

pair-lines of the second γ -ray overlap the pair-line of the 3.22-Mev γ -ray and the photoline of a third γ -ray, respectively. The microdensitometer trace of the energy region in question is shown in Fig. 2, top. The unresolved doublets are in the region *BC* and *EF*. The next lower trace resulted from 2-crystal operation when the second crystal was oriented such that the line joining the crystals was at 135° with respect to the incident γ -ray beam. Using this trace, the pair-line of the second γ -ray was found at *B*; the γ -ray has an energy of 2.10 ± 0.03 Mev, and its photoline and "135° edge" should be located at *E* and *D*, respectively. It will be noticed that the calculated line *D* does not pass through the center of the 2-crystal Compton line: this is because the recoil electron energy changes very slowly with scattering angle beyond 135° . Using this information, line *A* was drawn for the "135° edge" of the third γ -ray whose energy is then computed to be 1.16 ± 0.03 Mev. The photoline of this γ -ray should lie at *C*. The bottom trace of Fig. 2 results on 3-crystal operation; only the pair-lines of the 3.22- and 2.10-Mev γ -rays remain.

It is a pleasure to thank Professor J. R. Richardson for much helpful advice in the course of this experiment.

* This work was assisted by the joint program of the ONR and AEC.
¹ R. Hofstadter and J. A. McIntyre, *Phys. Rev.* **80**, 631 (1950). The author is also indebted to Dr. Hofstadter for many helpful suggestions.
² L. Ruby and J. R. Richardson, *Phys. Rev.* **80**, 760 (1950).
³ Ramsey, Meem, and Mitchell, *Phys. Rev.* **72**, 639 (1947).
⁴ R. Hofstadter and J. A. McIntyre, *Phys. Rev.* **78**, 619 (1950).

Paramagnetic Resonance in Liquids*

MICHAEL TINKHAM, ROY WEINSTEIN, AND ARTHUR F. KIPT
*Research Laboratory of Electronics, Massachusetts Institute of Technology,
 Cambridge, Massachusetts*
 (Received October 4, 1951)

PARAMAGNETIC resonance absorption in solutions containing Mn^{++} ions has been observed in solutions sufficiently dilute for the hyperfine structure (hfs) to be easily observed. These solutions are as much as 100 times as dilute as those reported by Halliday and Wheatley,¹ in which no hfs was observable, and are about the same concentrations as those observed by England and Schneider.² The microwave apparatus used included a Pound

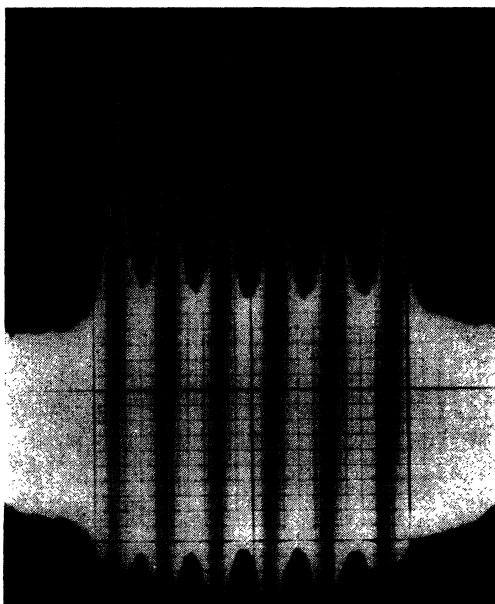


FIG. 1. Absorption spectrum of 0.15M $MnCl_2$ solution at $80^\circ C$.

stabilized oscillator, 6 kc/sec crystal modulator, magic Tee, and rectangular cavity (TE_{012} mode). The magnetic field was swept through the resonance region with a period of about 7 seconds. Figure 1 is an example of the observed absorption spectrum.

All observable structure is explained by the simple Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S},$$

where g is the g value of a free electron. The Hamiltonian given by Bleaney and Ingram³ for the Mn^{++} ion in crystals reduces to this form if spherical symmetry is assumed. It predicts absorption lines ($M \leftrightarrow M-1$) when

$$H = \frac{h\nu}{g\beta} - Am - \frac{A^2 g\beta}{2 h\nu} \left[\frac{35}{4} - m^2 + m(2M-1) \right] \quad \begin{array}{l} m = -5/2, \dots, 5/2 \\ M = -3/2, \dots, 5/2. \end{array}$$

The term in $(2M-1)$ gives only a broadening, with no shift of the center of each of the hfs lines. The observed lines fit this form with

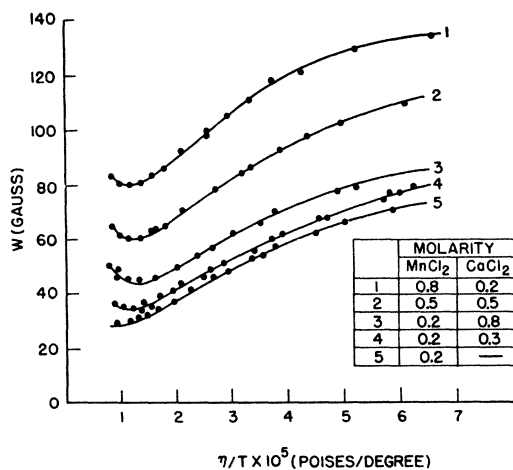
$$g = 2.001 \pm 0.001 \quad \text{and} \quad A = 95 \text{ gauss.}$$

The g value was established by comparison with an organic radical mounted directly on the sample capillary, and the distances of the 6hfs lines from this reference were determined by use of a synchronous flip coil.⁴ This observed g value is within experimental error of the free electron value, the values obtained by Bleaney and Ingram in two dilute manganese salts, the value obtained by England and Schneider for Mn^{++} activators in a ZnS phosphor,⁵ and their value for Mn^{++} ions in solution. The A value differs markedly from the 68 gauss obtained by England and Schneider for the phosphor, but not so strongly from the approximately 100 gauss obtained by Bleaney and Ingram and the 98 gauss given by England and Schneider for solutions. These differences indicate that the strength of the configurational interaction which produces the hfs depends on the ionic environment more strongly than might have been anticipated.

Line widths have been inferred from the ratio of the depth of the valley between lines to the height of one line, using the assumption of a Lorentz line shape. These widths have been interpreted in terms of electric and magnetic perturbations produced on the absorbing ion by its ionic neighbors and by the sheath of water molecules surrounding it. These perturbations broaden the energy levels in two general ways: by causing small randomly distributed shifts in the positions of the levels and by shortening the lifetimes by inducing transitions. To get a quantitative dependence on temperature, the random Brownian motion is decomposed into a noise spectrum,⁶ the intensity of which depends on frequency by the factor $\tau_c / (1 + \omega^2 \tau_c^2)$, where τ_c is the "correlation time" of the random motion. The first general mechanism is produced by electric and magnetic fields with frequency components ω small compared to the frequency width of the line; that is, by fields which do not "average out" over the lifetime of a state. Thus the noise factor approximately reduces to τ_c , and this contribution to line width increases with τ_c . The second mechanism acts through components near the Larmor frequency. With X-band frequencies, this makes $\omega \tau_c > 1$, causing this contribution to depend approximately on $1/\omega^2 \tau_c$. Since τ_c is proportional to η/T , where η is the viscosity, it turns out that the line width W between half-maximum points for a given sample should be approximately expressible in the form

$$W = C_1 / (\eta/T) + C_2 [W(\eta/T)]^{\frac{1}{2}}.$$

The coefficients C_1 and C_2 depend on the nature and concentration of the ions in solution, and may be approximately fairly well by linear combinations of these concentrations. Figure 2 shows the experimental results for samples containing various concentrations of $MnCl_2$ and $CaCl_2$ solutions. These results fit curves of the above form as well as expected in view of the number of approximations involved. For example, the approximation of $\tan^{-1} 2\tau_c/\tau$ by $2\tau_c/\tau$ eliminates the observed leveling off at large τ_c . By holding total ionic strength constant in three of these runs, the effect of the magnetic ions is largely isolated. It should be noted that with dilute solutions and high temperatures the width can be reduced

FIG. 2. Line width W as a function of η/T .

below 30 gauss. This corresponds to a relaxation time of about 4×10^{-9} second.

Other measurements have been made at room temperature to test the dependence of the width W on ionic concentrations. It was found that W is very nearly a linear function of Mn^{++} ion concentration when total ionic strength is constant, and also of total ionic concentration when a solution of a nonmagnetic salt was added, holding the Mn^{++} ion concentration constant. To test the effect of the anion, line widths were measured with 0.15- M solutions of $MnCl_2$, $MnBr_2$, $Mn(NO_3)_2$, $Mn(C_2H_3O_2)_2$, and $MnSO_4$. The first three widths were all 43 gauss within experimental error. The width in the acetate was 60 gauss and that in the sulfate was 64 gauss. These results can be interpreted in terms of the effect of ionic size on τ_c and the effect of ionic charge on the magnitude of the perturbation.

Further work on liquids is in progress.

* This work has been supported in part by the Signal Corps, the Air Materiel Command, and the ONR.

† Now at the Department of Physics, University of California, Berkeley, California.

¹ D. Halliday and J. Wheatley, *Phys. Rev.* **74**, 1724 (1948).

² T. S. England and E. E. Schneider, *Physica* **17**, 221 (1951).

³ B. Bleaney and D. J. E. Ingram, *Proc. Roy. Soc. (London)* **A205**, 336 (1951).

⁴ R. D. Arnold and A. F. Kip, *Phys. Rev.* **75**, 1199 (1949).

⁵ T. S. England and E. E. Schneider, *Nature* **166**, 437 (1950).

⁶ Bloembergen, Purcell, and Pound, *Phys. Rev.* **73**, 679 (1948).

Order of Gamma-Ray Emission in the Decay of In^{111} *

M. M. MILLER, C. H. PRUETT, AND R. G. WILKINSON
Department of Physics, Indiana University, Bloomington, Indiana
 (Received September 17, 1951)

THE identification of the 247-kev gamma-ray emitted following orbital electron capture in In^{111} with a 0.08- μ sec excited state in Cd^{111} at 247 kev seems to have been well established indirectly by several methods. One of these methods¹ depends upon noting that only the 247-kev gamma-ray is common to the activities of In^{111} and Cd^{111m} . Thus the order of emission of the gamma-rays following the decay of In^{111} can be inferred, the 0.08- μ sec level found by Deutsch and Stevenson² giving rise to the 247-kev gamma-ray. These conclusions have been substantiated in another way by Engelkemeir,³ who has shown the existence of a beta-ray group in Ag^{111} which feeds a 0.1- μ sec level in Cd^{111} . The present work shows the assignment is correct by demonstrating that the 247-kev gamma-ray following the decay of In^{111} is delayed with respect to the 172-kev gamma-ray associated with the same decay.

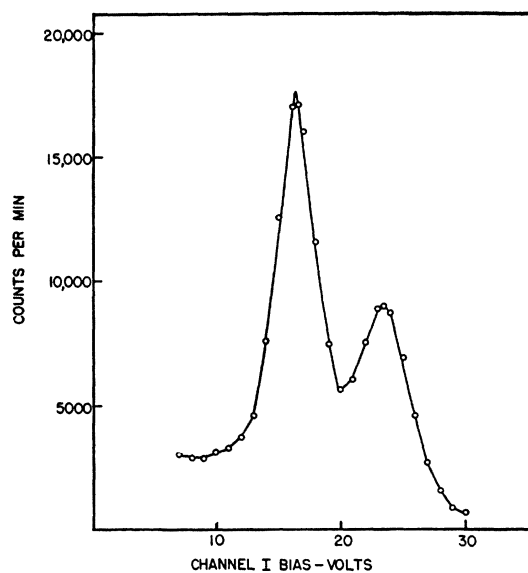


FIG. 1. Single-crystal pulse-height distribution for In^{111} obtained in channel I. The two photoelectron peaks are caused by gamma-rays at 172 and 247 kev.

In this experiment two scintillation spectrometers were used in coincidence. Each channel consisted of a $\frac{3}{4}$ -inch NaI(Tl) cube mounted on a RCA 5819 photomultiplier, a cathode follower pre-amplifier, an Atomic Instruments Model 204-B linear amplifier, and a conventional differential discriminator of variable slit width. The discriminator outputs were mixed in a coincidence circuit of approximately 0.2- μ sec resolving time. Delays in the form of RG 65/U cable were introduced in either channel between the linear amplifier and the differential discriminator. Attenuation of pulse height caused by the delay line was completely compensated

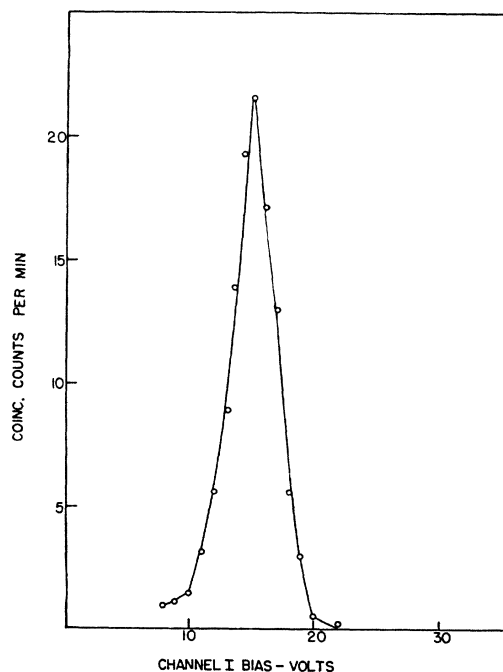


FIG. 2. Coincidence spectrum obtained when channel II transmits only the 247-kev peak while channel I surveys the whole spectrum. No delay has been introduced into either channel.

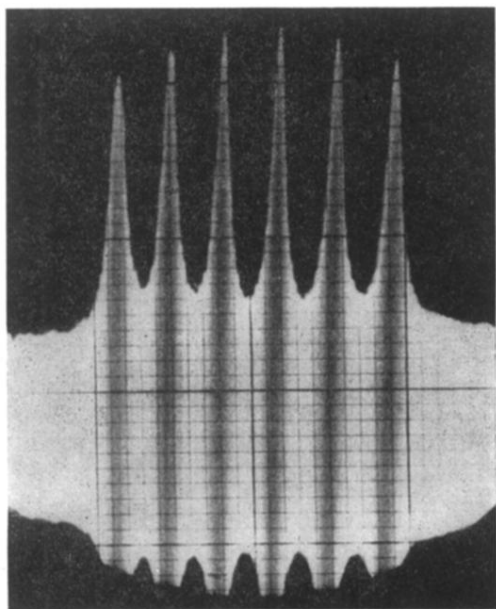


FIG. 1. Absorption spectrum of 0.15M MnCl_2 solution at 80°C.