# Cryogenic Luminescence Studies of $Eu^{3+}$ in $LiEuCl_4$

HARRY G. BRITTAIN*

*Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079*

AND GERD MEYER

*Institut für Anorganische und Analytische Chemie, Justus-Liebig Universität, Heinrich-Buff-Ring 58, 6300 Giessen, West Germany*

The luminescence associated with the $Eu^{3+}$ ion in $LiEuCl_4$ has been studied at cryogenic temperatures under conditions of high resolution. Emission was observed to originate from both the $^5D_0$ and $^5D_1$ excited states, and transitions to the $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ ground levels were observed. The fine structure observed within these emission bands was found to be consistent with the existence of an effective $D_4$ site symmetry for the emitting $Eu^{3+}$ species, even though the europium polyhedron was found to be that of a bisdisphenoid. © 1985 Academic Press, Inc.

## Introduction

Analysis of the luminescence spectroscopy associated with crystalline $Eu^{3+}$ compounds has received a great deal of attention, since it is relatively simple to relate the observed spectral patterns with details of the immediate coordinative environment of the emitting ion (*1*). Anhydrous $Eu^{3+}$ halide compounds form a series of systems in which the coordination polyhedron of the lanthanide ion can often be described with accuracy (*2*). For obvious theoretical reasons, most of the work carried out to date has concentrated on systems in which the $Eu^{3+}$ ion occupies sites of high symmetry. For instance, an extensive literature now exists regarding the emission spectroscopy of $Eu^{3+}$ doped into hexagonal ($P6_3/m$) $LaCl_3$

(*3*), or cubic ($Pa3$) systems isomorphous with elpasonite ($K_2NaAlF_6$) (*4*). Recently, the data obtained in these and other systems has been assembled into a compendium (*5*).

Appreciable self-quenching in many $Eu^{3+}$ halo compounds has prevented analogous studies from being performed on $Eu^{3+}$ complexes in environments characterized by lower metal ion site symmetries. However, in a recent work the luminescence spectrum of $K_2EuCl_5$ was obtained under conditions of high resolution at cryogenic temperatures, and quite reasonable emission intensities were observed (*6*). An interesting result obtained after data analysis was that the effective coordination polyhedron of the $Eu^{3+}$ ion appeared to be of higher symmetry than that required on the basis of its crystal structure. This result was taken to imply that the crystal field interaction ex-

* Author for correspondence.

perienced by the $Eu^{3+}$ ion within this host system was short-ranged in its extent, and that the $Eu^{3+}$ crystal field splitting patterns were determined only by the most immediate interactions.

We have continued this line of study through an analysis of the luminescence of the $Eu^{3+}$ ion in a different system, $LiEuCl_4$. The crystal structure of the isomorphous $LiGdCl_4$ salt was recently reported (7), where it was found that the $Eu^{3+}$ polyhedron could be described as that of a bisdisphenoid (triangulated dodecahedron). In the present work, we will detail the results of studies concerning the electronic structure of $Eu^{3+}$ in $LiEuCl_4$. The luminescence data which will be reported were all obtained at cryogenic temperatures under high-resolution conditions.

## Experimental

$LiEuCl_4$ was prepared in a manner similar to that which has been reported (7). Equimolar amounts of $Eu_2O_3$ and $Li_2CO_3$ were dissolved in concentrated hydrochloric acid together with a fourfold excess of $NH_4Cl$, thus producing $(NH_4)_2EuCl_5$ and $LiCl$. The solution was evaporated to dryness, and the residue was heated at 200°C in a HCl gas stream for 2 days. The mixture of $(NH_4)_2EuCl_5$ and $LiCl$ thus obtained was then heated at 350°C under vacuum. This process serves to sublime off the excess $NH_4Cl$ and initiates the thermal decomposition of the $(NH_4)_2EuCl_5$. To complete the conversion to $LiEuCl_4$, the reaction mixture was heated under argon at 350°C for 3 days.

X-Ray powder patterns of the materials were obtained using the Guinier–Simon technique, employing $CuK\alpha1$ radiation. The observed patterns were found to be completely free of extra lines corresponding to either $EuCl_3$ or $LiCl$. The tetragonal lattice constants were calculated from the data using 14 lines calibrated against low

quartz, and these were $a = 6.4686(9)$ Å, and $c = 13.189(3)$ Å. These numbers may be compared to the crystallographic data reported for $LiGdCl_4$; here it was found that $a = 6.463(2)$ Å and $c = 13.163(3)$ Å (7).

All luminescence spectra were obtained on a high-resolution emission spectrometer constructed at Seton Hall University. Samples were excited by the 350-nm output (100 mW) of an Ar-ion laser, and the emission was analyzed at $1\text{-}cm^{-1}$ resolution by a 1-m grating monochromator (Spex Model 1704). The emission was detected by a cooled photomultiplier tube (S-20 response), and processed through the Spex digital photometer. In most works, the sample temperature was held between 8.5 and 9.0 K, with the low excitation power being desirable in that sample heating could be minimized. The $LiEuCl_4$ sample was mounted on a Cu block bolted onto the cold stage of a closed-cycle cryogenic refrigerator system (Lake Shore Cryotronics Model LTS-21).

## Results and Discussion

The $[EuCl_8]$ polyhedron in $LiEuCl_4$ has been described as that of a bisdisphenoid (triangulated dodecahedron), exhibiting a $I4_1/a$ space group (7). A drawing of the $[EuCl_8]$ polyhedron is shown in Fig. 1. This particular crystal structure is identical to that of $LiYF_4$ (8), a material which has found extensive use as a laser host system (9). If the $Eu^{3+}$ coordination polyhedron was exactly that of a bisdisphenoid, then the polyhedron would exhibit an overall symmetry of $D_{2d}$ and the lanthanide ion would occupy a site of $S_4$ symmetry.

However, the assignment of coordination polyhedra to 8-coordinate species is recognized as a difficult problem, since the energy barriers between the different forms are often small (10, 11). Detriangulation of the 8,18,12-dodecahedron proceeds via the 8,17,11-4, 4-bicapped trigonal prism to yield the 8,16,10-square antiprism (12).
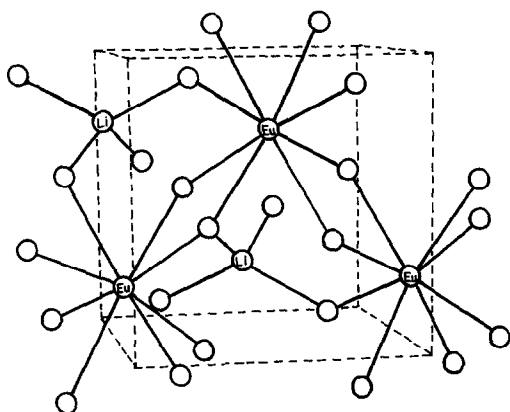
FIG. 1. Structure of the $[EuCl_8]$ polyhedra within the $LiEuCl_4$ material. The structure is isomorphous with that reported for $LiGdCl_4$ (7).

One could easily envision a polyhedron whose properties lie in between the two extremes, and which would exhibit an intermediate symmetry. It will be demonstrated eventually that the spectroscopic results can only be interpreted by the assumption of this intermediate symmetry case.

With the sample cooled to cryogenic temperatures, it was found that UV excitation resulted in the observation of reasonably strong photoluminescence. This observation indicates that self-quenching of the $Eu^{3+}$ centers through energy transfer is not a major problem in the $LiEuCl_4$ system. The luminescence was found to originate from both the $^5D_0$ and $^5D_1$ excited states, and a sequence of transitions to the various $^7F_J$ levels of the ground state was observed. Assignments of the various band systems may be easily obtained after comparison to the known free ion values (13). Experimental constraints limited our investigations to transitions terminating in the $^7F_J$ levels characterized by $J = 0, 1, 2, 3,$ or 4. For the sake of simplicity, we will henceforth refer to the various $f$-$f$ transitions by their defining $J$ quantum numbers.

As may be seen in Figs. 2–8, each luminescent transition contains a wealth of fine structure, and is found to occur in a charac-
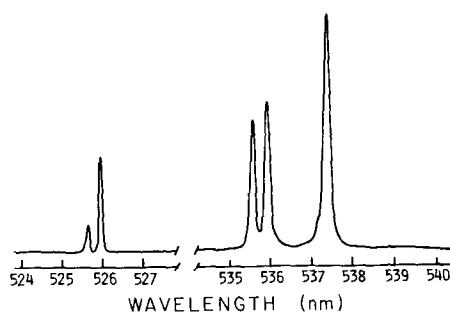


FIG. 2. Luminescence spectra of the $^5D_1 \rightarrow ^7F_0$ and $D_1 \rightarrow ^7F_1$ transitions of $Eu^{3+}$ in $LiEuCl_4$, obtained at 9.0 K. The 1–0 band system is located at shorter wavelengths relative to the 1–1 system.

teristic spectral region. None of the $^5D_J \rightarrow ^7F_J$ transitions overlaps to any significant extent with any other emission band. All of the band systems were found to consist of sharp features no more than 5 cm$^{-1}$ wide, and no evidence for the existence of vibronic bands was evident in the spectra. Thus, we have assigned all spectral features to genuine electronic transitions having allowed electric dipole character. A tabulation of the wavelengths and energies corresponding to all major peaks has been collected in Table I.

No crystal field is capable of splitting the nondegenerate levels corresponding to $J = 0$. Consequently, transitions from the $^5D_0$ and $^5D_1$ emitting states to the $^7F_0$ ground level are particularly useful in locating the energies of any and all emitting levels of the excited states. The number of crystal field components associated with the $^5D_1$ excited state must equal the number of peaks ob-
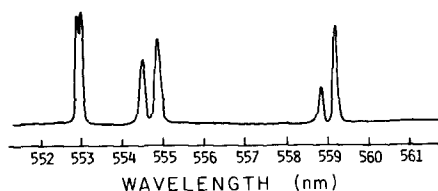


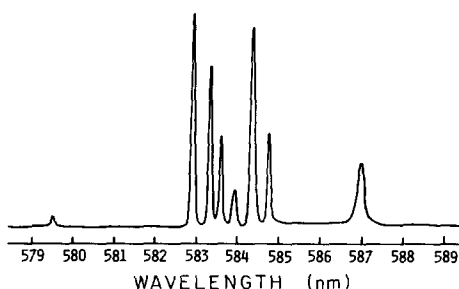FIG. 3. Luminescence spectrum of the $^5D_1 \rightarrow ^7F_2$ transition of $Eu^{3+}$ in $LiEuCl_4$, obtained at 9.0 K.

FIG. 4. Luminescence spectra of the $^5D_0 \rightarrow {^7F_0}$ and $^5D_1 \rightarrow {^7F_3}$ transitions of $Eu^{3+}$ in $LiEuCl_4$, obtained at 9.0 K. The sole 0–0 peak is the very weak feature located at the extreme left.

served within the 1–0 band system. Two peaks were found within the 1–0 band system (19,025 and 19,013 cm$^{-1}$), and hence we conclude that the $^5D_1$ emitting state is split into two crystal field states. The 0–0 transition was found to yield a single, but exceedingly weak, band at 17,257 cm$^{-1}$, and, of course, this transition cannot be split by any crystal field.

The $^5D_0$ level is thus the origin associated with each of the 0–$J$ transitions, and each component of the $^5D_1$ level may be considered as an origin for the 1–$J$ transitions. Each peak reported in Table I may thus be assigned as a transition from one of these three origins to the crystal field components
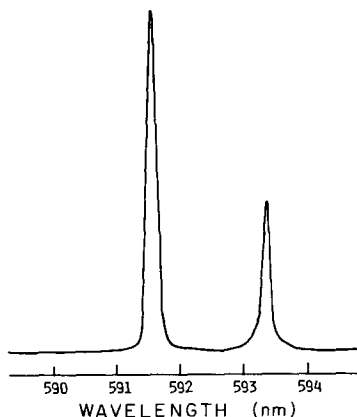


FIG. 5. Luminescence spectrum of the $^5D_0 \rightarrow {^7F_1}$ transition of $Eu^{3+}$ in $LiEuCl_4$, obtained at 9.0 K.

TABLE I

WAVELENGTHS, ENERGIES, AND ASSIGNMENTS OF THE LUMINESCENCE PEAKS OBSERVED FOR LiEuCl$_4$

| Wavelength (Å) | Energy (cm$^{-1}$) | Assignment |
|---|---|---|
| (a) 1–0 Band system | | |
| 5256 | 19,025 | 1(B)–0(A) |
| 5260 | 19,013 | 1(B)–0(A) |
| (b) 1–1 Band system | | |
| 5355 | 18,672 | 1(B)–1(A) |
| 5359 | 18,660 | 1(A)–1(A) |
| 5374 | 18,610 | 1(A)–1(B) |
| (c) 1–2 Band system | | |
| 5528 | 18,090 | 1(A)–2(A) |
| 5529 | 18,087 | 1(A)–2(B) |
| 5544 | 18,039 | 1(B)–2(C) |
| 5547 | 18,027 | 1(A)–2(C) |
| 5587 | 17,900 | 1(B)–2(D) |
| 5590 | 17,889 | 1(A)–2(D) |
| (d) 0–0 Band system | | |
| 5795 | 17,257 | 0(A)–0(A) |
| (e) 1–3 Band system | | |
| 5819 | 17,184 | 1(A)–3(A) |
| 5823 | 17,174 | 1(A)–3(B) |
| 5825 | 17,168 | 1(B)–3(C) |
| 5829 | 17,155 | 1(A)–3(C) |
| 5831 | 17,150 | 1(B)–3(D) |
| 5834 | 17,141 | 1(A)–3(D) |
| 5849 | 17,098 | 1(A)–3(E) |
| (f) 0–1 Band system | | |
| 5916 | 16,905 | 0(A)–1(A) |
| 5934 | 16,853 | 0(A)–1(B) |
| (g) 0–2 Band system | | |
| 6146 | 16,271 | 0(A)–2(C) |
| (h) 1–4 Band system | | |
| 6164 | 16,222 | 1(B)–4(A) |
| 6167 | 16,211 | 1(A)–4(A) |
| 6187 | 16,163 | 1(B)–4(B) |
| 6193 | 16,147 | 1(A)–4(B) and 1(B)–4(C) |
| 6198 | 16,135 | 1(A)–4(C) |
| 6201 | 16,127 | 1(A)–4(D) |
| 6212 | 16,098 | 1(A)–4(E) |
| 6216 | 16,088 | 1(B)–4(F) |
| 6221 | 16,074 | 1(A)–4(F) |
| 6228 | 16,056 | 1(A)–4(G) |
| (i) 0–3 Band system | | |
| 6494 | 15,398 | 0(A)–3(C) |
| 6500 | 15,386 | 0(A)–3(D) |
| 6517 | 15.344 | 0(A)–3(E) |
| (j) 0–4 Band system | | |
| 6955 | 14,378 | 0(A)–4(C) |
| 6985 | 14,317 | 0(A)–4(F) |
| 6994 | 14,299 | 0(A)–4(G) |
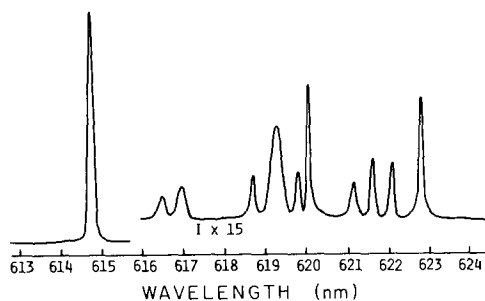
FIG. 6. Luminescence spectra of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_4$ transitions of Eu³⁺ in LiEuCl₄, obtained at 9.0 K. The intensity scale for the 0–2 peak at the left is 15 times that for the 1–4 series of peaks.



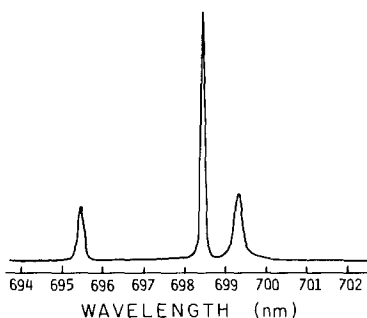FIG. 8. Luminescence spectrum of the $^5D_0 \rightarrow {}^7F_4$ transition of Eu³⁺ in LiEuCl₄, obtained at 9.0 K.

of each $^7F_J$ manifold. The actual number of peaks observed within a given band system depends on the site symmetry of the emitting Eu³⁺ ion.

The selection rules governing the 0–$J$ and 1–$J$ transitions of Eu³⁺ do not appear to have been worked out for $S_4$ symmetry. These have been summarized in Table II. If the crystal field of the Eu³⁺ ion was indeed that of a dodecahedron, then the state splitting induced by the crystal field would lead to the observation of zero 0–0 peaks, one 0–1 peak, three 0–2 peaks, four 0–3 peaks, and four 0–4 peaks. At the same time one should observe one 1–0 peak, three 1–1 peaks, seven 1–2 peaks, nine 1–3 peaks, and eleven 1–4 peaks. Such patterns were definitely not observed in the luminescence

spectra as summarized in Table I. These observations indicate that as far as spectroscopic requirements go, the effective site symmetry of the Eu³⁺ ion in LiEuCl₄ cannot be taken as $S_4$.

Comparison of the observed 0–$J$ patterns with those predicted by Forsberg (*14*) reveals that only one possible site symmetry fits the observed data. Were the Eu³⁺ ion to experience a site of $D_4$ symmetry, then the



FIG. 7. Luminescence spectrum of the $^5D_0 \rightarrow {}^7F_3$ transition of Eu³⁺ in LiEuCl₄, obtained at 9.0 K.

TABLE II

SELECTION RULES GOVERNING THE $^5D_J \rightarrow {}^7F_J$ Eu³⁺ LUMINESCENT TRANSITIONS IN $S_4$ SYMMETRY

| Ground state | | ES[a] = A [$^5D_0$] | ES = A [$^5D_1$] | ES = E [$^5D_1$] |
|---|---|---|---|---|
| $^7F_0$ | A | − | − | + |
| $^7F_1$ | A | − | − | + |
| | E | + | + | + |
| $^7F_2$ | A | − | − | + |
| | 2 B | + + | + + | + + |
| | E | + | + | + |
| $^7F_3$ | A | − | − | + |
| | 2 B | + + | + + | + + |
| | 2 E | + + | + + | + + |
| $^7F_4$ | 3 A | — | — | + + + |
| | 2 B | + + | + + | + + |
| | 2 E | + + | + + | + + + + |

*Note.* A (+) sign implies an electronic dipole transition, and a (−) sign signifies that the transition is electronic dipole forbidden.
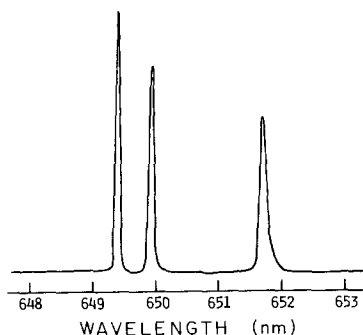
[a] Electronic state.

observed spectrum would consist of no 0–0 peak, two 0–1 peaks, one 0–2 peak, three 0–3 peaks, and three 0–4 peaks. The selection rules governing the various $J$–$J$ luminescence transitions in $D_4$ symmetry are collected in Table III. For these transitions, two 1–0 peaks, three 1–1 peaks, six 1–2, seven 1–3 peaks, and eleven 1–4 peaks would be anticipated. Comparison of these predictions with the actual results of Table I indicates the presence of an exact match for the 0–$J$ and 1–$J$ sequence of luminescence transitions. Consequently, one may conclude that as far as spectroscopic considerations go, the $Eu^{3+}$ ion experiences a crystal field described by $D_4$ symmetry.

Since the entire emission sequence associated with the transitions out of the $^5D_0$ and $^5D_1$ excited states can be interpreted with the assumption of $D_4$ symmetry, the remainder of the discussion will be based on considerations associated with this particular group. The $^5D_0$ level must not split in

TABLE III

Selection Rules Governing the $^5D_J \rightarrow {}^7F_J$ $Eu^{3+}$ Luminescent Transitions in $D_4$ Symmetry

| Ground state | | ES = $A_1$ [$^5D_0$] | ES = $A_2$ [$^5D_1$] | ES = $E$ [$^5D_1$] |
|---|---|---|---|---|
| $^7F_0$ | $A$ | – | + | + |
| $^7F_1$ | $A$ | + | – | + |
| | $E$ | + | + | + |
| $^7F_2$ | $A$ | – | + | + |
| | $B$ | – | – | + |
| | $B$ | – | – | + |
| | $E$ | + | + | + |
| $^7F_3$ | $A$ | + | – | + |
| | $B$ | – | – | + |
| | $B$ | – | – | + |
| | $2E$ | ++ | ++ | ++ |
| $^7F_4$ | $2A$ | – – | ++ | ++ |
| | $A$ | + | – | + |
| | $A$ | + | – | + |
| | $B$ | + | – | + |
| | $B$ | – | – | + |
| | $2E$ | ++ | ++ | ++ |

*Note.* A (+) sign implies an electronic dipole transition, and a (–) sign signifies that the transition is electronic dipole forbidden.

$D_4$ symmetry, and is characterized by $A_1$ symmetry. The fine structure within the various 0–$J$ transitions allows one to determine the energies of the $A_2$ and $E$ components of the ground $^7F_J$ levels, as transitions from the $A_1$ excited state to the $A_2$, $B_1$ and $B_2$ ground states are not permitted in $D_4$ symmetry.

The $^5D_1$ state must split into $A_2 + E$ components, and one would anticipate that emission out of both crystal field components ought to occur. Two transitions are possible within the 1–0 band system, and both are allowed in $D_4$ symmetry. The transitions out of the 19,013-cm$^{-1}$ level are normally found to be more intense than the corresponding transitions out of the 19,025-cm$^{-1}$ level, and hence one might assign $E$ symmetry to the 19,013-cm$^{-1}$ component. Supporting this assignment is the empirical observation that 1–$J$ transitions from this level are observed to every predicted level of the ground $^7F_J$ terms, with no exceptions. The 19,025-cm$^{-1}$ origin is not found to result in transitions to all $J$ levels of the ground $^7F_J$ terms, and hence cannot be the $E$ level.

One may use the data of Table I to calculate the energies corresponding to the crystal field substates of the $^5D_J$ and $^7F_J$ levels, and these are located in Table IV. In this process, we have assumed that the energy of the $F$ level equals zero.

Assignment of the symmetries associated with each level is not difficult, due to the relatively high symmetry associated with the $D_4$ point group. For the 0–$J$ transitions, only the $A_1 \rightarrow A_2$ and $A_1 \rightarrow E$ transitions can be observed. For the 1–$J$ transitions, one may observe the $A_2 \rightarrow A_1$ bands, the $A_2 \rightarrow E$ bands, the $E \rightarrow A_1$ bands, the $E \rightarrow A_2$ bands, and the $E \rightarrow E$ bands. Thus, symmetry labels for all $A_1$, $A_2$, and $E$ levels are readily assignable. One may use these general rules to determine which states are of either $B_1$ or $B_2$ symmetry, since these can only be observed in the 1–$J$ transitions originating with the $^5D_1$ level of $E$ symmetry.

TABLE IV

Energies of the Various Crystal Field Components of the Eu(III) States in LiEuCl$_4$ as Deduced from the Luminescence Spectra

| State | Symmetry | Energy (cm$^{-1}$) |
|---|---|---|
| $^7F_0$ Level | | |
| (A) | $A_1$ | 0 |
| $^7F_1$ Level | | |
| (A) | $E$ | 353 |
| (B) | $A_2$ | 404 |
| $^7F_2$ Level | | |
| (A) | $B_1/B_2$ | 923 |
| (B) | $B_1/B_2$ | 926 |
| (C) | $E$ | 986 |
| (D) | $A_1$ | 1125 |
| $^7F_3$ Level | | |
| (A) | $B_1/B_2$ | 1829 |
| (B) | $B_1/B_2$ | 1839 |
| (C) | $E$ | 1858 |
| (D) | $E$ | 1873 |
| (E) | $A_2$ | 1914 |
| $^7F_4$ Level | | |
| (A) | $A_1$ | 2802 |
| (B) | $A_1$ | 2866 |
| (C) | $E$ | 2879 |
| (D) | $B_1/B_2$ | 2886 |
| (E) | $B_1/B_2$ | 2915 |
| (F) | $E$ | 2940 |
| (G) | $A_2$ | 2958 |
| $^5D_0$ Level | | |
| (A) | $A_1$ | 17,257 |
| $^5D_1$ Level | | |
| (A) | $E$ | 19,013 |
| (B) | $A_2$ | 19,025 |

Note. Levels having either $B_1$ or $B_2$ symmetry cannot be uniquely assigned on the basis of the luminescence data. The empirical level labeling follows that of Table I.

No further symmetry determination can be made for these levels, however. The symmetry labels for the various Eu$^{3+}$ crystal field states may also be found in Table IV.

It is again noted that the effective site symmetry of the Eu ion is apparently higher than might be suspected from the crystal structure. In the case of LiEuCl$_4$, this situation implies that the crystal field experienced by the Eu$^{3+}$ ion is intermediate between that of a square antiprism ($D_{4d}$ symmetry) and a dodecahedron ($D_{2d}$). This observation and our earlier result concerning K$_2$EuCl$_5$ (6) provides some evidence that in these anhydrous chloride host systems of low symmetry, the crystal field interactions appear to be exceedingly short range in their nature. It is planned that these effects will be investigated further to learn of the possible generality of the phenomena.

## Acknowledgments

## References

1. S. Hufner, "Optical Spectra of Transparent Rare Earth Compounds," Academic Press, New York (1978).
2. G. Meyer, Prog. Solid State Chem. 14, 141 (1982).
3. G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals," Interscience, New York (1968).
4. J. P. Morley, T. R. Faulkner, and F. S. Richardson, J. Chem. Phys. 77, 1710 (1982).
5. C. A. Morrison and R. P. Leavitt, in "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gschneider, Jr., and L. Eyring, Eds.), Chap. 46, North-Holland, Amsterdam (1982).
6. H. G. Brittain and G. Meyer, J. Solid State Chem. 54, 156 (1984).
7. G. Meyer, Z. Anorg. Allg. Chem. 511, 193 (1984).
8. R. E. Thoma, G. D. Brunton, R. A. Penneman, and T. K. Keenan, Inorg. Chem. 9, 1096 (1970).
9. A. A. Kaminskii, "Laser Crystals," Springer-Verlag, New York (1981).
10. J. L. Hoard and J. V. Silverton, Inorg. Chem. 2, 235 (1963).
11. S. J. Lippard and B. J. Russ, Inorg. Chem. 7, 1686 (1968).
12. R. B. King, J. Amer. Chem. Soc. 91, 7211 (1969).
13. G. S. Ofelt, J. Chem. Phys. 38, 2171 (1963).
14. J. H. Forsberg, Coord. Chem. Rev. 10, 195 (1973).