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Electron Paramagnetic Resonance in Irradiated CsCl

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Two paramagnetic species have been observed in CsCl after irradiation at low temperatures with 2-Mev electrons. One of these, an anisotropic, "hole"-type center, has not yet been positively identified. The resonance signal from the other center has all the properties expected of the CsCl F center. The F-center parameters are $g=1.984\pm0.001$, $A=49.5\pm1.0$ gauss, and the envelope width at half maximum is approximately 800 gauss. The partially resolved hyperfine lines due to the nearest-neighbor Cs nuclei have an estimated width at half maximum of 17 ± 5 gauss. Due to the low signal-to-noise ratio only 38 of the expected 57 lines have been observed.

INTRODUCTION

ELECTRON paramagnetic resonance (EPR) has been observed for the F center in a number of the alkali halides possessing body centered structure.[1–5] However, no EPR work has been reported for the F center in the three salts CsCl, CsBr, and CsI which exist in the body-centered cubic structure.

Recent optical work on irradiated CsCl and CsBr has shown structure in the optical absorption band associated with the F center.[6,7]

The present work was undertaken to see whether EPR measurements of the ground state of the F center would show unusual characteristics.

APPARATUS

The resonance data was taken with a conventional hybrid-T bridge spectrometer operating at 9.3 kMc/sec. The minimum spin sensitivity was 10^{13} spins of DPPH. The applied field was produced by a 12-in. Varian electromagnet on a rotary base, and field measurements were made with a Numar proton magnetometer.

The crystals were mounted in a rectangular brass cavity using the TE_{101} mode. The end wall of the cavity was milled to a thickness of about 0.002 in. over a $\frac{1}{4}$-in. diam area which provided a window for electron irradiations. During an irradiation, the cavity was vertical with the end wall uppermost and the sample rested on the inductive coupling iris. A demountable cup containing the coolant (liquid N_2 or dry ice—trichlorethylene) surrounded the cavity and a stream of dry He was forced into the cavity. After irradiation the open end of the waveguide connected to the cavity was sealed with a glass-metal microwave window, and the cavity was inverted and immersed in a conventional glass liquid N_2 Dewar for EPR observation. During the process the sample temperature did not rise above the cryostat temperature.

All irradiations were performed with 2-Mev electrons from a Van de Graaff generator. A depth-dose curve for CsCl was obtained for CsCl at this energy by stacking alternate thin plates of CsCl and Mylar sheets.[8] All quoted dose values are for absorbed dose and are expected to be only accurate to ±50% since the cavity geometry was unfavorable for measurement.

The concentration of F centers, obtained by additively coloring in Cs vapor for one week at five degrees below the fcc–bcc phase change, was also too low to be observed. Crystals heated in Cs vapor to temperatures above the phase change apparently have nearly unlimited amounts of excess Cs present (perhaps due to the low Cl binding energy). However most of the Cs excess is apparently in the form of colloidal metal since no EPR signal could be obtained from samples containing up to 5×10^{19}/cc of Cs as determined chemically. The crystals could also be colored by x rays but the center concentrations were too low to observe EPR lines.

Most of the work was done with samples from a one inch cube of melt-grown CsCl crystal obtained from Semi-Elements Corporation. It was made up of oriented grains 2–10 mm in dimension. The grains appear to have a common orientation to within 1° to 5°.

A few runs were also made on small samples of CsCl grown from a 0.05% Ce-doped CsCl solution.[9] Although the crystals[10] contained less than 5 parts per million (ppm) of Ce, they had many small oriented inclusions which gave the material an opalescent appearance when polished. These samples were used only to make sure that the resonance data was not sample dependent.

Since CsCl does not cleave, samples were rough-sawed with a wet string and water polished to about 3 mm thickness with an area which completely filled the cavity cross section.

F-CENTER THEORY

On the basis of the deBoer[11] model for the F electron and on previous EPR results for the other alkali halides,

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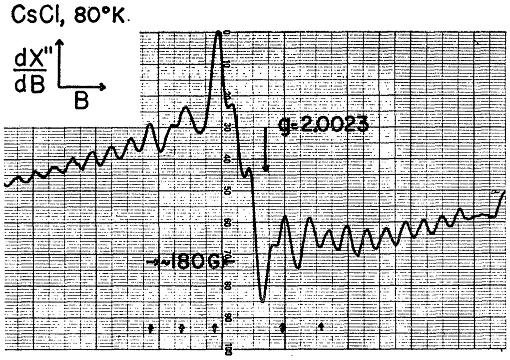

FIG. 1. Absorption derivative vs magnetic field. CsCl; Semi-Elements Corporation, after 3×10^8 r at 80°K. $B_{\text{mod}}=5$ gauss; $(B_{\text{rf}})^2\sim0.4$ mw. With this sensitivity, 1.5×10^{16} spins of DPPH produced full-scale deflection on recorder.

the CsCl F center may be expected to behave as an unpaired spin, interacting rather strongly with the $N=8$ spins of the nearest-neighbor Cs nuclei. This interaction should produce $(2I_n+1)^N$ spin states distributed among $2NI_n+1$ levels (Appendix I). The effects of the succeeding nuclei shells usually appear as broadening of the hyperfine lines.

The system spin Hamiltonian will be

$$H=g\beta\mathbf{B}\cdot\mathbf{S}+H_{\text{hfs}}, \tag{1}$$

where terms of the form $\mathbf{B}\cdot\mathbf{I}$ have been neglected since they are of the order of the present experimental error. H_{hfs} is made up of terms of the form $A_l(\mathbf{I}_l\cdot\mathbf{S})$.

Experimentally, one expects g shifts due to spin orbit terms not included in Eq. (1). There may be also a small g shift and a variation in line spacing due entirely to the hyperfine interaction.[12] If the nuclear spin angular momentum is summed properly,[13] the resonance conditions are given by the usual equation

$$h\nu=g\beta B+AM_i,\quad(-28\leq M_i\leq 28). \tag{2}$$

It will be shown in Appendix II that the hyperfine g shift and the line spacing variations can be expressed as small corrections to Eq. (2).

RESULTS

Figure 1 shows the paramagnetic absorption derivative vs applied magnetic field for a CsCl sample after electron irradiation at 80°K. The arrows at the bottom show the field positions of a number of lines which are apparently due to a single anisotropic center with a g value greater than that of a free electron. The main structure is due to the F center. At this concentration ($\sim10^{19}/\text{cm}^3$) all lines show dipolar broadening. Only 38 of the expected 57 lines have been observed to date.

The centers produced under these conditions had sample-dependent production rates, thermal bleaching rates, and power saturation parameters. The saturation of center production vs radiation dose obtained in the Semi-Elements material was a factor of 10 higher than in the solution-grown material. However, EPR lines showed no field variation among the different samples.

Since the optical density of the material is so high (OD ~ 10–100) after irradiation, optical irradiation with Xe–He arc lamps and with incandescent lamps produced very little change in the EPR signal. A series of experiments was performed where the cavity was removed from the liquid nitrogen bath, immersed in a higher temperature bath for a period of time, and the EPR spectrum was remeasured at 80°K. The number of both centers decreased after such a treatment; the "hole" center bleaching at a slightly greater rate than the F center. Some bleaching took place at 90°K, with increasing amounts occurring at 225°K, 260°K, and 280°K. However, at any given bleach temperature both species reached a steady state after 10–20 min and could only be further decreased by increasing the bleaching temperature. Thus the bleaching kinetics are of second or higher order in these crystals.

Figure 2 shows the absorption derivative vs applied field for a CsCl sample after electron irradiation at 230°K. The "hole" center is not present in detectable amounts.

The relative intensities of the F-center lines are approximately as computed. Ten to twenty percent of the original population exists after thermally bleaching for 24 hr at room temperature. The line shape remains the same at room temperature although the relaxation parameters are expected to be different from those of the 80°K measurements.

No angular variation in the hfs resolution was observed.[14] However, such an effect could be masked by the crystal grain misorientation.

The population showed in homogeneous power saturation.[15] The data of Fig. 1 were taken in the region where signal is proportional to power. Since the saturation behavior was slightly sample dependent no precise relaxation measurements will be made until better samples are available.

The centroid of Fig. 2 could not be determined from relative intensity measurements since the population differences (1–5%) of the levels near the center are of the same order as the noise level. Field measurements were made on the higher concentration samples of Fig. 1 and correlated with those of Fig. 2. The small apparent shift of hyperfine lines away from the centroid on Fig. 1 type curves (due to concentration broadening) amounted to only about ±0.001 in the g value and caused no confusion. An apparent centroid shift could be caused in a curve of this type by variations in field sweep rate and by variations with field of H_{mod} (due to possible magnetoresistive effects in the cavity walls).

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[12] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

[13] The expression $H_{\text{hfs}}=A(\mathbf{I}\cdot\mathbf{S})$ where $I=\Sigma_{l=1}^{8}I_n^{\,l}=28$ leads to an incorrect expression for the energy levels.

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These effects were investigated and found to be negligible. It would be desirable to repeat the measurements with a spectrometer of higher sensitivity so that the centroid determination could be made directly with concentrations of the level of Fig. 2 ($\sim 10^{17}-10^{18}/\text{cm}^3$).

The centroid of Fig. 2 occurs at $h\nu/\beta B = 1.984 \pm 0.001$. The precision is limited by the line breadth. The fit using Eq. (2) and corrections from Appendix II gave a value of $A = 49.5 \pm 1.0$ gauss which implies $[\varphi(0)]^2(\text{Cs nucleus}) = 1.6 \times 10^{24}$ cm^{-3}. No attempt was made to obtain the hyperfine line width by curve fitting since ENDOR[16] measurements are planned for the near future. However, using Wolga's plots[4] of line shape vs (A/line width), the hyperfine line half-width is estimated to be $W = 17 \pm 5$ gauss.

Calculations similar to those of Kahn and Kittel[17] show that a spin-orbit term due to an admixture of $6s$ and $6p$ wave functions can give a maximum value of $\Delta g = -0.032$. This can account for most of the observed g shift.

It was not found possible to obtain a hole center population without F centers in the undoped materials. However, a small sample of CsCl, doped to less than 30 ppm of Tl, showed an enhancement in the hole center production rate; at doses of about one-half those of Fig. 1, there was no appreciable F-center concentration. This sample, which was the only one available, was too small for accurate orientation and the data will not be presented until more crystals are available.

The hole center is anisotropic and consists of 7–9 lines—about 10–20 gauss wide. With the exception of the linewidth, it resembles the Cl_2^- center observed by Castner and Kanzig.[18] The hyperfine splitting is about 70 gauss and the g value for $H \| [100]$ is about 2.04. The large linewidth is probably due to the crystal grain misorientation.

SUMMARY

Two paramagnetic species have been observed in CsCl after irradiation with 2-Mev electrons at low temperature. One center shows all the properties expected of the F center: (1) $\Delta g < 0$; (2) g independent of crystal orientation; (3) inhomogeneous power saturation; (4) hyperfine structure with approximately the proper theoretical intensity ratios. The EPR results for the F-center ground state show no unusual characteristics.

The other center is anisotropic and all data is consistent with its tentative assignment as the $Cl_2^-(V_K)$ center.

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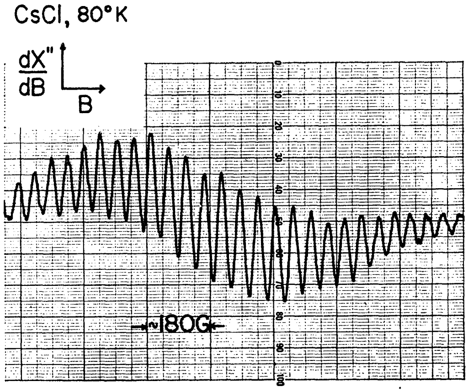

FIG. 2. Absorption derivative vs magnetic field. CsCl; Semi-Elements Corporation, after 6×10^8 r at 230°K. $B_{\text{mod}} = 5$ gauss; $(B_{\text{rf}})^2 \sim 0.4$ mw. Same sensitivity as Fig. 1. The centroid is at $h\nu/\beta B = 1.984 \pm 0.001$.

APPENDIX I

Relative Statistical Weights among the Cs Hyperfine Levels

In computing the hyperfine intensity ratios, it has been assumed[2] that the nuclei nearest the F center are aligned with the magnetic field and that the projection on the field, of an individual nuclear spin can be randomly chosen from the set $-I_n \leq M_i \leq I_n$. Utilizing the system symmetry, the intensity of the M_ith line is taken to be proportional to the number of ways one can arrange the individual M_i to form the sum $M_i = \sum_{l=1}^{8} m_i^l$ for the eight Cs nearest neighbors. The results appear to agree with experiment.[2,4]

It can be shown[19] that if the F center interacts with N similar nuclei in octahedral symmetry, with odd nuclear spin **I**, then in a magnetic field the F-electron hyperfine

TABLE I. Statistical weights of the hyperfine lines.

$\pm M_i$	ω_i	$\pm M_i$	ω_i
0	1 012 664	15	71 184
1	1 001 568	16	47 748
2	968 976	17	30 864
3	916 896	18	19 160
4	848 443	19	11 376
5	767 544	20	6427
6	678 588	21	3432
7	586 056	22	1716
8	494 166	23	792
9	406 568	24	330
10	326 124	25	120
11	254 808	26	36
12	193 705	27	8
13	143 088	28	1
14	102 552		

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[18] T. G. Castner and W. Kanzig, J. Phys. Chem. Solids **3**, 178 (1957).

[19] H. Rosenstock and A. A. Maradudin (to be published).

levels, $\pm M_i$, will each have a statistical weight, ω_i, given by the coefficient of the $Z^{(NI_n-|M_i|)}$ term in the expansion of $[(1-Z^{2I_n+1})/(1-Z)]^N$. For an F center surrounded by 8 Cs nuclei $(I_n=\frac{7}{2})$, ω_i is the weight for the $\pm M_i$ levels and is given by the coefficient of the $Z^{(28-|M_i|)}$ term in the expansion of $[(1-Z^8)/(1-Z)]^8$. Since the computation is rather tedious it seems worthwhile to list the values for future work.

APPENDIX II

Discussion of Eq. (2)

For the F center in CsCl the nuclear hyperfine splitting is so large that the usual "strong field" approximation is not quite valid. Assuming Russell-Saunders coupling and first summing the nuclear angular momentum,[20] one finds that an individual F-center system has a range of total nuclear angular momentum eigenvalues $I_t^2=I^\gamma(I^\gamma+1)$ where $0\leq I^\gamma\leq 28$. For each subset, I^γ, there will be a range of projection angular momenta I_z^γ such that $-I^\gamma\leq M_i\leq I^\gamma$. For each subset there will be a secular equation with solutions[12]:

$$\epsilon_\pm{}^\gamma=-\tfrac{1}{4}A\pm\tfrac{1}{2}g_\gamma\beta B \times\left\{1+\frac{2A(M_i{}^\gamma\pm M_s)}{g_\gamma\beta B}+\frac{A^2(I^\gamma+\frac{1}{2})^2}{[g_\gamma\beta B]^2}\right\}^{\frac{1}{2}}, \quad \text{(IIa)}$$

where $h\nu$(microwave)$=\epsilon_+{}^\gamma-\epsilon_-{}^\gamma$ for the $\Delta M_i{}^\gamma=0$, $\Delta M_s=\pm 1$ transitions.

The intensity relations will be not quite those obtained from the usual theory for an LS multiplet.[21] To conform to the strong-field intensity scheme set forth in Appendix I, each I^γ set should be weighted by a quantity α_γ. The α_γ are related to the ω_γ (Appendix I) by $\alpha=\omega_\gamma-\omega_{\gamma+1}$, where $0\leq\gamma\leq 27$ and $\alpha_{28}=\omega_{28}$.

The expansion of Eq. (IIa) in powers of A/B gives the resonance conditions

$$h\nu=g_\gamma\beta B\left\{1+\frac{A^2}{2(g_\gamma\beta B)^2}[I^\gamma(I^\gamma+1)-(M_i{}^\gamma)^2]+\cdots\right\} +AM_i{}^\gamma. \quad \text{(IIb)}$$

The experimental line will be made up of a sum of equations of type (IIb) weighted as α_γ. One expects that g_γ will vary with $1/(2\gamma+1)$ and that the center of symmetry of the I^γ multiplets will not coincide.[21] In fact the adjacent centers of symmetry should be separated by an energy difference given by the Landé interval rule. The energy differences should be of the order of the **B·I** terms which have been neglected in Eq. (1). Sample calculations indicate that this energy shift plus the lifting of the $M_i{}^\gamma$ degeneracy will contribute less than 2 gauss to the line width. Therefore the effect will be directly observable only as an apparent shift in the experimental peak position calculated from Eq. (2).

In this system the average g value will be that given by the experimentally observed centroid. Experimentally a small decrease in the hyperfine interval (of the order of the experimental error) is observed for two or three hyperfine lines on either side of the centroid. Away from the centroid the intervals appear uniform. This is consistent with the treatment given above. To be completely consistent with Eq. (2) perhaps one could calculate a small M_i dependent correction term for A, in Eq. (2).

Note added in proof. Since the completion of this work, Lewis and Pretzel have made a calculation similar to that of Appendix II [J. Phys. Chem. Solids **19**, 139 (1961)].

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