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ABSTRACT

The polarized absorption spectrum and some effect studies were conducted on crystals of lanthanum trichloride and lanthanum ethylsulfate containing 0.1 and 5 mol % of Pu^{3+} at various low temperatures. The ground-state levels as well as several excited states are well characterized. Attempts at fitting the positions of levels to 5f hydrogenic field-ion states give good agreement for $F_2 = 245 \text{ cm}^{-1}$ and $\zeta = 2290 \text{ cm}^{-1}$.

THE ABSORPTION SPECTRUM OF Pu^{3+} IN
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I. INTRODUCTION

The absorption spectrum of trivalent plutonium in single crystals has not yet been analyzed. Only Freed and Leitz¹ reported on the spectra of some actinides, including plutonium in anhydrous trichlorides. They observed groups of sharp lines, as in the spectra of the rare earths, and concluded that the actinides form a series similar to the rare earths, as had been suggested earlier. This would mean that in the actinides series the 5f electronic shell is filled successively—with the 6s and 6p shells completely filled. In the meantime the spectra of several actinides have been investigated in detail, and the position of the actinides in the periodic table proposed earlier is now considered to be correct.

Therefore, it seemed worth while to try an analysis of the plutonium spectrum. This way one should be able to tell something about the Coulomb and spin-orbit interactions of the 5f electrons. Furthermore, it is interesting to investigate the influence of external perturbing fields on these electrons and to compare it with the effects already known for the rare earths.

We have studied the absorption and fluorescence spectra of Pu^{3+} in two hexagonal crystals in the visible and infrared spectral regions at low temperatures, between 4.2 and 77°K. The Zeeman effect was also examined. Below 21 000 cm^{-1} , 14 groups of absorption lines and eight groups of emissions

lines were observed. They are discussed in detail in Sec. IV and analyzed as far as possible. Above $21\,000\text{ cm}^{-1}$ the numerous absorption lines do not appear in distinct groups. Therefore they will not be treated in this paper. Section II describes the experimental procedures, and in III the theoretical background is reviewed briefly.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Crystals

The plutonium, which was available as a concentrated $\text{Pu}^{4+}(\text{NO}_3)_4$ solution in HNO_3 , was reduced by $\text{NH}_2\text{OH} \cdot \text{HCl}_3$.² Single crystals of lanthanum trichloride containing 0.1 to 5 mol % of Pu^{3+} were grown from the melt following the method of Gruen et al.³

The lanthanum (plutonium) ethylsulfates with the same Pu concentration as the trichlorides were prepared in the same manner as rare-earth ethylsulfates. The crystals were grown by evaporation from the hydrous solution. In order to avoid oxidation, an excess of $\text{NH}_2\text{OH} \cdot \text{HCl}_3$ was added to the solution, and the crystals were grown in a nitrogen atmosphere. Fractionated crystallization took place, so that the crystals always contained more plutonium than the solution.

We also tried to prepare the double nitrates $\text{La}_2(\text{Pu}_2)\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, but got only the pure lanthanum crystals.

The trichloride and ethylsulfate crystals were stable during the whole period of the experiments, and were not destroyed by the α radiation of the decaying plutonium.

B. Equipment

The absorption and fluorescence spectra were photographed on a Jarrel-Ash (Ebert mount) grating spectrograph with a reciprocal linear dispersion of about $5 \text{ \AA}/\text{mm}$. Also, a Cary Model-14 and a Beckman IR-5 infrared recording spectrophotometer were used. Light sources were a mercury lamp (BH6) and a tungsten lamp.

The crystals were oriented by means of a polarizing microscope and put into a small brass holder, with glass windows, which was uncontaminated on the outside. The cooling liquid helium, hydrogen, or nitrogen was contained in a double dewar system of pyrex or quartz. Tiny slits in the crystal holder allowed the cooling agent to penetrate and wet the crystal.

Homogeneous magnetic fields up to 28 000 Oe were produced by a Varian magnet.

III. THEORETICAL BACKGROUND

A. The Free Ion

The Pu^{3+} ion has five $5f$ electrons and, like samarium (Sm^{3+}), 198 levels characterized by the total angular momentum J . The levels of the free ion can be calculated with the procedure first developed by Racah.⁴ In such calculations one encounters the matrix elements of the Coulomb interaction and the spin-orbit interaction, which are evaluated for the f^5 configuration by Elliot et al.⁵ and by Wybourne.⁶ Using a program developed by Wybourne, we have calculated the levels for $5f^5$ as a function of the Slater parameters F_2 , F_4 , and F_6 and the spin-orbit parameter ζ . This program also computes the g values and the eigenfunctions of the levels as linear combinations of Russell-Saunders functions.

B. The Levels in Perturbating Fields

The characteristic behavior of a level in the electrostatic crystal field and an external magnetic field has been described extensively in connection with the analysis of the rare earths. Fortunately the effects of these fields on Pu are observed to be of the same order of magnitude as in the salts of the rare earths, so we can use the same methods.

For completeness we give a brief outline of the theoretical background: In both salts the Pu^{3+} ion is in a field of the symmetry C_{3h} . In such a field the levels split into $J+1/2$ Kramer's doublets, which are characterized by the crystal quantum numbers $\bar{\mu} = \pm 1/2, \pm 3/2, \pm 5/2$ first introduced by Hellwege.^{7,8} If we write the corresponding eigenfunctions $U_{i\bar{\mu}}$ as linear combinations of the wave functions $\psi_{\gamma JM}$ of the free ion, only the $\psi_{\gamma JM}$ with $M \equiv (\bar{\mu} \pm 3) \pmod{p}$ are present.

For the electrical dipole radiation we have the selection rules⁷

$$\langle \bar{\mu} | P_x \pm iP_y | \bar{\mu}' \rangle \neq 0 \text{ only, for } \Delta \bar{\mu} = \pm 1, \pm 4.$$

$$\langle \bar{\mu} | P_z | \bar{\mu}' \rangle \neq 0 \text{ only, for } \Delta \bar{\mu} = \pm 3.$$

Here P_x , P_y , and P_z are the electric dipole operators in the x, y, and z directions, respectively.

The splitting of the levels by the external magnetic field is not isotropic, but is a complex algebraic function of the field strength. In former papers, for small J values, explicit expressions for the splittings are given as a function of the g value of the free ion and the crystal field matrix elements $K_{MM'}$, together with equations for the calculation of g and the $K_{MM'}$ from the observed Zeeman splitting.^{9,10,11} For the larger J values explicit formulas are not available. Therefore we diagonalized

the matrix of the combined perturbation of the crystal field and the magnetic field.

IV. RESULTS

1. General Remarks

a. Absorption.

As already mentioned above, at low temperatures the spectra of the plutonium are very similar to those of the rare earths. That means that below $21\,000\text{ cm}^{-1}$ well-separated groups of polarized sharp lines are observed. Each group in the chloride corresponds to a group of the ethylsulfate. Their centers of gravity are shifted by about 100 cm^{-1} . In the ethylsulfate we found only three groups of sharp lines. All other groups are so broad that the Zeeman effect could not be investigated. In the chloride, however, we observed more sharp lines. As in the rare earths, the high-energy lines of a group are broader than the low-energy ones.

The plutonium spectrum is much more intense than the samarium spectrum. With the concentrations used, only transitions of electrical dipole radiation, which are forbidden for the free ion, are observed. In the samarium,¹⁰ however, we found magnetic and electric dipole radiation of comparable intensity. Presumably, stronger admixtures of other configurations to $5f$ are present in the Pu^{3+} than in Sm^{3+} .

In order to give a survey of the plutonium spectrum, we show in Fig. 1 a photometer curve of the PuCl_3 , taken with the Cary spectrophotometer at 77°K with unpolarized light. To the right of Fig. 2 are the absorptions or the centers of gravity of the groups for both salts.

First we treat the four levels with sharp components that allow the determination of J , g , and $K_{MM'}$. By use of these results the total energy level scheme is calculated. Then the remaining levels with broader components are discussed and compared with theory.

b. Fluorescence.

Plutonium fluorescence has been reported by Cunningham et al.¹² We found eight groups of emission lines, which represent transitions from the three excited levels H, I, O to the two first excited levels and the ground level. We discuss them together with the absorption in the far infrared spectral region.

2. The Ground Level

In the following discussion we denote the three ground-level crystal field components by I, II, III and the components of the excited levels by a, b, c, ... with increasing energy.

In an earlier paper¹³ we have reported the crystal field splitting and the paramagnetic resonance spectrum of the ground level ${}^6H_{5/2}$. In order to give a complete description here we include values of the components and the splitting factors, in Tables I and II.

Since the earlier paper we have determined the splitting factors s_{\parallel} of the $\bar{m} = \pm 3/2$ components. In the ethylsulfate I has the \bar{m} value $\pm 3/2$. Because there is no magnetic dipole radiation, all transitions arising from I are completely σ or π -polarized, and are split therefore only into two Zeeman components in an external magnetic field parallel to the crystal axis. Therefore, s_{\parallel} (I) cannot be determined directly. If we make the assumption that the splittings of the crystal field components of the "0" level with $J = 3/2$ are related as three to one, we can determine s_{\parallel} (I) from the observed Zeeman splittings of the two lines of group O at 4.2°K . The value obtained under this assumption is given in Table II. We believe that this

assumption is justified because the g factor of the excited level calculated in this way is in good agreement with g determined in the perpendicular field.

3. Group H

In the trichloride, four absorption lines and two emission lines are observed at 4.2° K. Also, a further absorption line appears in the perpendicular magnetic field. At 20° K, and higher, temperatures three more lines are observed. Figure 3 shows the complete energy-level scheme as it was found. The observed transitions are included. The values of $\bar{\mu}$ and the M values of the eigenfunctions $\psi_{\gamma JM}$ of the free ion, which are predominant in the crystal eigenfunctions $U_{i\bar{\mu}}$, are also given. The selection rules are well followed. We find the center of gravity at $14\ 858\text{ cm}^{-1}$. The angular momentum of the level is clearly $J = 11/2$, as it is split into six Kramers' doublets. The matrix elements $K_{MM'}$ and the splitting factors s_{\parallel} and g were first determined by using the linear parallel Zeeman effect. With these values, the perturbation matrix for the perpendicular magnetic field was numerically diagonalized as a function of the magnetic field H . The calculated curves $E(H_{\perp})$ were in rather good agreement with the experimental curves. The agreement could be improved by slight variation of the $K_{MM'}$ and g values. We consider these new $K_{MM'}$ as more precise, since in the case in which two crystal field components with the same $\bar{\mu}$ are well separated, the perpendicular Zeeman effect is more sensitive to variations of $K_{MM'}$ than is the parallel effect. Therefore, these values are given in Table III. Besides the position of the components, Table I contains also s_{\parallel} , s_{\perp} , and the values of g calculated from them. The obtained mean value is $g = 1.40$. The departures of the single values from the mean are small; however, they are higher than the experimental error. These deviations must be

ascribed to admixtures of levels with different J values by the crystal field.

The ethylsulfate spectrum resembles the trichloride spectrum. Data are given in Fig. 4 and Tables II and III. The center of gravity is found 100 cm^{-1} higher than in the trichloride at 14957 cm^{-1} . The overall splitting is only about half as wide, 39 cm^{-1} , compared with 77 cm^{-1} for the chloride. The order of the crystal field components does not agree for the two salts. If however, one compares the two approximately valid M values corresponding to one $\bar{\mu}$ value, one finds that in both salts the higher values are at lower energies. The mean value of g is 1.39 which is in good agreement with the value for the trichloride. This value is close to the Russell-Saunders g value (1.455) of the ${}^6F_{11/2}$ level. From this we assume that the level H is a ${}^6F_{11/2}$.

The crystal field matrix elements $K_{MM'}$ can be calculated explicitly by following the procedure of Stevens¹⁴ if the crystal is considered as a point-charge lattice. However, in many cases the constants of the crystal field $A_{\ell}^m \langle r^{\ell} \rangle$ have been determined by using the $K_{MM'}$ obtained from the experiment. The parameters $A_{\ell}^m \langle r^{\ell} \rangle$ should not vary appreciably inside a series of homologous salts of the actinides. To correlate the $A_{\ell}^m \langle r^{\ell} \rangle$ with the matrix elements $K_{MM'}$ one has to know the factors for the operator equivalences α, β, γ of the eigenfunctions of the free ion.¹⁴ In several cases, where the $A_{\ell}^m \langle r^{\ell} \rangle$ were adjusted by using the ground multiplet only, it was sufficient to work with the Russell-Saunders values of α, β, γ . If we apply this procedure to the ${}^6F_{11/2}$ level, we obtain for $A_{\ell}^m \langle r^{\ell} \rangle$ the values in Table IV. For comparison we have added the results from the samarium ${}^6F_{11/2}$ level.¹⁵ The four values for $A_{\ell}^m \langle r^{\ell} \rangle$ given in Table IV were obtained by applying the method of least-squares fit to the nine

experimental $K_{MM'}$ in Table III. We see from Table IV that $A_4^0 \langle r^4 \rangle$ and $A_6^0 \langle r^6 \rangle$ become positive in the case of plutonium, whereas they are negative for the samarium. Gruber,¹⁶ who measured the americium spectrum, found negative values for $A_4^0 \langle r^4 \rangle$ and $A_6^0 \langle r^6 \rangle$ in the case of the ground multiplet. By performing the same calculations for the plutonium ground level, we can fix $A_2^0 \langle r^2 \rangle$ and $A_4^0 \langle r^4 \rangle$. But $A_4^0 \langle r^4 \rangle$ again comes out positive. So this rough approximation is not sufficient in the case of plutonium.

4. Group 0

In both salts at 4.2 and 20°K, group 0 consists of very sharp lines which start at I and II. Hence it was possible to determine $s_{||} (\bar{\mu} = \pm 3/2)$ of the ground level from these lines (as was already mentioned in connection with the ethylsulfate). The data of level 0 are given in Tables I and II. The angular momentum is $J = 3/2$. The difference between the centers of gravity of the chloride, $19\,380\text{ cm}^{-1}$, and the ethylsulfate, $19\,637\text{ cm}^{-1}$, is rather large. The position of this level seems to depend sensitively on the crystal field. The values of g obtained from the different splitting factors agree very well. The mean value for g is 2.00, which lies between the Russell-Saunders g values of ${}^6P_{3/2}$ ($g = 2.400$) and ${}^4P_{3/2}$ ($g = 1.733$). Therefore, level 0 is probably essentially a mixture of the ${}^6P_{3/2}$ and ${}^4P_{3/2}$ levels.

5. Group I

A second level with $J = 3/2$ is found at $16\,000\text{ cm}^{-1}$ (see Tables I and II). But the components of this level are broader, and the results of the Zeeman-effect measurements do not agree as well with each other. Four values obtained for g are close together and give a mean value of

0.96, but the fifth one, of $g = 1.5$, does not fit at all.

6. Group N

Besides the three groups treated above, the ethylsulfate spectrum contains only broad lines. But for the trichloride one more J value can be measured. The level N at $18\,250\text{ cm}^{-1}$ has $J = 7/2$. However, the lines are not sharp enough, so only one splitting factor s_{\parallel} ($\bar{\mu} = \pm 3/2$) could be determined, giving $g = 0.97$. This value is very close to the Russell-Saunders g value of ${}^4G_{7/2}$ ($g = 0.984$). Hence we assume that this level is predominant in N.

7. Comparison with theory

Using the four levels identified in the last chapter, we can determine the parameters F_k and ξ and give a first comparison between theory and experiment. In the course of the analysis of the rare-earth spectra we found that the 4f one-electron wave functions can be very well approximated by hydrogenic wave functions. We have tried to calculate the plutonium levels by using the 5f hydrogenic functions. In this case, for the F_k the relations $F_4/F_2 = 0.1422$, $F_6/F_2 = 0.0161$ hold and only the parameters F_2 and ξ are to be determined. The values of ξ and $\chi = \xi/F_2$ should increase slightly along the series of the actinides. It is reasonable to try values for χ close to $\chi = 11.55$, which was found by Gruber and Conway¹⁷ for americium, by using Russell-Saunders coupling. They fitted this atom with $\xi = 2600$ and $F_2 = 225\text{ cm}^{-1}$. Hence for $\chi = 9, 10$, and 11 , the energies were calculated in units of F_2 . For each χ the F_2 was adjusted so that the level $H = {}^6H_{11/2}$ was situated at $14\,800\text{ cm}^{-1}$. The results are given on the left side of Fig. 2. If we compare the four analyzed levels H, I, N, O with the calculated-levels scheme, we find levels with the same J values

close to the measured levels. Table V gives the predominant eigenfunctions and the calculated g values for $\lambda = 9.35$. For group O the calculated and the experimental g value which was reported in Subsec. 4 coincide, and ${}^6P_{3/2}$ are really the main levels. In N, 4G is predominant as proposed and the calculated g is only very little higher than the one found experimentally. In the case of level I, only J agrees. The computed g value is much smaller than the observed one. Since this value is smaller than those of all neighbouring levels, the deviation can easily be explained by admixtures of other levels by the crystal. If one considers all the levels below ${}^6F_{11/2}$ in Fig. 2, everywhere that the theory predicts a level, one is found experimentally. Since, however, the groups mostly contain broad lines, J and g cannot be determined uniquely. Nevertheless, the experimental findings do not contradict the theory. In the following discussion these groups and the remaining groups in the visible region will be treated in detail.

Comparing the whole calculated-level scheme with the one found experimentally, we see that most of the calculated and measured levels coincide best with $\lambda = 9.35$, $F_2 = 245 \text{ cm}^{-1}$ and $\xi = 2290 \text{ cm}^{-1}$. In the frame of this approach we feel that the agreement is surprisingly good. In order to determine the parameters more precisely, better one-electron eigenfunctions should be used. Also, admixtures of different configurations should be considered.

8. Group C

Group C lies at the limit of the photographic infrared spectral region up to $11\,650 \text{ cm}^{-1}$. The hypersensitized fresh Kodak I-Z plates were sufficiently exposed in 14 h. In both salts the excited level is split relatively wide, about 300 cm^{-1} . One sharp component is situated 100 cm^{-1}

below the rest of the group. The other components are up to 15 cm^{-1} broad. Hence the Zeeman effect could not be investigated and the $\bar{\mu}$ values cannot be given uniquely. Figure 2 shows that it is very likely that this level corresponds to the ${}^6\text{H}_{11/2}$ level. This is confirmed by the observation of six intense lines in the ethylsulfate. Four are σ -polarized and represent transitions Ia to Id with $\bar{\mu}(\text{a-d}) = \pm 1/2$ and $\pm 5/2$. Two lines are π -polarized and go from I to e and f with $\bar{\mu}(\text{e,f}) = \pm 3/2$. Then the two very weak lines at higher energies must be considered as superpositions of vibrations. In the chloride the analysis is more complicated because of emission lines, which partly coincide with the absorptions so that it is difficult to decide whether there are two absorption lines present or only one. But on the other hand, there is no indication that the level C should not be ${}^6\text{H}_{11/2}$.

9. Group D

In the trichloride crystal group D (9600 cm^{-1}) consists of three kinds of lines: very close together, very sharp lines of mean intensity; near-together broad intense lines; and very weak sharp lines between the first two kinds. If we consider the first two kinds only, we obtain for the excited level four components a, b, c, d and, therefore, for $J = 7/2$ and $g \approx 1.2$. The theory predicts a ${}^6\text{F}_{7/2}$ level at this energy with $g = 1.314$ (for $\lambda = 10$). This agreement is satisfactory. Then the weak lines have to be attributed to crystal field hyperfine structure.¹⁸ Otherwise we have to assume three more components a', b', c' (see Table I), and J would have a higher value. The ethylsulfate spectrum consists of a 20-cm^{-1} -broad band only and does not help to clear up the situation.

10. Group E

Group E, situated at $10\ 850\ \text{cm}^{-1}$, has four sharp lines at the low-energy side, which are the transitions Ia, IIa, Ib, and IIB—a and b having $\bar{\mu} = \pm 1/2$. The splitting factors are found as $s_{\parallel}(a) = 1.0$, $s_{\parallel}(b) = 2.0$, giving $g = 1.0$. Besides these lines some more weak, sharp, and some broad, lines exist, but J cannot be determined. The situation is similar in the ethylsulfate. So it is very well possible that level E is the ${}^6\text{H}_{13/2}$ postulated by the theory.

11. Group F.

Group F is spread out from $12\ 100\ \text{cm}^{-1}$ to $12\ 900\ \text{cm}^{-1}$. In the ethylsulfate it consists of at least eight broad polarized lines. In the chloride one observes on the low-energy end several sharp lines of different intensity. Some of the $\bar{\mu}$ values and splitting factors could be determined (Table I). The rest of the lines are broad. It is very probable that we are dealing with two excited levels. Otherwise it would not be possible to observe as many lines in the chloride. This is consistent with theory, which gives a ${}^6\text{H}_{15/2}$ and a ${}^6\text{F}_{9/2}$ level in the energy region under discussion.

12. Group G

At $14\ 000\ \text{cm}^{-1}$ theory predicts a ${}^4\text{G}_{5/2}$ level. Actually we observe three very weak lines in both salts at $13\ 500\ \text{cm}^{-1}$. So we believe that this level is identical to the ${}^4\text{G}_{5/2}$ level. The splitting factors could not be determined.

13. Groups K, L, and M

If we compare the calculated and the observed positions of the levels in the visible spectral region which were not discussed in the preceding sections, no absorptions are observed between 14 900 and 16 000 cm^{-1} and between 18 300 and 19 400 cm^{-1} , where two levels with $J = 15/2$ and $J = 17/2$ should be found. In both cases the most contributing level belongs to the 4M multiplet. One simple explanation is that the transition probabilities are so small that no absorption can be observed with the small plutonium concentrations used. Another possible explanation will be given below.

Between 16 000 and 18 000 cm^{-1} three groups are observed: in the ethylsulfate they contain only broad bands. In the trichloride crystal group K (at 16 500 cm^{-1}) consists of sharp intense lines with lattice vibrations superposed on the high-energy side, Group L, situated at 17 150 cm^{-1} , has also sharp lines. Between 17 300 and 17 900 cm^{-1} many broad bands are observed which we call group M. There are two possibilities to explain these observations, if we consider that probably not all components are observed.

The first possibility is that K is the $J = 15/2$ level, which was missed at lower energies. This interpretation is supported by the fact that three components with $\bar{\mu} = \pm 3/2$ are observed corresponding to the M values $\pm 3/2$, $\pm 9/2$, and $\pm 15/2$. In that case two components with $\bar{\mu} = \pm 5/2$ which are not observed had to be searched among the vibrational lines. The difficulty with this interpretation is that the $J = 3/2$ and $J = 15/2$ levels have "crossed". By varying λ within reasonable limits of the theoretical values these levels should not cross. Thus one had to consider that the one-electron wave functions are not represented by 5f hydrogenic wave functions, and that there are other effects, for instance, configuration

mixing. In this case level L is the $J = 9/2$ level and group M contains all transitions to the $J = 11/2, 13/2,$ and $5/2$ levels. This interpretation is somewhat supported by the observations in the ethylsulfate. Among the broad bands between $17\ 100$ and $18\ 000\ \text{cm}^{-1}$ at 4.2°K , seven are π -polarized, which means that there are seven components with $\bar{\mu} = \pm 3/2$ in that region. This is the number occurring in the levels $J = 9/2, 11/2, 13/2,$ and $5/2$ all together.

The second possibility is that the $J = 15/2$ level is really not observed, K is identical with the $J = 9/2$ level, and L and M contain the $J = 11/2, 13/2,$ and $5/2$ levels. In this case the "crossing" of the $J = 3/2$ and $15/2$ levels is not necessary. In order to find out whether the last interpretation is correct more calculations should be done.

14. Groups A and B, and fluorescence

Two more groups are observed in the far infrared at wavelengths of 3μ and $1.5\ \mu$.

a. Group A.

Using the Beckman spectrometer one finds two absorption-lines at room temperature: one σ line at $3.19\ \mu$, and one unpolarized line at $3.08\ \mu$. They correspond to two crystal field components: at $3136\ \text{cm}^{-1}$ with $\bar{\mu} = \pm 3/2$, and at $3245\ \text{cm}^{-1}$ with $\bar{\mu} = \pm 1/2$. The only level in this energy region is the ${}^6\text{H}_{7/2}$ and it should be split into four components in this crystal. By analyzing the fluorescence, we tried to find the two components which are missed in the absorption spectrum.

The fluorescence spectrum was taken at 77°K with unpolarized light. Between $11\ 000$ and $20\ 000\ \text{cm}^{-1}$ seven groups of emission lines are observed, and an eighth at $8\ 700\ \text{cm}^{-1}$. No exposures were made in the region in between.

Each of these groups corresponds to a transition between one of the levels H, I, and O and the ${}^6H_{5/2}$, ${}^6H_{7/2}$, or the levels contained in B. The observed lines are given in Table VIII. The resonance groups were omitted, since they do not furnish new results. In the second row the transitions are listed, as far as an identification was possible. The low-energy lines are mostly broad. Probably they correspond to transitions to vibrational levels of the lower levels. Three of the observed groups go from H, I, and O to the ${}^7H_{7/2}$ level. Many transitions to the two components at 3136 and 3245 cm^{-1} are found. But no other additional components can be identified. It may be that one or both missing components lie very close to 3245 cm^{-1} (say at 3240 or 3250 cm^{-1}). The lines in brackets in Table VIII are very near to the intense neighboring lines. But it may be possible that the 3245 cm^{-1} component is broad and has a structure or satellites, and that the two remaining components are to be found at higher energies. Some emission lines appear in the absorption spectrum already. These served for determination of the Zeeman effect of the $\bar{m} = \pm 3/2$ component at 4.2°K: $S_{\parallel} = 1.32 \pm 0.05 = 3/2 g$, which gives $g = 0.88$ and $s_{\perp} = 0$. The theory predicts $g = 0.87$ for $\lambda = 10$, which is in good agreement with the experimental value.

b. Group B

At about 3000 cm^{-1} higher than the ${}^6H_{7/2}$ level the theory predicts the four levels ${}^6H_{9/2}$, ${}^6F_{1/2}$, $3/2$, $5/2$ which lie very close together. The absorption spectrum taken with the Cary spectrometer at 77°K shows a broad band in that region containing several maxima (see Fig. 1). However, the crystal field components could not be resolved. On the other hand, it would be very useful to know the centers of gravity of the levels. As can be seen in Fig. 2 the relative position of the four levels varies much with λ . In particular, for the small λ the ${}^6H_{9/2}$ level lies far below the

6F levels, whereas all levels come together at higher λ values. So—knowing the ${}^6H_{9/2}$ position—one is able to determine λ . How far this relationship will be influenced by the crystal field, especially the K_{00} part, should be investigated separately. The fluorescence spectrum does not answer the question totally, but somewhat indicates that the smaller λ values are preferred, as we shall discuss now.

Transitions between the O and B levels should be found from 11 500 to 13 500 cm^{-1} . Three groups of lines are observed in this region. The one in the middle, at 12 800 cm^{-1} , is not of interest here, since it represents a transition between the levels I and A. The second, at 13 200 cm^{-1} , yields the components at 5980/82, 6081, and 6101 cm^{-1} . To all these components, transitions occur from both components of the O level. This means that these components can have $\bar{\mu}$ values of $\pm 1/2$ and $\pm 3/2$ only, according to the selection rules. The third group at 12 500 cm^{-1} presents components about 600 cm^{-1} higher, between 6700 and 6850 cm^{-1} , whereas nothing is observed in the area of 600 cm^{-1} . Though the lines of the last groups are sharp, the positions of the components cannot be evaluated uniquely, because the distance between the two components of level O (34 cm^{-1}) is not observed. Therefore we assume that several components have $\bar{\mu} = \pm 5/2$ and cannot be reached from the $\bar{\mu} = \pm 5/2$ component of O by electric dipole radiation. Thus we conclude that group B is split into two subgroups. At lower energies the ${}^6H_{9/2}$ level is situated, which has only one $\mu = \pm 5/2$ component, while the upper group exhibits the three levels ${}^6F_{1/2, 3/2, 5/2}$ with three $\bar{\mu} = \pm 5/2$ components. Of course this interpretation should be supported further by additional exposures at 4.2°K with polarized light.

The emission lines at 8700 cm^{-1} were obtained with the absorption spectrum. Therefore, it may very well be that Table VIII is incomplete.

Probably this group can be interpreted as transition between the levels $H = {}^6F_{11/2}$ and ${}^6H_{9/2}$. Some lines go to the components at 6081 and 6100/01, which were found already. One further component could be situated at 6170 cm^{-1} .

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FOOTNOTES AND REFERENCES

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Table I. Data of the groups with sharp lines in $\text{La}(\text{Pu})\text{Cl}_3$.

Level center of gravity (cm^{-1})	Com- ponent	Wave number (cm^{-1})	Energy (cm^{-1})	$ \bar{\mu} $	s_{\parallel}	g (s_{\parallel})	s_{\perp}	g (s_{\perp})
Ground level 46.3	I	0	-29.7	5/2	0.292	0.585	0.4375	0.291
	II	13.0	-16.7	3/2	0.44	0.29		
	III	76	46.3	1/2				
D 9 586.6	a	9 543.4	-43.2	1/2	+1.8	1.2		
	b	9 547.6	-39.0	5/2	-1.12	1.12		
	c	9 625.5	+38.9	1/2	-0.6	1.2		
	d	9 629.9	+43.3	3/2	1.8	1.2		
	a'	9 557.7						
	c'	9 639						
F (broad components are listed in Table VI)	a	12 128.7		3/2	5.13		0	
	b	12 135		3/2			0	
	c	12 202.2		3/2	1.2		0	
	d	12 230.5		1/2	1.7		± 2.5	
	e	12 240		5/2	± 2.6 ± 0.9		0.87	
H 14 857.8	a	14 816.72	-41.08	5/2	+7.52	1.37		
	b	14 844.91	-12.89	1/2	+3.18	1.43	2.83	1.37
	c	14 847.69	-10.11	3/2	+6.12	1.41	0	1.45
	d	14 864.15	+ 6.35	1/2	-1.85	1.41	2.95	1.37
	e	14 879.92	+22.13	3/2	-1.85	1.45	0	1.45
	f	14 893.4	+35.6	5/2			4.08	1.37
I 15 992.5	a	15 988.69	- 4.1	3/2	1.59	1.06	0	--
	b	15 996.44	+ 4.1	1/2	0.4	0.8	1.03	1.03

Table I (contd.)

Level center of gravity (cm^{-1})	Com- ponent	Wave number (cm^{-1})	Energy (cm^{-1})	$ \bar{\mu} $	s_{\parallel}	g (s_{\parallel})	s_{\perp}	g (s_{\perp})
K	a	16 357.8		3/2	4.74		0	
	b	16 382.3		3/2	± 1.2 ± 0.29			
	c	16 387		5/2				
	d	16 393		1/2	± 2.3 ± 0.29			
	e	16 418		3/2				
	f	16 432		1/2	± 3.2 ± 0.29			
	g	bands						
L	a	17 122.5		5/2	(0.5)		1.9	
	b	17 176.8		3/2				
	c	17 178.5		1/2	2.88			
	d	17 205.6		3/2	2.7 ₅			
	e	?						
N	a	18 245	-41.8	5/2				
	b	18 271.9	-14.9	3/2	1.46	0.97	0	
	18 286.8	c	18 296.6	+ 9.8	1/2			
	d	18 333.8	+470	1/2				
O	a	19 363.88	-16.22	3/2	+2.988	1.992	0	
	19 380.1	b	19 396.27	+16.2	1/2	+0.995	1.995	1.988 1.988

Table II. Data of the groups with sharp lines in $\text{La}(\text{Pu})(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

Level center of gravity (cm^{-1})	Com- ponent	Wave number (cm^{-1})	Energy (cm^{-1})	$ \bar{\mu} $	s_{\parallel}	g_{\parallel} (s_{\parallel})	s_{\perp}	g_{\perp} (s_{\perp})	
Ground level 18.8	I	0	-18.8	3/2	0.44	0.293	0	--	
	II	20.1	1.3	5/2					
	III	36.4	17.6	1/2					
14 956.7	H	a	14 937.48	-19.24	1/2	+3.08	1.45	2.94	1.35
	b	14 949.59	- 7.13	3/2	+5.63	1.46	0	--	
	c	14 953.87	- 2.85	1/2	-1.53	1.37	2.94	1.35	
	d	14 957.23	+ 0.51	5/2	+7.32	1.37	≈ 0	--	
	e	14 966.56	+ 9.84	3/2	-1.26	1.46	0	1.40	
	f	14 975.6	+19.88	5/2			3.77	1.30	
16 014.4	I	a	15 984.14	-30	3/2	2.28	1.52	0	--
	b	16 044.7	+30	1/2			0.97	0.97	
19 636.8	0	a	19 628.87	- 8.0	3/2	3.036	2.024	0	--
	b	19 644.72	+ 8	1/2	1.012	2.024	1.94	1.94 ± 0.02	

Table III. Crystal field matrix elements $\langle r_{JM} | \mathcal{V} | r_{JM'} \rangle = K_{MM'}$
 divided by $\hbar c$ in cm^{-1} for the ${}^6F_{11/2}$ level.

Matrix element	Trichloride	Ethylsulfate
$K_{1/2, 1/2}$	35.44	19.39
$K_{3/2, 3/2}$	20.84	8.05
$K_{5/2, 5/2}$	2.08	6.63
$K_{7/2, 7/2}$	- 8.62	-15.47
$K_{9/2, 9/2}$	- 8.82	- 5.34
$K_{11/2, 11/2}$	-40.12	1.01
$ K_{1/2, -11/2} $	3.54	3.1
$ K_{3/2, -9/2} $	6.32	5.21
$ K_{5/2, -7/2} $	8.00	6.90

Table IV. Crystal field parameters $A_l^m \langle r^l \rangle$ of the $\text{La}(\text{Pu})\text{Cl}_3$ and $\text{La}(\text{Pu}) (\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ calculated from the experimental crystal matrix elements K_{MM} , given in Table III by using the Russell-Saunders operator equivalence factors α, β, γ . (For comparison the samarium values are listed.)

		PuCl ₃	PuEth.	SmEth.
	$\alpha \times A_2^0 \langle r^2 \rangle$	-0.726	-0.149	-0.373
	$\beta \times A_4^0 \langle r^4 \rangle$	$+0.806 \times 10^{-3}$	$+2.949 \times 10^{-3}$	-1.177×10^{-3}
	$\gamma \times A_6^0 \langle r^6 \rangle$	-4.981×10^{-5}	-3.026×10^{-5}	$+2.732 \times 10^{-5}$
	$\gamma \times A_6^6 \langle r^6 \rangle$	4.58×10^{-4}	3.84×10^{-4}	3.67×10^{-4}
${}^6\text{F}_{11/2}$:	$A_2^0 \langle r^2 \rangle$	+179.7	+37.0	+92.4
	$A_4^0 \langle r^4 \rangle$	+ 13.1	+48.0	-19.2
	$A_6^0 \langle r^6 \rangle$	+ 66.6	+40.5	-36.5
	$A_6^6 \langle r^6 \rangle$	612.6	513.1	490.9

Table V. Energy levels for Pu^{3+} calculated for $F_2 = 245 \text{ cm}^{-1}$, $\zeta = 2290 \text{ cm}^{-1}$ by using 5f hydrogenic wave functions. The SLJ label states are underlined.)

Energy (cm^{-1})		Eigenfunctions		g
0	5/2	67.5%	$\underline{6H} + 12.4\% \underline{4G}$	0.416
3 268	7/2	81.3%	$\underline{6H}$	0.862
6 192	9/2	86.6%	$\underline{6H}$	1.067
6 942	5/2	49.5%	$\underline{6F} + 13.1\% \underline{4F}$	1.148
6 982	3/2	69.7%	$\underline{6F} + 11.4\% \underline{4F}$	0.973
7 299	1/2	82.4%	$\underline{6F}$	-0.531
8 672	11/2	81.9%	$\underline{6H}$	1.174
9 746	7/2	68.5%	$\underline{6F} + 11.3\% \underline{4F}$	1.324
10 802	13/2	72.2%	$\underline{6H} + 14.4\% \underline{4I}$	1.228
12 356	15/2	49.8%	$\underline{6H} + 21.8\% \underline{4I}$	1.212
12 457	9/2	75.2%	$\underline{6F}$	1.377
14 100	5/2	34.1%	$\underline{6F} + 12.8\% \underline{6H} + 10.4\% \underline{4G}$	0.938
14 860	11/2	68.0%	$\underline{6F} + 10.4\% \underline{4G}$	1.371
15 361	15/2	51.2%	$\underline{4M} + 18.9\% \underline{6H} + 12.1\% \underline{2L}$	0.966
15 980	3/2	52.1%	$\underline{4F} + 18.8\% \underline{6F} + 11.9\% \underline{4F} + 11.1\% \underline{4F}$	0.555
16 883	9/2	50.9%	$\underline{4I} + 11.1\% \underline{4I}$	0.841
17 160	11/2	43.0%	$\underline{4K} + 15.5\% \underline{4I}$	0.912
17 253	13/2	44.6%	$\underline{4L} + 21.6\% \underline{4K} + 12.0\% \underline{6H}$	0.935
17 965	5/2	26.4%	$\underline{6P} + 26.3\% \underline{4P}$	1.422
18 307	7/2	20.9%	$\underline{4G} + 16.5\% \underline{4G} + 15.1\% \underline{6F}$	1.050
19 267	17/2	66.9%	$\underline{4M} + 16.9\% \underline{4L}$	1.007
20 152	1/2	33.2%	$\underline{2P} + 22.5\% \underline{2P} + 11.1\% \underline{6F} + 9.9\% \underline{4D}$	0.432
20 570	3/2	54.5%	$\underline{6P} + 30.2\% \underline{4P}$	2.011

Table VI. Data of the groups with broad lines in $\text{La}(\text{Pu})\text{Cl}_3$.

Group	Wave number (cm^{-1})	Polarization	Transition	$ \mu $	Line width (cm^{-1})	Remarks
C	8 589.4	π (σ)	II a	1/2		
	8 602.4	σ	I a	1/2		} Disturbed by fluorescence
	8 708	π	II b	3/2		
	8 712	σ	II c	1/2		
	8 724	π σ	Ib, Ic	3/2, 1/2	6	
	8 740	π				Very weak
	8 756/72	π				Four weak lines
	8 779	σ				Very weak
	8 859	π				5
	8 872	σ				5
	8 877	σ				10
	8 889	σ				10
	E	10 845.7	σ	II a	1/2	
10 858.7		π σ	I a	1/2		
10 886.2		σ	II b	1/2		
10 888.8		π σ				Very weak
10 899.4		π σ	I b	1/2		
10 806		σ				Very weak
10 936		π				
10 957		π	II-	3/2	15	} Weak
10 964		σ	I			
10 971		σ	I	3/2		
10 981		π	II	3/2		
10 994		σ	I	3/2		
10 998		π	II			
11 005		π	II			
11 018		σ	I			10
11 021		π	II			
11 030	σ	II			10	
11 042	σ				Weak	
11 056	σ				10	

Table VI. (contd.)

Group	Wave number (cm^{-1})	Polarization	Transition	$ \bar{\mu} $	Line width (cm^{-1})	Remarks
F	12 115.8	π	II a			
	12 128.7	σ	I a	3/2		
	12 131	σ	I			Very weak
	12 135	σ	I b	3/2		
	12 162	$\pi \sigma$	III			
	12 189.2	π	II c			
	12 202.2	σ	I c	3/2		
	12 218	σ	II d			Very weak
	12 227	σ	II e	5/2		Very weak
	12 230.5	$\pi \sigma$	I d	1/2		
	12 235	π	I			
	12 244	σ	I f			
	12 336	π			8	
	12 355	π			10	
	12 367	π			70	
	12 392	π			6	
	12 399	π			6	
	12 355	π			10	
	12 367	σ			10	
	12 424	π				
12 537	$\pi \sigma$					
12 782	$\pi \sigma$			8		
12 793	$\pi (\sigma)$			8		
12 808	σ			8		
G	13 397					
	13 583	π	II a			
	13 596	σ	I a	3/2		
	13 665	$\pi \sigma$			5	
	13 698	$\pi \sigma$			5	
M	17 300 to 17 900					Many broad bands

Table VII. Data of the groups with broad lines in
 $\text{La}(\text{Pu}) (\text{C}_{25}\text{H}_{43}\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$.

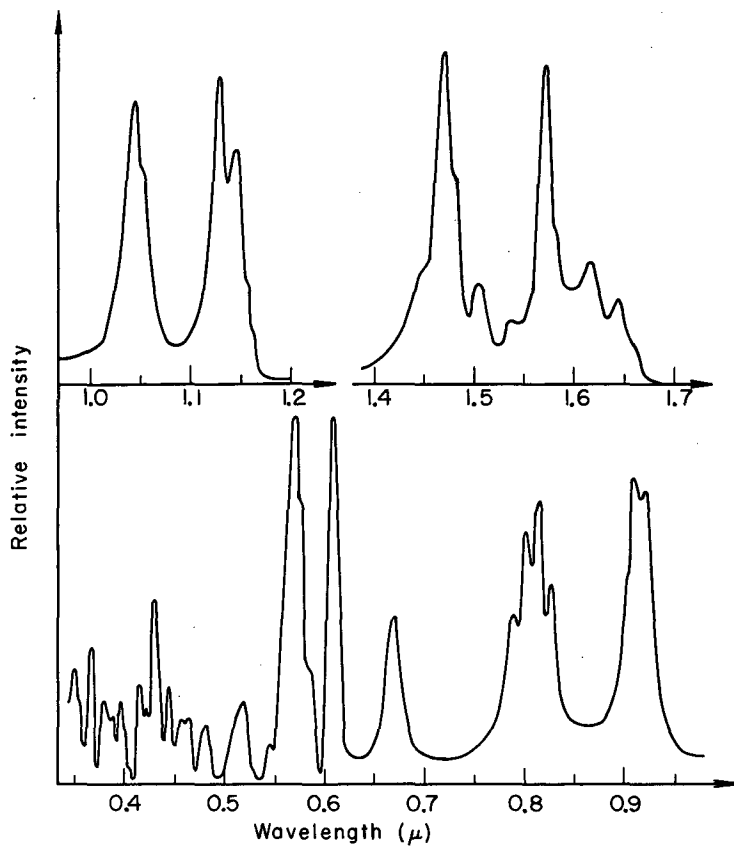
Group	Wave number (cm^{-1})	Polarization	Transition	$ \bar{\mu} $	Line width (cm^{-1})	Remarks
C	8 581	σ	I a	1/2, 5/2		
	8 728	σ	III c			Very weak
	8 745	σ	I b	1/2, 5/2	10	
	8 765	σ	I c	1/2, 5/2	7	
	8 782	σ	I d	1/2, 5/2	8	
	8 851	$\pi \sigma$	II e			Very weak
	8 871	π	I e	3/2	15	
	8 927	π	I f	3/2	15	
	8 993				6	Very weak
	9 030				6	Very weak
	D	9 712	π			21
9 725		σ			19	
E	10 877.0	$\sigma (\pi)$	I a			
	10 906.3	π	II c			Very weak
	10 909.0	π	I b			
	10 925.5	$\sigma \pi$	I c			
	10 967	π				Very weak
	10 982	π				
	11 003	π				
	11 027	π				
	11 055	π				
	11 021	σ				Very weak
	11 037	σ				
	11 051	σ				
	11 067	σ				
	11 080	$\pi \sigma$				
	11 091	$\pi \sigma$				
11 125	π				Very weak	
11 144	π					
11 176	π					
11 194	$\sigma \pi$					

Table VII. (contd.)

Group	Wave number (cm^{-1})	Polarization	Transition	$ \bar{\mu} $	Line width (cm^{-1})	Remarks
F	12 184	π	I a	3/2	10	
	12 248	π	I b	3/2	44	Very intense
	12 290	σ	I c		15	
	12 351	σ	I e		15	Very weak
	12 447	σ	I f	5/2, 1/2	22	Intense
	12 557	σ	I g		20	
	12 632	σ	I h		20	
	12941	π	I i	3/2	25	Intense
	G	13 635.7	π	I a	3/2	
13 744.8		σ			10	
13 767		β			10	
K	16 380 to 16 800					Many broad bands
	L	17 100 to 18 00				

Table VIII. Fluorescence lines and transitions in $\text{La}(\text{Pu})\text{Cl}_3$.

Wave number (cm^{-1})	Transition	Wave number (cm^{-1})	Transition
16 261	Ob - 3 136	12 648	
16 229	Oa - 3 136	12 611	Oa - 6 753
(16 158)	Ob - 3 240	12 569	
16 152	Ob - 3 245	12 525	Oa - 6 839
(16 125)	Oa - 3 240	\approx 12 494	
16 120	Oa - 3 245	11 757	Hf - 3 136
15 965		11 744	He - 3 136
15 895		11 712	Hc - 3 136
\approx 15 875		11 681	Ha - 3 136
\approx 15 863		11 648	Hf - 3 245
\approx 15 848		(11 639)	He - 3 240
\approx 15 832		11 636	He - 3 245
\approx 15 820		(11 573)	Ha - 3 245
\approx 15 785		11 567	Ha - 3 250
13 416	Ob - 5 980/2	\approx 11 584	
13 382	Oa - 5 980/2	\approx 11 464	
13 314	Ob - 6 081	\approx 11 447	
13 295	Ob - 6 101	\approx 11 442	
13 283	Oa - 6 081	8 807	
13 263	Oa - 6 101	8 794	Hf - 6 100/1
13 196		8 781	He - 6 100/1
13 182		8 758	
12 859	Ib - 3 136	8 752	
12 853	Ia - 3 136	8 736	Ha - 6 081
12 751	Ia - 3 245	8 733	
12 744	Ia - 3 245	8 723	Hf - 6 170
		8 710	He - 6 170
		8 702	



MU-23664

Fig. 1. Unpolarized absorption spectrum of a 3-mm La(Pu)Cl_3 crystal containing 1% plutonium at 77°K , recorded by a Cary Model 14 spectrophotometer.

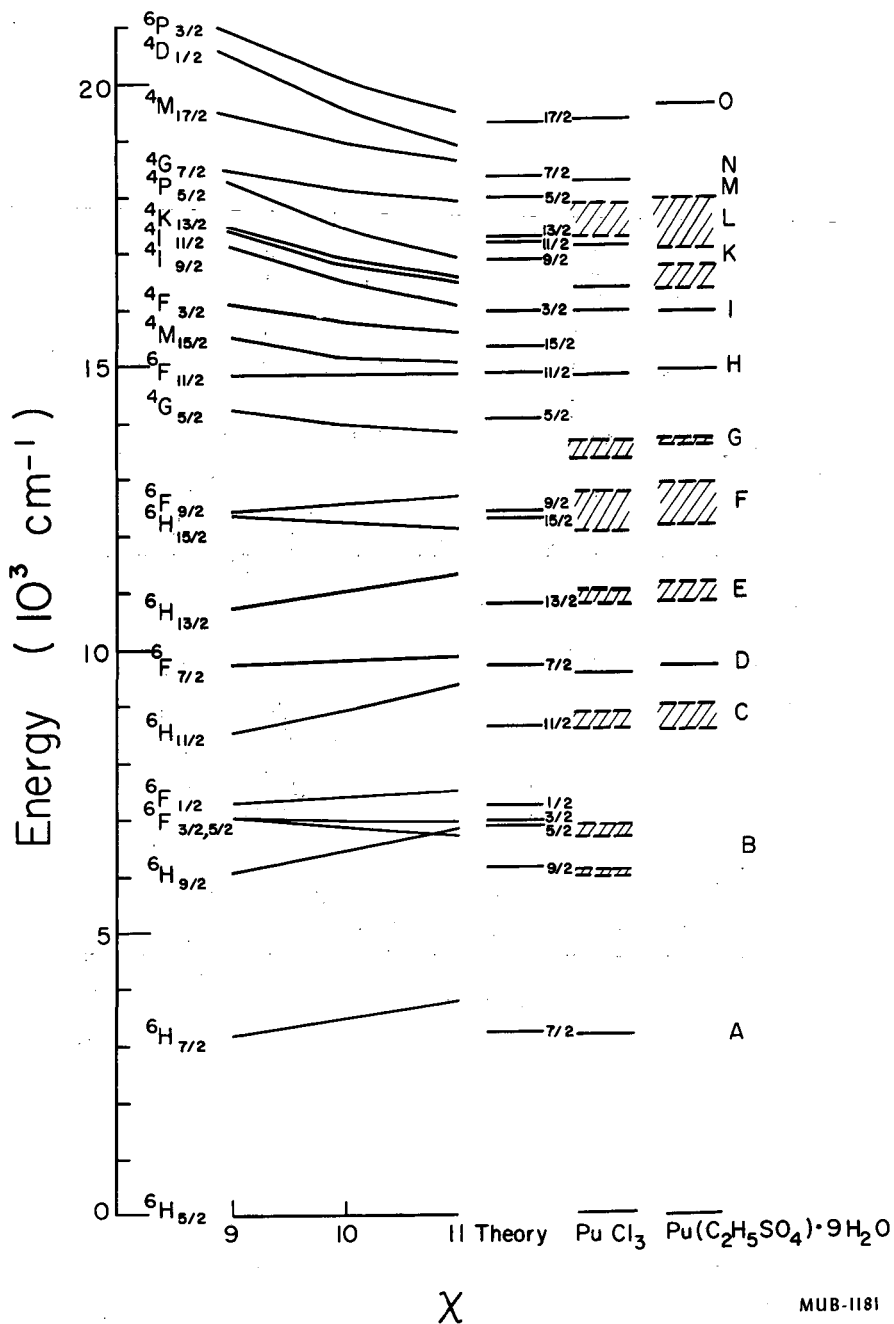
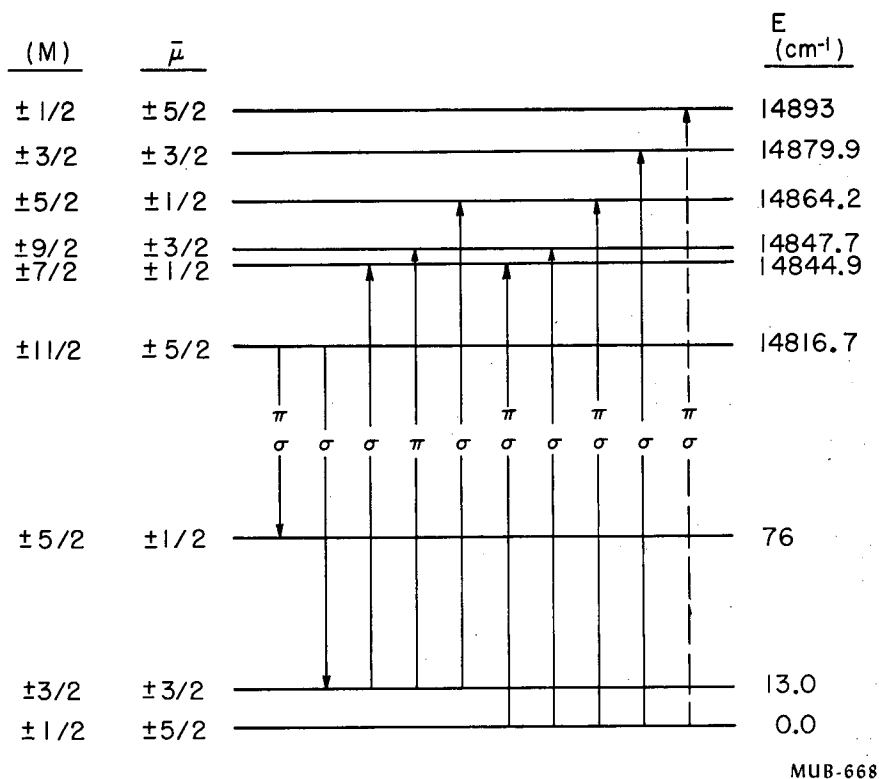
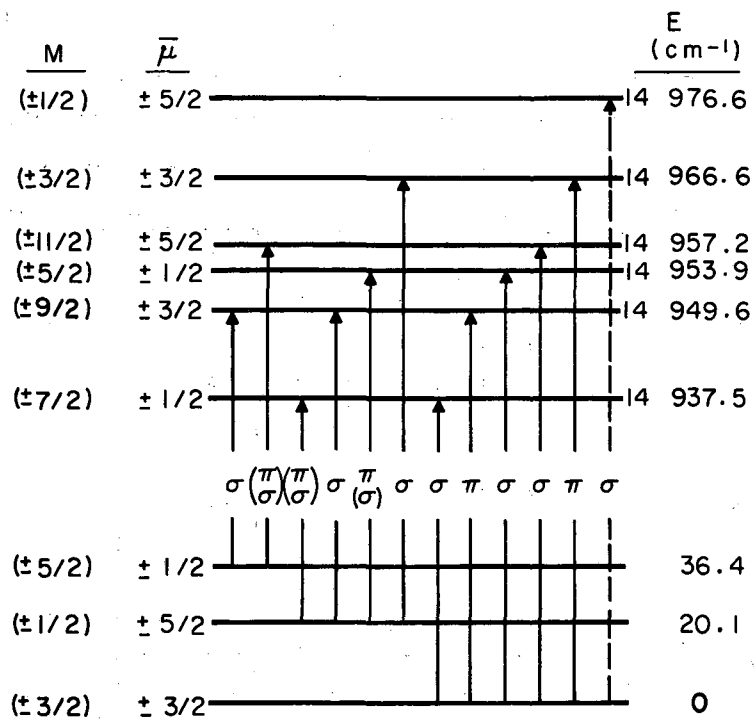


Fig. 2. Energy-level scheme of the trivalent plutonium between 0 and 20 000 cm⁻¹. Right side: the levels observed in the crystal of PuCl₃ and Pu(C₂H₅SO₄)₃ · 9 H₂O (A, B ... O are arbitrary designations of the levels). To the left: the free-ion levels calculated as functions of X for X = 9 to 11, adjusting 6H_{5/2} to 0 cm⁻¹ and 6F_{11/2} to 14 860 cm⁻¹. The states are labeled in the LSJ coupling scheme. The values for X = 9.35 (ξ = 2290 cm⁻¹, F₂ = 245 cm⁻¹) are considered the best fit.



MUB-668

Fig. 3. Energy-level scheme of the ${}^6F_{11/2}$ level in the PuCl_3 , and the observed transitions in electric dipole radiation parallel (π) and perpendicular (σ) to the optical axis of the crystal. The dashed line indicates a transition observed only in an external magnetic field perpendicular to the crystal axis ($\bar{\mu} \equiv$ crystal quantum number; $M \equiv$ approximately valid magnetic quantum number).



MU-27263

Fig. 4. Energy-level scheme of the ${}^6F_{11/2}$ level in the $\text{Pu}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, and the observed transitions. (markings are as in Fig. 3.)

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