

FIG. 1. Experimental arrangement.

It had no effect at St. Louis. At Climax it changed the  $N$  rate little; however, when 1 mm Cd sheaths were slipped over the neutron counters, the anticoincidence feature reduced the rate 40 percent. The "with Cd" rate at Climax was less than 5 percent of the "without Cd" rate. Certain refinements were found necessary at Climax' higher elevation. We added four anticoincidence  $C'$  counters in the top of the telescopes and also placed one cm of Pb in the telescopes. This discriminated against side showers and low energy stars in the telescope and filter.

Data were taken with and without the absorber. The results are given for neutrons coincident with apparent stoppings in the absorber ( $AB-C:N$ ) and neutrons coincident with apparent penetrations of the absorber ( $ABC:N$ ). The ( $AB-C:N$ ) results are shown in Table I, the ( $ABC:N$ ) results in Table II. The uncertainties given are the estimated statistical standard errors. The expected casuals are computed from the measured rates and neutron coincidence resolving time. The corrected rates are found<sup>5</sup> by subtracting the expected casual rates from the measured rates. The observed ( $AB-C:N$ ) rates without absorber may be attributed to accidentals. Previous experience has shown that the observed rates with Cd are always of the order of magnitude of the expected casuals. The factor of increase of the ( $AB-C:N$ ) coincidences from St. Louis to Climax is seen to be  $6.0 \pm 0.6$ . The factor of increase of the ( $ABC:N$ ) coincidences from St. Louis to Climax is seen to be  $16.3 \pm 1.2$  with absorber and  $18.9 \pm 1.7$  without absorber. These two factors are equal within the statistical uncertainty. The rate of apparent stoppings ( $AB-C$ ), corrected for the zero effect, increases 2.8 times, in agreement with Kraushaar's<sup>6</sup> results for  $\mu$ -mesons. The intensity of the hard component ( $ABC$ ), increases 2.1 times.

Three possible causes of ( $AB-C:N$ ) events are known,  $\mu^-$ -capture,  $\pi^-$ -capture, and low energy proton stars (type  $0_p$  in the Bristol notation<sup>7</sup>). The first should increase by a factor of 2.8. We consider the second and third together as events of nucleonic origin. It is known<sup>8</sup> that the factor of increase for both low and high energy nuclear interactions is greater than 10. It is unlikely that the nucleonic component giving rise to ( $AB-C:N$ ) events increases less rapidly. If we use the factor of increase for the ( $ABC:N$ ) events (17.3), we find 75 percent for the fraction of ( $AB-C:N$ ) events at sea level due to  $\mu^-$ -mesons, and 35 percent at Climax.

TABLE II. Neutrons associated with penetrations ( $ABC:N$ ).

	Climax	St. Louis
With absorber (115 g/cm <sup>2</sup> Pb)	33.7 $\pm$ 1.1/h	2.04 $\pm$ 0.13/h
Expected $\pm$ 1.1/h Casuals		Expected $\pm$ 0.04/h Casuals
Corrected rate 32.6 $\pm$ 1.1/h		Corrected rate 2.00 $\pm$ 0.13/h
Sans absorber (0.69 g/cm <sup>2</sup> brass in counter walls)	19.4 $\pm$ 1.2/h	1.02 $\pm$ 0.07/h
Expected $\pm$ 0.7/h Casuals		Expected $\pm$ 0.03/h Casuals
Corrected rate 18.7 $\pm$ 1.2/h		Corrected rate 0.99 $\pm$ 0.07/h

The author wishes to express his thanks to Professor R. D. Sard for his advice and guidance during the course of this work.

- \* Work supported by the joint program of the ONR and the AEC.  
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<sup>6</sup> W. L. Kraushaar, Phys. Rev. **76**, 1054 (1949).  
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<sup>8</sup> For example, B. Rossi, Echo Lake Cosmic-Ray Symposium, 307 (1949).

## On the Shift of the Nuclear Magnetic Resonance in Paramagnetic Solutions\*

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May 18, 1950

IN the measurement of gyromagnetic ratios of nuclear spins, paramagnetic ions are often added to the liquid sample in order to reduce the relaxation time.<sup>1</sup> The resonance frequency depends, however, on this addition, because the effective magnetic field at the nucleus is given by

$$H_{\text{eff}} = H_0 + (4/3\pi - \alpha)M + qM. \quad (1)$$

Here  $H_0$  is the externally applied field. The second term represents the contribution to the local field from the magnetization of the sample outside a spherical cavity around the nucleus under consideration,  $\alpha$  being the demagnetizing factor and depending on the shape of the sample. For a sphere the second term vanishes.

The last term is the contribution to the local field at the nucleus from the paramagnetic ions inside a small sphere around the nucleus. This term has heretofore been put equal to zero. This is theoretically correct for pure dipole-dipole interaction in a liquid or in a solid with cubic symmetry.<sup>2</sup>

Experiments show, however, that this term cannot be neglected and represents an important correction in the comparison of gyromagnetic ratios. The value of  $q$  depends strongly on the type of chemical compounds used in the liquid sample. An example of the effect is shown in Fig. 1. More detailed experimental results covering different paramagnetic ions will be published in a subsequent paper by one of us (W.C.D.). Although  $q$  is usually positive, several cases of negative values of  $q$  have been observed.

The effect must not be confused with the chemical binding effect arising from the second-order paramagnetic correction in diatomic or polyatomic molecules.<sup>3-5</sup> The purpose of this letter is to present a possible explanation of the interaction factor  $q$ .

The paramagnetic ion in the liquid is subjected to strong varying electric fields. These are responsible for the quenching of the orbital momentum so that the effective magnetic moment of the ion is close to the "spin only" value.<sup>6</sup> Although the average electric field in the liquid will have spherical symmetry, the field at any instant will deviate from the average. Let us consider as a specific example the resonance of a F<sup>19</sup> nucleus in a solution containing both fluorine ions and paramagnetic ferrous ions. The electric field produced by the F<sup>-</sup> ion at the position of a neighboring Fe<sup>++</sup> ion will have cylindrical symmetry around the radius vector connecting the two ions. Let us take the overall effect of the other particles in the liquid into account by a dielectric polarization, which reduces the field of the F<sup>-</sup> ion by a factor  $\epsilon$ , where  $\epsilon$  is the dielectric constant of the solution. Now the effective  $g$ -value of the paramagnetic ion will depend on the angle between the axis of the electric field and the magnetic field  $H_0$ .

$$g^2 = g_{11}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta. \quad (2)$$

The values of  $g_{11}$  and  $g_{\perp}$  may be different by a considerable amount, as is well known from observations of the magnetic susceptibility

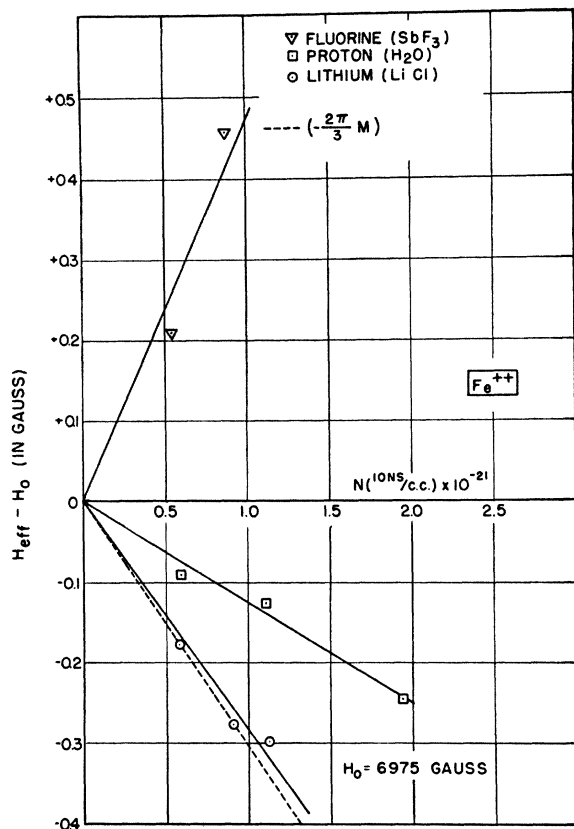


FIG. 1. The shift of the magnetic resonance of  $F^{19}$ ,  $H^1$ , and  $Li^7$  in aqueous solutions containing various amounts of  $FeCl_2$ . The samples have the shape of a long cylinder with the axis perpendicular to  $H_0$ . For  $q=0$  the dotted line would result.

in single crystals.<sup>7,8</sup> A static calculation of  $g_{11}$  and  $g_{\perp}$  is permissible if the motion in the liquid, and therefore the change in the electric field, is described by frequencies which are small compared to the multiplet splitting of the paramagnetic ion. This is a reasonable assumption. The magnetic moment of 1 cc of the solution, containing  $N$  ions, is then given by averaging the Langevin formula over all angles

$$M = Ng^2\beta^2 H_0 S(S+1)/3kT = N(g_{11}^2 + 2g_{\perp}^2)\beta^2 H_0 S(S+1)/9kT. \quad (3)$$

The time average local magnetic field at the position of the  $F^{19}$  nucleus is obtained by first multiplying the moment of a single paramagnetic ion averaged over the spin orientations by  $(-1+3\cos^2\theta)a^{-3}$ , where  $a$  is the distance between the two ions in the ion pair. Then we take the average over all angles, and finally multiply by the probability  $4\pi Nb^3/3$  to find a paramagnetic ion in the sphere of attraction of the  $F^{19}$  nucleus. The result, which in general will not vanish, is

$$qM = 4\pi Nb^3 a^{-3} (4/15)(g_{11}^2 - g_{\perp}^2)\beta^2 H_0 S(S+1)/9kT. \quad (4)$$

Dividing Eq. (4) by Eq. (3) an expression for  $q$  is found. The experimental value of  $q$  for the  $F^{19}$  resonance in a solution of  $FeCl_2$  can be explained by giving  $g_{11}^2 - g_{\perp}^2$  a value which is comparable to those observed in crystals. Of course, there is considerable uncertainty in the geometrical factor  $b^3 a^{-3}$ , which was introduced in a rather crude way. One must expect, however, that the  $q$  value for the  $Li^7$  resonance is much smaller, as has been observed experimentally. The average distance of approach between a  $Li^+$  and a  $Fe^{++}$  ion will be much larger and consequently not only the factor  $a^{-3}$  is smaller, but also the anisotropic electric field at the  $Fe^{++}$  ion, and therefore the anisotropy factor  $g_{11}^2 - g_{\perp}^2$ . In the case of protons, bound in water molecules, more elaborate con-

siderations would be necessary. Even for single ions the geometrical situation has been oversimplified. It seems fruitless to attempt to calculate the detailed configurations of ions and molecules in these concentrated solutions. An experimental determination of the shift for each different type of solution seems necessary. But the order of magnitude of the experimental shift can be understood from the theoretical model, which also leaves room for negative  $q$ -values.

It is conceivable that other effects of the same order of magnitude also contribute to the shift. An exchange effect between the  $F^-$  and  $Fe^{++}$  ion, in which an unbalanced electron spin has a small but finite probability to be found on the fluorine ion, has been suggested by Purcell.<sup>9</sup> The unbalanced spin would create a very large magnetic field at the  $F^{19}$  nucleus for a small fraction of the time. This exchange effect would also depend strongly on the distance  $a$ , and a much smaller shift for  $Li^7$  is again expected.

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

\*\* Society of Fellows.

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## Coincidence Studies of the Disintegration of $Sc^{44}$ \*

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May 10, 1950

INVESTIGATIONS of the radioactivity of  $Sc^{44}$  have been made by Smith<sup>1</sup> and by Hibdon, Pool, and Kurbatov.<sup>2</sup> These authors showed that the disintegration of  $Sc^{44}$  involves an isomeric transition in the parent nucleus since two periods, 52 and 4.1 hr. were found. Smith showed that the 52-hr. state lies higher than the 4.1-hr. state and feeds the lower state by an internally converted gamma-ray of 0.27 Mev energy. The 4.1-hr. state emits positrons of 1.45 Mev energy. Hibdon, Pool, and Kurbatov showed that an additional gamma-ray was emitted and determined its energy, by lead absorption, as 1.33 Mev.

In the present experiments coincidence and absorption techniques have been employed in order to get further information on the decay scheme of this element. The sources were prepared by

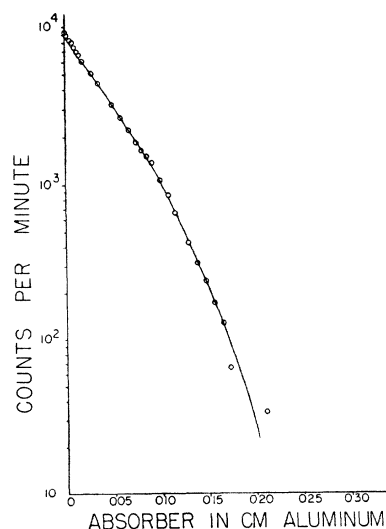


FIG. 1. Absorption of positrons in aluminum.