Excitons trapped at impurity centers in highly ionic crystals

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(Received 18 June 1985)

It is shown that there are several examples of impurity ions in ionic host crystals all of whose localized excited states lie above the ionization energy of the impurity in the crystal ($SrF_2:Yb^{2+}$, $BaF_2:Eu^{2+}$, and others). Excitation of the localized states followed by relaxation leads to a lowest excited state in which the electron resides in the host lattice while the hole remains trapped on the impurity ion. Heretofore unexplained luminescence bands result from the radiative decay of this "impurity trapped exciton."

In highly ionic crystals, the main spectroscopic features introduced by impurity doping are the localized transitions, namely, $d \rightarrow d$, $d \rightarrow s$, and $d \rightarrow p$ for transition-metal ions, $f \rightarrow f$ and $f \rightarrow d$ for rare earths, and $s \rightarrow p$ for post-transition-metal ions.[1] In addition, electron-transfer transitions, anion to metal-impurity ion, introduce strong absorption bands usually in the uv spectral range.[2,3] The reverse process, in which an electron on the metal-impurity ion moves to lattice states, is not often observed. The reasons for this are (1) the photoionization energy of the impurity in the host crystal is often greater than the band gap of the crystal, and (2) these transitions are inherently weak because of the small overlap of metal-impurity-ion orbitals with those of the host-crystal metal ion. In this Rapid Communication, however, we will show that such transitions have been observed in the past, but not recognized as such, and will show the conditions under which they may be found. The excited state of such a transition could be called an impurity-trapped exciton, since it consists of a bound electron-hole pair with the hole localized on the impurity and the electron on nearby lattice sites.

EXPERIMENT

The only new datum presented in this paper is the photoconductivity spectrum of $SrF_2:Yb^{2+}$. The crystal was grown by Harold Temple at RCA Laboratories. It had less than 0.1% of Yb^{2+} and smaller amounts of Yb^{3+}. The photoconductivity measurements were made using blocking electrodes and by the same methods as in Ref. 4. The results are shown in Figs. 1 and 2 for the temperatures 300 and 10 K, respectively. The current voltage plot in these experiments is linear and passes through zero.

DISCUSSION

In a systematic study of the photoionization thresholds of impurity ions in ionic host crystals[4] we have observed several cases in which all the localized excited states of the impurity ion lie in the conduction band of the host crystal. Examples are Yb^{2+} in SrF_2 (as shown in this paper), Cu^+ in $CdCl_2$, and $CdBr_2$,[5] Tm^{+2} in BaF (except for the low-
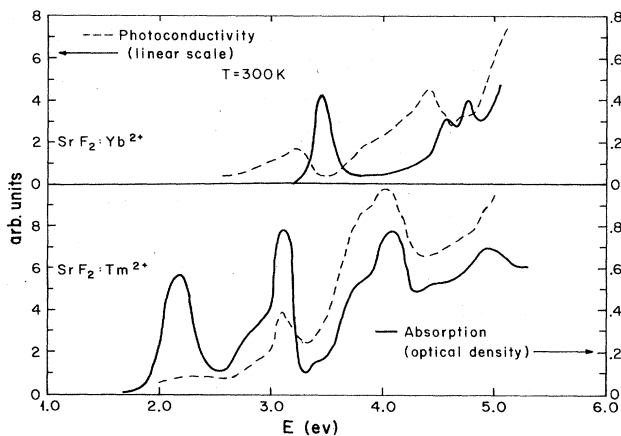

FIG. 1. A comparison of the photoconductivity and absorption spectra of $SrF_2:Tm^{2+}$ and $SrF_2:Yb^{2+}$. Data for the former are from Ref. 4, replotted, and for the latter from this work. All data are taken at $T = 300$ K. The photoconductivity is measured as electrons per incident photon and is plotted on a linear scale in arbitrary units. Crystal thickness 1.34 mm, 300 V applied for $SrF_2:Yb^{2+}$.

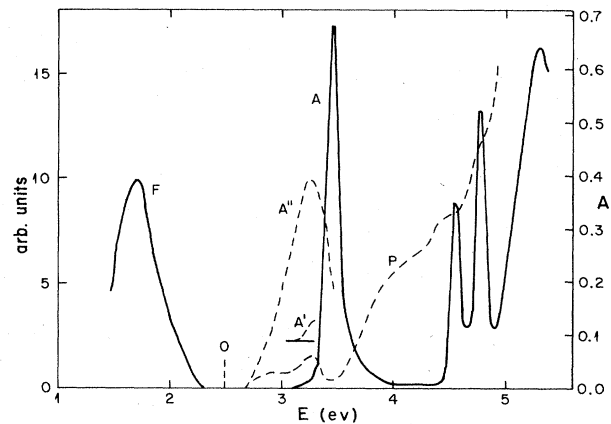FIG. 2. $SrF_2:Yb^{2+}$: Photoconductivity (P), at 10 K, linear scale at left; absorption (A) at 10 K, absorbance scale at right; forbidden absorption (A'), anomalous emission (F) at 80 K; estimated trapped exciton absorption (A'') at 80 K (see text); estimated zero-phonon line (0). The fluorescence spectrum shown is that given by Reut, Ref. 7.

lying $^2F_{5/2}f^{13}$ state).[4] These results are obtained by comparing the onset of photoconductivity with the onset of absorption due to the localized transition in the impurity. Two examples are shown in Fig. 1. The first is that of SrF_2:Tm^{+2}, a case in which the photoconductivity due to the ionization of Tm^{+2} begins within the first $f \rightarrow d$ absorption band. The second is SrF_2:Yb^{+2}, which shows a quite different photoconductivity spectrum. Photoconductivity is detected well below the onset of strong absorption, and below the onset of the absorption to the forbidden transition in Yb^{2+} (see below). The photocurrent is attenuated in the first absorption band, and it only becomes strong at higher energies. A similar behavior was observed for $CdCl_2$:Cu^+, $CdBr_2$:Cu^+,[6] and BaF_2:Tm^{2+},[4] and we can predict the same for BaF_2:Eu^{2+}. In the case of SrF_2:Yb^{2+} the onset of photoconductivity appears to lie at about 2.8 eV, while the first absorption is detected at about 3.2 eV. If we were to calculate the photoelectron yield per absorbed photon from such data, we would get indefinitely large yields from 2.8 and 3.2 eV. Clearly, there is a weak absorption which begins before the absorption to the localized states. It must be the direct absorption to conduction bandlike states. The object of this paper is to present some evidence as to the spectrum and intensity of this absorption and the corresponding emission.

There have been several examples of impurity ions in host crystals whose emission band is not the inverse of the localized transition seen in absorption, but is strongly red shifted relative to the expected emission band.[6] The case of SrF_2:Yb^{2+} has been studied in detail by Reut[7] and more recently by Ramasesha et al.[8]

The normally expected emission bands are the inverse of the absorption processes to the lowest states of Yb^{2+}, one a forbidden transition, $A_{1g} \rightarrow Eu$, T_{2u} near 3.2 eV, the other an allowed transition, $A_{1g} \rightarrow T_{1u}$ near 3.45 eV.[9] When Yb^{2+} is dissolved in $SrCl_2$, a crystal having the same structure type as SrF_2, one finds these normal emission bands at the expected places, and it is also apparent that the absorption spectra in the two host crystals are nearly identical.[10] Table I gives the spectral comparisons.

The actual emission band in SrF_2:Yb^{2+} peaks at 1.7 eV and is 0.5 eV in width at half height at 80 K; the normal emission bands would peak at 3.34 and 3.10 eV and have a width at half height of 0.08 eV. Figure 2 shows the emission band of SrF_2:Yb^{2+} and the positions of the allowed and forbidden absorption bands.

This comparison shows that light emission from SrF_2:Yb^{2+} is anomalous; it is not the inverse of the localized emission process which occurs in $SrCl_2$:Yb^{2+} as well as in other Yb^{2+}-doped crystals such as $NaCl$:Yb^{2+}.[11]

We now believe that the anomalous emission band is the radiation from an impurity centered exciton which is the lowest excited state of the impurity-crystal system. Excitation of any of the localized levels of the impurity ion leads either to photoionization or to radiationless decay into lower levels. Normally the lowest excited localized level would be the emitting level, but when this level lies above the exciton energy it may decay into it, and the delocalized exciton may then emit instead.

The trapped exciton geometry is probably that expected for a trivalent impurity ion, Yb^{3+} in our case, at a divalent site with an electron delocalized over the 12 next-neighbor metal-ion sites about 4.10 Å away. The collapse of the F^- cube around the Yb^{3+} could displace the F^- ions by about 0.2 Å, and would account for the large Stokes shift.

We do not know the binding energy of the trapped exciton, so as a first approximation let us consider the relationship between the photoionization energy in the lattice and the localized excitation energies. In our systematic study of the photoionization thresholds[4] E_{PI} we presented and tested an obvious electrostatic model, which gives

$$E_{PI} = I - E_m - \Delta E_m - E_{pol} - E_A \ ,$$

where I is the ionization potential of the impurity ion, E_m is the negative electrostatic potential energy at the metal-ion site in the pure crystal (related to the Madelung energy), ΔE_m is the correction for the previous term due to the distortion introduced by the impurity, E_{pol} is the polarization due to removal of an electron from the metal-ion site, and E_A is the electron affinity of the crystal. While some of these quantities are not well known, we can make reasonable estimates, and can use the formula for interpolating missing data points. Since we do not know the electron affinity values, and the ΔE_m values are not very accurate, we have used the calculated results to interpolate between the observed E_{PI} values to help estimate the unknown E_{PI} values.

For Yb^{2+} in the three fluorite structure crystals the only photoconductivity data are for the case of SrF_2:Yb^{2+}. For this case, the photoconductivity threshold at 3.0 eV indeed lies below the lowest localized transition whose origin is at 3.15 eV, and anomalous emission occurs. For BaF_2:Yb^{2+} no normal emission occurs and the anomalous emission may be entirely quenched.[7] In the case of CaF_2:Yb^{2+}, the estimated threshold, somewhat less than 4 eV, seems to lie above the observed zero-phonon line, 3.28 eV. But anomalous emission does occur with high yield. In this example it is clear that the binding energy of the exciton must be taken into account. It is not unreasonable to believe that it is around 0.5 eV, such as to permit the lowest localized level to decay into the exciton state.

In the Eu^{2+} examples, photoconductivity data exist only for CaF_2,[12] in which case the threshold lies above the absorption origin and the expected normal emission occurs. The extrapolated values of the threshold predict normal for SrF_2 and anomalous for BaF_2, in agreement with what is observed.[7]

In the Tm^{2+} series, the threshold lies below the absorption origin only for the case of BaF_2.[4] So far as is known, none of the Tm^{2+} systems emit visible light; however, because of the presence of the $f^{12}\,^2F_{5/2}f^{13}$ state, this state is the lowest of all and emits in the infrared. The trapped exciton, if it existed, could also decay into this localized excit-

TABLE I. Peak position of allowed and forbidden absorption and emission and anomalous emission of Yb^{2+} in three host crystals, in eV. $T = 80$ K.

System	Forbidden Abs.	Forbidden Em.	Allowed Abs.	Allowed Em.	Anomalous Em.	Ref.
SrF_2:Yb^{2+}	3.22	$\cdots$	3.45	$\cdots$	1.69	
$SrCl_2$:Yb^{2+}	3.15	3.04	3.41	3.28	$\cdots$ [a]	9,10
$NaCl$:Yb^{2+}	2.93	2.86	3.25	3.10	$\cdots$	11

[a]In addition to the normal emissions, $SrCl_2$:Yb^{2+} shows unexplained emission bonds under some conditions (Ref. 10).

ed state. This case needs more investigation.

We can conclude that the generalization regarding the occurrence of the anomalous luminescence is justified.

Most of the spectroscopic and photophysical data on the systems CaF_2, SrF_2, BaF_2:Yb^{2+}, and SrF_2, BaF_2:Eu^{2+} were published in a series of papers by Reut,[7] Kaplyanskii, Medvedev, and Smolyanskii,[13] and Zapasski and Feofilov.[14] Without the photoconductivity data, however, no positive interpretation of the anomalous emission bands was reached. Reut did mention the possibility that a charge-transfer state of some kind is the upper state of the SrF_2:Yb^{2+} emission band. The results of this series of papers can now be interpreted in terms of the impurity trapped exciton.

Reut measured the radiative decay rate for the anomalous luminescence of SrF_2:Yb^{2+} and its intensity, both as functions of temperature.[7] He showed that there are two emitting upper levels, the lower having a radiative rate $A_1 = 58$ sec^{-1} and the upper a rate $A_2 = 7900$ sec^{-1} and a spacing of 27 cm^{-1}. These data suggest how to determine the structure of the trapped exciton. This object consists of a Yb^{3+} core in its $^2F_{7/2}$ state which splits in the cubic field into $E_{5/2}$, G, and $E_{1/2}$, probably with $E_{5/2}$ lowest and the only level occupied below 100 K. The electron is probably distributed over the 12 nearest-neighbor Sr^{2+} ions, 4.10 Å away. The hole-electron coupling would give $E_{5/2}$ $\times E_{1/2} = T_2 + A_2$, both forbidden as electric dipole transitions to the ground state A_1. In addition, the hole-electron overlap is very small at this distance, making both transition moment and splitting small. Thus it is reasonable to account for the long lifetime and the 27-cm^{-1} splitting as the transitions from these states to the ground state of Yb^{2+}.

In an earlier paper, Chase measured microwave-optical double-resonance spectra of Eu^{2+} in CaF_2, SrF_2, and BaF_2.[15] He was able to measure the electron resonance in the emitting Γ_8 (or G) level in these hosts, detecting the resonances with the optical emission from this excited state via circular polarization modulation. In the case of BaF_2:Eu^{2+}, he used not the normal blue emission, which does not occur in this system, but the yellow anomalous emission. As he pointed out, one obtains information about the Γ_8 state in spite of the fact that it is decaying into some other state which gives rise to the anomalous emission. Chase, in fact, suggested that this state may be a Eu^{3+} plus lattice electron, in agreement with our conclusions. An interesting consequence of these measurements , which Chase pointed out, is that the spin polarization is preserved through the transfer from the Γ_8 state to the metastable state. Also, it is remarkable that the Γ_8 state lives long enough to be probed by the ESR method. Thus, one could conceivably measure the electron tunneling rate for this system.

If we are correct in ascribing the luminescence to an impurity localized exciton, there must be a corresponding absorption spectrum. The radiative decay rate given by Reut, $A_2 = 7900$ sec^{-1} (and confirmed by us[8,16]), leads to an oscillator strength (though $f = 1.5/\bar{\nu}^2 \tau$) of 10^{-5}. This is about 10^{-4} of the oscillator strength of the $4f \rightarrow 5d$ transition.[9]

If we plot the luminescence and photoconductivity spectra on the same scale, as is done in Fig. 2, we can estimate the position of the zero-phonon line for the exciton in SrF_2:Yb^{2+} to be near 2.5 ± 0.1 eV. A "mirror image" reflection of the emission spectrum about this point is shown in Fig. 2, and it gives us a first approximation of the absorption spectrum. Its shape and the position of its maximum

look reasonably like those of the long-wavelength portion of the photoconductivity spectrum. The true photoconductivity threshold, the dividing energy between bound and unbound states, must lie somewhere within this absorption band.

The absorption coefficients can now be found from the one-dimensional oscillator strength and the shape of the band. Using $f = 1.29 \times 10^{-8} \int \epsilon \, d\bar{\nu}$, where ϵ, the molar extinction coefficient, has units of l/mole cm, we find $\epsilon_{max} = 0.2$. This is indeed a weak absorption band; it is comparable to the intensity found in the broad spin forbidden d-d bands of Fe^{+3}. Nevertheless, direct observation of this band should be possible, and, in fact, it has apparently been observed in one-photon laser excitation experiments.[8] Once the precise absorption coefficients are known, it will be possible to test theroies of the wave function of the electron in the trapped exciton. Further photoconductivity studies may also reveal the true position of the photoionization threshold.

Reut studied the anomalous luminescence of Yb^{2+} in a series of mixed crystals $Ca_{1-x}Sr_xF_2$. Figure 3 shows the position of the band maximum and the value of the band half width as a function of x using data taken from his paper.[7] The remarkable feature of this diagram is that rapid changes in spectral properties occur as Sr is added to CaF_2, but not when Ca is added to SrF_2; and the main effect has occurred before $x = 0.1$. These facts are easily explained by the trapped exciton hypothesis, and they illustrate the nature of the electron distribution of the exciton. One first notes that the band gaps of CaF_2 and SrF_2 are 12.2 and 11.44 eV, respectively. Thus, in a mixed crystal, Sr sites will become low-potential-energy centers for electrons in the conduction band. With 10% of Sr in the CaF_2 lattice, the 12 metal sites at $\langle 110 \rangle$ positions around the Yb^{2+} are certain to have at least one Sr^{2+} ion, and because of its lower potential energy
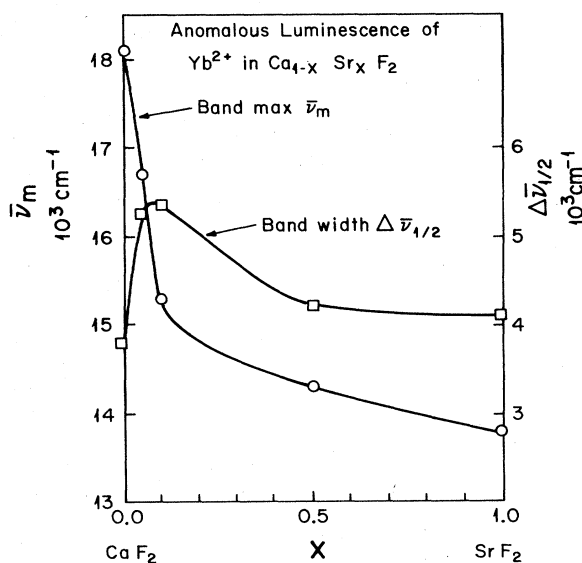

FIG. 3. A plot of the peak position of the anomalous luminescence of Yb^{2+} and its bandwidth at half maximum height vs composition of the mixed crystals $Ca_{1-x}Sr_xF_2$:Yb^{2+}. From data of Reut (Ref. 7); $T = 80$ K.

an electron would tend to stay in its vicinity. The total band shift of 0.53 eV almost equals the band-gap difference, 0.76 eV. The bandwidth results from the inhomogeneity of the surroundings as x changes from 0 to 1; but there is essentially no change beyond $x = 0.5$, because all of the sites have enough Sr to hold the electron in their lowered potential regions.

In a fuller account of this work we will discuss recent measurements on $SrF_2:Yb^{2+}$ (Ref. 8) and also relate the results of the present paper to previous work on $CdCl_2:Cu^+$ and $CdBr_2:Cu^+$.[6]

ACKNOWLEDGMENT

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