

material). Hence, it too can be neglected. [There will actually be an electron-hole generation region, just inside the surface, with  $(\phi_p - \phi_n)$  positive, followed by a recombination region, with  $(\phi_p - \phi_n)$  negative.]

For  $p$ -type bulk material (still assuming  $j_v=0$ ), the quasi-Fermi level variations, at least for electrons, will not be negligible when  $u_s \gtrsim u_b$  and the methods used in Sec. 7 will not apply. Here, there must be an electron-hole generation region, the electrons diffusing towards the surface and then being emitted while the holes diffuse away from the surface, towards the bulk region. For a sufficiently high value of  $j_e$ , the carrier generation may have to be enhanced by avalanche carrier multiplication.

Next, the case of predominant electron emission from the valence band will be considered. Here, there will be a recombination region near the surface. For  $p$ -type bulk material only, this is followed by a generation region. The expression for  $j_v$  will only be affected by the Fermi energy for the hole distribution at the surface if it is

degenerate. The only situation where this is likely to occur is for an initially degenerate  $p$ -type surface with a sufficiently high density of surface states to prevent appreciable field penetration. If this is associated with a  $p$ -type bulk region,  $\Delta\phi_p$  should be negligible as was  $\Delta\phi_n$  for the case of predominant conduction band emission from  $n$ -type material.

For those cases where the separation between the electron and hole Fermi levels at the surface is negligible (i.e., no net generation or recombination), they will also coincide with the Fermi level for surface states, provided there is no appreciable field emission from the surface states.

The probability that an electron in a surface state, incident on the surface barrier, be emitted is approximately given by Eq. (1) with  $\psi$  suitably defined. However, to compare the probabilities, per unit time, for field emission and emission into the conduction or valence bands, requires some knowledge of the surface-state wave functions.

## Magnetic, Thermal, and Optical Properties of the $F$ Center in $\text{NaH}^{\dagger*}$

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Thermal and optical bleaching and microwave saturation effects on the isotropic resolved electron paramagnetic resonance hyperfine structure of the  $F$  center in  $\text{NaH}$  have been studied. The results indicate that the thermal bleaching is a monomolecular process with an associated activation energy  $\epsilon_F = 0.38$  ev. A model similar to the print-out effect in silver halides is proposed for the bleaching mechanism. The wavelength of maximum optical absorption is 3.22 ev. The value of the characteristic spin relaxation time  $(T_1 T_2)^{\frac{1}{2}}$  is  $1.7 \times 10^{-9}$  second. The  $g$  value for the  $F$ -center electron is  $2.0025 \pm 0.0003$ .

### I. INTRODUCTION

THE resolved isotropic hyperfine structure of the electron paramagnetic resonance absorption of  $F$  centers in  $\text{NaH}$  was recently observed.<sup>1</sup> This paper reports the results of further measurements of the properties of this  $F$  center. Section II describes the experimental details. The results of thermal bleaching measurements, discussed in Sec. III, indicate that the  $F$ -center destruction is a monomolecular process. The thermal activation energy for this process is determined and a model involving the growth of colloidal sodium is proposed which is similar to the print-out effect in silver halides. Section IV is a description of the optical

bleaching measurements which give a value for  $\lambda_0$ , the wavelength of maximum optical absorption. An order of magnitude result for the characteristic spin relaxation time  $(T_1 T_2)^{\frac{1}{2}}$ , obtained from saturation measurements, is given in Sec. V. The  $F$ -electron  $g$  value, determined using the Breit-Rabi equation to second order, is given in Section VI. Section VII is a brief summary of the results.

### II. EXPERIMENTAL

All the measurements described here were made using a conventional superheterodyne paramagnetic resonance spectrometer employing phase-sensitive detection. The microwave frequency is approximately 9.1 kMc/sec. The sample cavity is rectangular and operates in the  $TE_{101}$  mode. The dc magnetic field is modulated at 560 cps. The microwave frequency was measured with a cavity wavemeter calibrated against  $WV$  using a frequency multiplier. The magnetic field

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<sup>1</sup> W. T. Doyle and W. L. Williams, Phys. Rev. Letters 6, 537 (1961).

strength was measured with the standard Hopkin's autodyne<sup>2</sup> proton resonance apparatus.

For the thermal bleaching measurements the cavity was sealed with a condom and immersed in a water bath at the various temperatures of observation. The temperature, measured with a thermocouple, remained constant for approximately two hours.

The optical bleaching measurements were made using a grating spectrometer with mercury and tungsten sources. The samples were colored in the cavity and the resonance absorption signal was observed. They were then illuminated for one hour at various wavelengths and the absorption signal again observed. The relative intensities of the bleaching wavelengths were determined using a chopper, thermistor bridge, and 10-cps amplifier.

For the saturation measurements the power on the detector of the i.f. strip was maintained at a constant level by adjusting an attenuator in the output arm of the *T* bridge to compensate for the change in power incident on the bridge, controlled by an attenuator in the input arm. The power incident on the cavity was measured with a thermistor bridge.<sup>3</sup>

The samples were commercial NaH powder. For all the experiments the samples were x-rayed for thirty minutes in the cavity. On irradiation the normally grayish-white powder becomes brownish. The bottom half of the cavity containing the sample was sealed with a quartz window during optical illumination and with cellulose tape during x irradiation as was the cavity coupling hole during the microwave runs. This prevents reaction of the hygroscopic NaH with atmospheric water vapor.

As reported earlier,<sup>1</sup> the NaH exhibited a strong resonance absorption signal which is attributed to con-

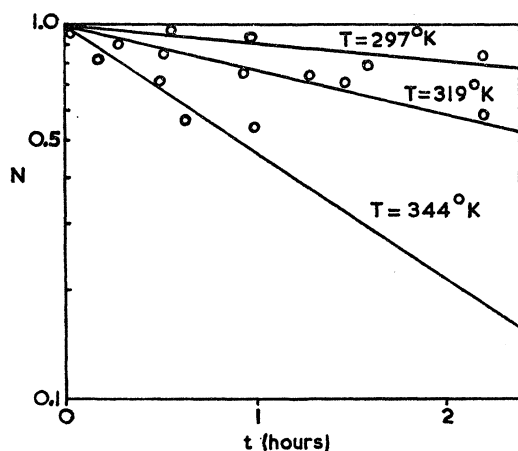


FIG. 1. Relative *F*-center concentration in NaH as a function of time at 297°, 319°, and 344°K.

<sup>2</sup> E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1955), p. 51.

<sup>3</sup> G. P. Harnwell, *Principles of Electricity and Electromagnetism* (McGraw-Hill Book Company, Inc., New York, 1949), 2nd ed., p. 174.

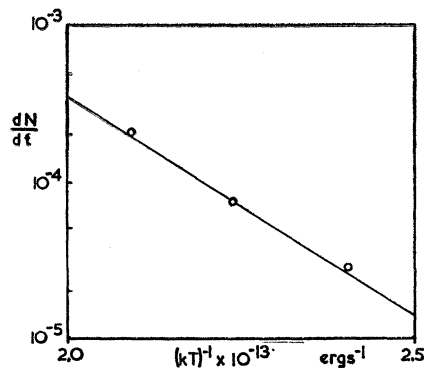


FIG. 2. Relative rate of change of *F*-center concentration in NaH as a function of  $(kT)^{-1}$ .  $\epsilon_F$  is the thermal activation energy for the monomolecular process.

duction electrons in colloidal sodium. The measured *g* value of  $2.0020 \pm 0.0004$ , and the Dysonian<sup>4</sup> shape and temperature independence of the signal are in agreement with the results of Feher and Kip.<sup>5</sup> Since the signal was constant under all the present experimental conditions it was used as a check on the stability of the apparatus throughout the course of the experiments.

### III. THERMAL BLEACHING

The thermal bleaching rate of the *F* centers in NaH was measured at 297°K, 319°K and 344°K. The paramagnetic resonance absorption signal, which is proportional to the *F*-center concentration, was observed as a function of time at each temperature. The results, normalized to the signals from the unbleached samples, are shown in Fig. 1. From these data the relative rate of change of *F*-center concentration as a function of  $(kT)^{-1}$  was determined. This result, shown in Fig. 2, indicates that the thermal bleaching can be interpreted in terms of a monomolecular process with an associated activation energy given by the slope of the line in Fig. 2. This activation energy is  $\epsilon_F = 0.38$  ev. This value may be compared with the value of 0.61 ev for KCl.<sup>6</sup> The *F* center in NaH, as in LiH which coagulates to form colloidal lithium at room temperature,<sup>7</sup> is also less stable than in the halides.

The monomolecular process proposed as the bleaching mechanism is quite similar to the print-out effect in silver halides.<sup>8</sup> It is well known<sup>9</sup> that metallic azides

<sup>4</sup> F. J. Dyson, *Phys. Rev.* **98**, 349 (1955).

<sup>5</sup> G. Feher and A. F. Kip, *Phys. Rev.* **98**, 337 (1955).

<sup>6</sup> E. E. Schneider, *Photographic Sensitivity* (Butterworths Scientific Publications, Ltd., London, 1951).

<sup>7</sup> W. T. Doyle, D. J. E. Ingram, and M. J. A. Smith, *Proc. Phys. Soc. (London)* **74**, 540 (1959).

<sup>8</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 227.

<sup>9</sup> W. E. Garner and I. Maggs, *Proc. Roy. Soc. (London)*, **A172**, 299 (1939); P. W. M. Jacobs and F. G. Tompkins, *Proc. Roy. Soc. (London)*, **A215**, 254 (1952); H. G. Heal, *Can. J. Chem.* **31**, 91, 1153 (1953); H. G. Heal, *Trans. Faraday Soc.* **53**, 210 (1957).

subjected to x rays or uv undergo photochemical decomposition accompanied by evolution of nitrogen gas and growth of metallic colloid at room temperature. Bach and Bonhoeffer<sup>10</sup> found that photodecomposition with evolution of hydrogen gas occurs when LiH is irradiated with uv. Their measured quantum yield of 5% indicates that hydrogen gas is trapped in the lattice. The release of gas indicates that a process similar to the print-out effect takes place during irradiation.

These results suggest the following model as the thermal bleaching process in NaH. During x irradiation electrons are ejected from anions into the crystal. This leaves a neutral H atom which moves through the crystal until it combines with another H atom to form H<sub>2</sub> which moves to the crystal surface and is released or is trapped in the crystal. This process leaves anion vacancies with which the freed electrons combine to form *F* centers. When the colored crystal is heated the *F* centers are ionized and an anion vacancy remains. Provided that the number of other types of traps is small, the electrons will be trapped by colloidal sodium present in the crystal. The metal colloid thus becomes negatively charged and reacts with the nearest neighbor metal ions resulting in its growth. The remaining anion vacancies can combine with cation vacancies.

Previous thermal bleaching measurements on<sup>11</sup> NaCl and<sup>6</sup> KCl showed a period of fast bleaching followed by a period of slow bleaching. The results for NaCl could not be analyzed in terms of a monomolecular process although those in KCl could be interpreted in terms of two monomolecular processes. Coagulation processes also occur in alkali halides although only under extreme conditions such as intense visible illumination at elevated temperatures<sup>12</sup> or neutron irradiation.<sup>13</sup> Since

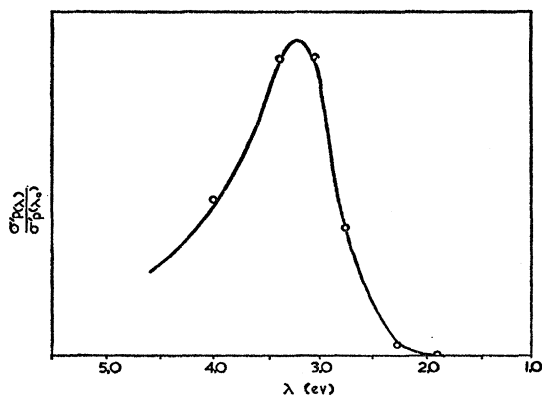


FIG. 3. Optical absorption band of *F* centers in NaH.  $\sigma_P'(\lambda)$  is a measure of the optical density.

<sup>10</sup> F. Bach and K. Bonhoeffer, Z. physik. Chem. **B23**, 256 (1933).

<sup>11</sup> I. L. Mador, R. F. Wallis, M. C. Williams, and R. C. Herman, Phys. Rev. **96**, 617 (1954).

<sup>12</sup> W. T. Doyle, Proc. Phys. Soc. (London) **75**, 649 (1960).

<sup>13</sup> P. J. Ring, J. G. O'Keefe, and P. J. Bray, Phys. Rev. Letters **1**, 453 (1958).

the capture cross section of an anion vacancy for an electron is much greater than the corresponding cross section of a metal colloidal particle, such a process can occur only if the metal is relatively more stable than the *F* center under the influence of a source of ionization.

In general, bleaching mechanisms for *F* centers in alkali halides are undoubtedly very complicated. It is possible, however, that the process can be interpreted in the simple manner described above for NaH. This model would not give the fast and slow bleaching curves as in NaCl and KCl since there is essentially no limit on the size to which the colloid can grow.

#### IV. OPTICAL BLEACHING

It has been shown<sup>11</sup> that if *F* electrons are transferred to the conduction band during optical bleaching, then in the limiting case when the capture cross section of a vacancy for a conduction electron is small the rate of change of *F*-center concentration is given by

$$dN/dt = -\sigma_F I N, \quad (1)$$

where *N* is the local *F*-center concentration, *I* the local intensity of bleaching light and  $\sigma_F$  the cross section for optical decomposition of an *F* center. For short times the bleaching can be described by

$$1 - N_F/N_0 = q\sigma_P I t, \quad (2)$$

where *N*<sub>0</sub> and *N<sub>F</sub>* are the initial and final *F*-center concentrations, *q* is the quantum efficiency (usually taken as unity) and  $\sigma_P$  is the *F*-center photon absorption cross section. The cross section  $\sigma_P = \sigma_P(\lambda)$  is finite for any wavelength lying within the optical absorption band and has a maximum at the center of the band. The relative intensities of the bleaching wavelengths divided by the corresponding optical energies, *hν*, give the relative number, *n<sub>P</sub>*, of photons incident on the sample at the various wavelengths. Thus,

$$\sigma_P'(\lambda) = \frac{(1 - N_F/N_0)}{n_P t}, \quad (3)$$

where

$$\sigma_P'(\lambda)/\sigma_P(\lambda) = hc/\lambda.$$

It was realized during the course of the experiment that considerable thermal bleaching occurred simultaneously with the optical bleaching. To the same approximation it is assumed that the thermal bleaching follows an equation of the form of (2) and that the two bleaching processes act independently. In this case

$$\left(1 - \frac{N_{FO}}{N_0}\right) = \left(1 - \frac{N_F}{N_0}\right) - \left(1 - \frac{N_{FT}}{N_0}\right) + 1, \quad (4)$$

where  $(1 - N_{FO}/N_0)$ ,  $(1 - N_{FT}/N_0)$ , and  $(1 - N_F/N_0)$  are the relative number of *F* centers destroyed optically and thermally and the relative total number of *F* centers destroyed, respectively.

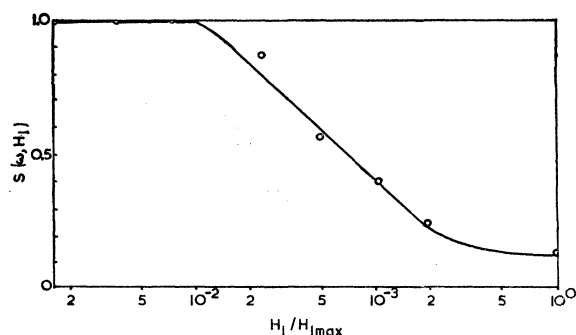


FIG. 4. Saturation parameter,  $S(\omega, H_1)$ , as a function of  $H_1/H_{1\max}$ .

Since the paramagnetic resonance signal is proportional to the *F*-center concentration, the values of  $(1 - N_F/N_0)$  were easily determined. Combining these results with the thermal bleaching data at 297°K, the values of  $(1 - N_{FO}/N_0)$  were used to determine  $\sigma_P'(\lambda)/\sigma_P'(\lambda_0)$  as shown in Fig. 3, where  $\lambda_0$  is the wavelength of maximum absorption. Measurement of  $\sigma_P'(\lambda)$  corresponds to measurement of the optical density. The value of  $\lambda_0$  is 3.22 eV. This can be compared with the value of 3.41 eV as calculated from Ivey's<sup>14</sup> empirical rule using Zintl and Harder's<sup>15</sup> value of 2.44 Å for the lattice spacing. Upon completion of this work it was found that Johnson<sup>16</sup> had observed the optical *F* band in NaH using thin films. The value of  $\lambda_0$  obtained here is in good agreement with his value of 3.43 eV.

It is not felt that the precise shape of the *F* band in Fig. 3 is meaningful due to the presence of thermal bleaching. The resemblance to the bell-shaped *F* band is reassuring, however, and the half-width of 0.95 eV is in fairly good agreement with the value of 0.8 eV for LiH,<sup>17</sup> although it may be too large. The agreement with Johnson indicates that the coloring due to x irradiation and the resulting paramagnetic resonance absorption, which supports the de Boer<sup>18</sup> model, is indeed due to the *F* center in NaH.

## V. ELECTRON SPIN RELAXATION TIME

The effect of variations in microwave power level on the paramagnetic resonance absorption signal of the NaH *F* center indicates that the width of the signal is due to inhomogeneous broadening. This has been treated thoroughly by Portis.<sup>19</sup> One result is that in the saturation region the imaginary part of the paramagnetic susceptibility,  $\chi''(\omega, H_1)$ , is proportional to  $1/H_1$ , where  $\omega$  is the microwave frequency and  $H_1$  is the

amplitude of the microwave magnetic field in the cavity. Since the detected absorption signal is proportional to  $\chi''H_1^2$ , then it should behave as  $H_1$  or the square root of the incident power. Figure 4 shows the results obtained for the saturation parameter  $S = \chi''(\omega, H_1)/\chi''(\omega, 0)$  as a function of  $H_1/H_{1\max}$  where  $H_{1\max}$  is the maximum value of  $H_1$ . As can be seen the results are in agreement with the theory of inhomogeneous broadening.

It was assumed that  $\omega_m T_1 < 1$ , where  $\omega_m$  is the frequency of the external modulation field and  $T_1$  is the electron spin relaxation time. This corresponds to slow-passage resonance and is equivalent to Portis's<sup>19</sup> case 1. For this case the saturation parameter is given by

$$S(\omega, H_1) = 1/(1 + \frac{1}{4}\gamma^2 H_1^2 T_1 T_2), \quad (5)$$

where  $\gamma$  is the gyromagnetic ratio and  $(T_1 T_2)^{1/2}$  is the characteristic spin relaxation time. Figure 5 shows  $\log_{10}(1/S - 1)$  vs  $\log_{10}(H_1/H_{1\max})^2$  for *F* centers in NaH. The intercept for  $H_1 = H_{1\max}$  is  $\log_{10}(\frac{1}{4}\gamma^2 H_{1\max}^2 T_1 T_2)$ . The value of  $H_{1\max}$  was calculated from the formula<sup>19</sup>

$$H_1^2 = 32\pi Q_u(1 - \Gamma^2)P/\omega V,$$

where  $Q_u$  is the unloaded cavity *Q*,  $\Gamma^2$  the cavity reflection coefficient, and  $V$  the cavity volume.

The value of  $(T_1 T_2)^{1/2}$  obtained from the intercept is  $1.7 \times 10^{-6}$  second. This can be compared with Portis's<sup>19</sup> value for KCl of  $7.6 \times 10^{-6}$  sec and the value for KI of  $106 \times 10^{-6}$  sec calculated from Noble's<sup>20</sup> data. This differs from the reported value which was calculated using Portis' case 4 which is not applicable under our experimental conditions.

The assumption made in applying Portis' case 1 is that the time of passage through a "spin packet"<sup>19</sup> is long compared to  $(T_1 T_2)^{1/2}$ . As the spin packet widths have not been determined directly, it is felt that the values of  $(T_1 T_2)^{1/2}$  are correct only to order of magnitude.

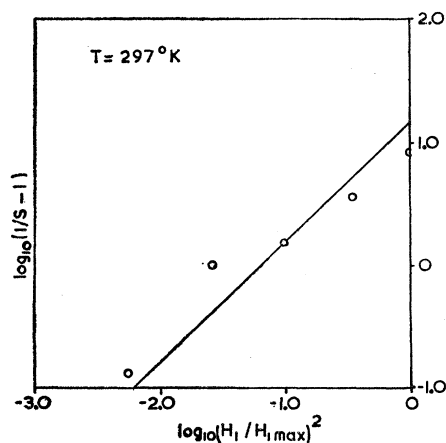


FIG. 5.  $\log_{10}(1/S - 1)$  versus  $\log_{10}(H_1/H_{1\max})^2$ .  $(T_1 T_2)^{1/2}$  is the characteristic electron spin relaxation time.

<sup>14</sup> H. F. Ivey, Phys. Rev. 72, 341 (1947).

<sup>15</sup> E. Zintl and A. Harder, Z. physik. Chem. B14, 265 (1931).

<sup>16</sup> F. Johnson, Columbia Radiation Laboratory Progress Report, 1955 (unpublished), pp. 30-35.

<sup>17</sup> F. E. Pretzel and C. C. Rushing, J. Phys. Chem. Solids 17, 332 (1961).

<sup>18</sup> J. H. de Boer, Rec. trav. chim. 56, 301 (1937).

<sup>19</sup> A. M. Portis, Phys. Rev. 91, 1071 (1953).

<sup>20</sup> G. A. Noble, J. Chem. Phys. 31, 931 (1959).

VI. *F*-ELECTRON *g* VALUE

It was previously reported<sup>1</sup> that the *g* value for the *F*-center electron in NaH was  $1.9979 \pm 0.0004$ , obtained using the Breit-Rabi<sup>21</sup> equation to second order and  $I=9$ , the maximum value of the first-shell spin. Lewis and Pretzel<sup>22</sup> have pointed out that this takes into account only 19 of the total 4096 possible first-shell nuclear spin states. It is actually necessary to average over all the total spin states,  $I$ , corresponding to a given value of  $\sum m_I$ . The weights of these states with total shell spin  $I$  are most simply obtained by taking differences of the successive weights of these states with given values of  $\sum m_I$ .<sup>23</sup> Lewis and Pretzel<sup>22</sup> have also shown that equivalent results are obtained if one works in the representation  $M_s, m_1, \dots, m_6$ .

This correction has been made giving a value of  $g = 2.0025 \pm 0.0003$  which, within the experimental error, is the free electron value. This value is obtained assuming that the centers of mass of the hyperfine peaks and the peak positions coincide. This is not exactly correct since the individual peaks are broadened due to the fact that each value of  $I$  has a slightly different correction term and the corresponding values of  $I(I+1)$  are weighted differently. An exact determination is quite formidable even with computer fitting, however, and no attempt was made to go beyond the simple weighted mean correction.

<sup>21</sup> G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

<sup>22</sup> W. B. Lewis and F. E. Pretzel, J. Phys. Chem. Solids **19**, 139 (1961).

<sup>23</sup> This result has also been obtained by Hughes and Allard to whom we are indebted for a preprint of their work on the cesium halides.

On the basis of a more complete table of calculated shapes it is now believed that the resolved hyperfine absorption curve is best fitted with  $2\sigma$  (rms width of the Gaussian hyperfine peaks)  $= 1.37 \pm 0.1$ . This gives a value for  $A(2)$ , the second-shell hyperfine interaction energy, of  $5.6 \pm 0.2$  gauss and a value of  $|\psi(2)|^2$ , the modulus of the *F*-electron wave function at the second-shell hydrogen nuclei, of  $0.24 \times 10^{23} \text{ cm}^{-3}$ .

## VII. SUMMARY

Thermal bleaching measurements of the *F* centers in NaH indicate that the bleaching is a monomolecular process with an associated activation energy of 0.38 ev. This process can be described qualitatively in terms of a model similar to the print-out effect in silver halides. The maximum of the NaH optical *F* band, as determined from optical bleaching data, is at 3.22 ev in agreement with previous results. The characteristic spin relaxation time  $(T_1 T_2)^{1/2} = 1.7 \times 10^{-6}$  second, in order-of-magnitude agreement with the value for KCl. The corrected *F*-electron *g* value is  $2.0025 \pm 0.0003$ .

## ACKNOWLEDGMENTS

The author wishes to thank Professor W. T. Doyle for his suggestions and encouragement during the course of this work. He would also like to acknowledge Professor A. Pytte for enlightening discussions of the Breit-Rabi equation. Finally, he thanks R. W. Hargraves and the Dartmouth Computation Center for calculating the curves with which the resonance absorption curve was fitted.