

Measurement of F -Center Concentration and Relaxation Time by Microwave Faraday Rotation*

D. T. TEANEY, W. E. BLUMBERG,[†] AND A. M. PORTIS

Department of Physics, University of California, Berkeley, California

(Received January 27, 1960)

The use of a bimodal cavity for the observation of electron spin resonance is described. The two samples of NaCl containing F centers used by Blumberg are investigated by electron spin resonance. Their F -center concentrations are found to be 4.4×10^{17} and 2.3×10^{18} electrons/cm³, respectively. The spin-lattice relaxation time at room temperature of the F -center electrons is found to be 1.7 microseconds.

INTRODUCTION

WE describe the use of a bimodal cavity¹ for the observation and comparison of absorption and dispersion signals in electron spin resonance. Application is made to the F -center resonance in NaCl. The two samples employed in the study of nuclear relaxation by F -center electrons² are investigated. We describe the determination of both the F -center concentration and spin-lattice relaxation time.

The method used is similar in principle to the method first used by Silsbee³ since both depend on the paramagnetic properties of F centers for their detection. Silsbee's method relies on the resonant absorption of microwave power by the precessing electrons in a cavity having a single resonant mode. The method herein described utilizes the transfer of power from one mode to the other of a bimodal cavity by the precessing electrons. Since these methods depend on the same physical property of the F -center, they have approximately the same ultimate sensitivity. However the fact that the bimodal cavity as used here has a stability much greater than that attainable for a microwave bridge as used by Silsbee gives this method a decided experimental advantage.

BIMODAL CAVITY

The bimodal cavity used here is similar to one developed for microwave Faraday rotation studies on semiconductors⁴ but has been modified by moving the entrance iris from the end of the cavity to the top. This change makes it possible to place a magnetic sample at the end of the cavity without seriously affecting the coupling to the cavity. The equivalent circuit theory already developed¹ may be applied without alteration to the present cavity. This theory relates the elements of the microwave susceptibility tensor to the variation in power P_2 coupled through the cavity as a function of

magnetic field. In practice the cavity is first adjusted so that no power is coupled through the cavity; thus the cavity modes are completely degenerate. Power is then coupled through the cavity by lifting this degeneracy either by a perturbation of the frequency match of the two modes or by a perturbation of the amplitude balance of the modes. The former type of unbalance is accomplished by inserting a metal plug oriented at 45° with respect to the direction of the waveguides, thereby lifting the degeneracy in the reactance of the normal modes along and perpendicular to the direction of the plug. We call this a reactive unbalance of the cavity. By increasing this unbalance in coupled power, $P_{2, \max}$ is ultimately reached. The latter type of unbalance is accomplished by inserting a resistive plug at 45° with respect to the direction of the waveguides, thus reducing the Q of the cavity mode along the direction of the plug, leaving the transverse mode unaffected. We call this a resistive unbalance of the cavity. With reactive unbalance the equivalent circuit analysis yields for the fractional variation in power coupled through the cavity

$$\frac{\delta P_2}{P_2} = -8\pi f Q_0 \frac{\omega}{\omega_0} \frac{\cot \theta}{[(1+\beta_1)(1+\beta_2)]^{\frac{1}{2}}} \chi'' \quad (1)$$

With resistive unbalance, we obtain

$$\frac{\delta P_2}{P_2} = +8\pi f Q_0 \frac{\omega}{\omega_0} \frac{\cot \theta}{[(1+\beta_1)(1+\beta_2)]^{\frac{1}{2}}} \chi', \quad (2)$$

where we have assumed that only a small fraction of the incident power is coupled through the cavity and that the magnetic resonance perturbs the cavity modes only slightly, so that $\delta P_2/P_2 \ll 1$. The quantities β_1 and β_2 are the voltage standing wave ratios in the input and output lines, respectively. The angle θ is defined in terms of the ratio of the power coupled through the cavity to the maximum power that may be coupled through the cavity: $\theta = \frac{1}{2} \sin^{-1}(P_2/P_{2, \max})^{\frac{1}{2}}$. The factor ω/ω_0 is the ratio of oscillator frequency to γH_0 , the Larmor precessional frequency, and f is the filling factor.

MEASUREMENT OF CONCENTRATION

The concentration of F centers in the samples employed in the preceding paper has been determined from

* Supported in part by the Office of Naval Research, the National Security Agency, and the U. S. Atomic Energy Commission.

[†] Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

¹ A. M. Portis and Dale Teaney, *J. Appl. Phys.* **29**, 1692 (1958).

² W. E. Blumberg and E. L. Hahn, *Bull. Am. Phys. Soc.* **3**, 318 (1958), and W. E. Blumberg, preceding paper [*Phys. Rev.* **119**, 1842 (1960)].

³ R. H. Silsbee, *Phys. Rev.* **103**, 1675 (1956).

⁴ A. M. Portis, *Proceedings of the International Conference on Semiconductors* [*J. Chem. Phys. Solids* **8**, 326 (1959)].

a measurement of the variation in coupled power on resistive unbalance. The microwave parameters may all be measured directly, and the sample filling factor f in Eqs. (1) and (2) is determined experimentally, as described below. This makes it possible to determine χ'' , the imaginary part of the microwave susceptibility. In the absence of saturation, χ'' for a Gaussian⁵ line is

$$\chi'' = [(\pi)^{1/2} \omega_0 / 2\Delta\omega] \chi_0 \exp[-(\omega - \omega_0)^2 / \Delta\omega^2]. \quad (3)$$

The static susceptibility is given by

$$\chi_0 = N \frac{g^2 \mu_B^2 S(S+1)}{3kT} = 2.08 \times 10^{-27} N, \quad (4)$$

at room temperature, so that we are ultimately led to the concentration of paramagnetic centers.

The samples were rectangular in shape, 0.8 cm × 0.8 cm × 0.4 cm for a volume of 0.26 cm³. In order to preserve cylindrical symmetry, the sample formed the central part of a slab of NaCl 0.4 cm thick which completely covered the end wall of the cavity. The frequency of the empty cavity was 9560 Mc/sec. With the slab of NaCl in place, the frequency was lowered to 8190 Mc/sec. The NaCl slab could not be considered as a perturbation of the cavity modes so that a calculation to obtain the average microwave field in the volume of the sample was not practical. Thus an experiment was made to determine this average by use of the microwave Faraday rotation caused by a sample of known susceptibility. For this purpose, a single crystal of CuSO₄·5H₂O was cut to the same size as the NaCl samples containing the F centers and placed in the NaCl slab in the same position.⁶ Since the dielectric constant of copper sulfate (7.8) is not far different from that of sodium chloride (6.12), it was assumed that the field configuration would be approximately the same for both samples. This assumption is strengthened by the fact that the change in frequency upon changing from the NaCl to the CuSO₄·5H₂O samples was only 20 Mc/sec. If the cavity were to be operated in the same manner as for the relatively dilute F -center samples, the large number of spins in the CuSO₄·5H₂O would give such a large absorption signal that the restrictions in $\delta P_2/P_2$ in Eqs. (1) and (2) would be violated. Therefore, we tuned the cavity to give a circularly polarized microwave field. In this case, the spins cause absorption when the external magnetic field is in one direction but not when it is in the other.

⁵ A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. **91**, 1066 (1953).

⁶ We could have used small samples imbedded in a slab of pure NaCl, following the procedure of Silsbee. However, since the number of spins in the full-size copper sulfate crystal could be measured more accurately and since the Faraday rotation of this crystal could easily be measured in the bimodal cavity, it was more advantageous to use the method described above. Of course, a conventional microwave bridge³ cannot handle the absorption from a full size paramagnetic crystal of this sort and the former method of calibration must be used for that apparatus.

To observe this phenomenon, the condition,

$$\csc 2\theta = -\frac{1}{2} \left(\frac{1+\beta_1}{1+\beta_2} \right)^{1/2} + \frac{1}{2} \left(\frac{1+\beta_2}{1+\beta_1} \right)^{1/2}, \quad (5)$$

must be satisfied. Then, at the center of the resonance line, the absorption signal is

$$\frac{\delta P_2}{P_2} = -8\pi f Q_0 \chi_0 \frac{\omega}{\Delta\omega} \frac{\csc 2\theta (1 + \cos 2\theta)}{[(1+\beta_1)(1+\beta_2)]^{1/2}}. \quad (6)$$

If β_1 and β_2 are nearly equal, we have $\csc 2\theta \cong 1$, and we may write

$$\frac{\delta P_2}{P_2} \cong -\frac{8\pi f Q_0 \chi_0 \omega}{\Delta\omega [(1+\beta_1)(1+\beta_2)]^{1/2}}. \quad (7)$$

From the observed strength of the absorption signal and the known static susceptibility of CuSO₄·5H₂O, $\chi_0 = 1.34 \times 10^{-5}$ cm⁻³, we obtained experimentally that the ratio of the average microwave power in the sample to the average power in the cavity was 9.8 times the ratio of the volume of the sample to the volume of the cavity, giving a value of 0.226 for the filling factor f .

To measure the F center concentration, the dispersion signal was observed in order to avoid anomalous saturation effects.⁷ Equation (2) was used to compute χ' from the microwave parameters.

For the low concentration sample, observations were made with $P_2/P_{2, \max} = 2.7 \times 10^{-4}$. A change in transmitted power of 0.0092 at the dispersion peak was observed. We obtain for the microwave parameters $\beta_1 = 0.16$, $\beta_2 = 0.05$, $Q_0 = 4200$. We calculate from Eq. (2) the maximum value of the dispersion, $\chi_{\max}' = 3.36 \times 10^{-9}$. The form of the dispersion curve associated with a Gaussian absorption has been given by Pake.⁸ Reading from his curves, we expect a peak absorption 1.65 times the peak dispersion, or $\chi_{\max}'' = 5.55 \times 10^{-9}$. Taking the root mean square width of the absorption from F centers in NaCl to be 69 oersteds or 193 Mc/sec, we obtain for the static susceptibility from Eq. (2),

$$\chi_0 = (8/\pi)^{1/2} (\Delta\omega/\omega_0) \chi_{\max}'' = 9.12 \times 10^{-10} \text{ cm}^{-3}. \quad (8)$$

Finally, by comparison with Eq. (4), we obtain $N = 4.4 \times 10^{17}$ electrons/cm³. In the same way, the concentration of the second sample was determined to be 2.3×10^{18} . The concentration ratio, which may be compared with the results of the preceding paper, is 5.2.

MEASUREMENT OF RELAXATION TIME

The spin-lattice relaxation time is determined from a comparison of the relative strength of absorption and dispersion signals and a calculation of the microwave field within the cavity. It has been shown that the line width of the F -center resonance arises from inhomogeneous

⁷ A. M. Portis, Phys. Rev. **91**, 1071 (1953).

⁸ G. E. Pake and E. M. Purcell, Phys. Rev. **74**, 1184 (1948).

geneous broadening.⁷ In this case, there is negligible coupling between spins,⁹ and we expect that the ratio of the peak absorption signal to the peak dispersion signal will be

$$\chi_{\max}''/\chi_{\max}' = 1.65/(1+\gamma^2 H_1^2 T_1^2)^{1/2}. \quad (9)$$

The klystron employed for these measurements, a Varian VA-6315/V-153, delivered 130 mw to a matched load as measured with a microwave bolometer. The actual power absorbed by the cavity is

$$P_a = [4\beta_1/(1+\beta_1)^2]P_0. \quad (10)$$

In this experiment we measured $\beta_1 = 0.16$ giving an absorbed power of 62 mw. The energy stored in the cavity may be calculated from the relation,

$$U = Q_0 P_a / \omega. \quad (11)$$

Under the experimental conditions, this amounts to 0.050 erg or, taking the cavity volume to be 11.1 cm³, the average energy density within the cavity is 4.5×10^{-3} erg/cm³. The magnetic energy density within the sample

⁹ P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

is larger than this by a factor of 9.8, as we have seen from the determination of the sample filling factor. Then, taking the energy density at the sample to be

$$(1/8\pi)(2H_1)^2 = 0.044 \text{ erg/cm}^3, \quad (12)$$

we compute $H_1 = 0.53$ gauss. At this level of microwave power, the ratio of dispersion to absorption is observed to be 16. We thus calculate from (9) a spin-lattice relaxation time of 1.7 microseconds.

In computing the relaxation time from saturation measurements, we should have used the quantity,

$$\langle H_1^2 / (1 + \gamma^2 H_1^2 T_1^2)^{3/2} \rangle, \quad (13)$$

where the average is taken over the sample. Instead, by introducing the filling factor, we have actually used the quantity,

$$\langle H_1^2 \rangle / (1 + \gamma^2 \langle H_1^2 \rangle T_1^2)^{1/2}. \quad (14)$$

Normally, with only a slight variation in magnetic field intensity over the sample, there is very little difference between the two expressions, and this difference becomes smaller as the ratio χ'/χ'' becomes larger. For our measurements, taken in the region of high saturation, we neglect the effects of this approximation.

Relation Between X-Ray Coloration and Optical Bleaching of KCl Crystals*

W. E. BRON

International Business Machines Research Center, Yorktown Heights, New York

(Received May 6, 1960)

Changes in the absorption of KCl crystals in the spectral region of 200 mμ to 1000 mμ have been observed during room temperature x-ray irradiation and subsequent bleaching with *F* light. It is observed that both coloration and bleaching of the *F* band occurs in two stages. Secondary centers such as *M*, *R*, and *V*_s centers grow primarily during the second stage of coloration, and the rate of growth of these centers during the second stage is enhanced by plastic deformation in a manner similar to that of the *F* band. It is found that the absorption change at the *F* band during the first stage of bleaching approximately equals that during the first stage of coloration. Furthermore, the initial rate of bleaching of the *F* band is proportional to the initial *F* band absorption in samples irradiated only into the first stage of coloration, but is essentially independent of the initial *F*-band absorption in samples irradiated into the second stage of coloration.

INTRODUCTION

IT has been known for some time that when NaCl and KCl crystals are irradiated with ionizing irradiation at room temperature the resultant growth of

tion. It is concluded from this and other evidence that the center responsible for the first stages of coloration and bleaching differs from the center responsible for the second stages of coloration and bleaching. A major point of difference is that the first stage centers are considered to be located in the bulk of the crystal, whereas the second stage centers are located in the vicinity of dislocations.

It is also observed that *M* centers which are formed from *F* centers during the first stage of bleaching can be bleached with *F* light. To explain the observations concerning this *M*-band bleaching, it is proposed that *M* as well as *F* centers are bleached when they are joined by mobile defects, possibly vacancy pairs. Some of the second stage centers located in the vicinity of dislocations are thought to compete with the centers located in the bulk of the crystal for the mobile defects.

the *F* band absorption occurs in two stages¹⁻³ During the first stage the increase in the absorption is rapid, while in the second stage the increase is much slower. (It has recently been shown^{4,5} that when alkali halides

¹ E. Goldstein, Z. Instrumentkunde **16**, 211 (1896).

² H. V. Harten, Z. Physik **126**, 619 (1949).

³ K. Przibram, *Irradiation Colours and Luminescence* (Pergamon Press, New York, 1956).

⁴ H. W. Etzel and J. G. Allard, Phys. Rev. Letters, **2**, 452 (1959).

⁵ P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **117**, 442 (1960).

* Part of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1959. This paper was originally presented at the International Symposium on Color Centers in Alkali Halides, at Oregon State College, September, 1959.