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Emission Spectra of $Cs_2NaEuCl_6$ and $Cs_2Na(Eu,Y)Cl_6$

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The emission spectra of $Cs_2NaEuCl_6$ and $Cs_2Na(Eu_xY_{1-x})Cl_6$ ($x = 0.01$ and 0.10) have been determined at room temperature and at 77 K. These compounds have a face-centered cubic structure and the rare earth ion lies on a site of perfect octahedral symmetry surrounded by six chloride ions. The emission spectrum of the europium(III) ion confirms this symmetry and is dominated by those transitions which obey magnetic dipole selection rules. Weak, broad vibronic transitions are observed in place of the electric dipole transitions which are forbidden by the selection rules for octahedral symmetry. In $Cs_2NaEuCl_6$ transitions are found between 4900 and 6500 Å and arise from the $^5D_0$, $^5D_1$, and $^5D_2$ excited states. In the doped compounds transitions are observed between 4500 and 6500 Å and arise from the $^5D_3$ excited state as well as from $^5D_0$, $^5D_1$, and $^5D_2$.

Introduction

There are very few compounds of the trivalent rare earth ions which have sixfold, octahedral coordination.[2] As a result, most spectroscopic work has been done with compounds in which the symmetry of the environment around the rare earth ion is lower than octahedral, a fact which introduces complicating factors. In previous studies of the rare earth ions in cubic sites, such as the eightfold coordination of the ions doped in CaF_2[3] or the sixfold, octahedral, coordination in CaO,[4] there are the additional problems of charge compensation and multiple-site occupancy. These arise because of the difference in charge between the trivalent rare earth ion and the divalent calcium ion. For example, in the case of Er^{3+} in CaF_2, in addition to the cubic sites, trigonal sites (C_{3v}), tetragonal sites (C_{4v}), and 16 other sites having more than one Er^{3+} ion have also been observed.[3]

There have been two recent detailed spectroscopic studies of rare earth ions in sixfold, octahedral, environments. Gruber, Mendel, and Ryan[5] have examined the absorption spectrum of $[(C_6H_5)_3PH]_3NdCl_6$ and found that the neodymium ion occupies two slightly inequivalent sites having essentially octahedral symmetry with a slight distortion along one of the axes. Butter and Seifert[6] have investigated the emission spectra of $(pyH)_3EuCl_6$ and $(pyH)_3EuBr_6$ and interpreted their results in terms of a weakly distorted octahedral symmetry about the europium ion. The emission spectrum of europium(III) doped into the compound Ba_2GdNbO_6[7] has also been studied. The rare earth ion in this compound is in a site of octahedral symmetry which was demonstrated by the appearance of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ and the vibronic transition $^5D_0 \rightarrow {}^7F_2$.

As part of a project to investigate the emission spectrum of europium(III) in compounds in which the ion has discrete octahedral symmetry but does not suffer from the disadvantages mentioned above, we have measured the spectra of $Cs_2NaEuCl_6$ and $Cs_2Na(Eu_xY_{1-x})Cl_6$ ($x = 0.01$ and 0.10). These compounds were first prepared by Morss[8] and belong to a broad class of compounds of the trivalent metal ions which have been shown to have the face-centered cubic structure. All of the rare earth ions can exist in this lattice and the ESR spectra and magnetic susceptibilities have been reported for some of the ions.[9-11] In all cases the results which have been obtained are in agreement with the rare earth ion occupying a site of essentially perfect octahedral symmetry. In addition the absorption and magnetic circular dichroism spectra have been reported for the Ce^{3+} ion doped into Cs_2NaYCl_6[12] and the transitions and vibronic analysis were found to be indicative of the octahedral symmetry around the Ce^{3+} ion. The fluorescence emission of the Nd^{3+} compound[13] has also been determined and the long fluorescence lifetime is in accord with the suggestion made previously by Dieke.[14]

Because the rare earth ion in these compounds lies on a site which has inversion symmetry, this is an ideal system in which to check the degree to which the selection rules for the various optical transitions in europium(III) are obeyed. In principle, only those electronic transitions allowed under the magnetic dipole selection rules should be permitted and the electric dipole transitions will be replaced by vibronic transitions.[15] After our initial emission measurements were made, we became aware of the work carried out by Schwartz on the visible absorption spectrum and magnetic circular dichroism spectrum of $Cs_2NaEuCl_6$.[16] The results of these measurements complement the emission results reported here.

Experimental Section

Preparation of $Cs_2NaLnCl_6$. The compound $Cs_2NaEuCl_6$ was prepared by dissolving 2 mmol of CsCl, 1 mmol of NaCl, and 0.5 mmol of Eu_2O_3 in 6 M HCl and evaporating the resulting solution to dryness (preparation E).[7] Analysis of the resulting microcrystalline material for europium by EDTA titration was in agreement with the expected formula. The x-ray diffraction pattern agreed well with that previously reported and gave no evidence for significant amounts of NaCl or CsCl. The doped compounds, $Cs_2Na(Eu_xY_{1-x})Cl_6$ ($x = 0.01$ or 0.10), were made by the same procedure with the exception that the Eu_2O_3 was replaced by sufficient Y_2O_3 to yield the desired formulation. Samples of large crystals of $Cs_2NaEuCl_6$ were also

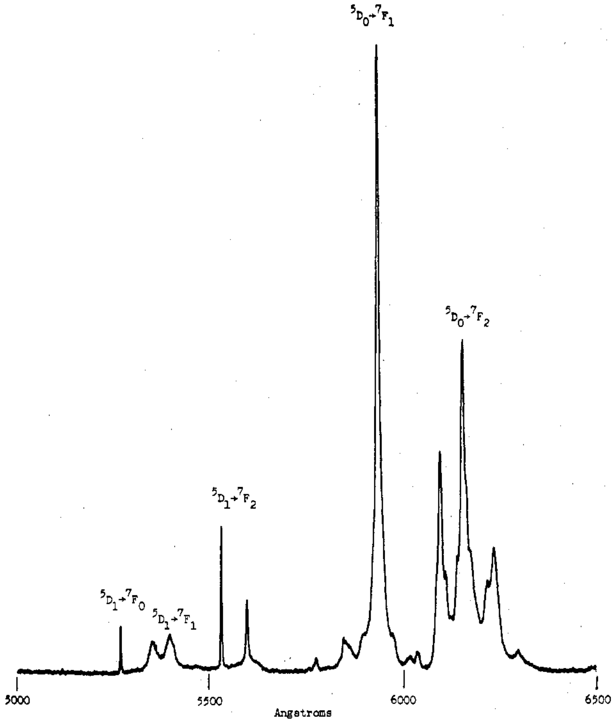

Figure 1. Emission spectrum of $Cs_2NaEuCl_6$ at room temperature.

generously supplied by Dr. Schwartz.

Spectral Measurements. The emission spectra were measured on a McPherson RS-10 spectrophotometer equipped with the Model 606 fluorescence attachment. The excitation source was a 100-W mercury lamp used in conjunction either with Corning CS-7-39 or CS-7-54 filters or with Baird-Atomic 2537- or 3650-Å interference filters. Other than for the differences in the intensities of the emitted radiation, the spectra obtained were essentially the same in each case. The monochromator slits were routinely set at 100 μ, which gave an instrumental resolution of 1 Å. When the instrumental resolution was increased to 0.5 Å, there was no change in the spectrum. For measurements at 77 K the solid compound was placed in a quartz tube of 3-mm i.d. and immersed in a Dewar flask which had a quartz tail and was filled with liquid nitrogen. For measurements at room temperature, the same system was used except for the absence of the liquid nitrogen. The wavelength scale of the spectrophotometer was calibrated with the lines from a low-pressure mercury lamp. The sharp peaks in the emission spectrum of the europium(III) compounds could be located to less than 1 Å and the weaker broad peaks could usually be determined within 2 Å.

Results

The emission spectrum of $Cs_2NaEuCl_6$ between 4900 and 6500 Å is found to consist of a number of sharp lines as well as some regions in which the lines are rather broad. At liquid nitrogen temperatures, some of these lines are quite narrow, having half-widths of 1–2 Å. In general it is found that the relative intensity of the broad bands compared to the narrow ones decreases as the temperature decreases, which strongly suggests that the former are vibronic in origin. The spectrum of a crystalline sample of $Cs_2NaEuCl_6$ at room temperature is shown in Figure 1 and the spectrum of the same sample at liquid nitrogen temperature is shown in Figure 2. (The intensities have not been corrected for the spectral response of the monochromator and detector but it can be noted that the response is about 6 times greater at 4500 Å than at 6500 Å.)

The positions of the peaks at room temperature are given in Table I,[17] and at liquid nitrogen temperature the corresponding peaks are given in Table II.[17] The transitions to which these correspond are also given in the tables. The various transitions originate on the $^5D_0$, $^5D_1$, and $^5D_2$ excited states of the europium(III) ion and terminate on the $^7F_0$, $^7F_1$, $^7F_2$, and $^7F_3$ components of the ground ^7F term.[18] Of particular interest is the observation that the $^5D_2 \rightarrow {}^7F_3$ and $^5D_2 \rightarrow {}^7F_2$ transitions are very much weaker than any of the transitions which originate on $^5D_0$ or $^5D_1$.

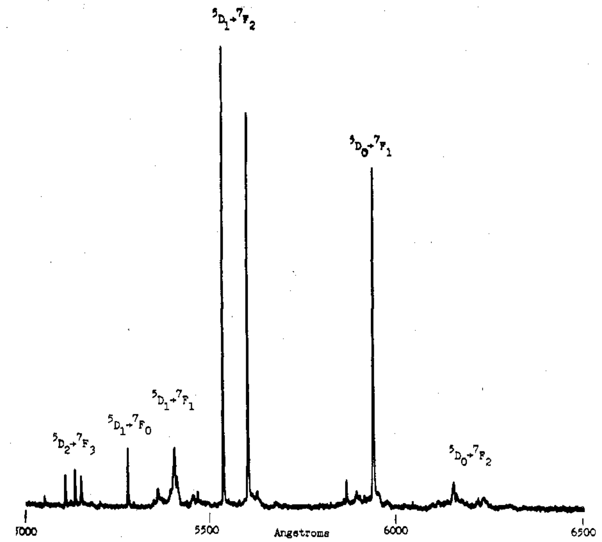

Figure 2. Emission spectrum of $Cs_2NaEuCl_6$ at 77 K.

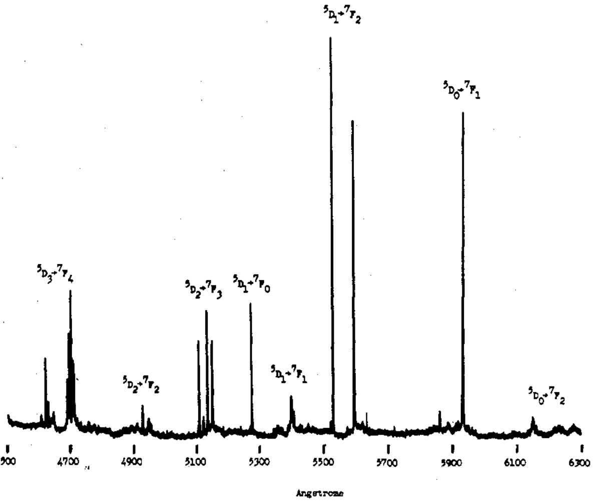

Figure 3. Emission spectrum of $Cs_2Na(Eu_{0.01}Y_{0.99})Cl_6$ at 77 K.

The doped compounds $Cs_2Na(Eu_xY_{1-x})Cl_6$ ($x = 0.01$ or 0.10) yield emission spectra that are the same as that of $Cs_2NaEuCl_6$ with two notable exceptions. In the doped compounds there are new bands that appear in the 4500–4900-Å region and the peaks between 4900 and 5200 Å are relatively much more intense than in the undoped compounds. Transitions in those regions originate on the $^5D_2$ and $^5D_3$ excited states.[18] The spectrum of the 1 mole % europium compound at 77 K is illustrated in Figure 3 and the peak positions are given in Table III.[17]

Discussion

When the europium(III) ion is located in an octahedral site and thus occupies a site having inversion symmetry, the only purely electronic transitions which can occur are those for which the magnetic dipole selection rule $\Delta J = 0, \pm 1$ (J and J' not both equal to zero) is obeyed.[19] Utilizing the fact that the f^6 electronic configuration of europium(III) has even parity and thus gives rise to terms which are symmetric with respect to inversion, the magnetic dipole selection rules given in Table IV can be derived for the transitions which would be expected in the wavelength range from 4500 to 6500 Å.

Transitions for which $\Delta J = 2$ are electric dipole in origin

Table IV. Magnetic Dipole Selection Rules for Eu^{3+} in an Octahedral Field

J	Irreducible representation[a]	J	Irreducible representation[a]
0	A_{1g}	3	$A_{2g} + T_{1g} + T_{2g}$
1	T_{1g}	4	$A_{1g} + E_g + T_{1g} + T_{2g}$
2	$E_g + T_{2g}$		
Allowed transitions			
$^5D_0 \rightarrow {}^7F_1$	$A_{1g} \rightarrow T_{1g}$	$^5D_2 \rightarrow {}^7F_3$	$E_g \rightarrow T_{1g}$
$^5D_1 \rightarrow {}^7F_0$	$T_{1g} \rightarrow A_{1g}$		$E_g \rightarrow T_{2g}$
$^5D_1 \rightarrow {}^7F_1$	$T_{1g} \rightarrow T_{1g}$		$T_{2g} \rightarrow A_{2g}$
$^5D_1 \rightarrow {}^7F_2$	$T_{1g} \rightarrow E_g$		$T_{2g} \rightarrow T_{1g}$
	$T_{1g} \rightarrow T_{2g}$		$T_{2g} \rightarrow T_{2g}$
$^5D_2 \rightarrow {}^7F_1$	$E_g \rightarrow T_{1g}$	$^5D_3 \rightarrow {}^7F_4$	$A_{2g} \rightarrow T_{2g}$
	$T_{2g} \rightarrow T_{1g}$		$T_{1g} \rightarrow A_{1g}$
$^5D_2 \rightarrow {}^7F_2$	$E_g \rightarrow T_{2g}$		$T_{1g} \rightarrow E_g$
	$T_{2g} \rightarrow E_g$		$T_{1g} \rightarrow T_{1g}$
	$T_{2g} \rightarrow T_{2g}$		$T_{1g} \rightarrow T_{2g}$
			$T_{2g} \rightarrow E_g$
			$T_{2g} \rightarrow T_{1g}$
			$T_{2g} \rightarrow T_{2g}$

[a] Magnetic dipole operator is T_{1g}.

and as such would be absent in a compound which has the europium(III) at a site with inversion symmetry. Coupling with the odd normal modes of vibration of the compound will, however, lead to a vibronic spectrum built upon the electric dipole transitions.[19] The intensities of such vibronically allowed transitions should decrease as the temperature is lowered. The most prominent example of this is the vibronic transition which occurs in the $^5D_0 \rightarrow {}^7F_2$ region and which has an intensity about 50% of that of the $^5D_0 \rightarrow {}^7F_1$ emission at room temperature but only about 10% of the intensity at 77 K.

The sharp peaks which are found in all cases are in the appropriate regions in which the magnetic dipole transitions are expected. For the undoped compound these are the $^5D_0 \rightarrow {}^7F_1$, $^5D_1 \rightarrow {}^7F_0$, $^5D_1 \rightarrow {}^7F_2$, and $^5D_2 \rightarrow {}^7F_3$ transitions. The transition $^5D_2 \rightarrow {}^7F_1$ was not found. These same transitions are found in the doped compounds with the addition of the transition corresponding to $^5D_3 \rightarrow {}^7F_4$. In the doped compound $^5D_2 \rightarrow {}^7F_1$ is only very weakly observed.

The only other allowed transitions which should be observed in the wavelength range covered in this study are $^5D_1 \rightarrow {}^7F_1$ and $^5D_2 \rightarrow {}^7F_2$. Both of these are found, but they are very weak and consist of several lines. Moreover, the intensities of these relative to the transitions which are clearly magnetic dipole in character vary significantly with temperature which establishes them as vibronic in origin. It has previously been shown by Judd[20] that the $^5D_1 \rightarrow {}^7F_1$ transition which is permitted by magnetic dipole selection rules is not observed in this mode because $g(^5D_1) = g(^7F_1)$. A similar situation probably applies to the $^5D_2 \rightarrow {}^7F_2$ transition.

When the europium(III) ion is in an octahedral crystal field, some of the degeneracy of the total angular momentum, J, is removed and a number of states is found. This removal of the degeneracy is indicated in Table IV. For $J = 0$ and 1, only a single state is found; for $J = 2$, two states are found; for $J = 3$, three states are found; and for $J = 4$, four states are found. The selection rules for magnetic dipole transitions then give the number of components that should be observed for each transition. Comparison with the experimental data shows that the agreement with the number of allowed components is excellent.

Since both $J = 0$ (A_{1g}) and $J = 1$ (T_{1g}) are not split by the octahedral field, the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_1 \rightarrow {}^7F_0$ must consist of single lines. The $^5D_1 \rightarrow {}^7F_2$ transition consists of two components since $J = 1$ (T_{1g}) is not split but $J = 2$ is split into two components, E_g and T_{2g}, with a separation of 220 cm^{-1}. The $^5D_2 \rightarrow {}^7F_3$ transition gives four allowed transitions between the $J = 2$ (E_g, T_{2g}) and $J = 3$ (A_{2g}, T_{1g}, T_{2g}) states and the $^5D_3 \rightarrow {}^7F_4$ transition consists of six of the eight transitions allowed between the state with $J = 3$ and that with $J = 4$ (A_{1g}, E_g, T_{1g}, T_{2g}). The two missing transitions can be identified as $T_{1g} \rightarrow A_{1g}$ and $A_{2g} \rightarrow T_{2g}$ from the fact that the six allowed transitions occur in two series with a separation of 27–33 cm^{-1}. Since there are three transitions which originate on each of the T_{1g} and T_{2g} components of $^5D_3$ and terminate on the T_{2g}, T_{1g}, and E_g components of $^7F_4$, these six transitions are identified.

Each of the strong magnetic dipole allowed transitions is accompanied by much weaker side bands that are vibronic in origin. Since the consideration of the vibrational structure in the absorption spectrum has been carried out in detail by Schwartz,[16] it will not be repeated here. Suffice it to say that in general the position of the vibronic bands relative to the pure electronic transition can be correlated in nearly all cases with one of the vibrational modes discussed by Schwartz. In addition, there are several transitions in the emission spectra that are due solely to vibronic interaction. The main transition considered by Schwartz, $^7F_0 \rightarrow {}^5D_2$, is also observed in the emission spectrum ($^5D_2 \rightarrow {}^7F_0$) but is very weak and overlaps the $^5D_3 \rightarrow {}^7F_4$ transition. The $^5D_0 \rightarrow {}^7F_2$ transition which occurs between the same two values of J, could, however, be studied. From the separation of 220 cm^{-1} found for the E_g and T_{2g} components of $^7F_2$ it was expected that many of the vibronic lines associated with each state would be separated by that amount. The data in Tables I–III[17] show that this expectation was met. Moreover, there is a good correspondence with the absorption data.

In the analysis of the vibronic structure of the $^7F_0 \rightarrow {}^5D_2$ transition, Schwartz found an almost constant difference of 110 cm^{-1} between the same vibration associated with the two electronic states (E_g and T_{2g} of $^5D_2$) at liquid helium temperature. This difference can be observed directly in the $^5D_2 \rightarrow {}^7F_3$ magnetic dipole allowed transitions in the emission spectrum and is found to be 111 cm^{-1} for one pair of the allowed transitions and 113 cm^{-1} for the other.

The other three transitions that are solely vibronic in origin are $^5D_0 \rightarrow {}^7F_0$, $^5D_1 \rightarrow {}^7F_1$, and $^5D_2 \rightarrow {}^7F_2$. These are observed in both the doped and the undoped compounds, but the last transition is very weak in the undoped compound. The $^5D_1 \rightarrow {}^7F_1$ emission closely resembles the $^7F_1 \rightarrow {}^5D_1$ transition in the absorption spectrum, although at room temperature only two vibronic lines are observed. The $^5D_2 \rightarrow {}^7F_2$ emission consists of a large number of vibronic lines which again have separations consistent with the vibrational analysis of Schwartz (provided $^5D_2$ is located as discussed below), as do the vibrational structures on the $^5D_0 \rightarrow {}^7F_0$ and $^5D_1 \rightarrow {}^7F_1$ transitions.

A partial energy level diagram for the europium(III) ion in these compounds can be constructed from the results of the emission measurements coupled with the results of the absorption measurements. The position of the $^5D_1$ excited state is obtained directly from both the emission and the absorption spectra and at 77 K is located at 18965 cm^{-1}. The $^7F_1$ state cannot be obtained directly, but if the two components of the $^5D_1 \rightarrow {}^7F_1$ emission at room temperature are taken to be the same distance from the origin, the transition would appear at 18612 cm^{-1}. Schwartz located this transition at 18615 cm^{-1} at room temperature. Using this value the corresponding transition at 77 K is determined to lie at 18605 cm^{-1}. Combining the values for these two transitions puts the $^7F_1$ level at 360 cm^{-1}. This value for $^7F_1$, coupled with the known energy of the $^5D_0 \rightarrow {}^7F_1$ transition, places $^5D_0$ at 17209 cm^{-1}. The two components of $^7F_2$ are obtained from the $^5D_1 \rightarrow {}^7F_2$ emission and the known position of $^5D_1$ and are found to be at 875 and 1095 cm^{-1}.

Schwartz was able to estimate the positions of the com-

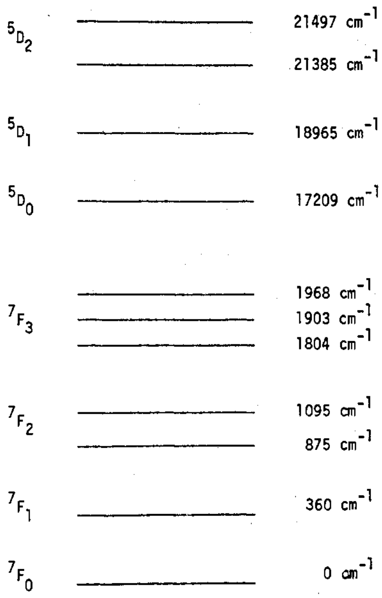

Figure 4. Partial energy level diagram for $Cs_2NaEuCl_6$.

ponents of the $^5D_2$ level from the $^7F_0 \rightarrow {}^5D_2$ absorption as 21405 and 21515 cm^{-1} at liquid helium temperature and at 21400 and 21505 cm^{-1} at room temperature. In the emission spectrum of the doped compound at 77 K there are two weak lines at 21026 and 21137 cm^{-1}. If these are assigned to the $^5D_2 \rightarrow {}^7F_1$ transition, then the components of $^5D_2$ would be located at 21386 and 21497 cm^{-1}, respectively. Although this assignment is not conclusive because of the weakness of these bands (even though they are allowed by magnetic dipole selection rules), it should be noted that the calculated position of $^5D_2$ at 77 K is less than at room temperature as is usually found.[21] Schwartz's assignment puts these at a lower energy at room temperature than at liquid helium temperature. If our values are used, however, the vibronic transitions on the $^7F_0 \rightarrow {}^5D_2$ absorption band can still be assigned with the exception that the highest vibration occurs at 256 cm^{-1}, which is not an unreasonable value.[22] Moreover, our assignment allows the vibronic structure on the $^5D_2 \rightarrow {}^7F_2$ transition to be analyzed. Also, it should be noted that the $^5D_0 \rightarrow {}^7F_2$ transition and the $^5D_1 \rightarrow {}^7F_1$ transition also give the highest vibronic line at 250–256 cm^{-1} from the calculated positions of the pure electronic transition. Once again it must be pointed out, however, that because of the breadth of some of these vibronic lines, the possible presence of small amounts of emitting impurities, and the overlap of emissions in some of these regions, the assignment of the vibrational modes is subject to some error.

If the $^5D_2$ levels are placed at 21386 and 21497 cm^{-1}, then these can be combined with the $^5D_2 \rightarrow {}^7F_3$ transitions to place the $^7F_3$ levels at 1804, 1903, and 1968 cm^{-1}. With the available data it is not possible to place the $^5D_3$ and $^7F_4$ levels on this energy scale. The partial energy level diagram is given in Figure 4.

The observation of emission from the excited $^5D_3$ level deserves some comment. Transitions from the higher excited ^5D levels in europium are rarely observed[19] since the lifetimes of these higher excited levels are generally very short. Consequently it is usually found that the emission spectrum of europium compounds originates on $^5D_0$, $^5D_1$, and, to a much lesser extent, $^5D_2$. It was suggested by Dieke,[14] however, that the excited states of rare earth ions in a perfect octahedral environment might have long relaxation times, a suggestion which is supported by these emission measurements. The fluorescence lifetimes for $Cs_2NaNdCl_6$ have been measured[13] and were found to be the longest yet reported. Moreover, it is interesting to note that transitions originating on $^5D_2$ and $^5D_3$ are more intense in the doped compounds. (In fact those from $^5D_3$ were not observed in $Cs_2NaEuCl_6$.) This suggests that even in $Cs_2NaEuCl_6$ where the europium(III) ions are separated from one another by a rather large distance (0.76 nm) there is still some interaction between the ions.

The value of the fourth-order crystal field parameter B_0^4 is obtained from the splitting of the $^7F_2$ level and is found to be 1384 cm^{-1}. This can be compared with the value of 1272 cm^{-1} found by Butter and Seifert for europium(III) in $(pyH)_3EuCl_6$.

In summary, it has been found that the europium(III) ion in $Cs_2NaEuCl_6$ and doped into Cs_2NaYCl_6 lies on a site of exact octahedral symmetry. The selection rules for this symmetry require that the only pure electronic transitions must be of magnetic dipole character and that all other transitions be vibronic in origin. The experimental results are in conformance with these selection rules. Moreover, the lifetimes of the excited states are sufficiently long that in the doped compounds emission is observed from the $^5D_3$ level as well as the $^5D_2$, $^5D_1$, and $^5D_0$ levels.

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Registry No. $Cs_2NaEuCl_6$, 27880-12-2; Cs_2NaYCl_6, 27880-16-6.

Supplementary Material Available: Tables I–III listing the emission wavelengths for $Cs_2NaEuCl_6$ at room temperature and 77 K and for $Cs_2Na(Eu,Y)Cl_6$ at 77 K (6 pages). Ordering information is given on any current masthead page.

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(22) The assignment of the vibronic lines on the $^7F_0 \rightarrow {}^5D_2$ absorption band is being changed to reflect this: R. W. Schwartz, private communication.