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High-Resolution Measurements of Absorption, Fluorescence, and Crystal-Field Splittings of Solutions of Divalent, Trivalent, and Tetravalent Uranium Ions in Fluoride Crystals

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Energy levels of dilute solutions of valence-pure divalent, trivalent, and tetravalent uranium in fluoride crystals are derived from absorption and fluorescence measurements. Fluorescence is observed which results from transitions between split ground-state and next higher split levels of trivalent uranium and divalent uranium in alkali-earth fluoride lattices. A new explanation is proposed for the fluorescence characteristics of trivalent uranium laser crystals, based upon the competition of energy absorptions of impurity valence states with the fluorescent emission of trivalent uranium ions.

I. INTRODUCTION

URANIUM has an inner unfilled $5f$ shell, well shielded by higher-energy outer electrons which are (mainly) involved in the chemical bonding. Electrical and magnetic coupling of external fields involves an excitation of the inner "free" electrons and includes optical and magnetic resonance excitation. The ground state of uranium for the last filled shells is $5f^3 6d7s^2$ for U^0, $5f^3 6d7s$ for U^{1+}, $5f^3 6d$ for U^{2+}, $5f^3$ for U^{3+}, and $5f^2$ for U^{4+}.

Literature references[1] detailing electronic energy levels for U^0 and U^{1+} have been determined by arc and spark spectroscopic excitation studies.

The compounds UC, UN, and UO are known to have ionic crystal structures, in which any one of the three can be substituted isomorphously with the others.[1] Since the ionic radius of O^{2-} is about the same as that of F^-, it is possible that F^- could also be substituted in these crystals, with suitable vacancy conditions accounting for the difference in valence. In any case, the existence of the compounds implies the existence of divalent uranium.

In the Manhattan Project during World War II, successful production of trivalent uranium fluoride was achieved after considerable difficulty.[1] Recent optical maser work has involved the U^{3+} ion in many fluoride lattices.

Tetravalent uranium is a well-known and much-investigated ion. However, the forms in which it has been available have been such that mixed valences, lattice vibrations, and other causes have prevented a clarification of the character of the free electrons of this ion in solid solution. In the present report, we first consider the tetravelent uranium ion in solid solution and then proceed to the lower valence forms.

II. TETRAVALENT URANIUM IN CRYSTAL SOLUTION

Conway[2] prepared crystal solutions of uranium in calcium fluoride using carefully prepared UF_4 as the doping material. Conway did his work before the more recent extensive experimental work with $CaF_2:U^{3+}$ laser materials. He made spectroscopic studies of line spectra in the ultraviolet, visible, and infrared regions. Analyzing these data, he concluded that intermediate crystal-field conditions were involved, with considerable crystal-field mixing of levels.

Satten, Young, and Gruen[3] studied U^{4+} in crystals having U^{4+} octahedrally surrounded by chlorine ions. These were not dilute solutions, such as used by Conway and by us, but crystals of complex tetravalent uranium chlorides. Their work details the separation of many vibrational frequencies from electronic levels to arrive at the energy levels of the U^{4+} ion, and their analysis led them to the position that very strong crystal fields were involved, of the same order as the spin-orbit interaction. As a result they arrived at even stronger crystal-field mixing of levels than Conway. The work of Satten *et al.*[3] was extended further by Pollack.[4]

McLaughlin[5] studied single crystals of UCl_4 (again a pure uranium crystal, not a dilute solution) and found that many vibrational transitions were involved in the spectra. By theory and experiment, he arrived at an electronic energy-level diagram based on weak crystal-field interactions, and consequently a J splitting or free-ion-like spectrum.

Title *et al.*[6] studied what they concluded was a U^{4+} ion in calcium-fluoride and strontium-fluoride crystals. On the basis of spin-resonance data, and of comparison of absorption-spectrum data of Satten *et al.*,[3] Conway[2] and others[6] with their own spectroscopic data (in particular, see Fig. 4(a), p. 64 of Ref. 6 for uranium-doped CaF_2), they concluded that the ion involved was U^{4+}. This report departs from their conclusions in that the main aspects of the impurity optical absorption of trivalent-uranium-doped difluorides, particularly that in the 1.58-μ region, are attributed to U^{2+} ions.

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[1] J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium* (Dover Publications, Inc., New York, 1951).

[2] J. G. Conway, J. Chem. Phys. **31**, 1002 (1959).

[3] R. A. Satten, D. Young, and D. M. Gruen, J. Chem. Phys. **33**, 1140 (1960).

[4] S. A. Pollack, thesis, University of California, OTS US Department of Commerce Report No. PB-156077 (unpublished).

[5] R. M. McLaughlin, J. Chem. Phys. **36**, 2699 (1962).

[6] R. S. Title, P. O. Sorokin, M. J. Stevenson, G. D. Scardefield, and J. R. Lanard, Phys. Rev. **128**, 62 (1962).

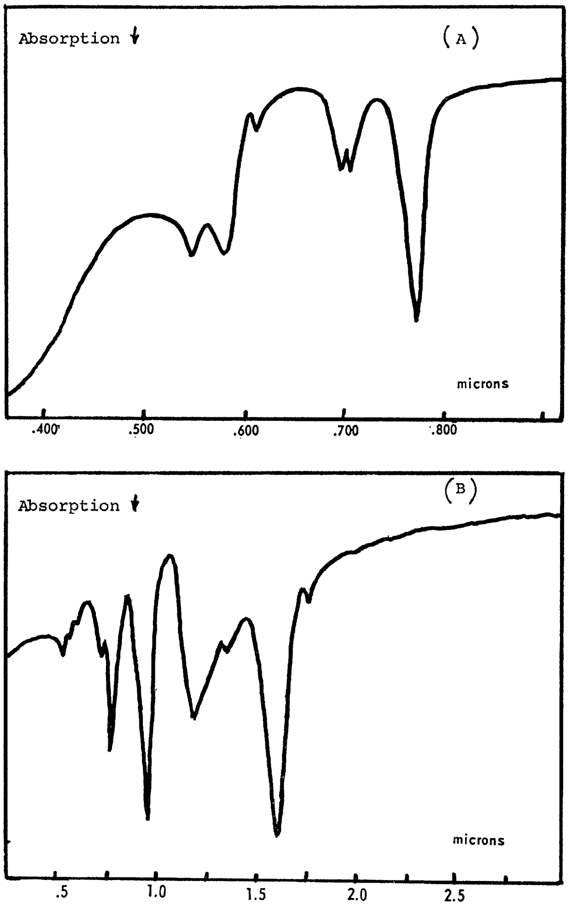

FIG. 1. Optical absorption spectra of $CaF_2:U^{4+}$ (0.05%) at 295°K: (a) in visible region; (b) in infrared region.

Yariv,[7] in an independent study similar to that of Title *et al.*,[6] came to about the same conclusions: that a certain contamination of U^{3+} laser materials, identifiable particularly by a broad 1.55-μ absorption band, was tetravalent uranium, and was the source of high-threshold difficulties in the U^{3+} lasers.

The following chemical reaction[1] is involved in the physical chemistry of preparation of $CaF_2:U^{3+}$ laser materials:

$$4UF_3 \rightarrow 3UF_4 + U^0. \qquad (1)$$

The melting point of UF_4 is about 960°C, and that of UF_3, above 1140°C. At about 1050°C, the above reaction moves strongly to the right, and under the conditions for growing uranium-doped CaF_2, tends to result in strong loss of uranium by vaporization of UF_4.

Under abnormal conditions, we have grown uranium-doped calcium fluoride crystals with low oxygen content (good scavenging conditions) but with almost complete conversion of uranium ions present to U^{4+} ions. This is done in accordance with Eq. (1) above by overheating in an interior section of the melt prior to growth. The crystal region grown in this way is called by us "yellow uranium CaF_2" and has been proven to be $CaF_2:U^{4+}$ The evidence is based upon the physical method of preparation, upon the energy-level system developed for the material, upon gamma-irradiation studies, and upon the general correlation of our experimental work with all of the valences of uranium in our fluoride crystals.

The $5f^2$ system of U^{4+} would be expected to yield an energy-level system of 13 lines. Twelve of these have been determined in the visible and infrared regions. Figures 1(a) and 1(b) show these levels in absorption spectra. Studies have been made with several grating instruments in the visible range, with long-exposure photographic measurements in the visible range using a prism instrument, with a standard double-beam infrared instrument, and with a high-resolution grating instrument in the 1- to 3-μ region. A very broad strong absorption occurs in the ultraviolet with a maximum at 3690 Å (27 174 cm^{-1}) but extending from 3000 to about 4800 Å. This is probably *d*-band absorption and

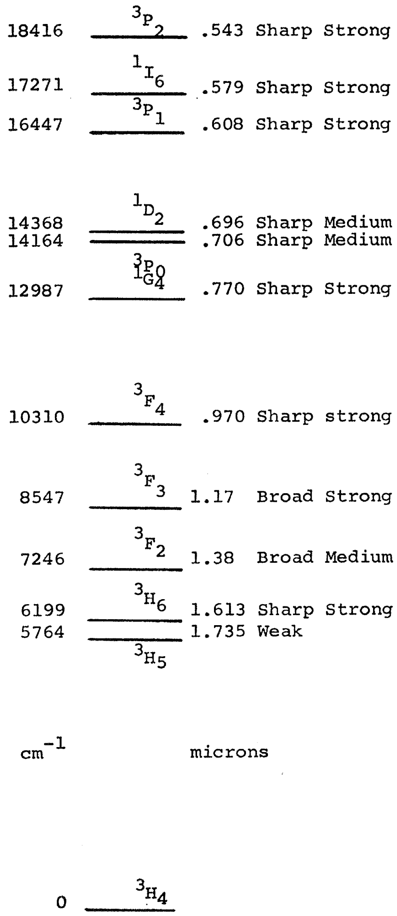

FIG. 2. Energy-level diagram of $CaF_2:U^{4+}$.

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[7] A. Yariv, Phys. Rev. **128**, 1588 (1962).

it accounts for the yellow color of the crystal, as a result of blue absorption. It is likely that the 13th level, the $^1S_0$ level, is somewhere above 20 000 cm^{-1}, obscured by the *d*-band absorption. Figure 2 shows the energy-level scheme based upon absorption measurements. Tentative term notations are assigned to the levels based upon the analogous $4f^2$ system and a free-ion-like spectrum. In view of the decreasing electron shielding in proceeding from U^{2+} to U^{4+} ions, it is very possible that the level-system assignments of Fig. 2 should be modified to allow for crystal-field mixing of levels.

The $CaF_2:U^{4+}$ has a strong absorption at 1.62 μ which can be mistaken for the absorption of U^{2+} in the 1.4- to 1.7-μ region. As will be shown shortly, the U^{2+} has many strong lines in that region, whereas U^{4+} has only one. In the visible region, the U^{2+} is very distinctive in the large number of resonant line transitions appearing there, characteristic of an f^4 electron system. Conversely the very small number of terms of an f^2 ion is a very distinctive characteristic of U^{4+}, and fortunately appears in this form in dilute CaF_2 solution, without vibrational complications.

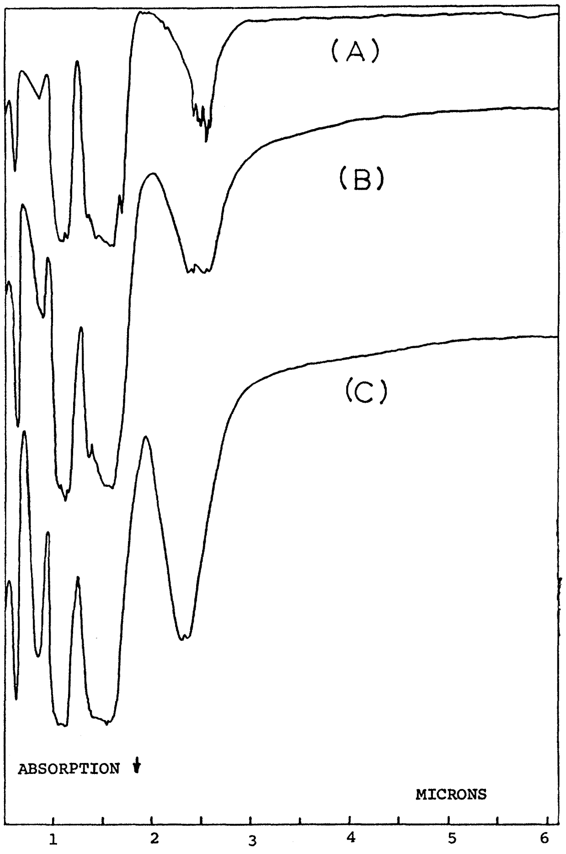

FIG. 3. Optical absorption spectra recorded with M-21 spectrometer: (a) of $CaF_2:U^{2+}$ (0.3%) at 77°K; (b) of $SrF_2:U^{2+}$ (0.3%) at 295°K; (c) of $BaF_2:U^{2+}$ (0.3%) at 295°K.

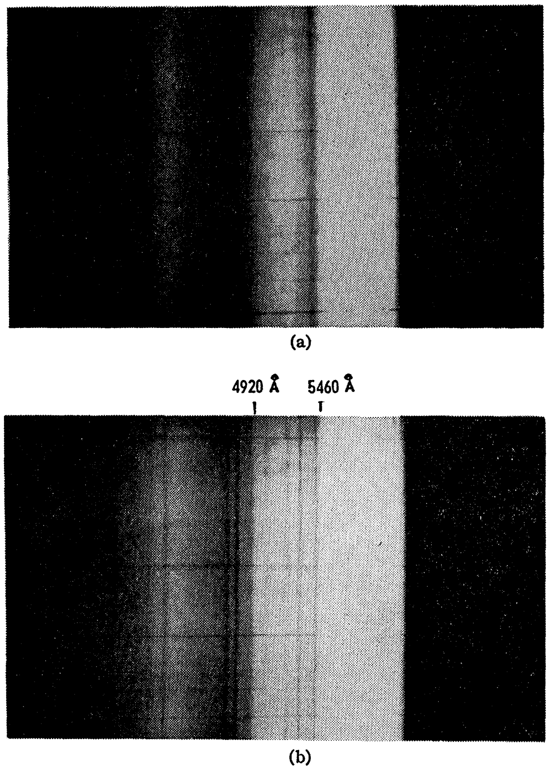

FIG. 4. Absorption spectra photographed in visible and near-ultraviolet spectral regions: (a) of $CaF_2:U^{2+}$ (0.3%) at 295°K; (b) of $CaF_2:U^{2+}$ (0.3%) at 77°K.

III. DIVALENT URANIUM

As a new discovery, I report observations on single crystals of divalent uranium in CaF_2, BaF_2, and SrF_2, and in other crystals such as NaF, LiF, CdF_2, and CeF_3, all of which have been prepared and identified spectroscopically as containing divalent uranium. The U^{2+} crystals are green colored in short path length but in long path length (2 in.) they are a deep red, very similar to the appearance of trivalent uranium in calcium fluoride. Figures 3(a), 3(b), and 3(c) show the absorption spectra of U^{2+} in CaF_2, SrF_2, and BaF_2, respectively, as recorded with our M-21 Perkin-Elmer spectrometer equipped with a CaF_2 prism. The broad absorption in the 1.5-μ region is the one attributed by Title *et al.*[6] and Yariv[7] to U^{4+}. Other characteristics of the $CaF_2:U^{2+}$ spectrum can be identified as the source of some of the impurities mentioned in various literature on $CaF_2:U^{3+}$; but the general features of this U^{2+} spectrum have not previously been reported.

Figures 4(a) and 4(b) are photographs of the absorption spectrum of $CaF_2:U^{2+}$ in the visible and near-ultraviolet regions, taken with a low-resolution glass prism instrument. Particularly at 77°K there is an interesting broad background absorption pattern. It is difficult to reproduce this satisfactorily, but in the original photographs there is a distinct long-wavelength threshold of a uniform dark background at 5460 Å

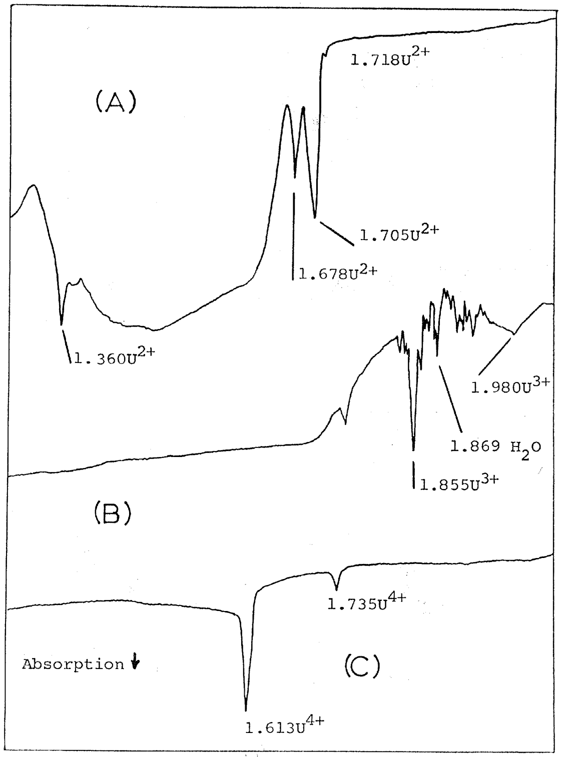

FIG. 5. High-resolution optical absorption spectra of U^{2+}, U^{3+}, and U^{4+} ions in CaF_2 at 77°K, as recorded in 1.5-μ region.

(18 300 cm^{-1}) and a second similar threshold to a darker uniform background at 4920 Å (20 325 cm^{-1}). These are probably related to the excitation of the *d* electron in U^{2+}, or to *f*- to *d*- band transitions.

The spectrum of Fig. 4(b) also shows a pattern of many sharp absorption lines superimposed on the broad-band background. A study of these has been made to determine the wavelength values of many of the U^{2+} electronic resonance lines in the visible spectrum. The strongest of these are shown in Fig. 8(a).

An interesting comparison of the spectra of the U^{2+}, U^{3+}, and U^{4+} uranium ions is seen in Figs. 5(a), 5(b), and 5(c) taken at high resolution in the 1.5-μ region at liquid-nitrogen temperature. All three spectra are distinctive. In Fig. 5(c), the U^{4+} ion has a strong sharp absorption at 1.613 μ and a weaker one at 1.735, both previously seen in the absorption curve of Fig. 1. There is no indication of crystal-field splitting here, and again we have evidence of the simple 13-line energy-level system shown in Fig. 2. Figure 5(a) for U^{2+}-ion absorption shows a number of strong sharp-line absorptions, and a region of unresolved strong absorption from 1.4 to 1.6 μ. This latter region probably involves near ground levels populated at 77°K.

The valence purity of the materials studied in this report can be judged by a comparison of the spectra of Fig. 5. The presence of U^{3+} is most readily seen by the very strong sharp absorptions at 2.15 and 2.20 μ, and these are not evident in Fig. 1 for yellow uranium $CaF_2:U^{4+}$ or in Fig. 3(a) for $CaF_2:U^{2+}$. Directly comparing Figs. 5(a) and 5(c), one sees no evidence of the presence of U^{2+} in our $CaF_2:U^{4+}$ or of U^{4+} in our $CaF_2:U^{2+}$.

It is of interest to make a comparison of the spectrum of Fig. 5(a) with that of Title *et al.*,[6] shown in their Fig. 4 (page 64), which has been discussed previously. They show three sharp lines at about 1.70 μ, which compare closely with the lines 1.678, 1.705, and 1.718 μ in Fig. 5(a) of this report. Also they show a region of general absorption between 1.4 and 1.6 μ similar to that in Fig. 5(a) and also to that in Fig. 3(a). Their spectrum shows no similarity to Fig. 1 or, in the 1.5-μ region, to Fig. 5(c).

Figures 6(a), 6(b), and 6(c) are high-resolution absorption spectra in the 2.5-μ region of U^{2+} in CaF_2, SrF_2, and BaF_2 made at liquid-nitrogen temperature. The instrument for this work was a Perkin-Elmer 98G grating monochromator, equipped with a PbS detector. The entrance slit was filtered with a Ge window, eliminating all input wavelengths below about 1.8 μ. The light source for absorption and fluorescent measurements was a 750-W tungsten lamp backed up by a large spherical reflecting mirror focusing on the crystal. Cooling of the crystal was obtained by large-area contact with the liquid-nitrogen-cooled copper block of a special vacuum cell equipped with CaF_2 windows. The fluorescent output of the crystal was focused to fill the instrument collimator mirror by means of a CaF_2 cylindrical lens.

In high resolution, I measured the crystal-field-split absorption lines of the first above-ground manifold

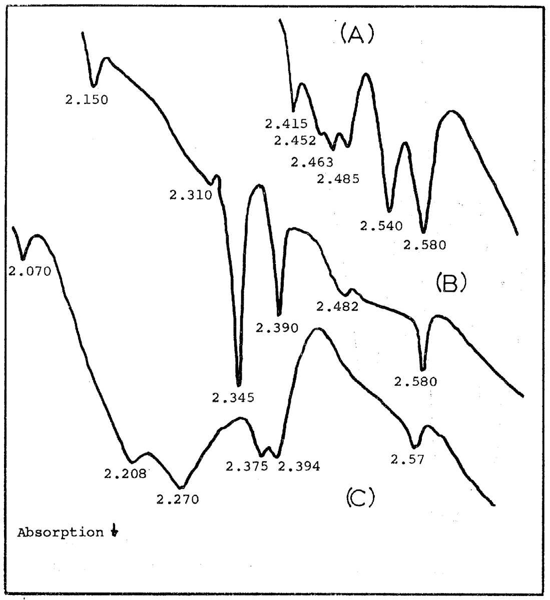

FIG. 6. High-resolution optical absorption lines ($^5L_7$): (a) of $CaF_2:U^{2+}$ (0.3%) at 77°K; (b) of $SrF_2:U^{2+}$ (0.3%) at 77°K; (c) of $BaF_2:U^{2+}$ (0.3%) at 77°K.

of CaF_2:U^{2+}, SrF_2:U^{2+}, and BaF_2:U^{2+}, which lines are in the 2.5-μ region. In a less precise way, the M-21 spectrometer gave splitting data at liquid-nitrogen temperature on these and several other infrared manifold regions.

Figures 7(a), 7(b), and 7(c) are fluorescence curves of CaF_2:U^{2+} SrF_2:U^{2+}, and BaF_2:U^{2+} never previously reported. The same 98G grating instrument was used to obtain these data. Fluorescence was looked for from 2.0 to 3.5 μ and seen only in the 2.8-μ region. However, the PbS detector used loses its high sensitivity somewhere in the region of 2.8μ, and wavelengths longer than 2.8 μ may not have been detected.

The fluorescences shown in Fig. 7 were observed with an ammonium dihydrogen phosphate crystal in the pumping beam, which cut off pumping radiation near 1.5 μ, and probably did not pump the 1.5-μ levels. Pumping through a water filter, which gives energy up to 1.1 μ, also excites the fluorescence, but not as well. Quantitative data on the effects of pumping in the visible green region have not been obtained, but it appears that the region is not particularly effective.

Figures 8(a), 8(b), and 8(c) show the results of the measurements as energy-level diagrams of the U^{2+} ions in CaF_2, SrF_2, and BaF_2. Figures 9(a) 9(b), and 9(c) detail in larger scale the two lower manifolds of the three systems.

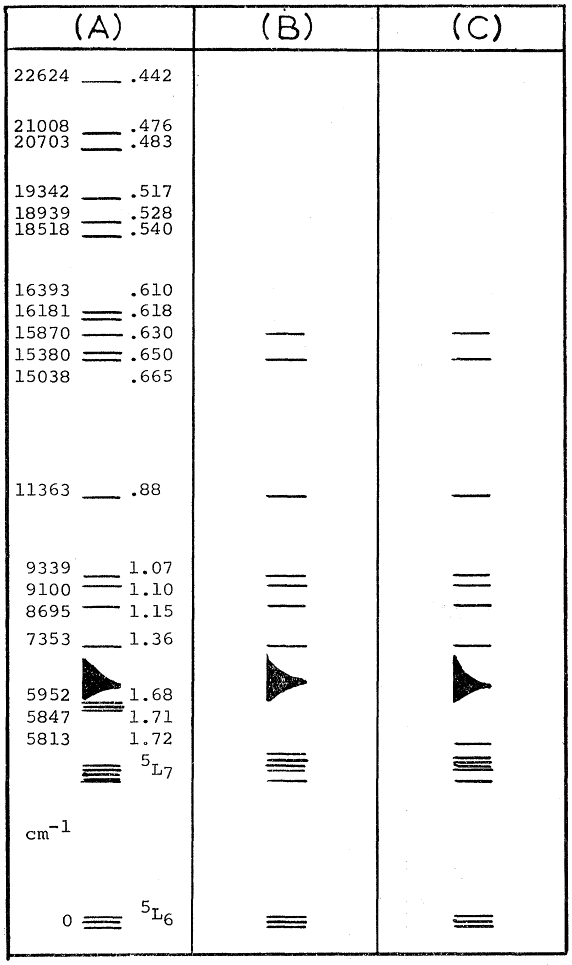

FIG. 8. Full energy-level diagrams: (a) of CaF_2:U^{2+}; (b) of SrF_2:U^{2+}; (c) of BaF_2:U^{2+}. In the visible and near-ultraviolet regions, only the levels derived from the strongest resonance-line absorptions are shown.

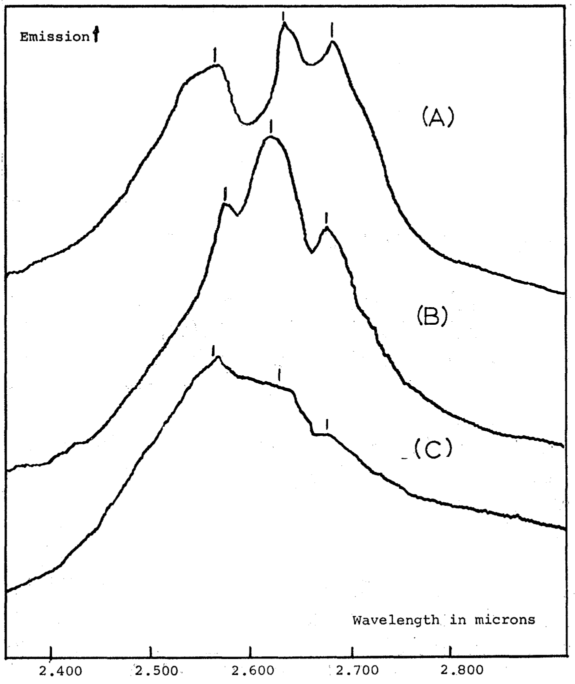

FIG. 7. Fluorescence spectra: (a) of CaF_2:U^{2+} at 77°K; (b) of SrF_2:U^{2+} at 77°K; (c) of BaF_2:U^{2+} at 77°K.

As discussed in Sec. II, CaF_2:U^{2+} has the unfilled shell structure $5f^36d$.[8,9] If in our CaF_2:U^{2+} there is a direct *substitution* of U^{2+} for Ca^{2+} ions, then we are concerned with a cubic symmetry. For a four-electron system, the lowest term of the ^5L manifold would be $^5L_6$, followed by $^5L_7$ and $^5L_8$.[8] According to El'yashevich,[9] the splitting of $J=6$ level is 6, that of $J=7$ is 6, and that of $J=8$ is 7 in a cubic field, assuming J splitting applies. Site configurations with other symmetries are possible, such as the *addition* of U^{2+} ions along with compensating fluorine ions into the open interstitial fluorite structure. This would involve other than cubic symmetry. Present information is not adequate, but further work on this is in progress to clarify the question.

The energy-level diagrams of Fig. 9 have six levels

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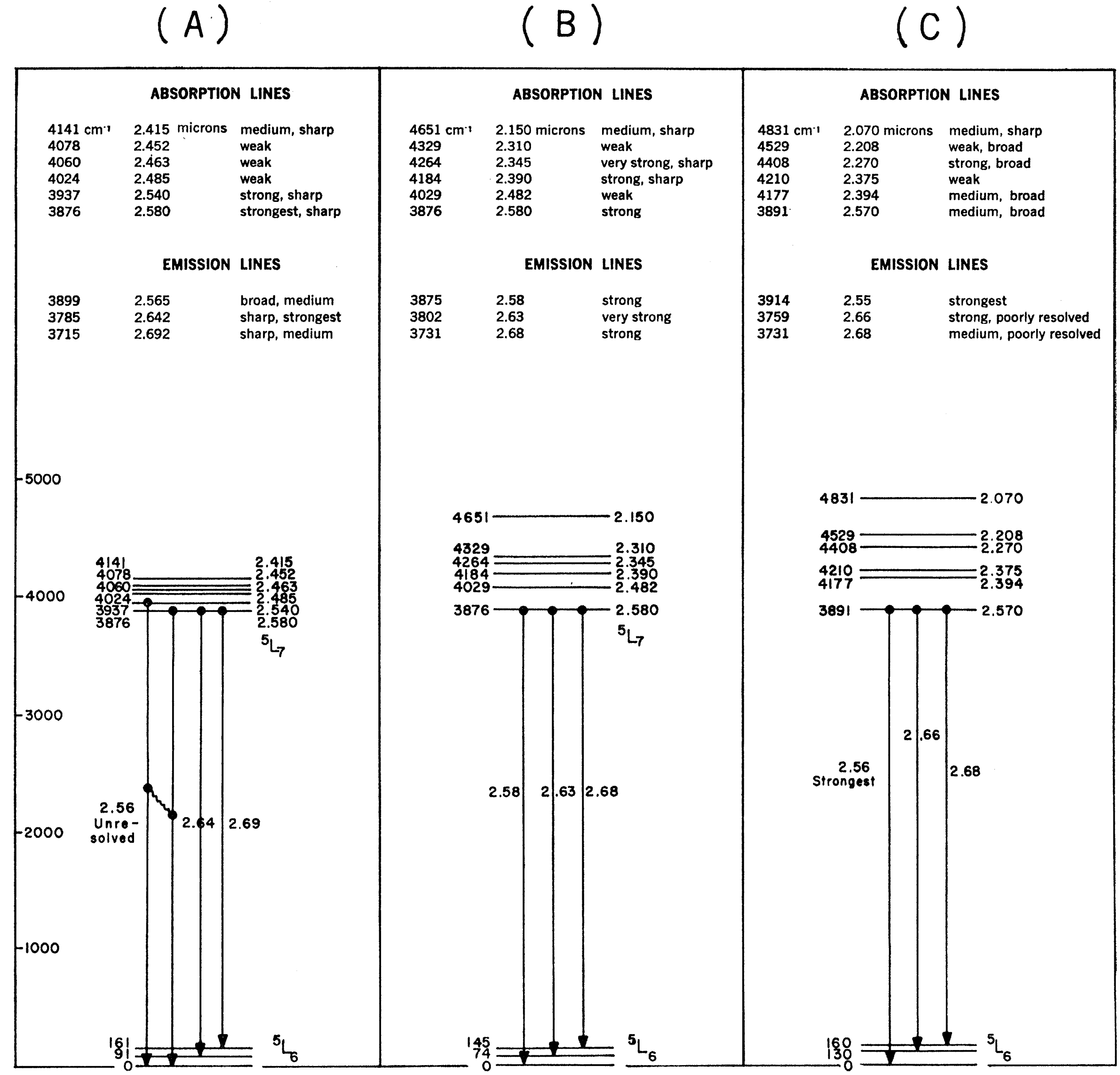
[8] *American Institute of Physics Handbook*, edited by Dwight E. Gray *et al.* (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., pp. 7–15.

[9] M. A. El'yashevich, U. S. Atomic Energy Commission Report No. USAEC-tr-4403, Book 1, p. 170 (unpublished).



(A)

ABSORPTION LINES

4141 cm⁻¹	2.415 microns	medium, sharp
4078	2.452	weak
4060	2.463	weak
4024	2.485	weak
3937	2.540	strong, sharp
3876	2.580	strongest, sharp

EMISSION LINES

3899	2.565	broad, medium
3785	2.642	sharp, strongest
3715	2.692	sharp, medium

(B)

ABSORPTION LINES

4651 cm⁻¹	2.150 microns	medium, sharp
4329	2.310	weak
4264	2.345	very strong, sharp
4184	2.390	strong, sharp
4029	2.482	weak
3876	2.580	strong

EMISSION LINES

3875	2.58	strong
3802	2.63	very strong
3731	2.68	strong

(C)

ABSORPTION LINES

4831 cm⁻¹	2.070 microns	medium, sharp
4529	2.208	weak, broad
4408	2.270	strong, broad
4210	2.375	weak
4177	2.394	medium, broad
3891	2.570	medium, broad

EMISSION LINES

3914	2.55	strongest
3759	2.66	strong, poorly resolved
3731	2.68	medium, poorly resolved

FIG. 9. Energy-level diagrams for the two lowest split levels: (a) of $CaF_2:U^{2+}$; (b) of $SrF_2:U^{2+}$; (c) of $BaF_2:U^{2+}$.

in the $^5L_7$ manifold. In the $^5L_6$ manifold, only the ground and several other levels are derived from fluorescence measurements, but there are indications in the fluorescence curves that other levels could be resolved at lower temperatures than 77°K.

There was an obvious possibility that the U^{2+} ions were U^{4+} ions having a compensating mechanism much different from that of our "yellow uranium" U^{4+} crystals. In the following paragraphs, evidence is given that such is not the case, and that divalent uranium ions are involved.

Gamma radiation has been used to partially convert trivalent ions to divalent ions in fluoride crystals.[10,11] This technique was applied to crystals of U^{2+}, U^{3+}, and U^{4+} in calcium fluoride. Figures 10(a), 10(b), and 10(c) are M-21 curves of the absorption spectra at room temperature of gamma-irradiated crystals of the different valences.

After irradiation the $CaF_2:U^{2+}$ retained its characteristic green color and absorption spectrum. The $CaF_2:U^{3+}$ also retained the bright red color and the distinctive U^{3+} absorption-spectrum characteristics except for the appearance of a U^{2+} absorption band at 6300 Å. The strong band at 1.55 μ which characterizes U^{2+} in its infrared spectrum is very weak. It is possible that a small amount of U^{4+} present in the original crystal (which was not of highest U^{3+} purity) converted to U^{2+} to give the 6300-Å absorption. The U^{3+} ions in tetragonally compensated sites (F^- as a next-neighbor

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[10] J. R. O'Connor and H. A. Bostick, J. Appl. Phys. **33**, 1868 (1962).

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

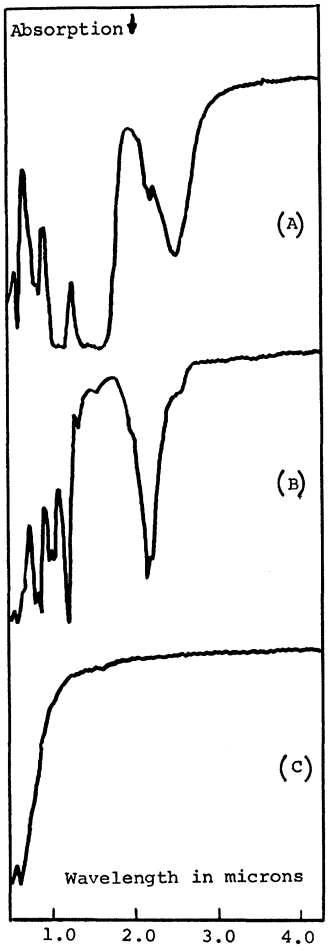

FIG. 10. Optical absorption spectra at 295°K, recorded after gamma irradiation: (a) of $CaF_2:U^{2+}$, (b) of $CaF_2:U^{3+}$; (c) of $CaF_2:U^{4+}$.

ion of U^{3+})[12–15] cannot be converted by gamma irradiation without the concurrent removal of the compensating F^- ions.[11]

The "yellow uranium" calcium fluoride $CaF_2:U^{4+}$ converted to a dense dark-green crystal showing the typical U^{2+} transmission band at 5300 Å and the typical U^{2+} absorption band at 6300 Å. The lack of U^{2+} absorptions in the infrared might be explained by the presence of compensating ions for the original U^{4+} still in the lattice, but this interesting problem is outside the scope of the present paper.

We have prepared many CaF_2 crystals double-doped with uranium ions and rare-earth ions, and find from spectroscopic analysis that they have almost 100% U^{3+} content, with the concurrent presence of considerable rare earth in divalent form. The various absorption curves for these will not be shown in the present paper, but strong concentrations of Sm^{2+}, Nd^{2+}, Tm^{2+}, and Dy^{2+} combined with almost 100% U^{3+} were obtained without gamma irradiation, under growing conditions which normally would have resulted in larger U^{2+} concentrations if the rare-earth ions were not present. My studies indicate that the following is a general reaction analogous to the CaF_2:Sm–Eu system which has been studied by Feofilov[16] and more recently by Welber[17,18]:

$$RE^{3+}+U^{2+}\rightarrow U^{3+}+RE^{2+}, \qquad (2)$$

where RE is any rare earth. Irradiation of these double-doped crystals with ultraviolet produced more RE^{2+} but also increased the U^{2+} content. This is not a reversal of the reaction above, and there is not yet an adequate explanation. For the main purpose of the present discussion involving divalent uranium, the chemical equation referred to above involving the double-doped ions could not be explained if the U^{2+} ion on the left side of the equation were replaced by U^{4+}.

Finally we come to the chemistry of the preparation of our green U^{2+} fluoride crystals. In the production of our optical fluoride crystals and in the production of our optical-maser crystals, we use the chemical PbF_2 as a scavenging agent, mainly to eliminate oxygen content caused by hydrolysis. The $CaF_2:U^{3+}$ crystals tetragonally compensated with F^- ions are prepared by a proper balance of initial PbF_2 addition and crystal processing and growing conditions. The scavenging reaction can be expressed in the following equations, which involve all of the important reacting materials and products when the operation is carried out in a graphite crucible:

$$3PbF_2+Ca(OH)_2+CaO\rightarrow 2CaF_2+3PbO+2HF \qquad (3)$$

$$PbO+C\rightarrow Pb+CO. \qquad (4)$$

We prepare our green U^{2+} by the same methods that we use for the U^{3+} crystals with the exception that we use much higher quantities of PbF_2.

Excellent on the chemistry of uranium is the publication by Katz and Rabinowitch.[1] On p. 223 of that book it is shown that UC can be prepared from uranium and carbon, but at a much higher temperature (over 2000°C) than involved in our reactions. However, the UC can be prepared readily at 1100°C by reaction with methane or carbon monoxide. We have a source of carbon monoxide in our scavenging process, but it is likely that U^0 melted in a graphite crucible with CaF_2 in presence of oxygen will readily produce UC. UC is a stable compound at room temperature. I believe the following chemistry represents closely the processes

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[12] E. Zintl and A. Udgard, Z. Anorg. Allgem. Chem. **240**, 150 (1939).

[13] B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) **B69**, 858 (1956).

[14] J. M. Baker, W. Hayes, and M. C. M. O'Brien, Proc. Roy. Soc. (London) **A254**, 273 (1960).

[15] W. Hayes and J. W. Twidell, J. Chem. Phys. **35**, 1521 (1961).

[16] P. P. Feofilov, Opt. i Spektroskopiya **12**, 531 (1962) [English transl.: Opt. Spectry. (USSR) **12**, 296 (1962)].

[17] B. Welber, J. Chem. Phys. **42**, 4262 (1965).

[18] B. Welber, J. Appl. Phys. **36**, 2744 (1965).

involved:

$$U_2O_3+U^0+2CaF_2+4C(\text{crucible}) \rightarrow 2CaF_2:U^{3+}+UC+3CO. \quad (5)$$

The above reaction has been observed when no PbF_2 is added to the original crystal stock. The crystals have optical scattering due to precipitated CaO platelets, have a layer of uranium carbide on the exterior, and are fairly free of U^{2+}, as shown by absorption measurements.

Concerning ourselves now with UF_3 in CaF_2 solution and treating this solution with the Pb^0 available as a product of PbF_2 scavenging reactions and of scavenger decomposition:

$$CaF_2:U^{3+}+Pb^0 \rightarrow CaF_2:U^{2+}+PbF_2. \quad (6)$$

There is always some $CaF_2:U^{4+}$ produced in accordance with Eq. (1), but the high vapor pressure of UF_4 at the crystal-growing temperature eliminates this fairly well.

Copious amounts of PbF_2 will yield adequate Pb^0 for the complete conversion of uranium ions to $CaF_2:U^{2+}$. The usually available PbF_2 is itself a source of Pb^0, since hydrolysis of the PbF_2 results in PbO, which decomposes to $Pb^0+\frac{1}{2}O_2$. For this reason, the graphite crucible is not essential to the process, as was determined by using another crucible material.

An understanding of the chemical processes discussed above leads to a rather clear picture of the valences of uranium obtained in CaF_2 crystals under various conditions. Also the following group of special experiments confirm the identification of valences of uranium in this report:

(a) We have readily converted $CaF_2:U^{2+}$ to $CaF_2:U^{3+}$ by remelting and regrowing in the absence of PbF_2. Also we have converted $CaF_2:U^{3+}$ to $CaF_2:U^{2+}$ by remelting and regrowing in the presence of a large amount of PbF_2. In addition to graphite crucibles, inert crucibles such as molybdenum and platinum have been used, so there is no question of the reducing action of a graphite crucible involved.

(b) Our "yellow uranium" $CaF_2:U^{4+}$ reduces to red $CaF_2:U^{3+}$ when remelted and regrown in the presence of approximately equal amounts of calcium metal and uranium. The characteristic optical absorption and emission spectra of $U^{3+}:CaF_2$ are obtained in this case.

(c) Our "yellow uranium" $CaF_2:U^{4+}$ partially reduces to green $CaF_2:U^{2+}$ when the yellow crystal is remelted and regrown in presence of a large excess of calcium metal over uranium. Mainly the change is observed in the visible-region optical absorption characteristics.

(d) Our "yellow uranium" $CaF_2:U^{4+}$ partially reduces to green $CaF_2:U^{2+}$ in visible-region optical characteristics when electrolyzed at 700°C and 90 V, in a process similar to the electrolytic reduction of rare-earth ions to divalent form previously reported.[19]

(e) Irradiation of our "yellow uranium" $CaF_2:U^{4+}$ by 2600-Å ultraviolet light results in a conversion to the visible region optical characteristics of $CaF_2:U^{3+}$. I have previously discussed the effect of gamma irradiation on our yellow uranium $CaF_2:U^{4+}$.

This report establishes that several previous papers[6,7] are incorrect in assigning to U^{4+} ions an optical absorption spectrum which is correctly that of U^{2+} ions. But in addition, ESR measurements have been made recently by McDonald, Jensen, and Wilkinson[20] on our "green uranium" $CaF_2:U^{2+}$ crystals. Some unexplained lines at $g=2$ were present, but a major constituent was seen to be a trigonally sited, even-valenced ion, with $g_\perp=0$ and $g_\parallel=3.2$. This is essentially the same as the ESR results of the previous papers.[6,7] Accordingly, both the optical absorption, and the ESR spectra of $CaF_2:U^{2+}$ have been determined.

To explain the trigonal ESR spectrum, it may be necessary to consider interstitial sites for the U^{2+} ion in CaF_2. The approximate ionic radius of U^{2+} can be calculated from x-ray data on UO crystals,[1] as 1.10 Å. This indicates that U^{2+} ions may be somewhat large to allow substitution of them for Ca^{2+} ions. But the U^{2+} may go interstitially into the open F^- ion cube structure of CaF_2 (just as every F^- ion cube contains a cation in the NaCl-type monovalent fluorides, such as NaF). Charge compensation of the U^{2+} ions would then be possible by F^- ions in nearest, normally empty, interstitial sites. Two F^- compensating ions in two such sites which have a contiguous edge, would present a trigonal resultant field on an interstitial U^{2+} ion in CaF_2. The possibility of O^2-compensation is not considered, since O^2- is not present to any considerable extent in our $CaF_2:U^{2+}$ crystals.

Recently McLaughlan[21] has reported ESR identification of trigonally sited uranium ions in CaF_2 with $g_\perp=0$, and $g_\parallel=4.02$ and 5.66. No sign of trigonal ions with $g_\parallel=3.2$ were seen. The report indicates that oxidizing conditions were present in the preparation of the crystals, and such conditions would not be conducive to the presence of U^{2+} ions. Independently of the McLaughlan report,[21] Stettler, McDonald, Meyer, and Donaho[22] have determined $g_\perp=0$ and $g_\parallel=4.1$ values for trigonally sited ions in our "yellow uranium" $CaF_2:U^{4+}$ crystals, using electron spin-resonance (ESR) and ultrasonic paramagnetic-resonance (UPR) techniques. Consequently, both the optical absorption spectrum, and the ESR spectrum of $CaF_2:U^{4+}$ have been identified.

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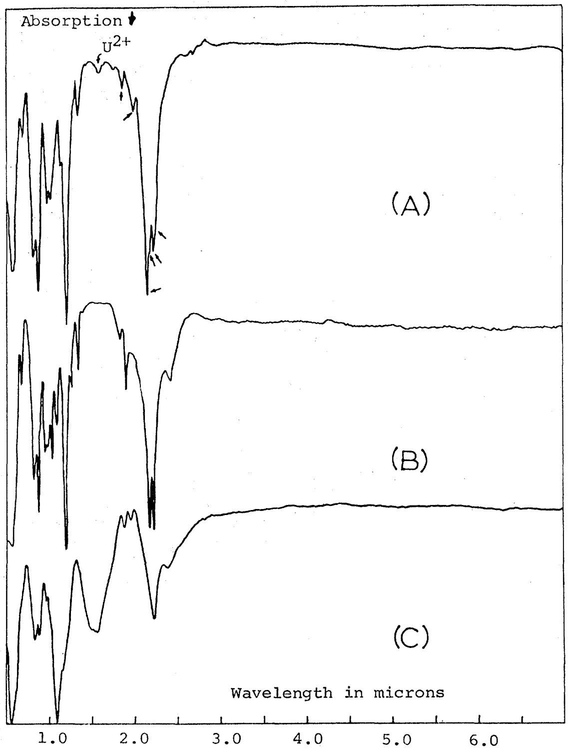

FIG. 11. Optical absorption spectra recorded with M-21 spectrometer; (a) of $CaF_2:U^{3+}$ (0.05%) at 77°K; (b) of $SrF_2:U^{3+}$ (0.05%) at 295°K; (c) of $BaF_2:U^{3+}$ (0.05%) at 295°K.

IV. TRIVALENT URANIUM

Trivalent uranium in calcium fluoride has been of particular interest, since it was one of the first laser materials discovered,[23] and has been successfully lased continuously at a high power level with low input power.[24,25] The fluorescence of the system was first observed by Galkin and Feofilov.[26,27]

Figures 11(a), 11(b), and 11(c) are absorption curves of single-valence U^{3+} in CaF_2, SrF_2, and BaF_2 made with our Perkin-Elmer M-21 spectrometer equipped with a CaF_2 prism. The $BaF_2:U^{3+}$ is included for completeness but is not of valence-pure material, which we have not yet produced. With the moderate resolution of this instrument there is some separation of the individual split levels of the lower manifolds at 77°K, as seen in Fig. 13(a).

Figures 12(a), 12(b), and 12(c) are high-resolution absorption curves of single-valence U^{3+} in CaF_2, SrF_2, and BaF_2 taken at 77°K in the grating instrument described in Sec. III. Calibrations were made with slits set for high resolution of the 1.87- and 2.67-μ water absorption groups, which have excellent sharp-line spectra carefully calibrated by infrared spectroscopists. In addition a large-scale graphical calibration was prepared using various harmonics of the mercury arc spectrum for the 1.8- to 2.8-μ region (and a less precise curve for longer wavelengths). Absorption measurements in the region are accurate to an estimated $\pm 0.003\ \mu$ for the sharp $CaF_2:U^{3+}$ absorption lines of the $^4I_{11/2}$ manifold at 2.150, 2.182, 2.220, and 2.250 μ; to about $\pm 0.01\ \mu$ for the other lines of $^4I_{11/2}$; and to about $\pm 0.01\ \mu$ for the broader U^{3+} fluorescent lines; but to $\pm 0.003\ \mu$ for the sharp strong 2.605-μ fluorescent line.

For U^{3+} in tetragonal symmetry, six levels would be predicted[9] for the weak-field splitting of the $J=11/2$ level. These six levels are shown in absorption (Fig. 12), in fluorescence (Fig. 13), and in energy-level diagrams (Figs. 14 and 15). This is believed to be the first accurate presentation of the tetragonal-sited $J_{9/2}$ and $J_{11/2}$ multiplets of U^{3+}.

The splittings of the $^4I_{9/2}$ manifold were determined by fluorescence studies with the grating instrument. Figures 13(a) and 13(b) are typical fluorescence curves of very "pure" U^{3+} (low U^{2+} and U^{4+}) in predominantly tetragonal sites. The fluorescence of $BaF_2:U^{3+}$ is included but is not of a completely "pure" crystal, as

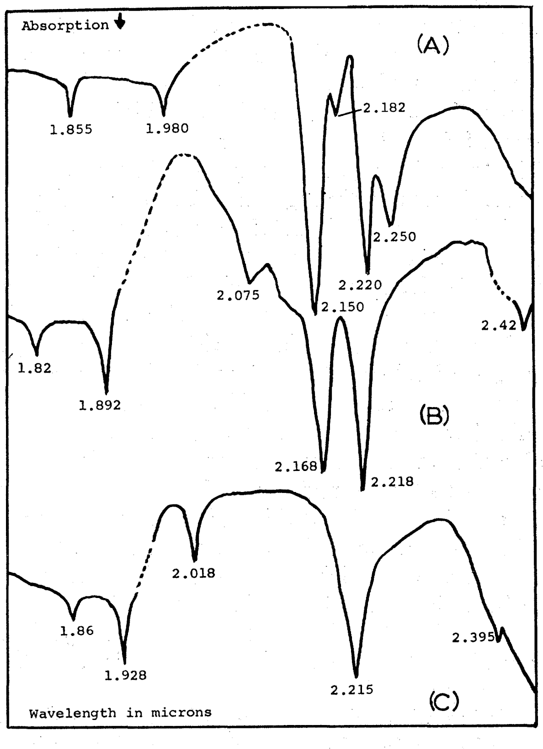

FIG. 12. High-resolution optical absorption lines ($^4I_{11/2}$) at 77°K: (a) of $CaF_2:U^{3+}$; (b) of $SrF_2:U^{3+}$; (c) of $BaF_2:U^{3+}$.

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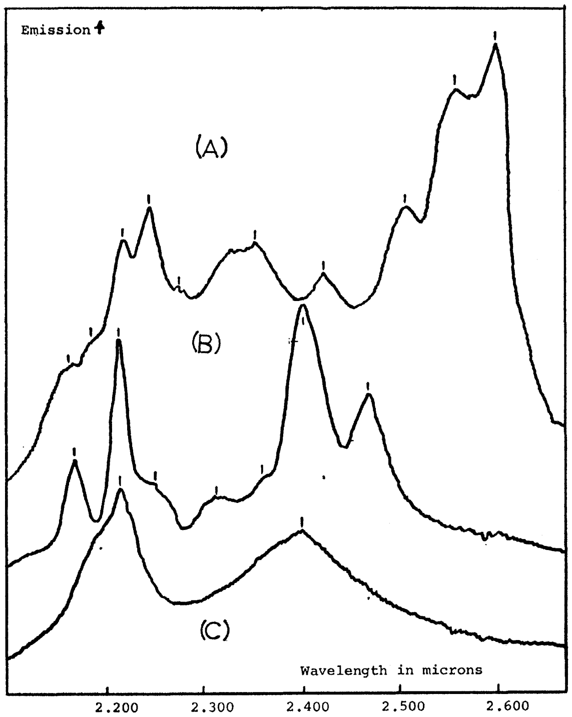

FIG. 13. Fluorescence spectra at 77°K: (a) of $CaF_2:U^{3+}$; (b) of $SrF_2:U^{3+}$; (c) of $BaF_2:U^{3+}$.

mentioned previously. The curves were obtained using germanium as an entrance-slit filter and an ammonium dihydrogen phosphate (ADP) as a pumping filter, with the tungsten lamp source referred to in Sec. III. Entrance slits and exit slits were set at 100 μ. For measurements of weak fluorescences sometimes much broader slits were used, but the very high fluorescence energy of the U^{3+} allowed the narrow slits.

The "pure" $CaF_2:U^{3+}$ pumps well in many spectral regions. Pumping through an (ADP) crystal pumps well the bands of U^{3+} from 0.50 μ out through the strong 1.20-μ levels but does not transmit energy into the strong U^{3+} 2.2-μ levels (which the experiments also show to be an effective pumping region). A water filter has similar transmission in the visible to the ADP but cuts off earlier, before 1.2 μ. Pumping through the water filter produces about one-half the fluorescent energy obtained when an ADP crystal filter is used. By combining the water filter with a green-transmitting filter, the 0.50- to 0.60-μ region was isolated for pumping. The result indicated that this region pumped about one-tenth as well as with the water filter. For a tungsten lamp operated at high temperature the energy available in a given wavelength band at 0.53 μ is several times less than that in a similar band at, say, 0.90 μ. Qualitatively the green region therefore is a relatively good pumping region.

Differing with other reports, I have found that the effect of changing the spectral region of pumping for single-valence $CaF_2:U^{3+}$ was to change the fluorescent output of all wavelengths in roughly the same proportion. There is no evidence that certain pumping regions would produce certain fluorescent peaks and not others.

Some reports made on the pumping of $CaF_2:U^{3+}$ have indicated the isolation of certain wavelength regions by means of Wratten, Corning, and other such filters. The details of the way in which these were used is not known, but it might be well to point out some experimental pitfalls connected with optical "leaks" in these and multilayer filters. Care must be taken that measurements are not confused by mistaking these "leaks" for fluorescence, and that the "leaks" are not neglected as sources of pumping radiation. The glass filters such as the Wratten filters are designed for filtering visible radiation, but they transmit very well in the infrared and have to be carefully used in series with other filters if it is desired to isolate a certain pumping region. Pumping solely into the 1.20-μ band of $CaF_2:U^{3+}$ is very effective for producing fluorescence. Thus "pumping in the green" by use of a Wratten red

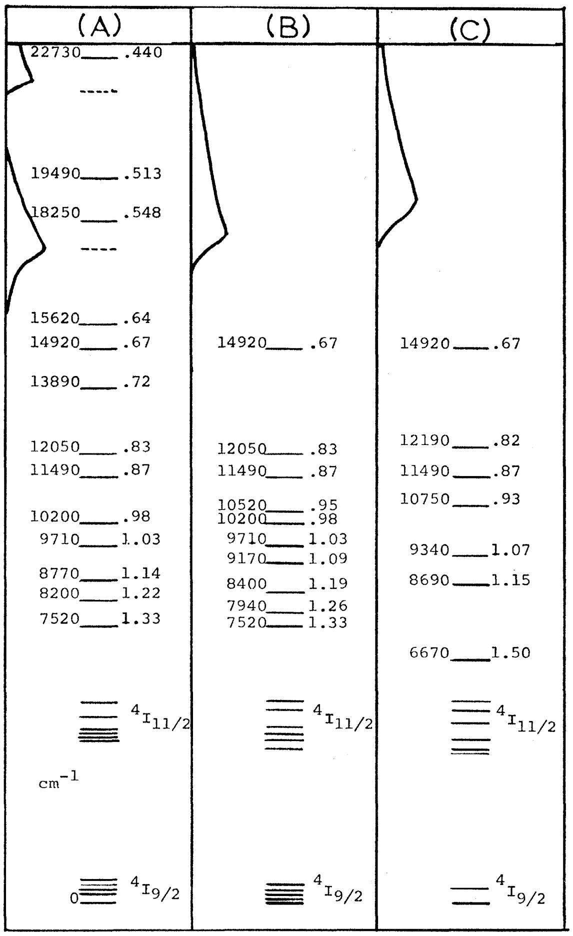

FIG. 14. Full energy-level diagrams: (a) of $CaF_2:U^{3+}$; (b) of $SrF_2:U^{3+}$; (c) of $BaF_2:U^{3+}$. In the visible and near-ultraviolet regions, only the levels derived from the strongest resonance-line absorptions are shown.

(A)

ABSORPTION LINES

5376 Cm^{-1}	1.86 microns	weak, sharp
5050	1.98	weak,
4651	2.150	very strong, sharp
4583	2.182	weak, sharp
4504	2.220	strong, sharp
4444	2.250	medium, sharp

EMISSION LINES

4612 (a)	2.168	very weak, broad
4556 (b)	2.195	very weak, broad
4500 (c)	2.222	weak, sharp
4444 (d)	2.250	medium, sharp
4386 (e)	2.280	very weak, sharp
4237 (f)	2.360	strong, very broad
4115 (g)	2.430	medium, broad
3981 (h)	2.512	medium, broad
3906 (i)	2.560	strong, broad
3839 (j)	2.605	very strong, sharp

(B)

ABSORPTION LINES

5494 Cm^{-1}	1.82 microns	weak, sharp
5285	1.892	medium, sharp
4819	2.075	weak
4613	2.168	strong, sharp
4509	2.218	very strong, sharp
4132	2.42	medium, sharp

EMISSION LINES

4608 (a)	2.170	medium, sharp
4509 (b)	2.218	strong, sharp
4444 (c)	2.250	weak, broad
4310 (d)	2.320	weak, broad
4243 (e)	2.357	weak, broad
4153 (f)	2.408	very strong, sharp
4049 (g)	2.470	medium, sharp

(C)

ABSORPTION LINES

5376 Cm^{-1}	1.86 microns	weak
5187	1.928	weak
4955	2.018	medium, sharp
4515	2.215	strong, sharp
4175	2.395	weak
4049	2.470	weak

EMISSION LINES

4505	2.220	strong, sharp
4158	2.405	strong, broad

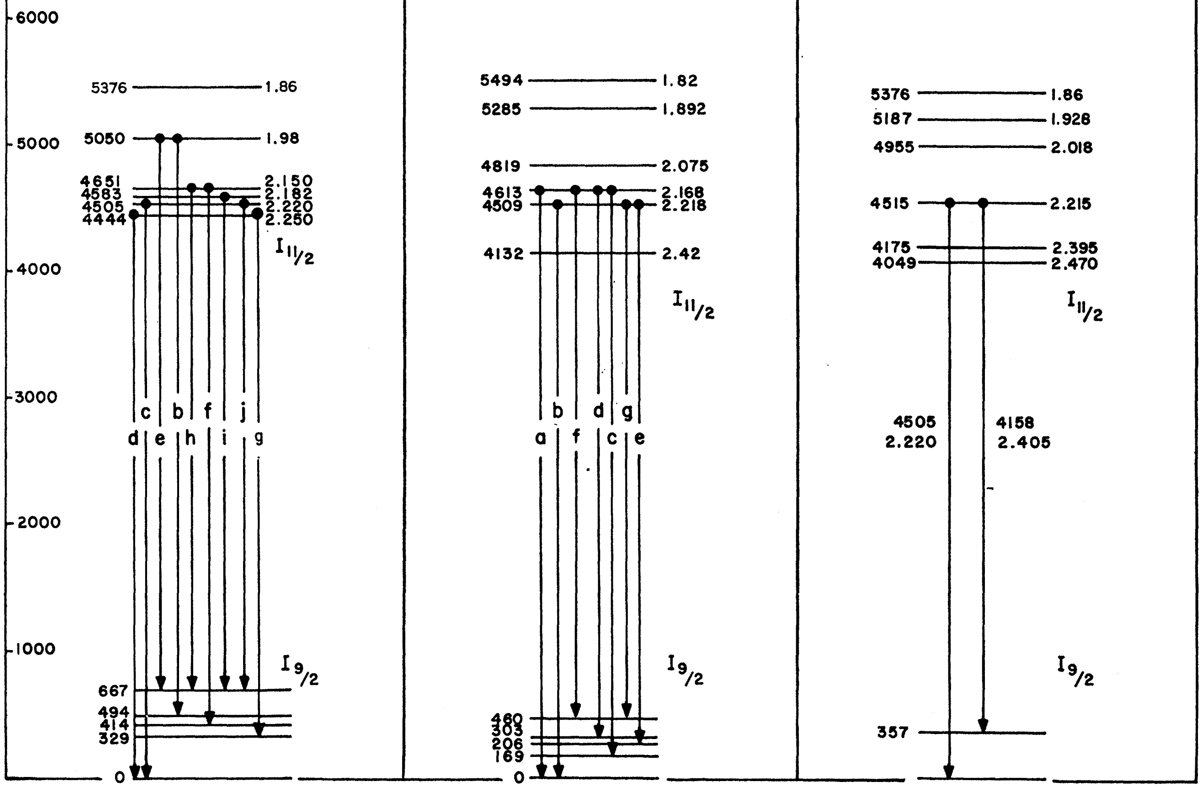

FIG. 15. Energy-level diagrams for the two lowest split levels: (a) of CaF_2:U^{3+}; (b) of SrF_2:U^{3+}; (c) of BaF_2:U^{3+}.

filter alone would not be a test of the effectiveness of the green region for pumping, since the filter would also be pumping well in the infrared region.

With some exceptions, in all systems the strongest lines in fluorescence arise from the strongest absorption levels. The 2.56-μ fluorescence of CaF_2:U^{3+} arises from a rather weak absorption level, but the terminal level of the 2.56-μ emission is the highest split-ground-state level, and this may explain why it has been observed as a room-temperature lasing wavelength. The 2.605-μ line also terminates on the same high ground-state level, but originates from one of the two strongest upper levels, resolved by cooling.

V. APPLICATION OF RESULTS TO U^{3+} LASER PHENOMENA

Various papers have discussed the lasing of CaF_2:U^{3+} on the basis of there being different or mixed states of

U^{3+} in the crystal, radiating independently of each other. Porto and Yariv,[28] on the basis of considerable spin-resonance work, propose the presence of orthorhombic and tetragonal U^{3+} sites as the origin of various lasing wavelengths. Wittke *et al.*[29] suggest "isolated ion" and "high concentration" fluorescent spectra. Bazhulin *et al.*[30] found "mechanical mixtures" to explain why some crystals which showed stimulated emission only at 2.6 μ had fluorescence at 2.5 , 2.55, and 2.6 μ, while some which showed stimulated emission only at 2.5 μ did not show 2.6-μ fluorescence at all.

My emphasis is on the fact that all $CaF_2:U^{3+}$ lasers that have been studied have contained some $CaF_2:U^{2+}$ as a contaminant and that this $CaF_2:U^{2+}$ has an absorption and fluorescing region just in the stimulated-emission wavelength region of $CaF_2:U^{3+}$. Absorption and energy transfer can therefore take place.

There is evidence of energy transfer between U^{2+} ions and U^{3+} ions in CaF_2. Both in the U^{3+} 0.98- and 1.03-μ absorption levels, and in the 2.15- and 2.22-μ absorption levels, changes in relative intensity of the line pairs with changes in U^{2+} concentration are seen. The 2.15- to 2.22-μ region is the more important in that it includes some $^4I_{11/2}$ split levels which are the source of U^{3+} laser fluorescence. The 2.15- and 2.22-μ lines are the strongest absorptions of the $^4I_{11/2}$ multiplet and are seen readily in Fig. 11(a), the M-21 absorption curve. Normally in valence-pure $CaF_2:U^{3+}$ the 2.15-μ level is the strongest, as it is in Fig. 11(a). But I have studied crystals with increasing U^{2+} relative to U^{3+}, and have noted that the 2.22-μ band increases in strength relative to the 2.15-μ band with increasing U^{2+} concentration as monitored by the 1.55-μ absorption band of U^{2+}. For an approximately 10% 1.55-μ absorption (in a 7-mm path), the 2.15- and 2.22-μ bands are about equal. (It might be mentioned that valence-pure $CaF_2:U^{2+}$ has no absorptions in the 2.2-μ region.) The 2.15-μ level is the origin of the 2.512 fluorescence of the U^{3+}, and the 2.220-μ level is the origin of the 2.605-μ fluorescence. A mechanism is proposed to fit the observations. The energy of fluorescence of U^{3+} can be short-circuited through the resonance absorption of the U^{2+} $^5L_7$ levels. This decreases the observed fluorescence in the longer U^{3+} wavelengths (2.56- and 2.605-μ laser wavelengths) but would not affect the 2.51-μ wavelength as much, or at all, as evidenced by the absence of U^{2+} fluorescence in the vicinity of this wavelength. A short-circuiting path for the 2.605-μ fluorescence would increase the absorption seen in the 2.220-μ level from which the 2.605-μ radiation originates—a prediction in agreement with my observations.

My explanation for the manifestations of $CaF_2:U^{3+}$ laser action at various frequencies as reported in the literature is a new one in that I attribute the causes not to the presence of separate fluorescing systems, but to one system of U^{3+} fluorescing ions with selective energy absorptions due to the presence of U^{2+} impurity ions.

ACKNOWLEDGMENTS

The author thanks P. W. Waugh of Optovac, Inc., for many contributions of skill in crystal growing. Also Dr. J. R. O'Connor, of MIT Lincoln Laboratory, has kindly contributed gamma-irradiation, facilities and suggestions for fluorescence-measuring equipment. Gratitude is also expressed to scientists (listed in Refs. 20 and 22) of Redstone Arsenal, Huntsville, Alabama, for their cooperation in making ESR measurements on $CaF_2:U^{2+}$, and for their permission to quote spin-resonance results on $CaF_2:U^{2+}$ and $CaF_2:U^{4+}$ in advance of papers to be published by them on these subjects.

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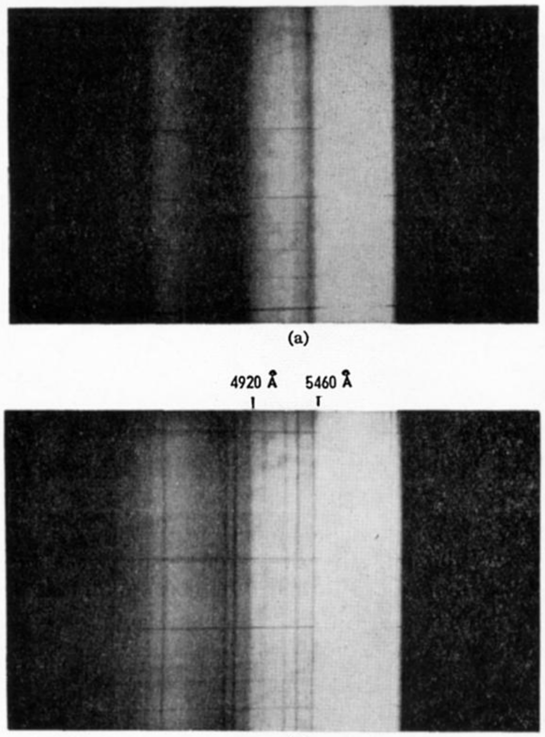

(a)

(b)

FIG. 4. Absorption spectra photographed in visible and near-ultraviolet spectral regions: (a) of CaF_2:U^{2+} (0.3%) at 295°K; (b) of CaF_2:U^{2+} (0.3%) at 77°K.