Polarization of Mn^{55} Nuclei: Cryogenic Aspects*

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A brief discussion of certain cryogenic aspects of nuclear polarization is given. This discussion is applied to Mn^{55} in the paramagnetic salt $Mn(ND_4)_2(SO_4)_2\cdot 6D_2O$. Measurements on this salt of the temperature in the range $0.12°\leq T\leq 0.35°K$ and of magnetic moment up to 90 percent of saturation as a function of magnetic field in the range $660\leq H\leq 4560$ gauss and for an entropy $S/R=0.514$ are described. These measurements are used to calculate the nuclear polarization as a function of field in this magnetic field range and at this entropy, and they form the cryogenic basis for Mn^{55} polarization experiments reported previously.

INTRODUCTION

THIS paper is concerned with cryogenic aspects of work on the polarization of Mn^{55} nuclei. Results of observations on the interaction of these polarized nuclei with polarized thermal neutrons have been described.[1]

The polarization of nuclear magnetic moments by the use of hyperfine structure coupling has been suggested independently by Rose[2] and Gorter.[3] In their procedure, it was proposed to use the hfs coupling occurring in salts of suitable paramagnetic ions to obtain a splitting of the different nuclear spin orientations comparable to kT. As this coupling may be equivalent to a magnetic field at the nucleus of the order of several hundred thousand gauss, temperatures of the order of 0.1°K may give a useful nuclear polarization f_N of order 10 percent.

Because the splitting of the nuclear levels is produced by interactions internal to the salt many of the problems of the "brute force" method proposed earlier by Gorter[4] and by Kurti and Simon[5] are minimized or eliminated. For example, the time required for the electron spin system to cool the nuclear spins, i.e., the electron spin-nuclear spin relaxation time, may become quite short since the electron spin system, which is cooled by the adiabatic demagnetization, is directly coupled by the hfs coupling to the nuclear spins.

Thus, if the "free" electron spins of the paramagnetic ions are oriented, i.e., magnetized by an applied magnetic field H, and if the temperature is then lowered to a value having kT comparable to the hfs splitting, nuclear polarization will result. Equation (1) which describes this has been given by Rose,[2] and has been further discussed by Rose, Simon, and Jauch:[6]

$$f_N=S_e(I+1)(Ahc/3kT)\cdot f_e(H,T). \quad (1)$$

Here A is the coupling constant in the hfs operator, $A\mathbf{I}\cdot\mathbf{S}_e$ and f_e is the electron magnetization expressed as the fraction of magnetic saturation, S_e is the electron spin, I is the nuclear spin, k is the Boltzmann constant, T is the absolute temperature, h is Planck's constant, and c is the velocity of light *in vacuo*. Thus, knowing A, we may calculate f_N from Eq. (1) and measurements of H, f_e, and T.

To obtain the largest available value of the nuclear polarization f_N, the electron magnetization must be brought close to saturation, $f_e\cong 1$, and the temperature T must be made small. The path of an adiabatic demagnetization is suited to these requirements. If a sufficiently large magnetic field H is isothermally applied to the paramagnetic sample at $\sim 1°K$ to bring f_e close to unity, and H is then removed adiabatically, the temperature will fall initially almost in proportion to H, and f_e will remain very nearly constant, as shown by deHaas and Wiersma[7] and by Casimir.[8] This behavior of T will continue until the magnetic field has fallen to a value such that the magnetic field term in the Hamiltonian for the salt becomes comparable in magnitude with the internal interaction terms. For values of H less than this, the temperature will remain roughly constant while f_e will fall to zero at $H=0$. Thus, in this nuclear polarization procedure, there is an optimum final field for which the maximum value of nuclear polarization f_N will be obtained. This is the field at which f_e/T is maximum.

POLARIZATION OF Mn^{55} NUCLEI IN $Mn(ND_4)_2(SO_4)_2\cdot 6D_2O$

The hfs Constant A

The hfs coupling constant has been measured by Bleaney and Ingram.[9] For $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$ they found this coupling to be almost isotropic and to give a term in the Hamiltonian for the salt of the form

$$\mathcal{H}_{\text{hfs}}=aS_3I_3+b(S_2I_2+S_1I_1), \quad (2)$$

* Presented at the Chicago meeting of the American Physical Society [Phys. Rev. **93**, 935 (1954)].

[1] Bernstein, Roberts, Stanford, Dabbs, and Stephenson, Phys. Rev. **94**, 1243 (1954).

[2] M. E. Rose, Oak Ridge National Laboratory Report ORNL-48, 1948 (unpublished); Phys. Rev. **75**, 213 (1949).

[3] C. J. Gorter, Physica **14**, 504 (1948).

[4] C. J. Gorter, Physik. Z. **35**, 923 (1934).

[5] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **149**, 152 (1935).

[6] Rose, Simon, and Jauch, Phys. Rev. **84**, 1155 (1951).

[7] W. J. de Haas and E. C. Wiersma, Physica **3**, 491 (1936).

[8] H. B. G. Casimir, *Magnetism and Very Low Temperatures* (Cambridge University Press, Cambridge, 1940).

[9] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **205**, 336 (1951).

with $|a|=0.00911$ and $|b|=0.00943$, both in cm^{-1}. For a powder sample the spatial average A of the hfs coupling is $A=|a|/3+2|b|/3=0.00932\ cm^{-1}$. This measurement of a and b was made on a magnetically very dilute salt while a polarized neutron observation of the nuclear polarization must be performed on the normal and relatively concentrated salt. It seems reasonable to assume that the values of a and b are very little dependent on Mn^{++} concentration in that they have been found to have essentially the same values in a number of dilute salts with chemically very different anions.[9,10] The salt was deuterated to avoid incoherent neutron scattering by protons. It was assumed that the hfs coupling was not affected thereby.

Measurement of f_e

In 1940, Casimir[11] proposed a method for determining magnetic moments of paramagnetic materials which consists in applying to the sample a small measuring field H_0 at right angles to the magnetizing field H_e. If $H_0 \ll H_e$, and the sample is isotropic and spherical, the application of H_0 rotates both the total field and the magnetic moment through the same small angle at essentially constant magnitude. When H_0 is applied, an induction pickup coil (or secondary) coaxial with the coil producing H_0 and centered on the sample, delivers a signal proportional to the component of magnetic moment along H_0 if the usual bucking arrangement, familiar from susceptibility measurements, is used.[5,12] The apparatus is thus the usual ballistic susceptibility measurement arrangement, with the addition of the Weiss magnet which produces H_e.

Because of crystalline electric field effects, a single crystal of manganous ammonium sulfate is magnetically anisotropic; but a powder sample will, of course, have "net" magnetic properties which are independent of direction. If we adiabatically demagnetize a powder sample slowly compared to the time for thermal equilibrium among the crystallites of the powder, the total entropy of the sample will be constant, and in the final field H_e all of the crystallites will have the same temperature. When the small field H_0 is applied, the total field will be rotated and slightly increased. This change will produce temperature changes in the individual crystallites which will vary from one to another depending on their orientation. For $H_0 \ll H_e$, however, these temperature changes will be negligible compared to the sample temperature.[13] Thus, we conclude that the magnetic moment f_e of a powder sample may be measured by the above method if the demagnetization is performed slowly and $H_0 \ll H_e$. In these measurements, we used a $\frac{3}{4}$-inch sphere machined from a pressed powder cylinder of $Mn(ND_4)_2(SO_4)_2 \cdot 6D_2O$. The powder density was within 1–2 percent of the crystalline density; no corrections were made for this deviation which has a negligible effect.

It can be shown that the ballistic galvanometer deflection D, arising when H_0 is suddenly applied to the sample, is very closely given by

$$D/H_0=(\alpha/H_e)f_e+\beta(H_e), \tag{3}$$

where α is the ballistic sensitivity constant, and β reflects the residual unbalance of the coil system and the effect of the nearby iron pole tips. The dependence of β on H_e was minimized by making the length of the secondary coil approximately equal to the pole face diameter of the Weiss magnet. This dependence was almost negligible but was taken into account.

The accuracy with which Eq. (3) applies was determined in the liquid helium temperature region. Galvanometer deflections D were taken as a function of T from 1.2° to 4.2°K at constant H_e and H_0. By holding these fields constant, the effect of the iron magnet poles on β and H_0 was held constant. f_e was calculated for the various temperatures using the Brillouin function $B_{5/2}(H_e/T)$. Values of H_e up to 4560 gauss were used. This led to an over-all range of f_e for all combinations of H and T of $0<f_e\leq 0.5$.

In this range the linear relation between D and f_e was demonstrated to hold within 0.3 percent using the Royal Society Mond Laboratory liquid helium temperature scale (1948)[14] and to better than 0.1 percent using the corrections to this scale given by Kistemaker[15] and those recently obtained at this laboratory.[16] These measurements also showed that the coefficient of f_e [Eq. (3)] was inverse in H_e within 0.3 percent, i.e., the quantity α was constant.

After demagnetization, the magnetic moment f_e was calculated from readings of the galvanometer deflection D, using Eq. (3), with values for α and β obtained *for the particular* H_e as described above.

The cryostat used in these measurements was the same as that used for the nuclear polarization experiments[1] and was similar to one recently described by Erickson, Roberts, and Dabbs.[17] In the earliest of these experiments, building induced vibration of the pickup coil in the field H_e gave a large "noise" signal to the ballistic galvanometer which made precise observations of f_e very difficult. This situation was corrected by inserting a 7 henry air-core inductance in series with the galvanometer. The time constant introduced by this inductance was very short compared to the galvanometer period.

Figure 1 gives the observed variation of f_e with H_e at an entropy value $S/R=0.514$, where R is the gas

[10] T. S. England and E. E. Schneider, Nature **166**, 437 (1950); D. J. E. Ingram, Proc. Phys. Soc. (London) **A66**, 412 (1953); R. S. Trenhan, Proc. Phys. Soc. (London) **A66**, 118 (1953).

[11] See reference 8, p. 20.

[12] W. J. de Haas and E. C. Wiersma, Physica **2**, 335 (1935).

[13] L. D. Roberts and J. W. T. Dabbs, paper presented at the Southeastern Section meeting, American Physical Society, April, 1954 [Phys. Rev. **95**, 307(A) (1954)].

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[16] R. A. Erickson and L. D. Roberts, Phys. Rev. **93**, 957 (1954).

[17] Erickson, Roberts, and Dabbs, Rev. Sci. Instr. (to be published).

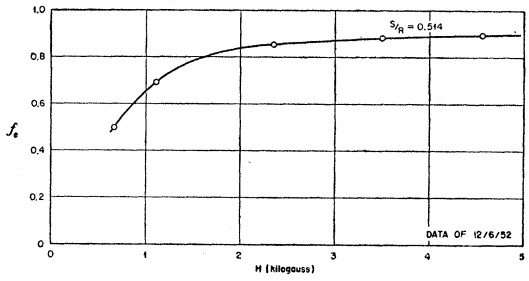

FIG. 1. The electron polarization f_e as a function of magnetic field H_e at constant entropy, $S/R=0.514$.

constant. This is the entropy value which was used in the nuclear polarization work.[1] Figure 2 shows a typical measurement of the f_e *versus* S/R relation at a final field H_e of 2350 gauss. This was obtained from a series of adiabatic demagnetizations at different entropies to the given H_e. The entropy values were calculated from the initial H_e and T ($\sim$1°K) assuming the salt to be an ideal paramagnetic material.

Temperature Measurements

Absolute temperature measurements below 1°K were made using the same apparatus and the same sample of $Mn(ND_4)_2(SO_4)_2\cdot 6D_2O$ as for determining f_e. Here f_e served as the "thermometric parameter"[18] for γ-ray heating experiments. One uses

$$T(H_e,S)=(\partial Q/\partial f_e)_H/(\partial S/\partial f_e)_H$$
$$=(\partial Q/\partial t)_H\cdot(\partial t/\partial f_e)_H/(\partial S/\partial f_e)_H, \quad (4)$$

where $\partial Q/\partial t$ is the heat input per unit time from the γ-ray source (assumed independent of temperature[19,20] and magnetic field), $(\partial f_e/\partial t)_H$ is the measured time rate of change of f_e during the γ-ray heating, and $(\partial S/\partial f_e)_H$ is the slope of the f_e-S curve, Fig. 2.

For these measurements, a pair of two-curie Co^{60} γ-ray "point" sources (furnished by the Radioisotopes Division of this laboratory) were used. They were placed 10 cm from the sample in Pb housings on opposite sides of the cryostat and on a line perpendicular to the axis of the Weiss electromagnet. The γ-ray heating could be turned "on" or "off" within one second by moving the sources within their housings. The ratio of the γ-ray intensity at the sample for the two positions was about 35.

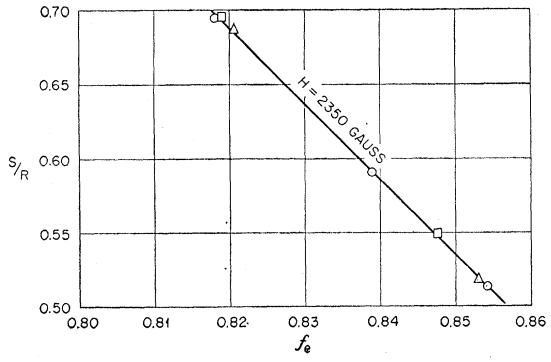

FIG. 2. The entropy S/R as a function of electron polarization f_e at constant $H=2350$ gauss for three separate experiments.

[18] D. de Klerk, thesis, Leiden, 1948 (unpublished).
[19] R. L. Platzman, Phil. Mag. 44, 497 (1953).
[20] N. Kurti and F. Simon, Phil. Mag. 44, 501 (1953).

Thermometric parameters which have been used previously[18] are the reactive and resistive components of the susceptibility and the magnetic remanence. The variation of these quantities with entropy is so small that they cannot be used in the magnetic field-entropy region of interest here. However, as is shown in Fig. 2, the variation of f_e with entropy is sufficiently large compared to the measurement errors to allow a satisfactory determination of $(\partial S/\partial f_e)_H$.

dQ/dt is obtained by measuring the rate of rise of temperature due to the γ rays in a temperature region of known specific heat. If this measurement is made near 1°K where the specific heat is usually well known,

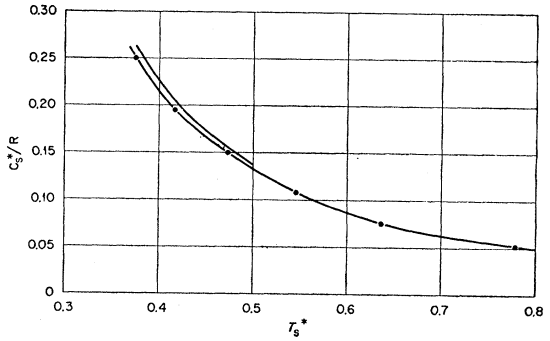

FIG. 3. The lower curve is the measured specific heat C_s^*/R as a function of the magnetic temperature T_s^*. The upper curve is calculated. See text.

the background heat leak is usually quite large compared to that at the lower temperatures and compared to the specific heat of the salt. If this calibration is made at lower temperatures where the salt specific heat is larger and the background heat leak relatively small and temperature independent, the specific heat is usually not well known. The resulting uncertainties in dQ/dt have been one of the larger sources of error in the measurement of temperature below 1°K by γ-ray heating. To reduce this error we have made a comparison of the γ-ray heating with a measured electrical heat input in the temperature region near 0.4°K where the thermal conductivity of the salt is adequate. At lower temperatures electrical heating would lead to serious temperature inhomogeneities, while γ-ray heating does not. At 0.4°K, the specific heat of the salt is sufficiently large compared to the "background" heat leak to permit precise measurements of susceptibility as a function of time for either heat source.

Figure 3 gives a curve of the specific heat $C_s^*=dQ/dT_s^*$ of $Mn(ND_4)_2(SO_4)_2\cdot 6D_2O$ as a function of

T_s^* (reciprocal susceptibility) as determined by electrical heating. For this measurement the salt was pressed into a slitted cylindrical Cu sleeve, $\frac{5}{16}$ in. in diameter$\times\frac{15}{16}$ in. long. A Constantan wire heater was wound on the Cu cylinder using baked Araldite to obtain thermal contact. Heater leads through the wall of the sample tube into the liquid He were made of 1-mil Pb-coated Constantan wire. Heater current and potential measurements were made using precision potentiometers and a standard resistor. The observed magnetic temperature T^* was corrected to that for a sphere T_s^* assuming the sample to be an ellipsoid with $c/a=3$. These measurements lead to a γ-ray heat input $dQ/dt=2890$ ergs/min for our $\frac{3}{4}$-in. spherical sample.

It is interesting to note in passing that the Constantan heater showed a minimum of electrical resistance at about 0.5°K.

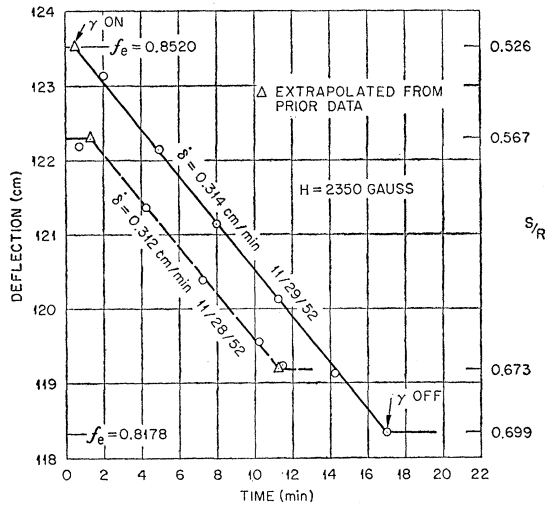

FIG. 4. Two typical warmup curves for the sample in a magnetic field of 2350 gauss showing the galvanometer deflection as a function of time.

A first term approximation to C_s^* is given by the specific heat[21] $0.0314R/T^2$ together with the T *versus* T_s^* relation given by Cooke.[22] This procedure yields a C_s^* in fair agreement with our measured values as is shown in Fig. 3. It is, however, not as acceptable in that this specific heat assumption is probably a few percent in error at the lower temperatures, and in that the T *vs* T_s^* relationship is normalized to a value based on a Stark splitting pattern recently shown to be incorrect.[9]

$(\partial f_e/\partial t)_H$ was obtained after demagnetization ($S/R<0.514$) by observing the galvanometer deflection D as a function of time, and using Eq. (3). Figure 4 gives typical results.

A substitution of the above results in Eq. (4) yields a temperature of 0.201°K at $S/R=0.514$ and $H_e=2350$ gauss.

[21] R. A. Erickson and L. D. Roberts (unpublished).
[22] A. H. Cooke, Proc. Phys. Soc. (London) A62, 269 (1949).

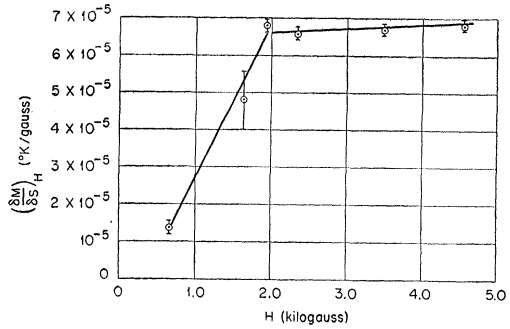

FIG. 5. $(\partial M/\partial S)_H$ as a function of magnetic field H at $S/R=0.514$.

Dependence of T on H_e

In order to obtain $T(H_e)$ at $S/R=0.514$ we use one of the Maxwell relations of magnetic thermodynamics, *viz.*, $(\partial T/\partial H)_S=-(\partial M/\partial S)_H$. Integrating this equation, we obtain the expression

$$T_2-T_1=-\int_{H_1}^{H_2}\left(\frac{\partial M}{\partial S}\right)_H dH$$
$$=-Ng\beta S_e\int_{H_1}^{H_2}\left(\frac{\partial f_e}{\partial S}\right)_H dH \quad (5)$$

for isentropic changes of temperature with applied field.[8] Here, N is Avogadro's number, g is the gyromagnetic ratio, and β is the Bohr magneton. Measurements similar to those shown in Fig. 2 were made for a number of fields in the entropy region $0.36\leq S/R\leq 0.9$. In this region as is illustrated in Fig. 2, the f_e-S function was remarkably linear for the H_e values covered. The slopes obtained from these measurements are plotted as a function of H_e for the entropy $S/R=0.514$ in Fig. 5. A numerical integration of these slopes, using Eq. (5) gives the temperature as a function of H_e when normalized to our γ-ray heating point at 0.201°K and 2350 gauss, as is shown in Fig. 6.

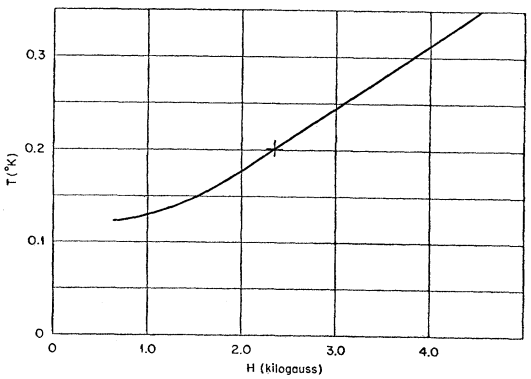

FIG. 6. Absolute temperature T as a function of magnetic field at $S/R=0.514$.

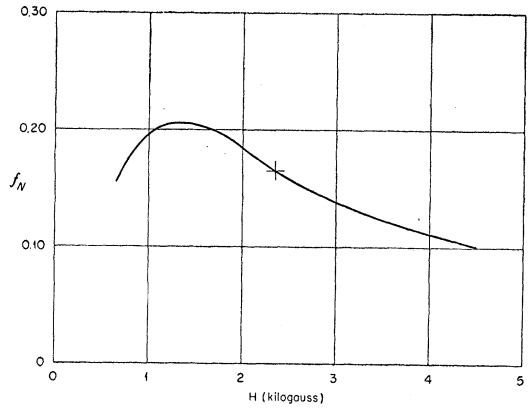

FIG. 7. The nuclear polarization f_N as a function of magnetic field H at $S/R=0.514$ as calculated from the measured f_e and T.

The measurement of the magnetic moment-entropy curve over a range of magnetic fields is especially convenient in that the same data are useful in γ-ray heating measurements and in experiments based on Eq. (5).

Calculation of f_N from Measured f_e and T

These measured values of f_e and T may now be substituted in Eq. (1) to obtain the nuclear polarization f_N as a function of H_e at $S/R=0.514$. This result is plotted in Fig. 7. It is seen that a maximum polarization $f_N=0.207$ is obtainable at a final field of 1300 gauss, and that the final fields (2260–2350 gauss) used in the nuclear polarization experiments[1] correspond to $f_N=0.165$ to 0.170 for the initial polarization of the nuclei.

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Resonant States of Mg^{24} Excited by Protons on Sodium*

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The gamma-ray yield from sodium was measured as a function of proton bombarding energy over the range 1.0 to 2.5 Mev using resolutions of 2.5 kev or better. In addition, the yield of α particles produced by the $Na^{23}(p,\alpha)Ne^{20}$ reaction and leading to the ground state of the residual nucleus was measured for proton energies of 1.0 to 2.2 Mev, with a resolution of 10 kev. Fifty-two resonances were observed in all. The resulting average level spacing is 28 kev at a mean excitation energy of 13.5 Mev in the compound nucleus Mg^{24}. The resonances vary in natural width from less than 0.3 kev to 50 kev. The energy spectra of the gamma rays from a number of resonances were investigated with a single-crystal NaI(Tl) scintillation spectrometer. The spectra consist mainly of two gamma rays, with energies of 0.45 ± 0.01 and 1.63 ± 0.02 Mev. These are interpreted as transitions from the first excited states of the residual nuclei formed by the reactions $Na^{23}(p,p')Na^{23}$ and $Na^{23}(p,\alpha')Ne^{20}$, respectively.

INTRODUCTION

THE interaction of fast protons with sodium nuclei was first observed by the detection of gamma radiation.[1] Curran and Strothers[2] studied the gamma-ray yield as a function of proton bombarding energy below 1 Mev and identified several maxima characteristic of resonance reactions. Measurements of the secondary electron absorption showed that many of the gamma rays were of high energy and hence presumably due to the radiative capture process. Burling[3] confirmed and more clearly resolved the resonances below 1 Mev and found a number of additional resonances in the region 1.0 to 1.9 Mev. However, even with the improved resolution of 10 to 25 kev, Burling concluded that the measured half-widths of the resonances were largely experimental in origin. Tangen,[4] using better resolution, found three new resonances in the low-energy region 0.25 to 0.50 Mev.

It was recognized that the (p,α) reaction is energetically possible and might give rise to gamma radiation of lower energy characteristic of the low-lying excited levels of the residual Ne^{20} nucleus. Curran aud Strothers showed that this was not a prominent mode of decay for resonances below 1-Mev proton energy. Burling did not undertake energy measurements of the gamma radiation. As one proceeds to higher proton energies,

* This work was jointly supported by the Bureau of Ships and the U. S. Office of Naval Research.
† Now at Oak Ridge National Laboratory, Oak Ridge, Tennessee.
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[1] Herb, Kerst, and McKibben, Phys. Rev. **51**, 691 (1937).
[2] S. C. Curran and J. E. Strothers, Proc. Roy. Soc. (London) **A172**, 72 (1939).
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[4] R. Tangen, Kgl. Norske Videnskab. Selskabs Skrifter Nr. 1 (1946).