

Letters to the Editor

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Hyperfine Structure of *F*-Center Spin Resonance in Lithium Fluoride and Sodium Fluoride*

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IN most *F* centers¹ the hyperfine broadening of the electron spin resonance has not been resolved by observation of the spin energy absorption. This is not the case for LiF² and NaF. Figure 1 shows the spin resonances of their x-ray-induced *F* centers. From these resolved structures it is possible to ascertain the basic model of the *F* center, the values of the wave function at the two nearest shells of nuclear sites, and the spectroscopic splitting factor with high precision.

In magnetic fields of around 3000 gauss when small radio-frequency field oscillations are used to cause electron spin transitions, the Zeeman energy difference³ is, to the first order,

$$W_1 - W_2 = g_J \mu_0 [H_0 + \sum_{\gamma} h_{\gamma} M_{\gamma}];$$

$$M_{\gamma} = -n_{\gamma} i_{\gamma}, \quad -(n_{\gamma} i_{\gamma} - 1), \quad \dots,$$

$$+ (n_{\gamma} i_{\gamma} - 1), \quad n_{\gamma} i_{\gamma}. \quad (1)$$

Here h_{γ} is the hyperfine field of the equivalent nuclei of the γ th shell surrounding the *F* center. If we neglect the small angular contribution to the hyperfine interaction from the *F*-center wave function, then

$$h_{\gamma} = -\frac{16\pi \mu_{\gamma}}{3g_J i_{\gamma}} |\psi(\gamma)|^2 \text{ gauss.} \quad (2)$$

Here $\psi(\gamma)$ is the value of the orthogonalized wave function at the nuclei γ .

In LiF and NaF, $h_1 \gg h_2$ and there results a resolved series of components centered at H_0 and separated by intervals of h_1 . All of the resonance patterns had these common characteristics: an odd number of components, 15 or more, and an intensity ratio of approximately 0.1 for the sixth component to the central one. Detailed consideration of the interstitial model⁴ shows that it cannot give rise to these characteristics except when special relations exist between $h_2(\text{F})$ and $h_1(\text{alkali})$. This is hardly likely in both crystals. On the other

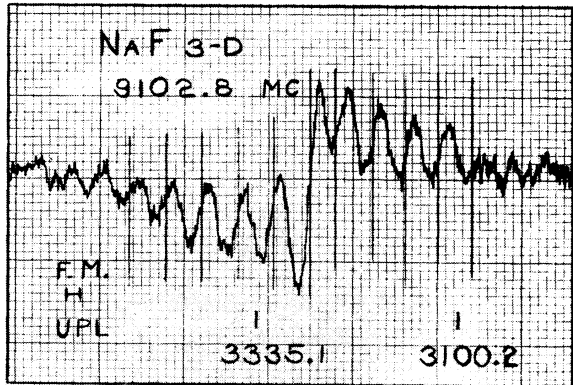
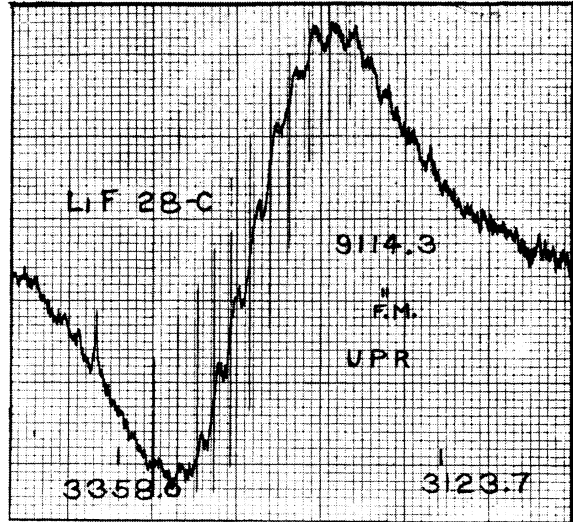


FIG. 1. The slope $d\chi''/dH$ of the spin resonance absorption in LiF and NaF for microwave frequencies of around 9000 Mc/sec in fields of around 3000 gauss. The amplitudes of field modulation used are labeled F.M. For LiF, $\sigma/h_1=0.57$. For NaF, $\sigma/h_1=0.39$.

hand, the vacancy model with $h_2(\text{F}) \ll h_1(\text{alkali})$ conforms very well without special relations.

For this model, the second moment, σ^2 , of the broadening of each component is mostly due to $h_2(\text{F})$. Then $h_2(\text{F}) \cong \sigma/\sqrt{3}$. The value of σ may be determined from the oscillations in the resonance pattern which depend only on σ/h_1 .

The splitting factor in (1), g_J , may be determined very accurately from the centroid, H_0 , of the pattern of components rather than from the envelope. Expansion of the Breit-Rabi formula yields a second-order correction which is appreciable for large h_1 . For $i = \frac{3}{2}$, H_0 is multiplied by $[1 + (5/4)(h_1/H_0)^2]$. The magnetic field is accurately determined by the resonance of protons in a water probe. The positions of the probe and sample are

TABLE I. Results: h in gauss, $|\psi|^2$ in cm^{-3} .

	$h_1(\text{alk.})$	$ \psi(\text{alk.}) ^2$	$h_2(\text{F})$	$ \psi(\text{F}) ^2$	g_J/g_e
LiF	14.1 ± 0.1	1.53×10^{23}	4.6 ± 0.5	0.21×10^{23}	1.00031 ± 0.00006
NaF	37.8 ± 0.3	6.05×10^{23}	8.6 ± 1	0.39×10^{23}	0.99999 ± 0.00010

interchanged in the magnetic field to cancel any difference. The accurately known ratio⁵ of free electron to proton magnetic moments is used to express the ratio of g_J to the free-electron value, g_e . All the results appear in Table I. The errors represent 95% confidence limits. A more detailed report is being prepared.

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Paramagnetic Resonance Spectrum of Curium*

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WE have observed the paramagnetic resonance spectrum of curium in anhydrous lanthanum trichloride at three-cm wavelength and room temperature. Seven lines can clearly be distinguished confirming the assignment of seven $5f$ electrons¹ and a ground state of $^8S_{7/2}$ analogous to the spectrum of gadolinium [(4f)⁷]. The spectrum can be described by the following Hamiltonian:

$$\mathcal{H} = g\mathbf{H} \cdot g \cdot \mathbf{S} + B_2^0 P_2^0 + B_4^0 P_4^0 + B_6^0 P_6^0 + B_6^6 P_6^6,$$

where P_m^n are operators and are given by Elliott and Stevens.² Following Bleaney *et al.*,³ one defines for convenience

$$b_2^0 = 3B_2^0, \quad b_4^0 = 60B_4^0, \quad b_6^0 = 1260B_6^0, \quad b_6^6 = 1260B_6^6.$$

From the measured absorption lines when H is perpendicular to the c axis, we find that at room temperature

$$g = 1.9914 \pm 0.0003, \quad b_2^0 = 8.2 \pm 0.2 \text{ gauss}, \\ b_4^0 = 2.2 \pm 0.2 \text{ gauss}, \quad (b_6^6 - 5b_6^0) \geq 3.7 \pm 0.5 \text{ gauss},$$

which can be compared with Jeffries' recent values⁴ of $g \cong 2.00$, $b_2^0 = 11$ gauss at 77°K. The analogous spectra of Gd^{+3} in $LaCl_3$ determined by Hutchison *et al.*⁵ gave the following parameters:

$$g = 1.991 \pm 0.001, \quad b_2^0 = 9.1 \pm 0.1 \text{ gauss}, \\ b_4^0 = 1.81 \pm 0.04 \text{ gauss}, \quad b_6^0 = 0.69 \pm 0.15 \text{ gauss}.$$

The small differences in the values of b_2^0 and b_4^0 are sufficient to give the appearance of different spectra for the two ions.

$LaCl_3$ single crystals were prepared by the method outlined by Anderson and Hutchison⁶ in narrow quartz tubes. The curium was carefully purified so as to be free from any other rare earth elements. The best spectrum was obtained with a single crystal containing 20 μg of Cm^{244} at a dilution of about one part in 2000. The radiation damage caused by the intense α radiation caused all transitions except for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition to disappear within 24 hours. Some lines caused by radiation damage were detected, but were of small intensity compared with the 7 fine structure lines. The crystal fluoresces very strongly with a light blue color. We have also observed the spectrum of Cm in a magnesium bismuth nitrate single crystal.⁷ Seven lines were observed in a crystal containing about 15 μg of Cm . Larger amounts of Cm caused so much radiation damage so as to obscure the spectrum of Cm . Three intense lines caused by radiation damage stood out in particular. They fall at $g = 2.003$ and with an average separation of 62 gauss with H parallel to the c axis. The three lines are characteristic of a hyperfine structure of N^{14} , the only isotope with nuclear spin 1 in this crystal. The radiation damage spectrum was not investigated in detail but there seem to be more than one nitrogen ion per unit cell.

In addition we have incorporated Cm into ThO_2 and $CaCl_2$. Many lines were observed, presumably caused by radiation damage. Similar lines were observed when these compounds were exposed to a cobalt source. We have also attempted, so far unsuccessfully, to find a hyperfine structure due to the nuclear moment of the odd isotope Cm^{245} . Work along this direction is being continued.

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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Radiation Damage Experiments in III-V-Compounds*

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SO far relatively few investigations on radiation damage have been published in which x-ray techniques were used to detect the effect of nuclear radiation on metals and semiconductors. It seemed of interest to see if x-rays could give information on the effect of radiation on the III-V-compounds. This group of compounds crystallizes in the zinc blende structure and

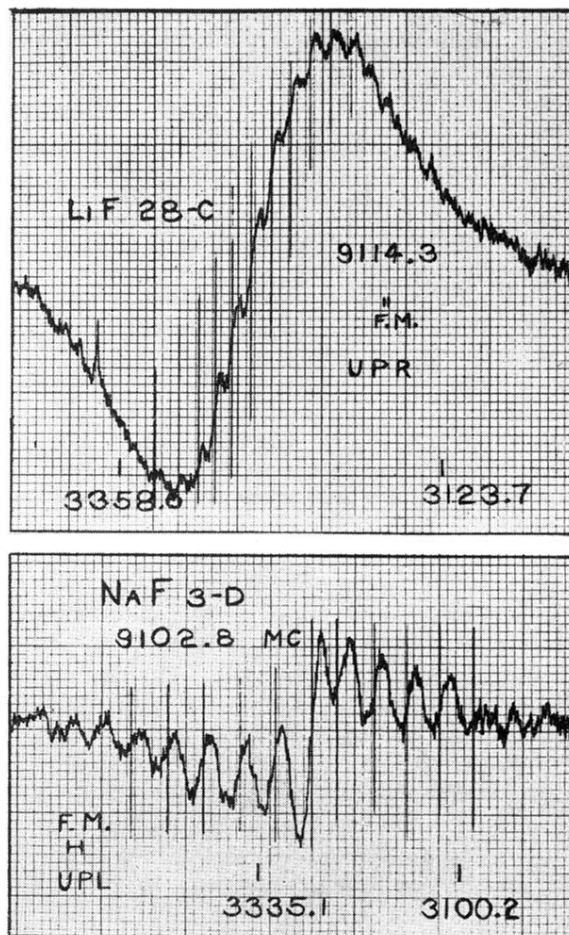


FIG. 1. The slope dx''/dH of the spn resonance absorption in LiF and NaF for microwave frequencies of around 9000 Mc/sec in fields of around 3000 gauss. The amplitudes of field modulation used are labeled F.M. For LiF, $\sigma/h_1=0.57$. For NaF, $\sigma/h_1=0.39$.