PHYSICAL REVIEW VOLUME 124, NUMBER 5 DECEMBER 1, 1961

Paramagnetic Resonance of Trivalent Pm^{147} in Lanthanum Ethyl Sulfate*

H. J. STAPLETON† AND C. D. JEFFRIES‡
Physics Department, University of California, Berkeley, California

AND

D. A. SHIRLEY
Chemistry Department and Lawrence Radiation Laboratory, University of California, Berkeley, California

(Received July 21, 1961)

Paramagnetic resonance absorption at 3-cm wavelengths is observed for trivalent Pm^{147} in a single crystal of lanthanum ethyl sulfate at 4.2°K. The observed spectra correspond to eight hfs transitions of a system described by the spin Hamiltonian $\mathcal{H}=g_{\|}\beta H_zS_z+AI_zS_z+\Delta_xS_x+\Delta_yS_y$, with $S=\frac{1}{2}$, $I=\frac{7}{2}$, $|g_{\|}|=0.432\pm0.004$, and $|A|/h=496.6\pm4$ Mc/sec. The value of $\Delta=(\Delta_x^2+\Delta_y^2)^{\frac{1}{2}}$ is not directly measured in this experiment but is known from nuclear alignment to be $\Delta/k=0.02\pm0.01$°K. The line shapes exhibit an asymmetry typical of non-Kramers doublets and become unobservable in a few days presumably due to broadening from radiation damage to the crystal. The experimental value of $g_{\|}$ is found to be in reasonable agreement with that predicted from crystal field theory. Effects from higher J level admixtures are taken into account in estimating the nuclear magnetic moment value $|\mu(Pm^{147})|=3.0\pm0.3$ nm.

I. INTRODUCTION

THE electronic configuration of trivalent promethium is that of Xe plus $4f^4$ and according to Hund's rules the free-ion ground level is $^5I_4$. When this ion is substituted for lanthanum in the ethyl sulfate, $La(C_2H_5SO_4)_3\cdot9H_2O$, the 9-fold degeneracy of the $J=4$ ground level is partially removed by the crystal field of C_{3h} symmetry, yielding three doublets and three singlets. For values of crystal fields interpolated from adjacent non-Kramers ions one would expect the lowest energy state to be a non-Kramers doublet.[1] Paramagnetic resonance of such non-Kramers doublets has been generally discussed by Baker and Bleaney[2] who have used a spin Hamiltonian of the form

$$\mathcal{H}=g_{\|}\beta H_zS_z+AI_zS_z+\Delta_xS_x+\Delta_yS_y. \qquad (1)$$

Here β is the Bohr magneton and the terms represent the Zeeman interaction of an effective spin S with an applied field H_z, the magnetic hyperfine interaction with nuclear spin I, and Δ_x and Δ_y represent the effects of random crystal field distortions and allow resonance to be observed. In this paper we report the observation of the paramagnetic resonance of Pm^{3+} in lanthanum ethyl sulfate and compare the results with those predicted from crystal field theory.

II. EXPERIMENTAL DETAILS AND RESULTS

Approximately 10 millicuries (5×10^{16} ions) of trivalent Pm^{147} were grown into a single crystal of lanthanum ethyl sulfate whose mass was about 300 mg; this corresponds to a 0.02 mole-% doping. Pm^{147} has a 2.64-yr half-life and emits weak γ rays and 0.22-Mev beta rays, which damage the crystal structure. The crystal was sealed with GE 7031 varnish, mounted in a rectangular TE_{101} mode cavity and placed in a metal helium Dewar between the poles of a magnet capable of producing fields up to 22 koe. The paramagnetic resonance spectrometer operated at ≈9 kMc/sec, and used video detection and modulation at 155 cps. The search for the Pm resonance was executed at 4.2°K at a frequency of 8.890 kMc/sec.

Eight broad equally intense and equally spaced resonance lines of asymmetric shape were observed at high magnetic fields for various crystal orientations. Figure 1 is a trace of the absorption derivative observed with the z axis of the crystal at an angle of 2.5° to the dc field $\mathbf{H}$. The absorption derivative exhibits the asymmetry typical of non-Kramers doublets[2] which reflects the randomness of Δ_x and Δ_y from one paramagnetic site to another and results in an absorption curve with a sharp high-field cutoff. It is also a characteristic of these doublets that the transition probability is a maximum when the rf magnetic field is parallel to the dc magnetic field.

The exact energy eigenvalues of Eq. (1) give rise to transitions when

$$h\nu=[(g_{\|}\beta H\cos\theta+Am)^2+(\Delta_x^2+\Delta_y^2)]^{\frac{1}{2}}, \qquad (2)$$

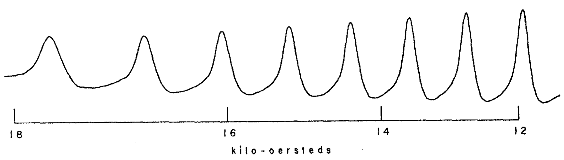

FIG. 1. Derivative of paramagnetic resonance absorption of 0.02 mole-% trivalent Pm^{147} in a single crystal of lanthanum ethyl sulfate at $\nu=8.890$ kMc/sec and $T=4.2$°K. The angle between $\mathbf{H}$ and the hexagonal crystal axis is 2.5°. The lines correspond to eight hfs transitions with $S=\frac{1}{2}$ and $I=\frac{7}{2}$. The absorption lines exhibit the asymmetric shape typical of non-Kramers doublets.

---

* This work was supported in part by the U. S. Atomic Energy Commission and the Office of Naval Research.

† Present address: Physics Department, University of Illinois, Urbana, Illinois.

‡ Associate Research Professor in the Miller Institute for Basic Research in Science.

[1] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).

[2] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

where ν is the rf frequency, m is the nuclear spin magnetic quantum number, and θ is the angle between the dc magnetic field and the hexagonal crystal axis z. The observation of eight hfs lines confirms the nuclear spin $I(\mathrm{Pm}^{147})=\frac{7}{2}$, previously obtained by optical[3] and atomic beam[4] measurements.

The angle θ was determined by the paramagnetic resonances due to Ce^{3+} also present[1] as an impurity in the crystal together with Sm^{3+} and Pr^{3+}. The spectrum was examined at four crystal orientations, each differing by about 10° and starting from a nearly parallel direction. The value of $\Delta=(\Delta_x^2+\Delta_y^2)^{\frac{1}{2}}$ in Eq. (2) could not be determined directly since the spectrum was observed at only one frequency, but Shirley *et al.*[5] have studied the γ-ray anisotropy from oriented Pm^{144} in neodymium ethyl sulfate and conclude that $\Delta/k=0.02\pm0.01$°K. Using this value and probable error for Δ, the magnetic field values for maximum absorption best fit Eq. (2) for $I=\frac{7}{2}$ and $S=\frac{1}{2}$ when

$$|g_{\parallel}|=0.432\pm0.004 \quad \text{and} \quad |A|/h=496.6\pm4 \text{ Mc/sec}. \tag{3}$$

The average deviation between all observed and predicted absorption peaks (derivative nulls) is then 23 oe (0.15%).

The linewidth can be described by the equation $\delta H \cos\theta=$ constant, where δH is the width between the high-field derivative peak and the derivative null. For the first crystal, which had been grown 12 hr prior to the resonance experiment, $\langle\delta H \cos\theta\rangle_{\mathrm{av}}=147\pm10$ oe. The same crystal was examined again after four days and no Pm resonance was observed, presumably because radiation damage to the crystal had broadened the lines excessively. A second crystal with approximately the same mole percent of Pm^{3+} was found to have a narrower linewidth, $\delta H \cos\theta$ being about 50 oe, when it was examined at 4.2°K within 4 hr of the end of its growth.

An electron-nuclear double resonance (ENDOR) experiment was attempted on a third newly grown crystal at 2.0°K at a microwave frequency of 8.520 kMc/sec. The transition corresponding to $m=+\frac{5}{2}$ in Eq. (2) was partially saturated while a second rf magnetic field whole frequency varied from 200 to 280 Mc/sec was introduced at the crystal site. No change in the amplitude of the electron resonance signal greater than noise (4%) was detected. Negative results were also obtained for the $m=-\frac{5}{2}$ transition.

Nuclear alignment experiments of Pm isotopes performed at Oxford[6] have indicated that when Pm^{3+} is grown into single crystals of concentrated cerium magnesium nitrate, a singlet state probably lies lowest with a doublet about 1 cm^{-1} higher. We have examined two lanthanum magnesium nitrate crystals containing 0.02 mole percent Pm^{3+} at various orientations at a frequency of 8.2 kMc/sec at a temperature of 2.0°K. No resonances due to Pm were observed for magnetic fields up to 22 koe.

III. THEORETICAL INTERPRETATION

The effect of a crystal field of C_{3h} symmetry on the levels of Pm^{3+} can be treated using the methods of Elliott and Stevens.[7] The operator corresponding to the crystal potential can be written as

$$\begin{aligned}\mathcal{H}_V=A_2^0\sum(3z^2-r^2)+A_4^0\sum(35z^4-30r^2z^2+3r^4)&\\ +A_6^0\sum(231z_6-315r^2z^4+105r^4z^2-5r^6)&\\ +A_6^6\sum(x^6-15x^4y^2+15x^2y^4-y^6)&\\ =V_2^0+V_4^0+V_6^0+V_6^6,&\end{aligned}\tag{4}$$

where the summation is extended over the coordinates of all electrons. The matrix elements of V_n^m in Eq. (3) can be evaluated by the operator equivalent method of Stevens[8] and involve $A_n^m\langle r^n\rangle$, a known function of J, J_z, and a reduced matrix element as tabulated by Elliott and Stevens.[7,9] The crystal field parameters $A_n^m\langle r^n\rangle$ which best fit the observed optical and paramagnetic resonance data for several other rare-earth ethyl sulfates have been given by Judd.[10] We take the average of his values for Pr^{3+} ($4f^2$) and Eu^{3+} ($4f^6$) to give approximate values for Pm^{3+} and find

$$\begin{aligned}A_2^0\langle r^2\rangle&=65\pm8\ \mathrm{cm}^{-1},\\ A_4^0\langle r^4\rangle&=-82\pm9\ \mathrm{cm}^{-1},\\ A_6^0\langle r^6\rangle&=-44\pm2\ \mathrm{cm}^{-1},\\ A_6^6\langle r^6\rangle&=585\pm38\ \mathrm{cm}^{-1},\end{aligned}\tag{5}$$

where the "errors" represent one half the difference between the corresponding best fitting values for Pr^{3+} and Eu^{3+}. With these center values the diagonalization of the crystal field interaction, Eq. (4), within the $J=4$ ground level results in a non-Kramers doublet lying lowest, whose wave functions are approximately

$$|\pm\rangle\approx0.63|J=4,\ J_z=\pm4\rangle-0.78|J=4,\ J_z=\mp2\rangle. \tag{6}$$

For this wave function the value of $g_{\parallel}$ is given by

$$g_{\parallel}=2\Lambda\langle+|J_z|+\rangle=0.44, \tag{7}$$

where $\Lambda=\frac{3}{5}$.[7] Although this is in good agreement with the observed value, Eq. (3), we feel that this may be fortuitous for the following reason. The predicted value of $g_{\parallel}$ is very sensitive to the assumed crystal field

---

[3] P. F. A. Klinkenberg and F. S. Tomkins, Physica **26**, 103 (1960).

[4] A. Cabezas, I. Lindgren, E. Lipworth, R. Marrus, and M. Rubenstein, Nuclear Phys. **20**, 509 (1960).

[5] D. A. Shirley, J. F. Schooley, and J. O. Rasmussen, Phys. Rev. **121**, 558 (1961).

[6] C. J. S. Chapman, M. A. Grace, J. M. Gregory, and C. V. Sowter, Proc. Roy. Soc. (London) **A259**, 377 (1960).

[7] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

[8] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

[9] We note that their $\langle J\|\gamma\|J\rangle$ for Pm^{3+} is correctly given by $2^3\times17\times19/3^3\times7\times11^3\times13^2$.

[10] B. R. Judd, Mol. Phys. **2**, 407 (1959).

parameters of Eq. (5). For example, a change in $A_6^0\langle r^6\rangle$ of 2 cm^{-1} (i.e., within its uncertainty) produces a 15% change in the calculated g value.

We note that the exact mixture of $|J=4,\ J_z=4\rangle$ and $|J=4,\ J_z=-2\rangle$ states required to yield the observed value of $g_{\parallel}$ is

$$|\pm\rangle=0.627|4,\ \pm4\rangle-0.779|4,\ \mp2\rangle. \tag{8}$$

Using this wave function we evaluate the magnetic hyperfine constant

$$A=4(\mu_n/I)\beta\langle r^{-3}\rangle\langle+|N_z|+\rangle, \tag{9}$$

taking $\langle r^{-3}\rangle=36.6\ \mathrm{A}^{-3}$ as given by Judd and Lindgren[11] to find $|\mu_n|=3.4$ nuclear magnetons for Pm^{147}. This value is surprisingly large since the unpaired proton of the nucleus would be expected to lie in a $g_{7/2}$ level from simple shell theory with resulting Schmidt and Dirac limits of $+1.72$ nm and $+3.11$ nm, respectively. Further, Klinkenberg and Tomkins[3] have estimated the nuclear moment to be 2.7 nm from optical data with an estimated error of less than 10%. We have not yet considered admixture from higher J levels and, as will now be shown, such admixtures affect the results critically.

Crozier and Runciman[12] have studied the optical spectrum of Pm^{3+} in solution and conclude that the energy difference between the $J=4$ and $J=5$ levels, mostly due to spin-orbit interaction, is about 1586 cm^{-1}. The effect of Eq. (4) operating within and between the $J=4$ and $J=5$ manifolds is to admix $|J=5,\ J_z=4\rangle$ and $|J=5,\ J_z=-2\rangle$ states with the $|J=4,\ J_z=4\rangle$ and $|J=4,\ J_z=-2\rangle$ states. The matrix of the spin-orbit and crystal field interactions [Eq. (4) with the values of Eq. (5)] between these four basis states can be calculated with the aid of the reduced matrix elements[13] and the result is

$$\begin{array}{c|cccc} & |4,4\rangle & |4,-2\rangle & |5,4\rangle & |5,-2\rangle \\ \hline \langle 4,4| & -27.5 & 67.7 & 100.0 & -68.8 \\ \langle 4,-2| & 67.7 & -56.1 & 135 & 9.7 \\ \langle 5,4| & 100.0 & 135 & 1584 & -25.1 \\ \langle 5,-2| & -68.8 & 9.7 & -25.1 & 1603.5 \end{array} \tag{10}$$

where the energies are expressed in cm^{-1} and the energy of the degenerate $J=4$ level is arbitrarily set equal to zero. The energy eigenvalues and eigenfunctions of this matrix have been calculated on an IBM 704 computer and the lowest energy eigenvalue is $E=-113.63\ \mathrm{cm}^{-1}$ as compared with the zero-order energy of $-111.0\ \mathrm{cm}^{-1}$. The associated eigenfunction is

$$\begin{aligned}|\pm\rangle=0.6125|4,4\rangle-0.7894|4,\ -2\rangle \\ +0.0271|5,4\rangle+0.0294|5,\ -2\rangle,\end{aligned} \tag{11}$$

yielding a calculated g value of $g_{\parallel}=+0.256$. As the coefficients of the two admixture terms from the $J=5$ level should not depend so critically on the values of the crystal field parameters, one might reasonably try to adjust the first two coefficients in Eq. (11), keeping the last two fixed to bring the calculated g value to 0.432. The result is the function

$$\begin{aligned}|\pm\rangle=0.6317|4,4\rangle-0.7741|4,\ -2\rangle \\ +0.0271|5,4\rangle+0.0294|5,\ -2\rangle.\end{aligned} \tag{12}$$

From Eq. (12) (which we feel to be the best over-all estimate of the wave function) one can calculate $\langle+|N_z|+\rangle=+0.565$, which yields

$$|\mu_n(\mathrm{Pm}^{147})|=3.0\ \mathrm{nm}, \tag{13}$$

using the same value of $\langle r^{-3}\rangle$ as before. We feel that this value may be in error by as much as 10% because of the critical dependence of $g_{\parallel}$ and $\langle+|N_z|+\rangle$ on the admixtures of higher states and the uncertainty in the crystal field parameters.

Because consideration of the $^5I_5$ level changed the theoretical value of $g_{\parallel}$ and μ substantially we have also computed the effect of the $^5I_6$ level, using the spin-orbit spacing $E(^5I_6)-E(^5I_4)=3305\ \mathrm{cm}^{-1}$ given by Crozier and Runciman.[12] The computation of the matrix elements of the crystal field terms in such a calculation is greatly facilitated by the use of Eqs. (25) and (26) given by Elliott, Judd, and Runciman,[14] which allow one to express such elements as $\langle J=4,\ J_z=4|V_2^0|J=6,\ J_z=4\rangle$, etc., in terms of tabulated $3-j$ and $6-j$ symbols.

An analysis was thus performed similar to that outlined above but considering the $^5I_6$ level as well as the $^5I_4$ and $^5I_5$ levels. Using the crystal field parameters given in Eq. (5), we obtained a theoretical value of $g_{\parallel}=0.213$ for the lowest doublet. After adjusting the $|4,4\rangle$ and $|4,\ -2\rangle$ coefficients to yield the experimental g value, one finds that the calculated $|\mu|$ value is affected by less than 0.5%.

ACKNOWLEDGMENTS

We wish to acknowledge numerous helpful discussions with Dr. R. J. Elliott and Dr. B. R. Judd.

---

[11] B. R. Judd and I. P. K. Lindgren, Phys. Rev. **122**, 1802 (1961).

[12] M. H. Crozier and W. A. Runciman (to be published).

[13] Reduced matrix elements required for the crystal field interaction in addition to those tabled by Elliott and Stevens (see reference 7) are: $\langle J=5\|\alpha\|J=5\rangle=29/3^2\times5\times11\times13$, $\langle J=5\|\beta\|J=5\rangle=2^3\times17/3^3\times5\times7\times11^2\times13$, and $\langle J=5\|\gamma\|J=5\rangle=-19/3^3\times7\times11^2\times13^2$. The additional reduced matrix elements required to calculate $g_{\parallel}$ and $\langle+|N_z|+\rangle$ are $\langle J=5\|\Lambda\|J=5\rangle=9/10$ and $\langle J=5\|N\|J=5\rangle=709/660$.

[14] J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) **A240**, 509 (1957).