COO-3245-2

OPTICAL SPECTROSCOPY OF Np^{237} IN CaF_2

Progress Report

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ABSTRACT

Green colored Np^{237} -doped CaF_2 monocrystal specimens have been grown on a reasonably reproducible basis. The optical absorption spectra of these samples were particularly simple ("A" spectrum) when Li^+ was added to the mix for charge-compensation purposes. The lowest absorption noted was at $2.2 \mu\text{m}$ which we attribute to the $^3\text{H}_4$ (ground state) $\rightarrow$ $^3\text{F}_2$ transition of $\text{Np}^{5+}(5f^2)$. Samples prepared without Li^+ compensation displayed "AB" spectra which were composites of the "A" spectrum and a new "B" spectrum. The observed B spectrum crystal-field splittings were much greater than those of the A spectrum, the lines were also more numerous. We are assigning the B spectrum also to Np^{5+} . To date we have not been able to grow crystals possessing just B type spectra. Tentatively we are associating the A spectrum with a nominal 3-fold symmetry axis and the B spectrum with a nominal 4-fold axis. Parametric analyses of the splittings of the levels are in progress.

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PERSONNEL SUPPORTED BY CONTRACT

Principal Investigator

Professor J. O. Artman	100% of effort	July-August 1972
	25% of effort	May-June 1972
		Sept. 1972-April 1973

Graduate Students

A. Natarajan	100% of effort	July 1972-April 1973
S.-D. Wang	100% of effort	July 1972-April 1973
R. Parenti	Supplement to NSF Traineeship	May-June 1972

NOTES ON PERSONNEL

Both Mr. A. Natarajan and Mr. S.-D. Wang passed the Ph.D. Qualifying Examination in the Physics Department in the Spring of 1972.

PUBLICATIONS

An abstract entitled "Optical Spectra of Neptunium-Doped CaF_2 Crystals" by A. Natarajan, S.-D. Wang and J. O. Artman has been submitted to the April 23-26 1973 meeting of the American Physical Society in Washington, D.C.

RESEARCH ACTIVITIES DURING THE PAST INTERVAL

The research during the past interval was primarily of a materials nature. In the previous interval¹ we had prepared samples of $\text{Np}^{237}\text{-CaF}_2$ which (when grown without charge compensation) were usually pink in color. We had attributed the spectra of these samples observed in the 0.55-2.5 μm region to a combination of Np^{4+} and of Np in another valence state, probably Np^{3+} . Na^+ addition to the starting mixtures yielded colorless crystals characterized by the Np^{4+} spectra. Li^+ addition did not seem to have any effect. The spectra were generally extremely complicated.

With changes in our crystal-growing apparatus in the past interval, we found that we could no longer prepare the pink samples. However we were able to prepare, on a reasonably reproducible basis, green-colored specimens. These specimens were grown in an induction furnace from CaF_2 powder (prepared from chips from very pure optical-quality crystals, the chips were furnished by Optovac) in carbon crucibles. The Np was added in the form of NpF_4 . (We had found that addition of Np in the form of NpF_3 made no difference as far as the optical state of the specimens were concerned). Helium gas was fed through the apparatus. The characteristic absorption spectra of these crystals were examined at room, liquid nitrogen, and liquid helium temperatures in the 0.3 to 2.5 μm wavelength region. We attribute these spectra to Np^{5+} .

The spectra of these green-colored $\text{Np}^{237}\text{-CaF}_2$ specimens became particularly simple (A-Spectrum) when Li^+ was added as a charge-compensator. The lowest absorption noted was at 2.2 μm which we are assigning to absorption from the ground state ($^3\text{H}_4$) to the lowest excited state ($^3\text{F}_2$). Other lines were seen at 1.25 μm (which we believe to represent transitions to the $^3\text{H}_5$ and $^3\text{F}_3$ levels) and between 0.5 and 0.9 μm which we are attributing in part to the presence of the $^3\text{F}_4$ and $^3\text{H}_6$ levels. The spectra in the shorter wavelength regions became progressively more complex.

In the non Li^+ -compensated samples, the spectra found (AB-Spectra) were composites of the previously discussed "A" Spectrum and a new "B" spectrum. The observed crystal-field splittings of the B spectrum were much greater than those of the A spectrum, the lines were also more numerous. Since the B patterns appeared in the same spectral regions as the A

patterns we attribute these also to Np^{5+} . To date we have not been able to grow crystals possessing just B type spectra. Additions of Na^+ to the starting mixtures also yielded spectra essentially of the AB-type; the B type spectra were somewhat stronger than the A but not enough for these samples to be of much use.

Our tentative interpretation is that the A-spectrum is due to Np^{5+} at a site of nominal 3-fold symmetry--this could be associated with partial compensation by two O^{2-} ions occupying the F^- sites at the opposite ends of a body diagonal of the F^- cube surrounding a Ca^{2+} site. Compensation of the Np^{5+} substituent by one more negative charge is required, possibly by an F^- at a nearby vacant cubic site. This of course would lower the symmetry and is consistent with the appearance of the spectra. We believe the B-spectrum to be due to Np^{5+} at a nominal 4-fold site. Parametric analyses of the splittings of the levels are in progress.

We have been guided in these interpretations particularly by the Np^{5+} results reported in CsNpF_6 ² and investigations of the isoelectronic U^{4+} system in CaF_2 ³. Unfortunately the Np^{5+} in CsNpF_6 is at a regular 6-fold coordinated site and does not exhibit low-order crystal field splittings. On the other hand the investigators of the U^{4+} - CaF_2 system were not able to distinguish the lower order crystal field splittings of the $^3\text{F}_2$ state.

An abstract prepared for the 23-26 April 1973 American Physical Society meeting in Washington, D.C. is appended.

The students associated with this project were Mr. A. Natarajan and Mr. S.-D. Wang. Mr. R. Parenti contributed to the research effort during May and June of 1972 and received supplementary support to his NSF Traineeship.

References

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3. R. McLaughlin, V. Abed, J. G. Conway, N. Edelstein and E. H. Huffman, J. Chem. Phys. 53, 2031 (1970).

Abstract Submitted

for the Washington, D.C. Meeting of the

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23-26 April 1973

Optical Spectra of Neptunium-Doped CaF_2 Crystals^{*}

A. NATARAJAN, S. D. WANG, and J. O. ARTMAN, Carnegie-Mellon U.--A number of Neptunium-doped CaF_2 crystals have been prepared. These specimens were usually green in color. Optical spectra were taken at room, liquid nitrogen and liquid helium temperatures in the wavelength region extending between 0.3 to 2.5 μm . The spectra became comparatively simple when the samples had been doped with Li^+ during growth. We believe the results to be consistent with the presence of the Np^{5+} state.

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