converged rapidly, and at most two terms were needed. If one uses only the first term, the results for ion s have the form

$$a(s) \cong A_s |\psi_F(s)|^2; \quad b(s) \cong B_s |(d\psi_F/dr)_s|^2,$$

where r is the distance from the center of the vacancy.[5] The coefficients A_s and B_s are properties of the ion and its nucleus alone, and ψ_F and its radial derivative are evaluated at the nucleus of the ion. The above formulas are useful for extrapolating results from one substance to another since the parameters of ψ_F vary smoothly with interionic distance.

The calculated results, in Mc/sec, are $a(K^{39}) = 35$, $b(K^{39}) = 1.0$, and $a(Cl^{39}) = 12$. Feher's experimental results are $a(K^{39}) = 21.6$, $b(K^{39}) = 0.95$, and $a(Cl^{39}) = 7.0$. The calculation of $b(Cl)$ has been omitted because of failure of the asymptotic series. More laborious methods could be used, but it is inadvisable in view of the sensitivity of calculations involving the negative ions to small changes in the variational parameters of ψ_F.

These results do show that the relatively simple wave function used can give the correct order of magnitude for most of the magnetic hfs constants. Consideration of these results and those of I indicates that the positive-ion results are the most reliable, the agreement improving with increasing interionic distance.

The author is indebted to Dr. G. Feher for the opportunity of seeing an advance description of his experiment. Miss Martha Neuman did the numerical calculations.

[1] G. Feher, Phys. Rev. **105**, 1122 (1957).
[2] First determined by Kip, Kittel, Levy, and Portis, Phys. Rev. **91**, 1066 (1953).
[3] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957). Hereafter referred to as I.
[4] K^+: D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **166**, 450 (1938). Cl^-: D. R. Hartree, Proc. Roy. Soc. (London) **156**, 45 (1936).
[5] Earlier, D. L. Dexter [Phys. Rev. **93**, 244 (1954)], and J. A. Krumhansl [Phys. Rev. **93**, 245 (1954)], proposed similar methods for calculating a. Krumhansl's method is used in I to get $a(K^{39}) = 29$ Mc/sec. However, their methods are not immediately applicable to the calculation of b.

Paramagnetic Resonance Hyperfine Structure of Np^{239}†

M. ABRAHAM, C. D. JEFFRIES, R. W. KEDZIE,
AND J. C. WALLMANN

*Radiation Laboratory and Physics Department,
University of California, Berkeley, California*
(Received May 2, 1957)

THE discrepancy between the spin value of Np^{239} as measured by Conway and McLaughlin[1] using optical hyperfine structure $(I = \frac{1}{2})$, and the value inferred from various decay scheme studies[2] $(I = \frac{5}{2})$ has led us to redetermine the spin by an independent

method: microwave paramagnetic resonance absorption.[3] Using this technique Bleaney, Llewellyn, Pryce, and Hall[4] have investigated the paramagnetic resonance of long-lived Np^{237} incorporated as NpO$_2^{+2}$ ions in a single crystal of UO$_2$Rb(NO$_3$)$_3$. Their results are in good agreement with a spin Hamiltonian:

$$\mathcal{H} = g_{||}\beta H_z S_z + g_\perp\beta(H_x S_x + H_y S_y) + A S_z I_z$$
$$+ B(I_x S_x + I_y S_y) + P[I_z^2 - \tfrac{1}{3}I(I+1)]; \quad (1)$$

where x, y, z are the crystalline field principal axes, $S = \frac{1}{2}$, $I(Np^{237}) = \frac{5}{2}$, $g_{||} = 3.40$, $g_\perp \cong 0.2$, $A = (+)0.1654$ cm^{-1}, $B = 0.0178$ cm^{-1}, $P = (-)0.0301$ cm^{-1}, $\beta =$ Bohr magneton. We have prepared 4 μg ($\sim$1 curie) of Np^{239} by thermal-neutron irradiation of U^{238} in the Materials Testing Reactor at Idaho Falls, Idaho. This was incorporated, together with 3 μg of Np^{237}, as NpO$_2^{+2}$ in a single crystal of UO$_2$Rb(NO$_3$)$_3$ weighing about 200 mg; KBrO$_3$ was added to the aqueous growing solution to maintain the Np (VI) oxidation state. The crystal was installed in the microwave cavity of the paramagnetic resonance apparatus previously described[5] with the crystalline z axis approximately parallel to the dc magnetic field H. Examination of the spectrum at 4.3°K showed a pair of lines near $g_{||} \cong 3.4$ which we attribute to Np^{239}. We thus conclude that $I(Np^{239}) = \frac{1}{2}$, confirming the earlier result of Conway and McLaughlin.[1] The Np^{239} resonance lines were first seen with a signal-to-noise ratio of about 20; this decreased to unity after about 12 hours because of radiation damage. No lines attributed to Np^{237} were observed, presumably because the large quadrupole interaction in this case makes them more susceptible to radiation damage. Thus our experiment does not rule out the possibility that there is perhaps an isomeric state of Np^{239} with $I = \frac{5}{2}$.

Detailed resonance data were obtained by rotating the wave guide and cavity containing the crystal about an axis perpendicular to the H field. The position of the two Np^{239} lines was found to fit within about 1% the first order theoretical expression $H_{\mathrm{res}} \cong (h\nu \pm \frac{1}{2}A)/g_{||}\beta \cos\theta$, which is obtained from the Hamiltonian (1) for $I = \frac{1}{2}$, assuming $\theta < 45°$, where θ is the angle between H and z, and ν is the microwave frequency (9380 Mc/sec in our case). The best fit is obtained by taking $g_{||} = 3.40$, $A(Np^{239}) = 0.0503 \pm 0.0005$ cm^{-1} and $\cos\theta = \cos\alpha \cos\psi$ where ψ is the (variable) angular position of the crystal about an axis perpendicular to H, and $\alpha \cong 19°$ is the fixed minimum angle between z and H. The angle α should be zero if the crystal were perfectly aligned in the cavity; in our case this is not true because the active crystal was quickly aligned by simply sighting with the eye. The excellent fit of the observed lines to the theory establishes them as certainly a hyperfine doublet, and we believe that the observed spectroscopic splitting factor $g_{||}$ establishes their chemical identity. They clearly could not be due to Pu^{239} $(I = \frac{1}{2})$ as PuO$_2^{+2}$, for which Bleaney et al.[4] report $g_{||} = 5.4$, $g_\perp \sim 0$, $A = 0.0862$

cm^{-1}, $B{\sim}0$ in the crystal used here. There remains the remote possibility that the Pu^{239} in the crystal, resulting from the decay of Np^{239}, exists as Pu (IV) and might be observed with, fortuitously, the g factor of NpO_2^{+2}. An experiment to rule out this possibility will be attempted.

A crystal containing 0.3 μg Np^{239} and 100 μg Np^{237} was also prepared. This showed only the Np^{237} lines (both allowed and forbidden), but the Np^{239} lines were too weak to be seen.

A separate experiment in which we attempted to dynamically polarize Np^{239} nuclei by saturating the forbidden paramagnetic resonance transitions as suggested by Jeffries[6] was also performed. No γ-ray anisotropy was observed ($\epsilon < 0.05\%$), which is consistent with $I(Np^{239}) = \frac{1}{2}$.

Using the value $A(Np^{237})$ of Bleaney et al.[4] and our value $A(Np^{239})$ quoted above yields the ratio of the nuclear g factors:

$$|g(Np^{237})|/|g(Np^{239})| = A(Np^{237})/A(Np^{239})$$
$$= 3.287 \pm 0.04.$$

Neglecting hyperfine structure anomalies, this gives for the magnetic moment ratio

$$|\mu(Np^{237})|/|\mu(Np^{239})| = 16.45 \pm 0.17.$$

Taking the value $|\mu(Np^{237})| = 6 \pm 2.5$ nm of Bleaney et al.,[4] we find $|\mu(Np^{239})| \cong 0.3$ nm.

We wish to thank Professor B. B. Cunningham for his helpful discussions and advice.

† Supported in part by the U. S. Atomic Energy Commission.
[1] J. G. Conway and R. D. McLaughlin, Phys. Rev. 96, 541 (1954).
[2] Hollander, Smith, and Mihelich, Phys. Rev. 102, 704 (1956); Smith, Gibson, and Hollander, Phys. Rev. 105, 151 (1957); J. M. Hollander, Phys. Rev. 105, 1518 (1957); Newton, Rose, and Milsted, Phil. Mag. (to be published); I. Perlman and F. Asaro, Annual Review of Nuclear Science (Annual Reviews, Inc., Stanford, 1954), Vol. 4, p. 157.
[3] See, e.g., B. Bleaney and K. W. H. Stevens, Repts. Progr. in Phys. 16, 108 (1953); K. D. Bowers and J. Owen, Repts. Progr. in Phys. 18, 305 (1955).
[4] Bleaney, Lewellyn, Pryce, and Hall, Phil. Mag. 45, 991, 992 (1954).
[5] Dobrowolski, Jones, and Jeffries, Phys. Rev. 101, 1001 (1956).
[6] C. D. Jeffries, Phys. Rev. 106, 164 (1957).

Electrical Properties of BaTiO₃†
Containing Samarium

GEORGE G. HARMAN

Electron Devices Section,
National Bureau of Standards, Washington, D. C.,
and University of Maryland, College Park, Maryland
(Received April 10, 1957)

THE properties of $BaTiO_3$ have been shown to be sensitive to impurities.[1,2] Work in this laboratory has revealed that $BaTiO_3$ containing samarium has very unusual electrical characteristics associated with its
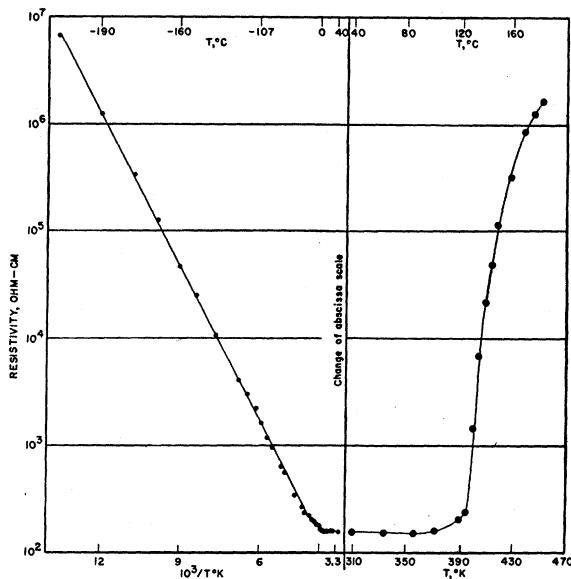

FIG. 1. Resistivity vs temperature for $BaTiO_3 + 0.1$ mole % Sm_2O_3. Note the change of abscissa scale from $10^3/T$ $(°K)^{-1}$ in the left-hand portion to $T°K$ in the right-hand portion.

crystallographic transitions (Fig. 1). In the tetragonal region (0—120°C) the resistivity is almost independent of temperature, but at constant temperature it decreases with increasing applied voltage (noted also in other temperature regions). This voltage dependence is too large to be explained by non-ohmic contact effects. As the temperature increases above the Curie point transition (about 120°C), the resistivity rises rapidly through several orders of magnitude until about 250°C (not shown in the figure) when the resistivity then decreases with increasing temperature. The resistivity in all temperature regions varies widely with a small change in the percentage of samarium.

Below the 0°C transition the material displays characteristics of a semiconductor with a small thermal activation energy (0.1 ev). The −80°C transition produces a very small jump in the curve (unnoticeable in Fig. 1) but results in no apparent change in properties. Thermal hysteresis is observed around the various transitions.

At room temperature the material gives large front to back resistance ratios, when tested with a phosphor bronze point contact using dc voltage. Alternating current, however, experiences little or no rectification.

Optical measurements indicate that samarium introduces one or possibly two absorption bands between 0.9 and 1.5 ev below the optical absorption edge (3.1 at room temperature).

The only electrodes employed so far have been silver paint, indium-gallium, and evaporated silver (soldered with indium). The latter two are by far the best, though not entirely ohmic. Aging effects at room temperature, in the form of an increase of resistance with time, are ascribed to contacts. Temperature