DIRECT OBSERVATION OF THE hfs OF A PARAMAGNETIC ION IN AN ANTIFERROMAGNET. NUCLEAR MAGNETIC RESONANCE OF Co^{59} IN CoF_2

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(Received December 29, 1958)

Indirect experimental evidence[1] for the existence of a Co^{59} $(I=7/2)$ hyperfine interaction in antiferromagnetic CoF_2 was found in the course of measuring the relaxation times of the F^{19} high-frequency nuclear magnetic resonance (NMR). The indirect observations consisted of two separate measurements: (1) measuring the frequency dependence of T_1^{19} and (2) measuring the degree of the "off-resonance" saturation of the μ^{19}.

We have now observed directly the high-frequency NMR of Co^{59} in a single crystal of CoF_2 in the range of frequencies of 160–190 Mc/sec in external fields extending to 10 kilo-oersteds and at temperatures of 1.3° to 4.2°K. The resonances occur at these high frequencies because of the intra-atomic hyperfine interaction of the Co^{59} magnetic moment with the huge fields of the unbalanced d electrons on the Co^{++} ion, and the spatial polarization of the Co^{++} spin moment in the ordered state.[2] Because of the nuclear electric quadrupole interaction, seven approximately equally spaced lines were seen, each of which is split in two by the external magnetic field. The latter effect results from the removal of the spatial degeneracy associated with the antiferromagnetic ordering.

With the external magnetic field parallel to the unique axis, [001], the Hamiltonian may be written as[2]

$$\mathcal{H}_0 = (A_z^{59}\langle S_z\rangle - \gamma^{59}\hbar H_z)I_z + \sum_{i=1}^{3} P_i I_i^2, \qquad (1)$$

where $\langle S_z\rangle$ is the time-average spin polarization per Co^{++} ion, A^{59} the magnetic hyperfine interaction constant, and

$$P_i = -\frac{eQ^{59}}{2I(2I-1)}\frac{\partial E_i}{\partial x_i};$$

Q^{59} is the Co^{59} nuclear quadrupole moment, $\partial E_i/\partial x_i$ is the x_ith electric field gradient component, and the directions x_i are the principal axes of the quadrupole interaction tensor, one of which coincides with [001]. If the quadrupole interaction be regarded as a perturbation, the eigenvalues of (1) correct to second order are given by

$$E_m = (A_z^{59}\langle S_z\rangle - \gamma^{59}\hbar H_z)m + \tfrac{3}{2}P_z m^2 + \frac{[(P_x - P_y)/2]^2}{A_z^{59}\langle S_z\rangle - \gamma^{59}\hbar H_z}\left[-m^3 + \frac{31}{2}m\right]. \qquad (2)$$

In Fig. 1 the field dependence of the 14 lines as a function of frequency is shown along with the experimental observations. The extrapolated zero-field splittings are given in Table I. The parameters determined from (2) with $H_{ext} = 0$

Table I. The experimentally determined parameters in the high-frequency NMR of $Co^{59}F_2$ at 1.3°K with H_{ext} parallel to [001].[a] The line widths, δH, represent the field separation of the extrema in the derivative of the line shape. Measurements of γ^{59} in diamagnetic cobalt compounds[b] have yielded $\gamma^{59}/2\pi = 1.01$ (kc/sec)/oe.

Line	$m \leftrightarrow m-1$	$\nu(H_{ext}=0)$ (Mc/sec)	δH (oe)	$\gamma^{59}/2\pi$ (kc/sec)/oe
a_0	±7/2 ↔ ±5/2	165.030±0.025	165±10	1.23 ±0.02
b_0	±5/2 ↔ ±3/2	170.120±0.030	222±12	1.25 ±0.01
c_0	±3/2 ↔ ±1/2	175.275±0.030	263±15	1.248±0.010
d_0	±1/2 ↔ ∓1/2	180.378±0.030	268±15	1.24 ±0.01
e_0	∓1/2 ↔ ∓3/2	185.383±0.040	242±15	
f_0	∓3/2 ↔ ∓5/2	190.530±0.100		
g_0	∓5/2 ↔ ∓7/2	195.800±0.200		

[a]In column 2, one must use either all the upper signs or all the lower signs.
[b]See reference 6.

are given in Table II. Since neither the sign nor the absolute magnitude of Q^{59} (or the gradient of the electric field) is known, only the quadrupole interaction energy is given and an uncertainty in the signs of the magnetic quantum numbers is necessarily present.

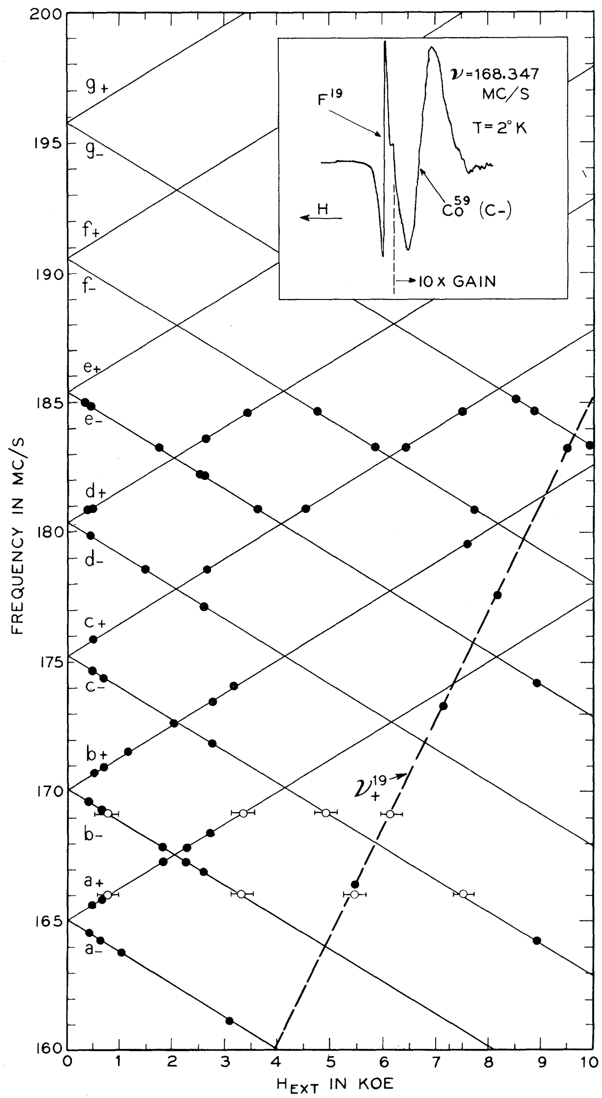

FIG. 1. The spectra of Co^{59} in antiferromagnetic CoF_2 at $T=1.3$°K and H_{ext} parallel to [001]. The dots are the experimental observations and the lines are the best fit to the data. The ν_+^{19} branch of the F^{19} in CoF_2 is included for completeness. The points with relatively large errors indicated at 166 and 169 Mc/sec are those corresponding to the "off-resonance" saturation of ν_+^{19} shown in Fig. 2 of reference 1. In the inset is a recorder trace of the derivative of the ν_+^{19} and ν^{59} (c_-) lines at a field of approximately 6000 oe (note the gain change). Nonlinearity of the field sweep and partial saturation contribute to the distortion of the two line shapes.

Moriya[3] has calculated A^{59} in the true $S=3/2$ manifold using Stout's[4] value of A^{59} derived from electron paramagnetic resonance measurements of Co:ZnF_2 in which the latter author, following Tinkham,[5] employed the fictitious effective spin $S'=1/2$. In this way an approximate mean value of $\langle S_z\rangle$ was determined.

Since the observed gyromagnetic ratios deviate by approximately 23% from the known[6] γ^{59}, and exhibit a negligible m dependence, the inadequacy of (1) in completely describing the observations is apparent. Phenomenologically we may add to (1) a term which allows for a field dependence of $\langle S_z\rangle$ in keeping with the known large parallel susceptibility of CoF_2 at 0°K.

$$A^{59}\langle S_z\rangle I_z \rightarrow [A_0^{59}\langle S_z\rangle_0 + A_H^{59}\langle S_z\rangle_H]I_z. \quad (3)$$

However, γ^{19} in CoF_2 at the same temperature deviates only by 3.2% from the known γ^{19} and, considering the ratio of $H_{hf}^{59}/H_{hf}^{19}=3.3$, it would follow that $\Delta\gamma^{59}/\gamma^{59}$ should be 10%. Thus a discrepancy still remains unless one assumes A_H^{59} to be quite different from A_0^{59}.

Table II. The derived values of the interaction constants using the data in Table I. Stout's value[a] for Co^{59}: ZnF_2 with $H_0 \| [001]$ is 225 Mc/sec ($S'=1/2$). Moriya's derived value[b] for $S=3/2$ is 132 Mc/sec.

$A^{59}\langle S_z\rangle = 180.4$ Mc/sec;	$\langle S_z\rangle_0 = 1.3$
$\lvert P_z\rvert = 1.70$ Mc/sec;	$\lvert P_x - P_y\rvert = 0\pm 2$ Mc/sec

[a]See reference 4.
[b]See reference 3.

The measured line shapes (see inset of Fig. 1) are more nearly Gaussian than Lorentzian. This fact combined with the large values of the line widths generally confirms the T_2 mechanisms proposed by Suhl[7] and Nakamura.[8] More precise measurements including relaxation time studies are in progress and will be reported shortly.

We believe these experiments to be the first direct observation of the NMR of a paramagnetic ion nucleus.

The author is indebted to J. L. Davis for experimental assistance, to Professor J. W. Stout of the University of Chicago for the CoF_2 crystals and to Dr. T. Moriya and Dr. H. Suhl for many stimulating discussions.

[1]V. Jaccarino (to be published elsewhere).
[2]T. Moriya, Progr. Theoret. Phys. (Japan) 16, 641 (1956). Though many, including the author, have inde-

pendently considered the possibility of observing such resonances it was Moriya who first showed the theoretical feasibility of such studies.

[3]T. Moriya (private communication).

[4]J. W. Stout (private communication).

[5]M. Tinkham, Proc. Roy. Soc. (London) A236, 535, 549 (1956).

[6]W. C. Proctor and F. C. Yu, Phys. Rev. 81, 20 (1951).

[7]H. Suhl, Phys. Rev. 109, 606 (1958).

[8]T. Nakamura (private communication).

PHOTODETACHMENT CROSS SECTION OF THE NEGATIVE HYDROGEN ION

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This Letter reports the results of the first precise measurement of the wavelength dependence of the photodetachment cross section of the negative atomic hydrogen ion in the range from 0.4 to 1.3μ.

The importance of absorption by H^- in determining the opacity of the solar atmosphere,[1] and general interest in the theory of two-electron systems[2] have stimulated considerable effort in the calculation of the continuous absorption coefficient, or photodetachment cross section, of H^-. In particular, Chandrasekhar and co-workers[3] have conducted a series of calculations of the cross section using various refinements of the wave functions of the bound and free states and considering the differences in results obtained using dipole-length, velocity, and acceleration matrix elements. Calculations of this cross section also have been carried out recently by Geltman.[4]

Experimental results bearing on this subject have been meager. The H^- emission continuum has been studied[5] in arc and shock tube spectra. Branscomb and co-workers[6] have developed a method for observing photodetachment by collecting free electrons produced at the intersection of crossed ion and photon beams in a high-vacuum apparatus. Branscomb and Smith[7] measured an absolute integrated H^- photodetachment cross section and obtained a check on the shape of the cross section in the visible spectrum using the continuous emission from a tungsten lamp modified by a set of absorption filters. More recently they have developed a set of band-pass filters utilizing interference reflection filters to make relative point-by-point measurements of slowly varying cross sections.[8]

The present authors have undertaken to refine the negative-ion beam apparatus to obtain an accurate relative H^- photodetachment cross section for comparison with and evaluation of theoretical calculations. This has been accomplished by improving signal-to-noise in the experiment through improvement of preamplifier detection sensitivity and elimination of background signals (such as photoelectric signals); and by developing a direct, reliable method for relative determination of light intensity in the photon beam. These problems will be discussed in a future publication.

The results of our measurement of the photodetachment cross section of H^- are given in Fig. 1. We used band-pass filter combinations with widths ranging from 250 to 500A. It should be noted that this is then a low-resolution measurement, because of the necessity for transmitting as much as a half-watt of radiation to the ion beam. Each point in Fig. 1 is the average value of from six to twelve measurements with a single filter combination, with rms errors indicated by the bars. The value for the cross section at each band pass filter was obtained relative to the value at one reference filter at 5280A for which no error bar is shown. The shape of the cross section is determined relative to the value at 5280A to an accuracy of about 2%.

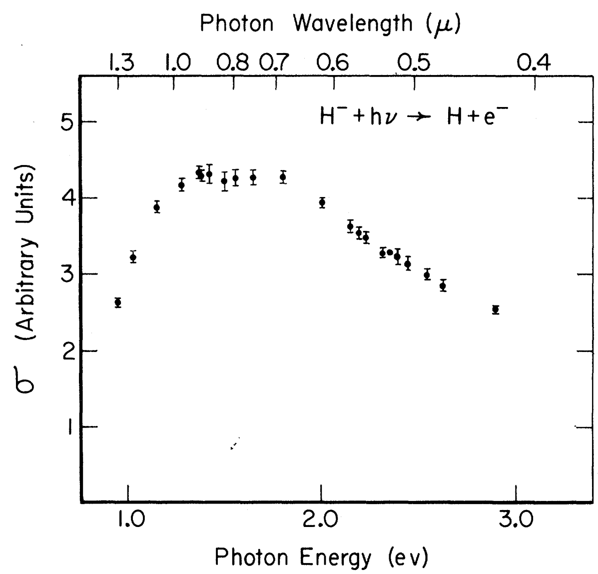

FIG. 1. Measured relative values of the photodetachment cross section for H^-.