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Annual Technical Report

PHOTOIONIZATION AND ELECTRON TRANSFER IN IONIC CRYSTALS

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I. Review of accomplishments July 1987 - March 1990

Three lines of work have been completed since our previously submitted proposal. These are:

- (A) Spectroscopy of $\text{Ce}^{3+}\text{-Na}^+$ pairs in CaF_2 and SrF_2
- (B) Photoionization studies of Sm^{2+} , Eu^{2+} and Yb^{2+} in CaF_2 and SrF_2
- (C) Infrared-detected two-photon spectroscopy of MgO:Ni^{2+} , and other two-photon spectroscopy studies.

A. $\text{Ce}^{3+}\text{-Na}^+$ Pairs.

The first of these projects will lead into next years work on photon-gated photoionization. Dee Pack carried out the laser-excited fluorescence and excitation spectroscopy of individual $\text{Ce}^{3+}\text{-Na}^+$ pairs in CaF_2 and SrF_2 host crystals. These pairs, illustrated in Figure 1, have been partially identified as to the relative lattice sites of the Ce^{3+} and Na^+ . Figure 2 shows the absorption spectrum of a crystal doped with Ce^{3+} 0.003% and Na^+ of about the same concentration. Since Ce^{3+} needs a charge compensator when substituting at a Ca^{2+} or Sr^{2+} site the Na^+ can fill this role when at such host crystal sites. The figure shows the zero-phonon lines of different Ce-Na pairs. For instance line 1 is the nearest neighbor pair with the Na^+ at the (110) site relative to Ce^{3+} . The broad band in the center is due to zero-phonon lines of the uncompensated or distantly compensated Ce^{3+} ions. After a long period of laser irradiation the spectrum shown in the lower part of the figure developed. The cubic, or uncompensated site has disappeared. We believe this means that the other sites have become ionized and that the uncompensated Ce^{3+} ions, being the best traps, have captured the electrons and have been reduced to Ce^{2+} . The latter has a spectrum in the IR and visible, far from the UV region of Figure 2.

This discovery is the most interesting result in Dee Pack's first paper and it needs further study¹.

In a second paper, the detailed laser spectroscopy results are given leading to the energy level schemes for the ground (4f) and excited (5d) states of Ce^{3+} in the presence of the Na^+ ion. These are shown in Table 1 for several types of pairs. What is interesting about these energy schemes is that they represent the effect of a Na^+ ion on the energy levels of the Ce^{3+} ion at a series of accurately known distances. We can try to explain the electronic splittings produced via crystal field theory or whatever else needs to be included. The results shown in Pack's second paper are that simple crystal field theory is not good enough. What can we add? Possibilities are that the electronic polarization fields of these ions interact or that the displacements, causing another kind of polarization field, interact.

The $\text{Ce}^{3+}\text{-Na}^+$ pairs constitute a series of entities about which clear and basic questions can be asked. The simplicity of these entities suggests that such questions are able to be answered and they should be pursued.

B. Photoionization studies of Sm^{2+} and Eu^{2+} .

These two rare earth ions are chemically stable in the divalent state. They also have the highest ionization potentials when incorporated in CaF_2 or SrF_2 ³.

A paper by Fuller deals with the rate of photoionization as determined from the analysis of one- and two-photon spectra^{4,5}. The broadening of either the f-d or the f-f spectra can be caused by vibronic coupling or by photoionization. We believe that we can argue for a particular mechanism in several cases. Figure 3 shows the case of $\text{BaF}_2\text{:Sm}^{+2}$ compared to $\text{SrF}_2\text{:Sm}^{+2}$ from Robert Fuller's thesis⁴. The excited state of Sm^{+2} in BaF_2 lasts for only 40 fsec according to

this analysis, before decaying into the lowest excited state of the manifold. The above example uses the one-photon $4f \rightarrow 5d$ spectrum. The two-photon spectra show the $4f \rightarrow 4f$ transitions and although these are observable for Sm^{2+} in CaF_2 and in SrF_2 , only the lowest such transition is observable in BaF_2 . This is the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ transition in which ${}^5\text{D}_0$ is the lowest excited state; the other transitions, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, ${}^5\text{D}_2$, ${}^5\text{D}_3$ are seen in CaF_2 and SrF_2 but not in BaF_2 . We have to assume that these transitions in BaF_2 are broadened into the noise level and thus have a lifetime less than 180 fsec. This upper limit is to be compared with the value of 40 fsec from the one-photon spectra.

A preliminary report on these studies was presented by Robert Fuller at the Conference on Dynamical Processes in Excited States of Solids, University of Georgia, August 1989, and has appeared in the Journal of Luminescence⁵. A complete account is in preparation.

The fourth paper gives the photoionization yields of Eu^{2+} in SrF_2 when Sm^{3+} is the electron trap and is taken from Robert Fuller's thesis⁶. It was found that the photoionization yield decreases with decreasing temperature from 300 K to 200 K and then remains constant. Figure 4 shows this behavior on a log rate vs $1/T$ plot from which an activation energy of about 3000 cm^{-1} is obtained. The absolute value of the ionization efficiency was also obtained and found to depend on the photon energy. It is 0.85% at 300 K when 240 nm radiation is used, for example and ten times higher at 218 nm.

This frequency dependence is expected for a model in which there is a threshold at about 4.9 eV and the energy above this value is given to the electron as kinetic energy. This excess kinetic energy is used to escape the coulomb field of the donor ion and allows the electron to find a trap.

The trap in these doubly doped crystals ($\text{Sm}^{3+} - \text{Eu}^{2+}$) is Sm^{3+} which is reduced by electron capture to Sm^{2+} . It was shown that charge compensated Sm^{+3}

is the major trap between 200 K and 300 K. The activation energy for the yield, shown in Figure 4, is a reasonable activation energy for the dissociation and diffusion of interstitial F^- ions. But this is just what would be expected if the electron upon combining with $Sm^{3+} - Fi^-$ has to eject the Fi^- charge compensator from its vicinity. The Fi^- then diffuses back to the donor ion which now is Eu^{+3} and uncompensated. We find that the uncompensated Eu^{+3} is created after the electron leaves but in a short time becomes $Eu^{+3} - Fi^-$, the charge compensated species.

Before these experiments on temperature dependence of yield we could not understand why the photocurrent was nearly independent of temperature. Afterwards it was even more puzzling - why should the photocurrent depend differently on temperatures than the electron yield? Aren't they measuring the same thing? The answer seems to be that when measuring photocurrent we are ionizing $\sim 10^{10}$ electrons per second, whereas when measuring yield we deal with $\sim 10^{15}$ electrons per second. The small number of electrons can be trapped either at the rare uncompensated sites or at compensated sites, but the rate of movement of F^- compensators back to the donor is enough to produce a reverse current which cancels the electron current to the compensated sites (above 200 K). Thus, the photocurrent measures trapping only at uncompensated sites. This also explains why at low temperatures (80 K) one produces only Sm^{2+} ions at cubic sites. It is not possible to trap an electron at a compensated site at temperatures below that needed to activate the dissociation of the $Sm^{3+} - Fi^-$ pair.

We found evidence that $Sm^{2+} - Fi^-$ pairs do exist, however, but the Fi^- may be more distant than at the nearest interstitial site. These pairs ionize at a lower energy than isolated Sm^{2+} and therefore give rise to the difficulty of determining a true threshold for photoionization; they give too low a value.

The conclusion of these studies is that electronic currents can drive ionic currents, and the proximity of charges to ionizable entities has a strong effect on the ionization threshold. Our work to date shows that this interrelationship exists and that its consequences may be very interesting and worth further exploration.

C. Two-Photon spectroscopy.

This technique is now a fairly standard one in our laboratory, but it requires a separate category here because of its special applications.

We completed another joint project with Paul Rabinowitz at Exxon Research and Engineering Laboratory, Annondale, NJ. This has resulted in a paper by Cecelia Campochiaro and Paul on MgO:Ni^{2+} .⁷ Special technology was needed here because Ni^{2+} emits at 1.2μ and photomultipliers cannot be used. Also, to get tunable infrared at 2.4μ we needed three Stokes shifts in hydrogen, and could only achieve this with the multipass cell in Rabinowitz' laboratory. The MgO:Ni^{2+} system is an important model for an ion in a crystal, and has been studied in every possible way except by 2-photon spectroscopy. Therefore, we wanted to do this case.

The results are quite interesting but have left us with a few puzzles. One is to explain the two-photon intensity and polarization in various transitions. A number of multiplet components we expected to see did not show up so we have tried to calculate their intensity from first principles. Cecelia has spent some time in London working with Colin Flint and Roberto Acevedo on these calculations under the auspices of a NATO grant. I expect that a separate paper on this subject will be written.

Another puzzle is the appearance of strong signals depending on the first power of the laser intensity which occur when the laser frequency is within 1000

cm^{-1} of a certain resonant level. This phenomenon apparently prevents us from seeing an interesting portion of the 2-photon spectrum.

D. Anomalous emission band of $\text{BaF}_2:\text{Eu}^{2+}$

A paper on this subject has been delayed several years until the completion of Fuller's work. The interpretation is now on firmer ground and we should be able to publish the results. It is work done by B. Moine of the University of Lyon, France while he was here at Princeton⁸.

II. Significance of This Research.

Our work on two-photon spectroscopy has helped us to use this method in several research projects and it is now considered a routine, though still challenging, experiment. It has helped us with our studies of photoionization, as shown in ref. 5.

The photoionization studies have resulted from earlier work aimed at finding photoionization thresholds as described in ref. 2. We were unhappy about the photoconductivity spectra and their interpretation. The work of Fuller, ref. 6, showed an important thing: the photocurrent and the photoionization yield measure different things. It showed how and where the electrons are trapped in the system he studied, $\text{SrF}_2:\text{Eu}:\text{Sm}$. Future studies of electrons in ionic crystals will have to take account of these findings.

The work on $\text{CaF}_2:\text{Ce}^{3+}:\text{Na}^+$ also led to the observation of a photoionization process. This had already been reported by Hamilton and his students⁸, who showed that it is a stepwise two-photon process. Our observation is that of the ionization of close Ce Na pairs, with trapping at widely spaced (uncompensated) pairs. We should now be able to measure the ionization potential of each type of pair by means of a two-laser experiment. This will show how a coulomb field (due to Na^+ at a Ca^{2+} site) affects the ability of the Ce^{3+} to lose an electron, and indirectly to understand the screening of a coulomb field in a typical ionic crystal. This is a fundamental problem which we now believe we have a chance to solve.

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Table 1. Summary of spectroscopic data for CaF_2 charge compensation sites. Energy units are cm^{-1} . Asterisks (*) refer to this paper.

Site	$\text{C}_3, \text{O}^{2-}$	C_4, H_1	C_4, F_1	C_3, F_1	C_2, Na^+	C_4, Na^+	C_3, Na^+	O_h
(1st)	(1/2 1/2 1/2)	(100)	(100)	(111)	(110)	(200)	(211)	
(R) (ϵ_0)	0.43	0.50	0.50	0.87	0.71	1.00	1.22	distant
Site	$\text{C}_3, \text{O}^{2-}$	C_4, H_1	C_4, F_1	C_3, F_1	C_2, Na^+	C_4, Na^+	C_3, Na^+	O_h
1	29553	-	-	32038.8	32291.0 ($\epsilon>$)	32326.5 ($\epsilon>$)	32331 ($\epsilon>$)	32325
2	29547	29251 ($\epsilon>$)	31922.2 ($\epsilon>$)	32057.4	32228.0 ($\epsilon>$)	32298.5 ($\epsilon>$)	32306 ($\epsilon>$)	32325
$2\text{F}_{7/2} \text{E}_{5/2}$	-	-	3562 ($\text{E}_{5/2}\text{E}_{3/2}$)	3896 ($\text{E}_{5/2}\text{E}_{1/2}$)	3847 ($\text{E}_{5/2}\text{E}_{1/2}$)	3840 ($\text{E}_{5/2}\text{E}_{3/2}$)	3838 ($\text{E}_{5/2}\text{E}_{1/2}$)	3832 ($\text{E}_{5/2}$)
$\text{G}, \text{E}_{1/2}$	-	-	2440 ($\text{OE}_{1/2}$)	2212 ($\text{OE}_{3/2}$)	2190 ($\text{E}_{1/2}\text{E}_{1/2}$)	2184 ($\text{E}_{1/2}\text{E}_{1/2}$)	2183 ($\text{E}_{1/2}\text{E}_{1/2}$)	2178 ($\text{E}_{1/2}$)
$\text{G}, \text{E}_{1/2}$	-	-	2307 ($\text{OE}_{3/2}$)	2190 ($\text{E}_{1/2}\text{E}_{1/2}$)	2171 ($\text{OE}_{1/2}$)	2170 ($\text{OE}_{1/2}$)	2167 ($\text{OE}_{1/2}$)	2163 (O)
$2\text{F}_{3/2} \text{E}_{5/2}$	-	577 ($\text{E}_{5/2}\text{E}_{3/2}$)	579 ($\text{E}_{5/2}\text{E}_{3/2}$)	558 ($\text{E}_{5/2}\text{E}_{1/2}$)	538 ($\text{E}_{5/2}\text{E}_{1/2}$)	532 ($\text{E}_{5/2}\text{E}_{3/2}$)	537 ($\text{E}_{5/2}\text{E}_{1/2}$)	532 ($\text{E}_{5/2}$)
G	60 ($\text{OE}_{1/2}$)	-	-100 ($\text{OE}_{1/2}$)	31 ($\text{OE}_{3/2}$)	14 ($\text{OE}_{1/2}$)	5 ($\text{OE}_{1/2}$)	9 ($\text{OE}_{1/2}$)	0 (O)
G	0 ($\text{OE}_{3/2}$)	0 ($\text{OE}_{3/2}$)	0 ($\text{OE}_{3/2}$)	0 ($\text{OE}_{1/2}$)	0 ($\text{OE}_{1/2}$)	0 ($\text{OE}_{3/2}$)	0 ($\text{OE}_{1/2}$)	0 (O)
$\nu(\text{A}_{1g})$ (emission)	56*	-	478	490	457	443	454	449
References	1,2	4	1,2,6	2*	.	.	.	.

FIG. 1. Model pictures of some Ce^{3+} charge-compensation pairs. Examples of both the Na^{+} substitutional sites and the F^{-} interstitial sites are shown.

FIG 2 High-resolution laser-excitation spectra of sample 4, Ce³⁺:Na⁺:CaF₂. (a) Initial 1.8-K spectrum. (b) Later 15-K spectrum. Note the hot bands and the appearance of a spectral hole at 32325 cm⁻¹.

Figure 3. UPPER: Absorption spectrum of $\text{BaF}_2:\text{Sm}^{2+}$ at 1.8K
 LOWER: Absorption spectrum of $\text{SrF}_2:\text{Sm}^{2+}$ at 1.8K
 with a blue shift of 860 cm^{-1} in order to align it with the $\text{BaF}_2:\text{Sm}^{2+}$ spectrum.
 MIDDLE: Lorentzian broadened $\text{SrF}_2:\text{Sm}^{2+}$ spectrum with a
 130 cm^{-1} bandwidth to fit the $\text{BaF}_2:\text{Sm}^{2+}$ spectrum above. This width
 corresponds to a decay time of 40 femtoseconds, a timescale of vibrational
 relaxation.

Figure 4. A plot of the relative efficiency of Eu^{3+} formation at 240 nm versus the inverse of temperature. This plot contains two clear regions, a region below 200K that is relatively insensitive to temperature and the region above 200K which corresponds to an activated process with a barrier of $2600 \pm 200 \text{ cm}^{-1}$ (0.32 eV). The value of this barrier is one half of the binding energy of a $\text{Sm}^{3+} \cdot \text{F}^-$ complex. Thus, the trapping of the ionized electron by $\text{Sm}^{3+} \cdot \text{F}^-$ centers determines the temperature dependence of the electron transfer reaction in the $\text{SrF}_2:0.01\%\text{Eu}, 0.02\%\text{Sm}$ crystals.

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