

validity of a molecular viewpoint. However, even the results reported here tend to support the application of this approach at higher velocities.

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Electron Paramagnetic Resonance of Photoexcited States of Nd^{+3} in Single Crystals of LaCl_3 †

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Electron-paramagnetic-resonance spectra of Nd^{+3} ions in the f^3 , $^4I_{13/2}$ and $^4I_{15/2}$ excited states were observed at $\sim 1.5^\circ\text{K}$ in a single-crystal LaCl_3 host. Values of the spin-Hamiltonian parameters which describe the spectra of the even-nuclear-spin species and of the $^{146}\text{Nd}^{+3}$ ion were determined. The excited states of Nd^{+3} were populated by energy transfer from photoexcited U^{+3} ions incorporated in the same crystal.

We have observed electron paramagnetic resonance (EPR) of the $^4I_{13/2}$ and $^4I_{15/2}$ photoexcited states of the configuration f^3 of Nd^{+3} ions substituted dilutely for La^{+3} ions in a LaCl_3 single crystal. This is the first observation of EPR in a photoexcited metastable state of a tripositive rare-earth ion.

The EPR spectra were observed at $\sim 1.5^\circ\text{K}$ from crystals prepared in the same manner as described previously,^{1,2} and which contained ~ 0.2 mole% each of Nd^{+3} and U^{+3} ions. The Nd was enriched³ in ^{145}Nd with nuclear spin $I = \frac{7}{2}$, and the U contained normal isotopic abundances.³ The crystals were held in, and irradiated through, fused silica cylinders, and were in contact with superfluid helium. A 1000-W mercury-xenon arc, whose light was filtered through a 5-cm thickness of a 100-g/l solution of CuSO_4 in H_2O ,⁴

was used for the photoexcitation. The superheterodyne-detection EPR spectrometer, with a carrier frequency of $\sim 23.8 \times 10^9$ Hz, was the same as that used previously⁵ in this laboratory for the study of photoexcited states of organic molecules in crystals.

Irradiation of the crystals produced two nine-line EPR spectra which decayed, upon cessation of irradiation, with measured values of 15 and 40 msec for their mean lifetimes, with an estimated standard deviation of 5 msec. Oscilloscope displays of these spectra are shown in Fig. 1. The eight lines corresponding to $I = \frac{7}{2}$ plus one line from the spinless species identified the lines as having their origin in the Nd^{+3} ions. The values of the decay times indicated that low-lying levels of the 4I manifold were being observed.⁶ Values of g_{\parallel} in the spin Hamiltonian^{1,7}

$$\mathcal{H}_S = |\beta| [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A S_z I_z + B (S_x I_x + S_y I_y) + P [I_z^2 - \frac{1}{3} I(I+1)], \quad S = \frac{1}{2}, \quad I = \frac{7}{2}, \quad (1)$$

for all crystal-field states of configuration f^3 have been computed by Eisenstein⁸ Nd^{+3} in LaCl_3 . He considered Coulomb, spin-orbit, and crystal-field interactions within the configuration f^3 . The values of g_{\perp} in (1) were evaluated for all the crystal-field states of $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ by using the crystal-field states for Nd^{+3} in LaCl_3 listed by Halford.⁷ He took into account only the interactions within the manifold described by J

$= \frac{9}{2}, \frac{11}{2}, \frac{13}{2}$. The values of g_{\perp} for the $^4I_{15/2}$ state were calculated assuming no interactions with other J levels. The crystal-field parameters and operator-equivalent factors given by Judd⁹ and the crystal-field matrix elements of Stevens¹⁰ and of Elliott and Stevens¹¹ were used in this last-mentioned calculation. All of these computed g values were compared with the g values ob-

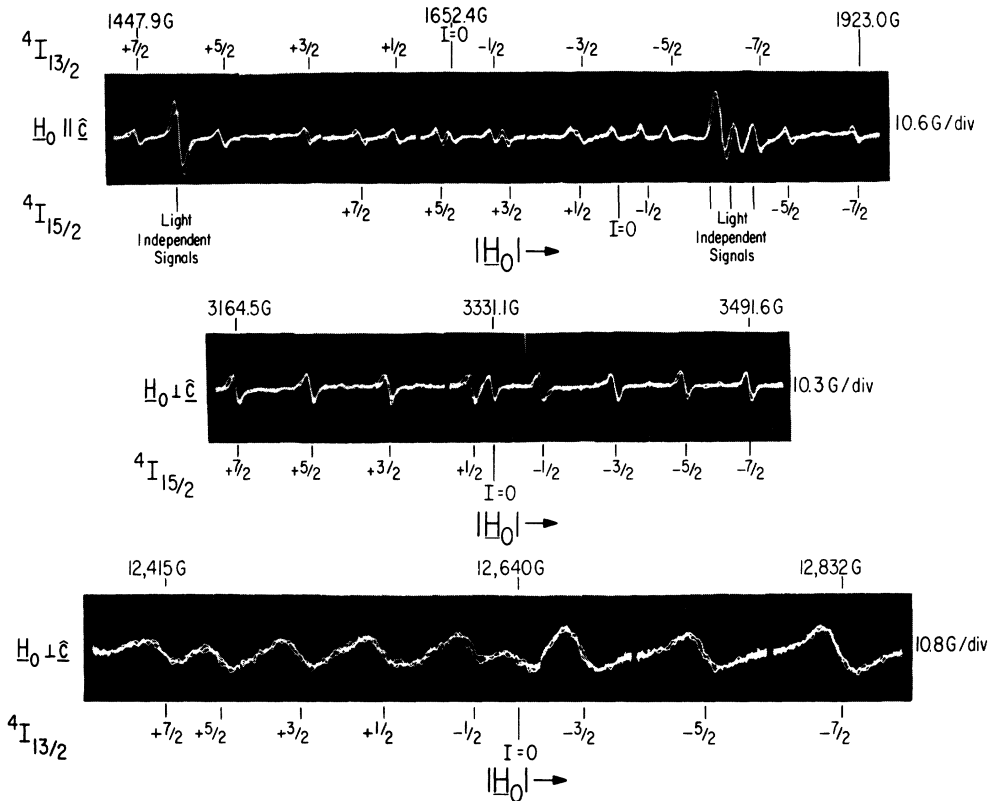


FIG. 1. EPR spectra. Photoexcited states of $^{145}\text{Nd}^{+3}$; 0.2 mole% $^{145}\text{Nd}^{+3}$, 0.2 mole% U^{+3} in LaCl_3 .

tained by fitting the first two terms of the spin Hamiltonian (1) to the single-line spectra shown in Fig. 1 for the spinless species. This comparison served unambiguously to identify the observed spectra as originating with the $^4I_{13/2}$, $2\mu = 1$ and $^4I_{15/2}$, $2\mu = 1$ states. These states were found by Carlson and Dieke¹² to lie 3391 and 5869 cm^{-1} , respectively, above the lowest-ener-

gy crystal-field state, $2\mu = 5$, of the ground $^4I_{9/2}$ manifold. Each of these observed states is the one of lowest crystal energy for its J manifold. The computed and observed g values for the two observed states are given in columns 4 and 5 of Table I. The agreement between observed and calculated g values in the case of the $^4I_{13/2}$ state is excellent. The poorer agreement for the val-

TABLE I. Values of parameters in the spin Hamiltonian, Eq. (1), for $^{145}\text{Nd}^{+3}$ in LaCl_3 single crystals. Estimated standard deviations are given in parentheses; μ is the crystal-field quantum number.

State	2μ	Comment	From even isotope $I=0$ lines		$ A /h$ (MHz)	$ B /h$ (MHz)	$ P /h$ (MHz)
			$ g_{\parallel} $	$ g_{\perp} $			
$^4I_{9/2}$	5	Ground state	3.9903 ^a	1.7635 ^a	790.736 ^a (0.016)	310.68 ^a (0.14)	0.0427 ^a (0.0022)
$^4I_{13/2}$	1	Observed	10.180 (0.005)	1.347 (0.004)	828.1 (5.0)	111.3 (2.0)	6.2 (1.0)
		Calculated	10.26 ^b	1.196
$^4I_{15/2}$	1	Observed	9.554 (0.005)	5.127 (0.005)	620.9 (4.0)	335.3 (2.0)	<1.0 ...
		Calculated	9.67 ^b	4.426

^aRef. 7.

^bRef. 8.

ue of g_{\perp} for the ${}^4I_{15/2}$ state reflects the much less accurate character of the state which was used in this case.

The lifetimes given above for the observed states are in reasonably good agreement with the lifetimes 31.4 ± 2.5 and 15.7 ± 1.0 msec for ${}^4I_{13/2}$ and ${}^4I_{15/2}$, respectively, measured by optical methods by Gandrud and Moos.⁶

The values of g_{\parallel} and g_{\perp} in (1) were kept fixed at the values determined as described above by the single-line spectra of the spinless species, and the other parameters were varied to give a fit to the lines for the ${}^{145}\text{Nd}^{+3}$. The approximate fitting procedure of Bleaney, Hutchison, Llewellyn, and Pope¹³ was used for this purpose. The values of the parameters for this fit are listed in Table I. It may be noted that the value of $g_{\parallel}B/g_{\perp}A$ is extremely close to 1 in both cases, indicating that the states are quite accurately eigenstates of \vec{J} .

The present work is of particular importance because of the vast number of previous magnetic resonance investigations¹⁴ of the ground states of the tripositive rare-earth ions in single crystals. It is a matter of considerable interest to extend magnetic resonance studies to the excited states of these ions which are so very well known in their ground states. The optical absorption of the tripositive rare-earth ions in the accessible regions of wavelength consists of relatively weak and narrow lines¹⁵ at low temperatures. Thus direct photoexcitation by conventional broad-band light sources is relatively inefficient. There have been a few reports of magnetic resonance studies of dipositive rare-earth ions in crystals by conventional methods^{16,17} and by the optical detection method,¹⁸ in which cases the broader and stronger optical absorptions make possible the attainment of the number of photoexcited ions required for conventional EPR investigations as estimated, e.g., by Clogston.¹⁹ In order to achieve sufficient numbers of photoexcited ions, U^{+3} ions were incorporated at La^{+3} ion sites in the LaCl_3 crystal in the present studies. The U^{+3} ions exhibit very strong and broad absorption² in the blue region of the visible spectrum. They thus form very efficient absorbing centers for the light from the mercury-xenon arc, and their excitation energy is also very efficiently used to populate excited states Nd^{+3} ions by energy transfer. The CuSO_4 filter transmits⁴ in just that wavelength region in which U^{+3} absorbs the light from the arc. In the absence of U^{+3} ions in a crystal containing ~1.0 mole% ${}^{145}\text{Nd}^{+3}$ ions (5 times the concentration for the

crystals used for the data of Fig. 1), it was possible to detect only the ${}^4I_{5/2}$ state with a signal-to-noise ratio somewhat less than 1, under the same experimental conditions as those for which the spectra in Fig. 1 were obtained.

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³The Nd contained the following atom percents of the various species: 90.56 ${}^{145}\text{Nd}$, 0.79 ${}^{143}\text{Nd}$, 8.26 even spinless species; the remainder is rare earth and other impurities. The natural-abundance U contains 99.28 at.% spinless species.

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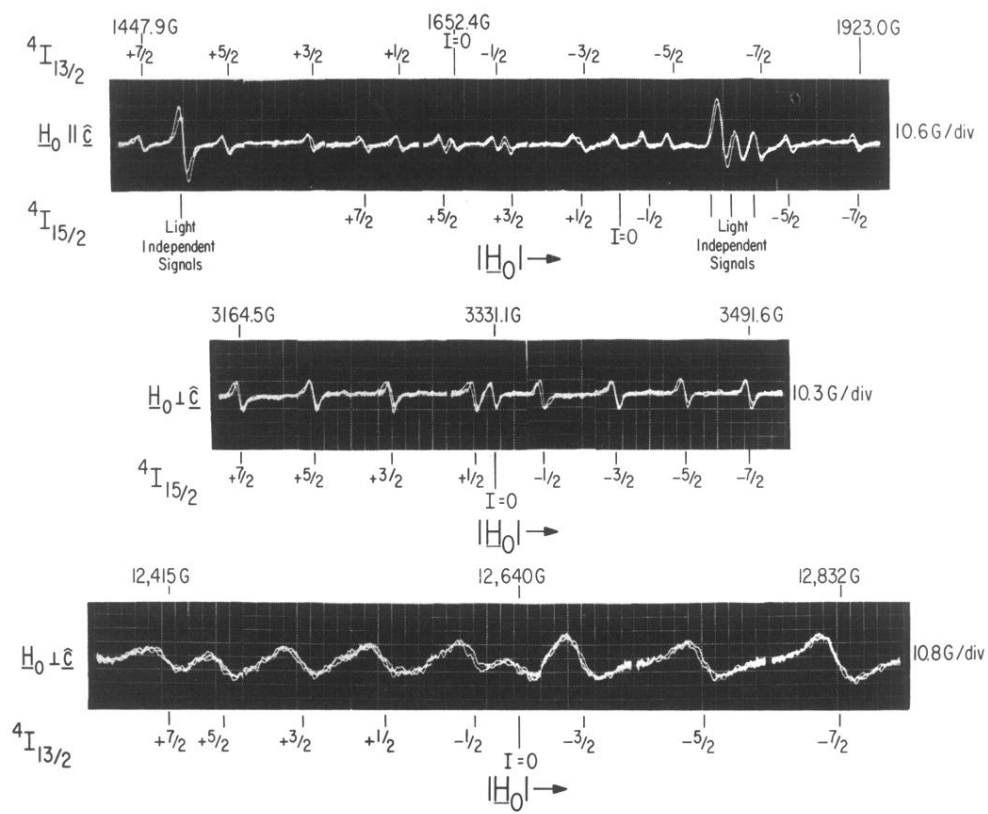


FIG. 1. EPR spectra. Photoexcited states of $^{146}\text{Nd}^{+3}$; 0.2 mole% $^{146}\text{Nd}^{+3}$, 0.2 mole% U^{+3} in LaCl_3 .