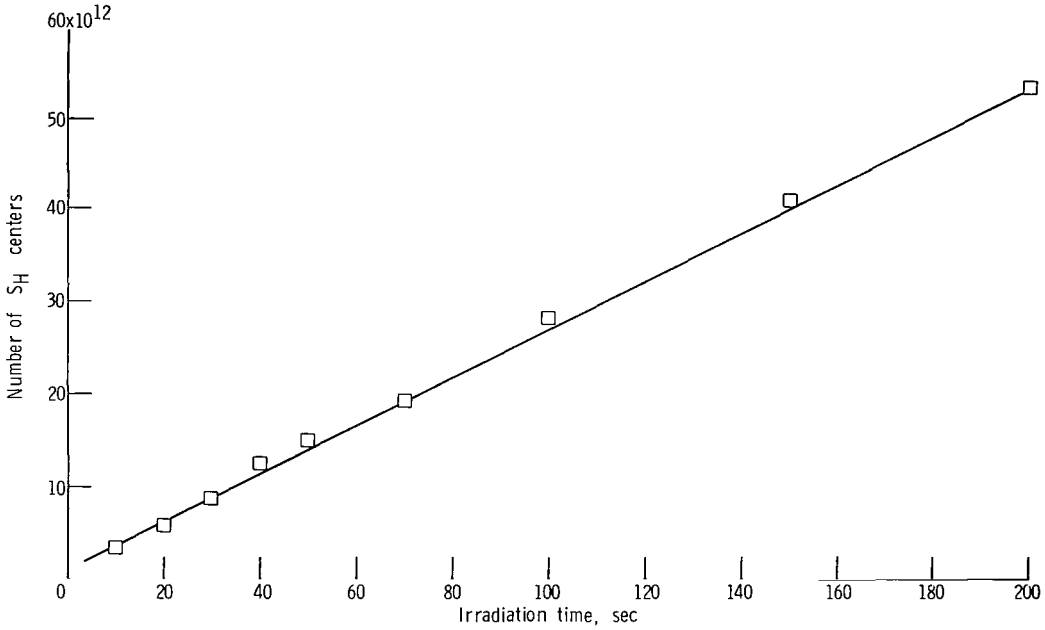

Figure 3. - Number of S_H centers as function of irradiation time on linear plot. Hydrogen pressure, 150 torr; distance between sample and source, 45.7 centimeters; number of S_H centers based on 1-centimeter length of sample.

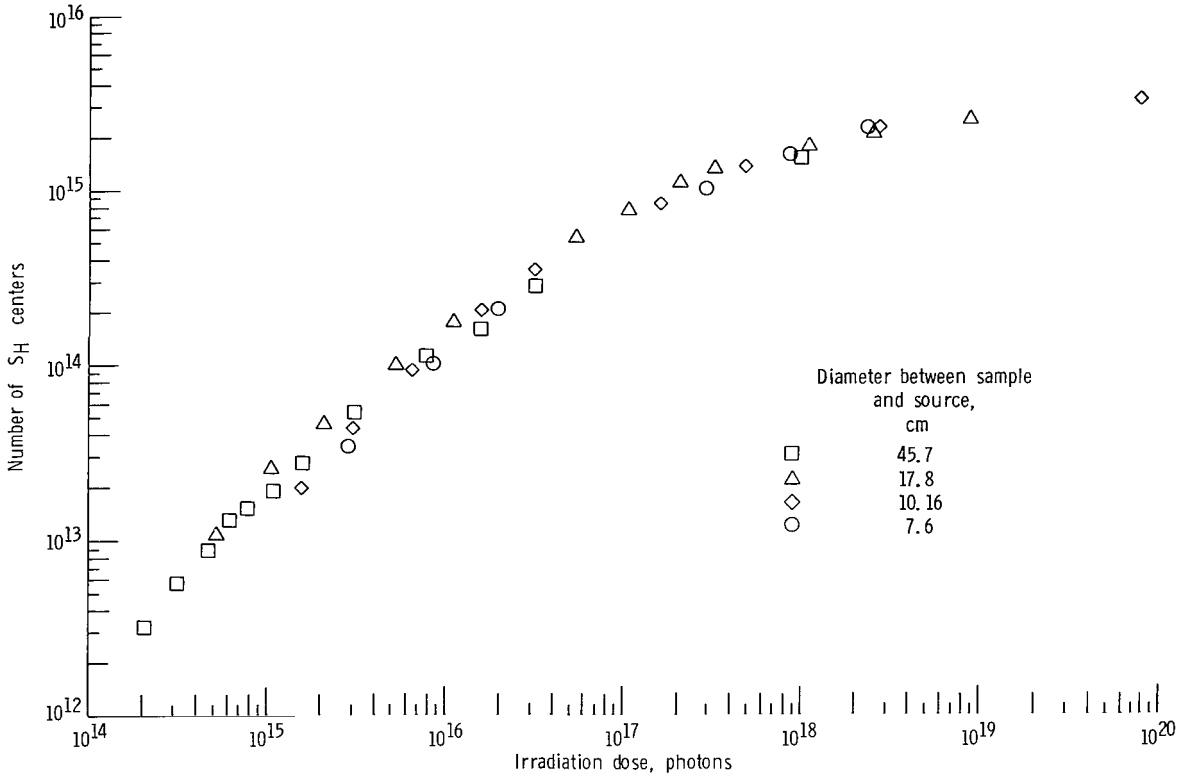

Figure 4. - Normalized growth curve for S_H center on MgO. Hydrogen pressure, 150 torr; 2537×10^{-10}-meter (2537-Å) radiation; number of S_H centers based on 1-centimeter length of sample.

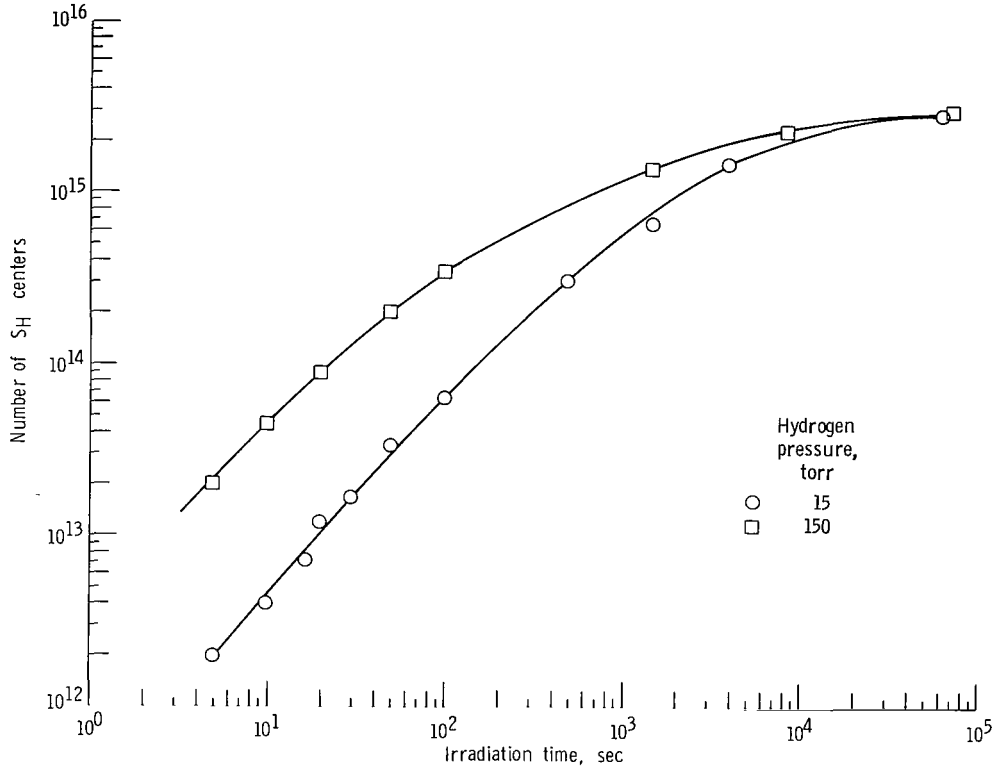

Figure 5. - Growth curves of S_H centers on MgO at two hydrogen pressures. Distance between source and sample, 10.16 centimeters; 2537×10^{-10}-meter (2537-Å) radiation; number of S_H centers based on 1-centimeter length of sample.

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