prediction based on a solid-sphere model. Since it is very difficult to measure the thermal expansion at low temperatures, the low-temperature $\gamma$ determined from the Grüneisen formula is no longer reliable. Therefore, it was suggested that an independent $\gamma$ determined from the low-temperature pressure derivatives of elastic constants [see Eq. (9a) and (9b)] can resolve this problem. However, as seen from Table V, the $\gamma$ calculated from these two formulas are not equal since the Grüneisen assumption does not apply for $CaF_2$; for instance, at 77.35°K the average mode $\gamma$ of the longitudinal wave is 1.66 and for the transverse waves, the $\gamma$ are 0.81 and 0.98. The $\gamma_0$ calculated from the pressure derivatives of elastic constants should be reasonably accurate at 78°K and below because of the high Debye temperature of $CaF_2$. Judging from our result, there is little change of $\gamma$ above 78°K. The value of $\gamma$ for temperatures below 78°K cannot be known until more measurements at low temperatures are completed. We plan to continue this experiment to low-temperature regions in the near future.

## ACKNOWLEDGMENTS

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# Electron Paramagnetic Resonance and Spectroscopic Study of $LaCl_3{:}Eu^{2+}$ and Associated Color Centers*†

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The electron-paramagnetic-resonance (EPR) spectrum of $LaCl_3{:}Eu^{2+}$ was observed to obtain the ground-state splitting of $Eu^{2+}$ in sites of $C_{3h}$ symmetry. A good fit to the observed energy levels in the ground manifold of $Eu^{2+}$ was provided by the parameters $b_2^0=427.20\times10^{-4}$ cm$^{-1}$, $b_4^0=5.48\times10^{-4}$ cm$^{-1}$, $b_6^0=-0.045\times10^{-4}$ cm$^{-1}$, $b_6^6=2.97\times10^{-4}$ cm$^{-1}$, $g_{\parallel}=1.9924$, and $g_{\perp}=1.9927$. The shift in $b_2^0$ from room temperature to 4.2°K was less than 5%. EPR spectra which could be attributed to europium ions in at least one other inequivalent site were observed but not analyzed in detail. The color centers produced in $LaCl_3{:}Eu^{2+}$ by ultraviolet radiation appeared to be due to electrons removed by the radiation from $Eu^{2+}$ ions, which were then trapped at certain crystal defects. The $Eu^{2+}$ donors were shown to reside in the normal $C_{3h}$ rare-earth sites, and the polarization of the color-center absorption spectrum indicated that the color-center defects had relatively high symmetry. If the color-center defects were due to anion vacancies such as one finds for certain color centers in alkali halide crystals, then the defect was probably a cluster of more than one chlorine vacancy.

## I. INTRODUCTION

THIS paper presents the results of an optical and electron-paramagnetic-resonance (EPR) study of $LaCl_3{:}Eu^{2+}$. The two significant features are the large splitting of the $^8S_{7/2}$ ground state and the polarized color-center absorption bands which are easily produced by ultraviolet radiation. A comparison of the splitting of the $^8S_{7/2}$ state of $Eu^{2+}$ and $Gd^{3+}$ is of interest since the explanation of this splitting is not yet complete.[1,2] Using EPR, the ground-state splitting of $Eu^{2+}$ in $C_{3h}$ sites in $LaCl_3$ has been determined to be approximately 50 times that of $Gd^{3+}$. This may indicate that configuration interaction is important in the splitting of the ground states of $Gd^{3+}$ and $Eu^{2+}$.

It has been previously reported[3,4] that color centers are formed in $LaCl_3$ containing divalent europium. [One of the striking features of this phenomenon is the relative ease with which these crystals can be colored and bleached. A modest amount of color can be induced in these crystals by subjecting them to the unfiltered ultraviolet radiation from a low-pressure mercury-discharge tube (pen lamp) for a few minutes at room temperature. Bleaching can be accomplished by heating the colored crystal to temperatures as low as 100°C.

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[†] This paper is based in part on a Ph.D. dissertation by Boris F. Kim, The Johns Hopkins University, 1967 (unpublished). For further details see the dissertation, available through University Microfilms, Ann Arbor, Michigan.

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[§] Alfred P. Sloan Foundation Fellow.

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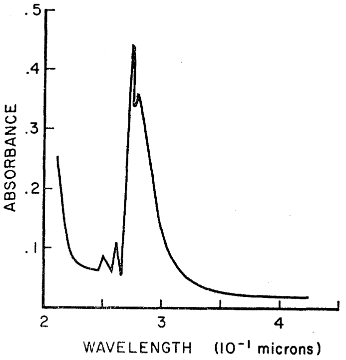

FIG. 1. Absorption spectrum of $LaCl_3$:[(1/16)%$Eu^{2+}$] at 77°K.

The bleaching process is accompanied by a blue fluorescence from the crystal.] It was also noted that, at room temperature, a blue phosphorescence was emitted from the crystal after ultraviolet irradiation. The decay of the intensity of this phosphorescence as a function of time is what one would expect from light emitted from typical electron traps. This can be understood by the explanation of the color-center phenomena discussed in this paper.

The interpretation of color centers in alkali halide crystals[5,6] as crystal defects which have trapped electrons or holes is undoubetedly applicable to the case of color centers in $LaCl_3$, although the details of the traps should be different because of the different crystal structure. The existence of color centers in $LaCl_3:Eu^{2+}$ from this point of view is not surprising, since the divalent ions in $LaCl_3$ are charge defects which require compensating defects of positive potential which could trap electrons. A spectroscopic study of $LaCl_3:Eu^{2+}$ has provided some insight into the nature of these color centers.

## II. EXPERIMENTAL TECHNIQUES

The sharp lines of the absorption spectra were obtained at 4.2° and 77°K with a 21 ft, *f*/36 Paschen spectrograph with a first-order dispersion of 1.2 Å/mm and a first-order resolution of approximately 180 000. A high-pressure mercury discharge lamp (GE AH-6) was used as a source of light. Polarization was determined with a calcite rhomb. The broad absorption bands were obtained with a Cary-14 recording double-beam spectrometer. A pair of matched glan prisms was used to obtain polarization of the two beams. The fluorescence of the broad bands was observed on a 1-m, two-mirror, *f*/6 spectrograph designed by William G. Fastie, using the technique of monochromatic excitation developed by Varsanyi.[7]

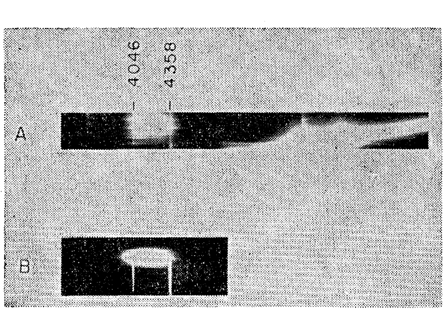

FIG. 2. (A) Fluorescence of $LaCl_3$:(1% $Eu^{2+}$) at 4.2°K. The spectrum of the exciting radiation is shown in second order to the right of the fluorescence. (B) Flourescence of $LaCl_3$:(1% $Eu^{2+}$). The fluorescence is excited by heating a deeply colored crystal at temperature in excess of 100°C.

The EPR spectra were obtained at *X*-band frequencies with a Varian V-4502-13 spectrometer system, and a Varian V-3401 magnet with 6-in. tapered pole faces. The system was used with 100-kc field modulation and detection.

Crystals doped with $Eu^{2+}$ were grown by the same procedure used to grow crystals doped with the trivalent rare-earth ions. Crystals doped with $Eu^{3+}$ are grown in an excess of chlorine vapor in this laboratory.

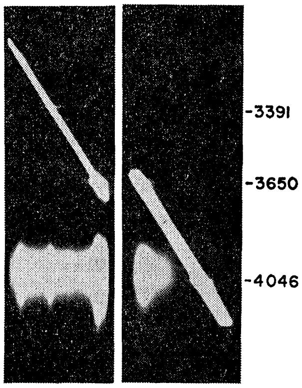

FIG. 3. Fluorescence of $EuCl_2$ at 77°K. The diagonal trace is the spectrum of the exciting beam.

## III. OPTICAL SPECTRA

### A. The Broad Absorption and Fluorescence Bands of $Eu^{2+}$

Broad absorption bands were observed in the ultraviolet with uncolored crystals with a europium concentration of approximately (1/16)%. Figure 1 shows an unpolarized absorption spectrum taken at 77°K. Crystals with a 1% europium concentration begin to absorb strongly at approximately 3900 Å. Broad bands observed in this spectral region for $Eu^{2+}$ in alkali halide crystals[8,9] have been attributed to transitions between

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the $f^7$ and $f^65d$ configurations. This is probably also the origin of the bands observed in the europium-doped $LaCl_3$ crystals. No sharp absorption lines which could be rttributed to $Eu^{2+}$ were observed in $LaCl_3$: (1% $Eu^{2+}$) in the spectral region from 2900 through 5000 Å, although the sharp absorption lines for the $^8S_{7/2}$-$^6P_{7/2}$ transition are easily observed in the region near 3000 Å for a 1% $Gd^{3+}$ doping in $LaCl_3$.[10] The sharp levels of $f^7$ are probably broadened in $Eu^{2+}$ by interaction with the $f^65d$ bands to such an extent that they are not observable.

Under uv excitation, a broad fluorescence band was observed at 4200 Å. This fluorescence at 77°K is shown in Fig. 2.[11] A broad fluorescence was also observed under uv excitation in a polycrystalline $EuCl_2$ sample but shifted to shorter wavelength, indicating that this fluorescence probably comes from $Eu^{2+}$. Figure 3 shows the fluorescence from $EuCl_2$ at 77°K.

### B. Spectroscopic Properties of the Color Centers

The color-center defects in $LaCl_3:Eu^{2+}$ could in fact be the defects which charge compensate the divalent europium ions. This would require that the color-center defects be of positive potential, serving as electron traps. The relative ease[12] with which the color centers are created indicates that the electron donors in the crystal are easily ionized by ultraviolet radiation. Since the divalent europium ions have absorption bands in the same region of the spectrum as the radiation which apparently creates the color centers, it is likely that some of the divalent europium ions are ionized when excited into the ultraviolet bands to provide the electrons for the color-center traps.

#### *1. Observations on the Coloring Process*

If this hypothesis is true, $Eu^{3+}$ absorption lines might appear as the color centers are formed. To check this, the absorption spectrum of $LaCl_3$: (1% $Eu^{2+}$) was observed with high resolution in the spectral region from 3900 through 6000 Å to determine whether or not any of the sharp lines of $Eu^{3+}$ would appear as the crystal was colored. No $Eu^{3+}$ absorption lines were observed in this spectral region with the uncolored crystal. The strongest $Eu^{3+}$ line in this region did in fact appear as the crystal was colored. The results of this experiment are shown in Fig. 4, which shows the spectra at 4650 Å with the light polarized perpendicular to the $C_3$ crystal axis. The first exposure was taken with the crystal at 77°K in the uncolored phase. The crystal

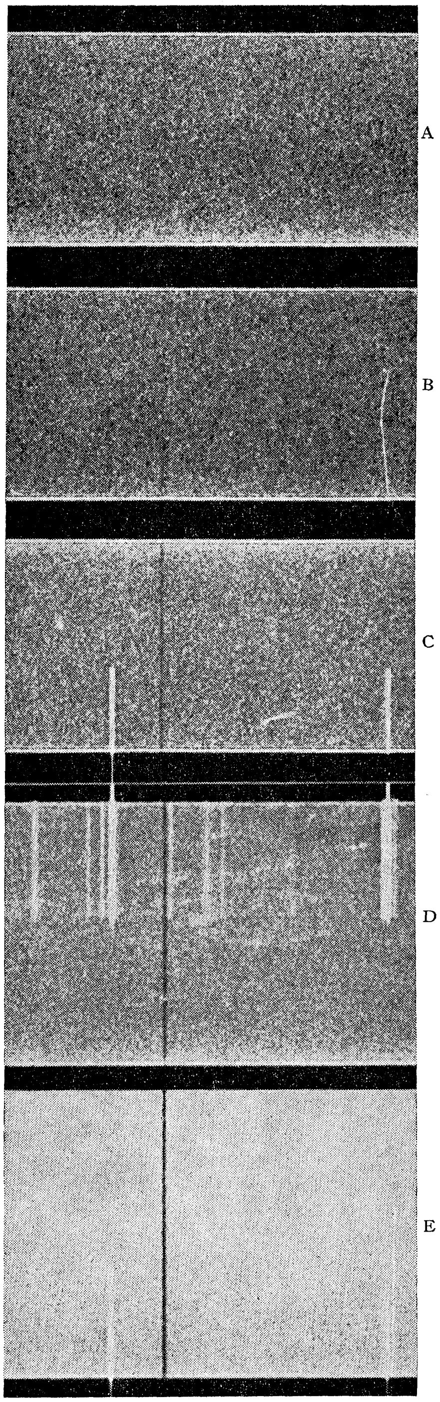

FIG. 4. Absorption spectra at 4650 Å: $\sigma$ polarization. (A) through (D) were taken with $LaCl_3$: (1% $Eu^{2+}$). (A) No prior ultraviolet irradiation (77°K). (B) Five minutes of ultraviolet irradiation prior to this exposure (77°K). (C) One hundred and fifty minutes of ultraviolet irradiation prior to this exposure (77°K). (D) Crystal deeply colored prior to insertion into the Dewar (4.2°K). (E) $LaCl_3$: (1%$Eu^{3+}$) at 4.2°K.

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[10] A. Piksis, dissertation The Johns Hopkins University, 1962 (to be published).

[11] This plate was taken by F. Varsanyi in this laboratory on the 1-m, *f*/6 spectrograph.

[12] Variations in the amount of color which could be induced were noted in different crystals cut from the same boule and were probably due to concentration gradients. The amount of color which a crystal could assume depended upon the temperature of the crystal when it was irradiated with ultraviolet light. Crystals were more difficult to color at low temperatures and tended to lose some of their color when subsequently subjected to higher temperatures. Crystals which were colored at room temperature before they were subjected to low temperature tended to retain their color when subsequently returned to room temperature.

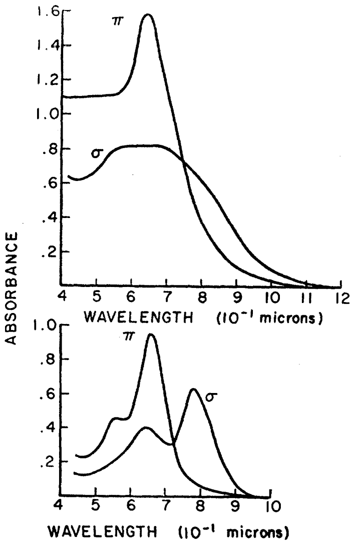

FIG. 5. Color-center absorption bands. The upper is at room temperature, the lower at 77°K. The band designations are: A: 7800 Å ($\sigma$) B: 6550 Å ($\pi$); C: 6500 Å ($\sigma$); and D: 5600 Å($\pi$).

was then irradiated for 5 min and a second exposure was made. The unfocused light from two small mercury-discharging lamps (pen lamps) was used to irradiate the crystals by placing the two pen lamps next to the Dewar windows. After the second exposure, the crystal was irradiated for 150 min, and the third exposure was made. These first three exposures were taken on the same photographic plate under identical optical conditions. The absorption line which appears clearly in the third exposure has been identified and classified as belonging to the $^7F_0$-$^5D_2(2)$ transition of Eu$^{3+}$ in LaCl$_3$.[4] The crystal, when removed from the Dewar, was colored, indicating that the ionizing radiation did in fact produce color centers in this experiment. The fourth exposure shown in Fig. 4 was taken at 4.2°K with a crystal which had been colored at room temperature with a GE AH-6 high-pressure mercury-discharge lamp prior to insertion of the crystal into the Dewar. A more pronounced coloring of the crystal was obtained, and the Eu$^{3+}$ line was correspondingly stronger. The last exposure shows the absorption spectrum taken with a crystal which had been grown with a doping of 1% Eu$^{3+}$. There was no measurable shift in the line. These results clearly show that Eu$^{3+}$ is ionized when the crystal is colored by ultraviolet radiation, and is consistent with the hypothesis that the Eu$^{2+}$ ions serve as electron donors for the color centers. The fact that the Eu$^{3+}$ absorption line which appeared in the colored LaCl$_3$: (1% Eu$^{2+}$) crystal was not measurably shifted shows that most of the donor Eu$^{2+}$ ions must reside in the normal $C_{3h}$ rare-earth sites.

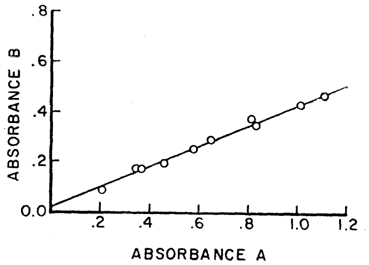

FIG. 7. Peak absorbance of the $A$ band versus the peak absorbance of the $B$ band at 77°K.

### 2. *Observations on the Bleaching Process*

Bleaching of the crystals by heat occurs as lattice vibrations dislodge the electrons from the color-center traps and they recombine with Eu$^{3+}$ ions. The recombination of electrons with Eu$^{3+}$ should result in Eu$^{2+}$ ions in excited states which fluoresce as they decay to the ground state. As previously stated, the crystal does fluoresce during bleaching. The spectrum of this fluorescence was photographed on the 1-m, $f/6$ spectragraph using ASA 10 000 Polaroid film. The results shown in Fig. 2(B) were obtained by heating a crystal, which was deeply colored, with a Veeco heat gun until the crystal was completely bleached. The broad fluorescence is unmistakably that of Eu$^{2+}$ as can be seen by comparing it with the fluorescence band of Eu$^{2+}$ under ultraviolet excitation in Fig. 2(A). These

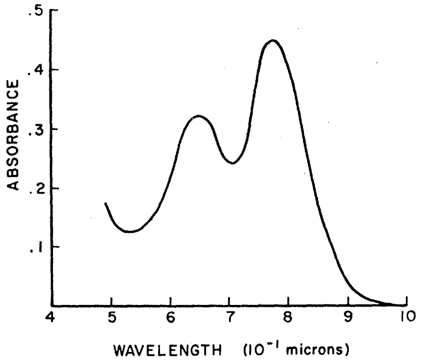

FIG. 6. Color-center absorption bands at 77°K in the axial polarization.

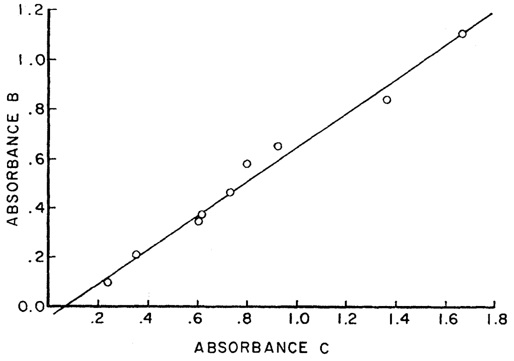

FIG. 8. Peak absorbance of the $B$ band versus the peak absorbance of the $C$ band at 77°K.

results further confirm the hypothesis that $Eu^{2+}$ ions provide the electrons for the color centers.

The weak phosphorescence observed[3,4] in these crystals is apparently due to the recombination process just described. The decay of the intensity of this luminescence is characteristic of the recombination times rather than of the source of the emitted light which should be, according to our interpretation, $Eu^{2+}$. It should be noted that the polycrystalline sample of $Eu^{2+}$ showed no phosphorescence or tendency to color, although the blue fluorescence band was observed.

### *3. The Color-Center Absorption Bands*

The absorption spectra of the color centers at room temperature and 77°K is shown in Fig. 5. At 77°K, there are four prominent bands which are polarized with respect to the $C_3$ axis of the crystal. Only one band is discernible at room temperature. The axial spectrum with respect to the $C_3$ axis shown in Fig. 6 indicates that the bands are due to electric dipole transitions as expected. No other bands were observed in the spectral region from 4000 through 20 000 Å.

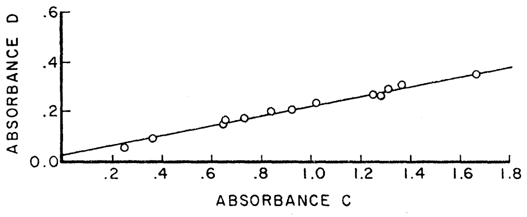

FIG. 9. Peak absorbance of the *C* band versus the peak absorbance of the *D* band at 77°K.

The bands, which are designated *A*, *B*, *C*, and *D*, were observed at 77°K as the crystal was bleached through several stages. The peak absorbances of the bands at each stage were plotted against one another in the following manner: *A* versus *B*, *B* versus *C*, and *C* versus *D*. The results are shown in Figs. 7–9. The fit of the data to straight lines indicates that the four absorption bands are all associated with the same species of color center.

## IV. CONJECTURES ON THE COLOR-CENTER STRUCTURE

Since the color-center bands are polarized, the color centers exist at sites of relatively high symmetry. This is useful information in considering the possibilities for the structure of the color centers, since the number of inequivalent sites of symmetry in the crystal is limited. Furthermore, since the available experimental information indicates that the color centers are of the type in which electrons are trapped, the color-center defects must have a positive potential. One might expect, therefore, that the color-center defects consist of a cluster of one or more chlorine vacancies or an interstitial positive ion.

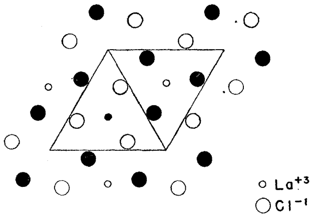

FIG. 10. The structure of $LaCl_3$. $C_3$ is perpendicular to the plane of the whole page. The plane which contains the white spheres lies half the distance of the unit cell in the $C_3$ direction above and below the plane which contains the black spheres. The dimension of the unit cell in the plane of the page is 7.428 Å, and perpendicular to the plane of the page is 4.312 Å.

A few chlorine-vacancy defect models which have some symmetry are constructed here from the known crystal structure of $LaCl_3$ to determine what defect symmetry types one might expect in this crystal. The electric dipole selection rules, which are known from group theory, can then be examined to see under what conditions one would expect polarized absorption from a particular model.

A single chlorine vacancy with a trapped electron, which is the model for an *F* center in the alkali halide crystals, would have a point symmetry $C_s$. This can be seen from Fig. 10 which shows the $LaCl_3$ crystal structure.[13] This model will be referred to as *C*-1. A high-symmetry chlorine-deficient defect can be constructed if one assumes that when two adjacent chlorine ions in the same plane of a unit cell are removed, the third assumes the position shown in Fig. 11. A similar ionic shift was suggested by Knox[14] to account for the inversion properties of the Seitz model of the *M* center in alkali halide crystals. The defect shown in Fig. 11, which should be electrostatically stable, has a symmetry $C_{3h}$ and is capable of trapping one or two electrons. The former case is denoted *C*-2 and the latter *C*-3. Because of the relatively high europium concentration, it is possible that one of the rare-earth ions above or below the defect along the $C_3$ axis might be a divalent ion. In this case, the symmetry of the defect is $C_{3v}$ and the defect can trap one electron. This model will be denoted *C*-4.

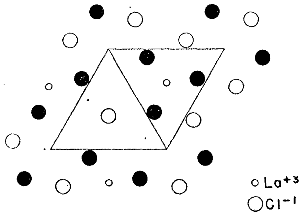

FIG. 11. Chlorine-deficient defect with two adjacent chlorine vacancies.

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[13] W. H. Zachariasen, J. Chem. Phys. **16**, 254 (1948).

[14] R. S. Knox, Phys. Rev. Letters **2**, 87 (1959).

Although other high-symmetry chlorine-deficient defects could be constructed, it does not appear that any with higher symmetry than those already considered could be constructed. One could also construct positive-ion defects with the symmetry properties of C-2, C-3, and C-4 by placing interstitial positive ions between two rare-earth ions along the $C_3$ axis. In addition, a defect centered about the obtuse corner of the parallelapiped unit cell of Fig. 10 would have a site symmetry of $C_{3i}$. Examination of the electric dipole selection rules[15,16] for all of the site symmetries considered indicates that all of the models can produce polarized spectra except C-1. In the alkali halides, the most prominent center, the *F* center, is an electron trapped at a single halide vacancy. On the basis of symmetry selection rules, the analogous defect in $LaCl_3$, a single $Cl^-$ vacancy, does not account for the optical properties of the color center. Even in this case though, the electron may not be highly localized, experiencing a potential which is predominantly of higher symmetry.

A search was made for an electron-paramagnetic-resonance signal from the color center. The overwhelming presence of $Eu^{2+}$ resonances made this especially difficult and no resonance which could be definitely attributed to the color center was found.

## V. THE $^8S_{7/2}$ GROUND STATE OF $Eu^{2+}$

### A. Experimental Results

The resonance spectrum of $LaCl_3:Eu^{2+}$ was observed at *X*-band frequencies. At least two $Eu^{2+}$ sites with comparable intensities were observed at low temperatures. At room temperature, the resonances from only one of the sites were observed. This site appeared to be the normal $C_{3h}$ rare-earth site in $LaCl_3$. The angular variation of the spectrum as the magnetic field was rotated perpendicular to and about the $C_3$ axis, exhibited a sixfold variation which is characteristic of $C_3$ symmetry.[17] Figure 12 shows the angular variation for the 3/2, 1/2, and $-3/2$, $-5/2$ electronic transitions. The angular variation was greatest for these two groups.

The resonances attributed to the $Eu^{2+}$-$C_{3h}$ sites were confirmed to be $Eu^{2+}$ transitions from the hyperfine structure. Each electronic transition between the eight states of the ground manifold consisted of twelve equally spaced hyperfine lines corresponding to the europium isotopes $Eu^{151}$ and $Eu^{153}$ which occurred in the crystal in approximately equal abundances. Figure 13 shows the structure of the $-1/2$, $-3/2$ transition with the magnetic field parallel to the $C_3$ axis. The observed hyperfine structure constants,

$$|A|=(31.8\pm0.6)\times10^{-4}\ \mathrm{cm}^{-1}\ (\mathrm{Eu}^{151})$$

and

$$|A|=(14.3\pm0.2)\times10^{-4}\ \mathrm{cm}^{-1}\ (\mathrm{Eu}^{153})$$

agreed well enough with that observed for $Eu^{2+}$ in other crystals[18–20] to confirm that the observed resonances were due to $Eu^{2+}$. The positions of the electronic transitions for the purpose of obtaining the crystal-field parameters and splitting factors were taken to be the center of gravity of the twelve hyperfine lines.

The operator Hamiltonian which describes the effect of the crystal field and magnetic field for $C_{3h}$ symmetry is[21]

$$\begin{aligned}H=&\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{J}+B_2{}^0[3J_Z{}^2-J(J+1)]+B_4{}^0[35J_Z{}^4-30J(J+1)J_Z{}^2+25J_Z{}^2-6J(J+1)+3J^2(J+1)^2]\\&+B_6{}^0(231J_Z{}^6-105J_Z{}^4[3J(J+1)-7]+J_Z{}^2[105J^2(J+1)^2-525J(J+1)+294]\\&-5J^3(J+1)^3+40J^2(J+1)^2-60J(J+1))+B_6{}^6\tfrac{1}{2}[J_+{}^6+J_-{}^6].\end{aligned}$$

In order to conform with the conventions of previous workers, the following parameters were used:

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

The crystal parameters $b_k{}^q$ and the perpendicular and parallel splitting factors $g_{\parallel}$ and $g_{\perp}$ were fit to the fourteen observed resonances (seven with the magnetic field parallel to $C_3$ and seven with the magnetic field perpendicular to $C_3$) with the method of least squares using a computer, by an exact diagonalization of the magnetic- and crystal-field interactions within the ground manifold for each resonance. The parameters for the crystal at room temperature were

$$b_2{}^0=(427.20\pm0.06)\times10^{-4}\ \mathrm{cm}^{-1},$$

$$b_4{}^0=(5.48\pm0.02)\times10^{-4}\ \mathrm{cm}^{-1},$$

$$b_6{}^0=(-0.045\pm0.020)\times10^{-4}\ \mathrm{cm}^{-1},$$

$$b_6{}^6=(2.97\pm0.12)\times10^{-4}\ \mathrm{cm}^{-1},$$

$$g_{\parallel}=1.9924\pm0.0001,$$

and

$$g_{\perp}=1.9927\pm0.0001.$$

The uncertainties indicated are the standard deviations estimated by the least-squares method with eight degrees of freedom for all the parameters except $b_6{}^6$.

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[16] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (The M.I.T. Press, Cambridge, Mass., 1963).

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The uncertainty indicated for $b_6^6$ is the estimated standard deviation with five degrees of freedom. The shift in $b_2^0$ from room temperature to 4.2°K was less than 5%.

The ordering of the Stark components in zero field was obtained from the relative intensities of the lowest- and highest-field resonances at 4.2°K in a 1% sample. The high-field resonance was observed to be more intense than the low-field resonance, indicating that the high-field resonance was due to the $-5/2$, $-7/2$ transition. From this it was inferred that the $\pm 1/2$ level lies lowest.

At low temperatures, saturation of the resonances was a problem. It was found that the high-field resonances saturated more than the corresponding low-field resonances. To determine the ordering of the Stark components the power was reduced to the extent that the low-field resonance was unsaturated. Some saturation of the high-field resonance was still present under these conditions. The observed ratio of the intensity of the high-field resonance to the low-field resonance was 1.56. The discrepancy between this value and the expected value of 1.72 can be attributed to the small amount of saturation of the high-field resonance.

### B. Theoretical Discussion

These results, when compared to those for Gd$^{3+}$ in LaCl$_3$,[1] indicate that the effects of configuration interaction may be prominent in the splitting mechanism for the ground state of Gd$^{3+}$ and Eu$^{2+}$ in LaCl$_3$. The difference in the splitting of Eu$^{2+}$ and Gd$^{3+}$ in LaCl$_3$ is approximately a factor of 50. Since the crystalline environment appears to be the same in each case, the difference in the splitting in each case should be due to the difference in the electronic properties of Eu$^{2+}$ and Gd$^{3+}$. The shift in the energies of excited configurations is probably the most striking difference in the electronic properties of Eu$^{2+}$ and Gd$^{3+}$, the difference being at least a factor of 3 for the $f^65d$ configuration.[22–24]

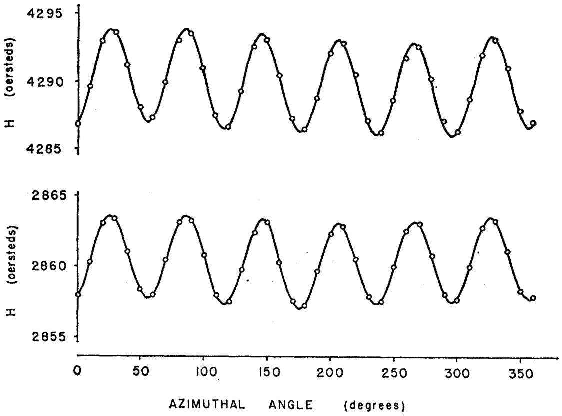

FIG. 12. Azimuthal variation of the $-\frac{3}{2}$, $-\frac{5}{2}$ and $\frac{3}{2}$, $\frac{1}{2}$ groups with the magnetic fields perpendicular to the $C_3$ axis at room temperature. These data were obtained from a crystal with 1% europium concentration.

Wybourne,[2] in a recent study of various ionic mechanisms for the splitting of Gd$^{3+}$ in lanthanum ethyl sulfate, was unable to account for the sign of $b_2^0$. The effects of configuration interaction, however, were not completely accounted for. If it could be shown for example that the mechanisms suggested by Hutchison *et al.*[18] to explain the splitting of Gd$^{3+}$ in LaCl$_3$ with configuration interaction included could account for the major portion of the splitting of Gd$^{3+}$ in LaCl$_3$, then these mechanisms would also be consistent with the present results for Eu$^{2+}$. It was suggested by Hutchinson *et al.* that the splitting was due primarily to two mechanisms, one being the effect of the crystal field with intermediate coupling which can be written

$$M_1 = \langle {}^8S_{1/2}|\Lambda|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|\Lambda|{}^6D_{7/2}\rangle \times\langle {}^6D_{7/2}|V|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|\Lambda|{}^8S_{7/2}\rangle / -W_P{}^2W_D,$$

where $\Lambda$ is the spin-orbit interaction, $V$ is the crystal-field interaction, and $W_P$ and $W_D$ are the energies of the ${}^6P_{7/2}$ abd ${}^6D_{7/2}$ states with respect to the ${}^8S_{7/2}$ energy. The second mechanism, originally suggested by Judd,[1] can be written

$$M_2 = \Big[\sum_X \langle {}^8S_{7/2}|\Lambda|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|V|{}^6X_J\rangle \times\langle {}^6X_J|V|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|\Lambda|{}^8S_{7/2}\rangle\Big] / -W_P{}^2W_X,$$

where the summation is over all intermediate states ${}^6X_J$, including those in higher configurations. Wybourne[2] obtained an expression for the splitting of Gd$^{3+}$ using these two mechanisms within the $f^7$ con-

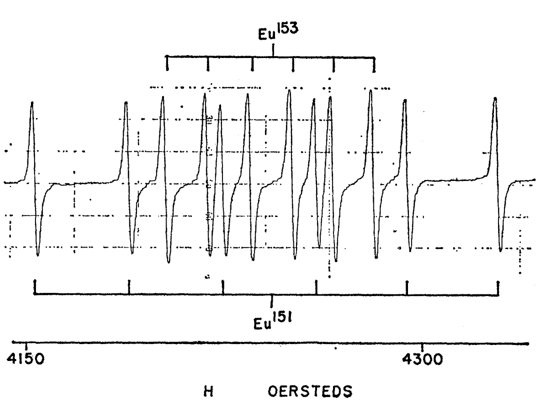

FIG. 13. The hyperfine structure of the $-\frac{1}{2}$, $-\frac{3}{2}$ transition with the magnetic field parallel to the $C_3$ axis at room temperature.

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[22] G. H. Dieke and H. M. Crosswhite, Appl. Opt. 2, 675 (1963).

[23] E. Loh, Phys. Rev. 147, 332 (1966).

[24] D. S. McClure and Z. Kiss, J. Chem. Phys. 39, 3251 (1963).

figuration. His result was

$$T(M)=\frac{b}{21}M^2\frac{2c}{(5)^{1/2}}C_2{}^0-\frac{b^2}{21}M^2\left[\frac{(C_2{}^0)^2}{25E_P}+\frac{5}{99}\frac{(C_4{}^0)^2}{E_G}+\frac{25}{1859E_I}(7(C_6{}^0)^2-22(C_6{}^6)^2)\right],$$

where the first term is the contribution from $M_1$ and the second term is the contribution from $M_2$. If one uses the values (from Wybourne[2])

$$b=0.1618,$$
$$c_2=-0.0123,$$
$$E_0=40\,320\text{ cm}^{-1},$$
$$E_G=50\,000\text{ cm}^{-1},$$
$$E_I=36\,360\text{ cm}^{-1},$$

and the values (from Piksis[10])

$$C_2{}^0=307\text{ cm}^{-1},\quad C_6{}^0=472\text{ cm}^{-1},$$
$$C_4{}^0=397\text{ cm}^{-1},\quad C_6{}^6=300\text{ cm}^{-1},$$

one finds the contribution to $b_2{}^0$ from $M_1$ to be $-260\times10^{-4}$ cm$^{-1}$ and the contribution from $M_2$ (from $f^7$) to be $-1.2\times10^{-4}$ cm$^{-1}$. If the portion of the splitting of $Gd^{3+}$ in $LaCl_3$ is due to these two mechanisms, then the contribution of configuration interaction in $M_2$ would have to be approximately $+270\times10^{-4}$ cm$^{-1}$ to account for the value of $8.46\times10^{-4}$ cm$^{-1}$ observed for $Gd^{3+}$ in $LaCl_3$. If one assumes that the energies of excited configurations are lower on the average for $Eu^{2+}$ from that of $Gd^{3+}$ by a factor of 3, the contribution of $M_2$ should increase by a factor of 3. One would then expect the value of $b_2{}^0$ for $Eu^{2+}$ to be

$$b_2{}^0=-261+3(270)=549\times10^{-4}\text{ cm}^{-1}.$$

It can be concluded, then, that if the mechanisms $M_1$ and $M_2$ can account for the major portion of the splitting of $Gd^{3+}$ in $LaCl_3$, these mechanisms should predict the proper sign for $b_2{}^0$ for $Eu^{2+}$ and also the large increase in $b_2{}^0$ from that of $Gd^{3+}$.

Wybourne[2] has raised an objection to mechanisms such as $M_2$ which reflect a portion of the splitting of the $^6P_{7/2}$ into the ground state because the ordering of the Stark components of $^6P_{7/2}$ is observed to be opposite from the ordering of the Stark components of $^8S_{7/2}$. He concludes therefore that mechanisms such as $M_2$ cannot predict the proper sign for $b_2{}^0$ for the ground state. This conclusion should be valid only if the relative importance of mechanisms which compete in the sign of $b_2{}^0$ is the same in the case of $^6P_{7/2}$ and $^8S_{7/2}$. It is not clear that this is true. The effect of intermediate coupling on the splitting should be greater in the case of $^6P_{7/2}$ than $^8S_{7/2}$. Piksis[10] was in fact able to account for the major part of the splitting of $^6P_{7/2}$ for $Gd^{3+}$ in $LaCl_3$ and in $La(C_2H_5SO_4)_3\cdot9H_2O$ from the intermediate-coupling mechanism alone, indicating that this mechanism is the major contribution to the splitting of $^6P_{7/2}$. It cannot be the major contribution in the case of $^8S_{7/2}$ since it predicts the wrong sign for $b_2{}^0$.

## VI. CONCLUSION

This paper reports an EPR and spectroscopic study of $LaCl_3:Eu^{2+}$ and the associated color centers. The 5*d* bands are similar to those in other crystals. The EPR gives two important results. (1) Many of the ions are in sites of $C_{3h}$ symmetry. This is in contrast to $LaCl_3Sm^{2+}$ where the optical spectra come from sites of low symmetry.[25,26] (2) The splitting is large, about 50 times that of $LaCl_3Gd^{3+}$. We have shown that configuration interaction may be important in the splitting mechanism.

The color centers have some unusual properties. They are easily colored and bleached. The same fluorescence accompanies bleaching as accompanies excitation of the *d* bands. High-resolution absorption spectra show increase in the number of $Eu^{3+}$ ions in sites of $C_{3h}$ symmetry as the crystal is colored, indicating that the $Eu^{2+}$ ions are the electron donors. This is in agreement with the hypothesis of Gruen *et al.*[3] The polarization of the color-center absorption bands indicates that the site symmetry is higher than that provided by a single $Cl^-$ vacancy.

## ACKNOWLEDGMENT

The authors wish to acknowledge many helpful discussions with Professor B. R. Judd.

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[25] G. H. Dieke and R. Sarup, J. Chem. Phys. **36**, 371 (1962).

[26] $LaCl_3:Sm^{2+}$ spectra from a site different from that of Ref. 25, but of undetermined symmetry, have been measured [W. D. Partlow (private communication)].

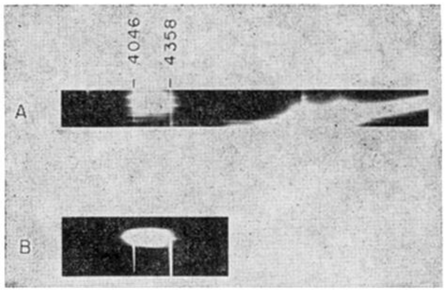

Fig. 2. (A) Fluorescence of $LaCl_3$:(1% $Eu^{2+}$) at 4.2°K. The spectrum of the exciting radiation is shown in second order to the right of the fluorescence. (B) Flourescence of $LaCl_3$:(1% $Eu^{2+}$). The fluorescence is excited by heating a deeply colored crystal at temperature in excess of 100°C.

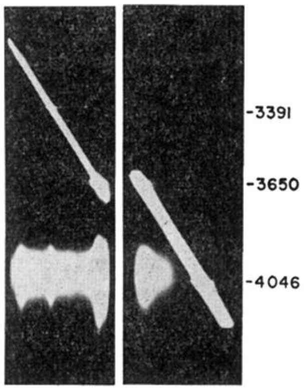

FIG. 3. Fluorescence of $EuCl_2$ at 77°K. The diagonal trace is the spectrum of the exciting beam.

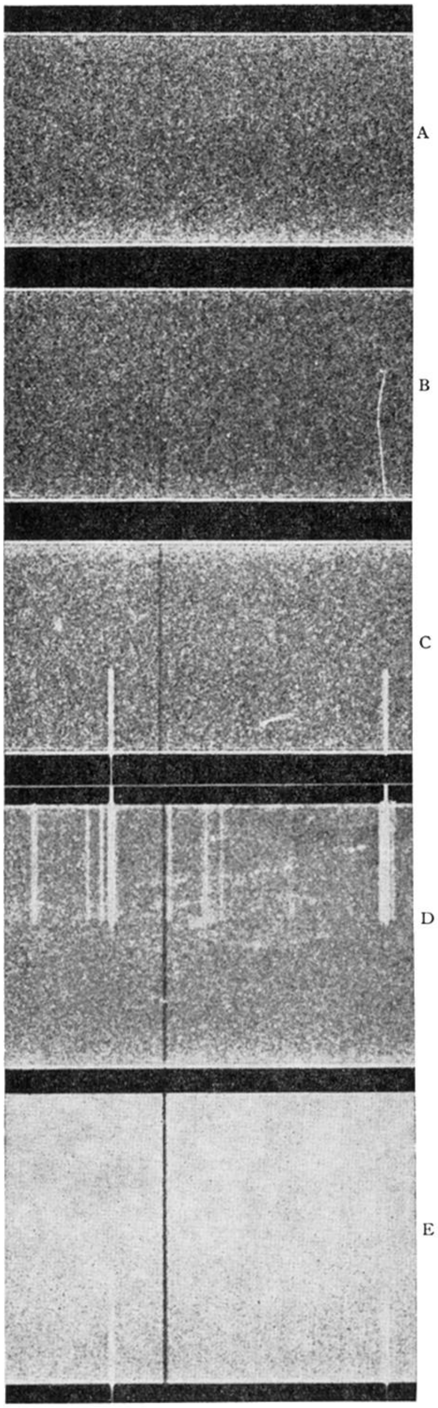

FIG. 4. Absorption spectra at 4650 Å: $\sigma$ polarization. (A) through (D) were taken with $LaCl_3$: (1% $Eu^{2+}$). (A) No prior ultraviolet irradiation (77°K). (B) Five minutes of ultraviolet irradiation prior to this exposure (77°K). (C) One hundred and fifty minutes of ultraviolet irradiation prior to this exposure (77°K). (D) Crystal deeply colored prior to insertion into the Dewar (4.2°K). (E) $LaCl_3$: (1% $Eu^{3+}$) at 4.2°K.