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Optical Absorption and Luminescent Emission of the I^- Center in AgCl

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The optical absorption and luminescent emission of AgCl crystals doped with small concentrations of AgI have been investigated. In such crystals, a narrow absorption band with intensity proportional to the iodide content can be resolved from the AgCl lattice absorption at low temperatures. Excitation in this (3.13-eV) band at low temperatures produces a distinct emission band peaking at 2.67 eV. The oscillator strength is found to be low (4×10^{-3}), whereas the radiative lifetime is rather long (6 μsec). A model is proposed in which the excited electronic states for absorption and emission are effective-mass states resulting in small overlap with the closed-shell ground state.

I. INTRODUCTION

IODIDE ions in AgCl or AgBr crystals produce an additional absorption in the visible and ultraviolet regions, which often appears as an extension of the fundamental absorption edge at room temperature.[1] The luminescent emission observed in the silver halides at low temperatures is also greatly modified by the presence of iodide.[2,3] However, previous measurements were not sufficiently detailed to decide whether the iodide impurity produced discrete absorption bands, or merely modified the absorption edge of the host crystal. Thus, it was not clear whether a description of the iodide absorption in terms of localized energy states, or in terms of perturbed-band states, was more appropriate. In the latter case, the absorption can be thought of as characteristic of the mixed crystal rather than as the sum of the individual components. For example, recent work by Joesten and Brown[4] indicates that the absorption of AgCl crystals containing bromide ions should be viewed as being characteristic of the mixed crystals. On the other hand, iodide or bromide ions, incorporated in KCl crystals, produce well-defined absorption bands resolved from the host absorption.[5,6] By examining the AgCl:I system in greater detail, we have been able to reveal discrete absorption and emission bands associated with iodide ions. The nature of the localized energy states involved is inferred from measurements of the absorption oscillator strength and radiative lifetime of the excited state.

II. MATERIALS AND EXPERIMENTAL METHOD

The AgCl:I crystals were grown from the melt either by a Bridgman technique[7] or as sheet crystals solidified between quartz plates.[8] Iodide concentrations were in the range 10^{16}–10^{19} I^- ions/cm^3. In Bridgman growth, the iodide ion shows a segregation in the direction of crystal growth, with an estimated segregation coefficient of about 0.2. This preferential solubility in the melt is probably due to the relatively large radius of the I^- ion compared to that of the Cl^- ion. Mahr[5] has noted a similar behavior of KI diluted in KCl crystals. In sheet crystals frozen rapidly there was little variation in iodide concentration across the sheet, and the observed absorption band was attributed to the nominal added iodide concentration.

The steady-state measurements of the absorption and emission bands were carried out with either a Spectracord Model 4000 or a Cary Model 14RI spectrophotometer. The excitation wavelengths used were the 405- or 365-nm lines from a mercury lamp. The 405-nm line is absorbed in the iodide band only, whereas the 365-nm line is strongly absorbed in the AgCl lattice. The emission spectra were corrected so that they could be presented as plots of the number of emitted photons as a function of photon energy (see Fig. 5).

III. EXPERIMENTAL RESULTS

A. Optical Absorption

Figure 1 shows the absorption edge, at liquid-helium temperature, of pure AgCl crystals, and the absorption of crystals containing about 9×10^{17} iodide ions/cm^3. The additional absorption due to the iodide ion is well resolved under these conditions. It has a peak at 3.13 eV, and a half-width of 0.13 eV. The band does not change with temperature, at least up to about 80°K. There is some broadening above this temperature, but no reliable data can be obtained, since the AgCl edge shifts rapidly toward longer wavelengths, and masks most of the iodide band. This iodide band has a Gaussian shape, as shown in Fig. 2.

In the range of 10^{17}–10^{19} iodide ions/cm^3, the band shape is independent of concentration, and the strength is proportional to concentration. Figure 3 shows the results of such measurements at 77°K. The three curves have been normalized to an iodide concentration of 10^{19} ions/cm^3. The absorption coefficient is about 60 cm^{-1} for this concentration.

These absorption data suggest that the iodide ion is

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[1] C. E. K. Mees and T. H. James, *The Theory of the Photographic Process* (Macmillan Company, New York, 1966), 3rd ed., pp. 23–24.

[2] G. C. Farnell, P. C. Burton, and R. Hallama, Phil. Mag. **41**, 157 (1950).

[3] F. Moser and F. Urbach, Phys. Rev. **106**, 852 (1957).

[4] B. L. Joesten and F. C. Brown, Phys. Rev. **148**, 919 (1966).

[5] H. Mahr, Phys. Rev. **125**, 1510 (1962).

[6] H. Mahr, Phys. Rev. **122**, 1464 (1961).

[7] N. R. Nail, F. Moser, P. E. Goddard, and F. Urbach, Rev. Sci. Instr. **28**, 275 (1957).

[8] W. West and V. I. Saunders, J. Phys. Chem. **63**, 45 (1959).

atomically dispersed in the lattice, and that the interaction between neighboring I^- centers is negligible. The absorption band is thus due to localized electron transitions at isolated I^- centers. The I^- ions are most likely present substitutionally for Cl^- ions. This conclusion is supported by x-ray data,[9] and by the dark ionic conductivity data shown in Fig. 4. It is seen that the ionic conductivity of pure and I^--containing crystals are very nearly identical over the entire temperature range; that is, the iodide impurity does not introduce any additional ionic disorder in the crystals.

Thinner sheet crystals of AgCl with as much as 1% AgI were examined for higher-energy absorption bands which might be associated with the iodide impurity. However, no such absorption bands were found out to about 4 eV.

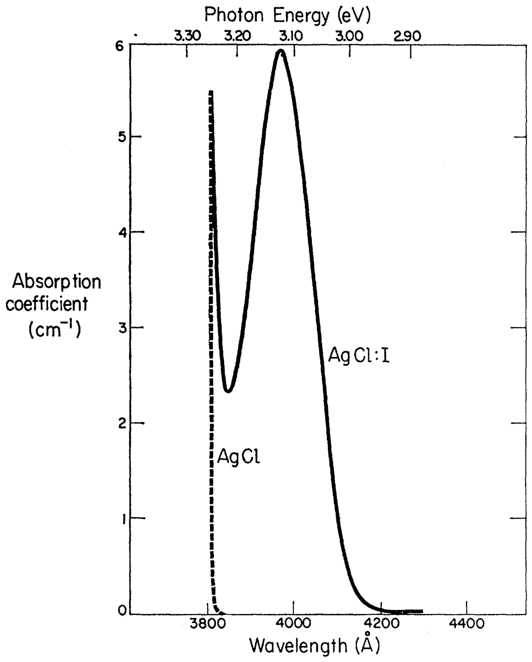

FIG. 1. Optical absorption at 5°K of a pure AgCl crystal (on left) and AgCl containing 9×10^{17} iodide ions/cm^3. The crystal is 4.2 mm thick.

The oscillator strength of this transition can be calculated by using the Smakula formula as given by Dexter.[10] This formula relates the oscillator strength f_{if} to the number of centers N by

$$N(\text{cm}^3)=8.7\times10^{16}\frac{n}{(n^2+2)^2}\frac{1}{f_{if}}\alpha_{\max}(\text{cm}^{-1})W_{1/2}(\text{eV}),$$

where n is the index of refraction of the host lattice at a wavelength corresponding to the band maximum; $\alpha_{\max}$ is the absorption coefficient at the band maximum; and $W_{1/2}$ is the width of the band at half-maximum. Using the values $n=2$, $N=10^{18}/\text{cm}^3$, $\alpha_{\max}=6$ cm^{-1}, and $W_{1/2}=0.13$ eV, one obtains $f_{if}=4\times10^{-3}$.

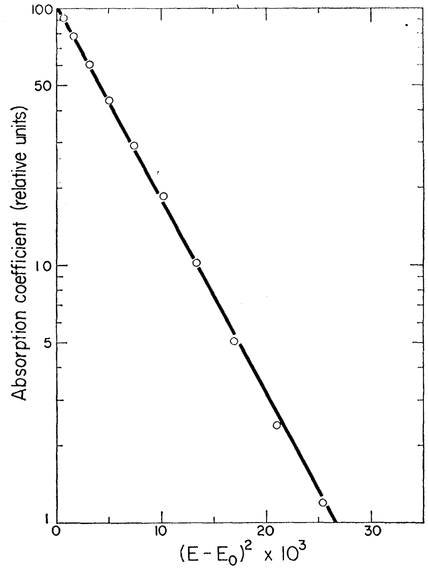

FIG. 2. Data of Fig. 2 replotted so as to reveal the Gaussian form of the iodide absorption band. Only the low-energy half of the band is shown. E_0 is chosen as 3.125 eV, and the half-width $W_{1/2}$ is 0.130 eV.

The iodide ion I^- is isoelectronic with the Xe atom. The ground state of that atom is a $5p^6$-electron configuration ($^1S_0$) and the lowest excited state is a $5p^56s$. This excited state is a P state, although in this heavy

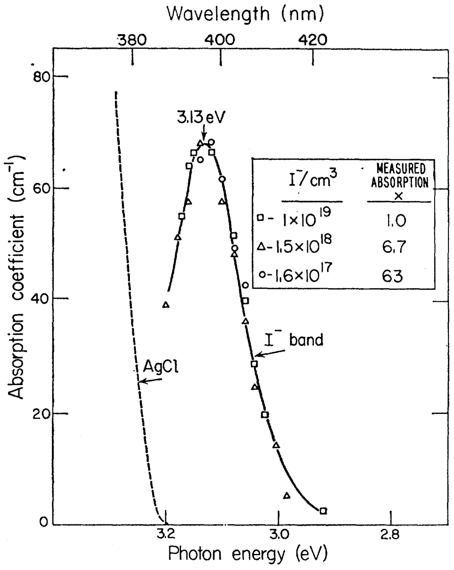

FIG. 3. Optical absorption of AgCl:I crystals at 77°K. The iodide band is shown for three different concentrations. The data for the two lower concentration samples were multiplied by the factor shown in order to normalize all the data at 3.13 eV. The *band* shape is seen to be independent of concentration in this range.

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[9] R. B. Wilsey, Phil. Mag. 42, 262 (1921).

[10] D. L. Dexter, Phys. Rev. **101**, 48 (1956).

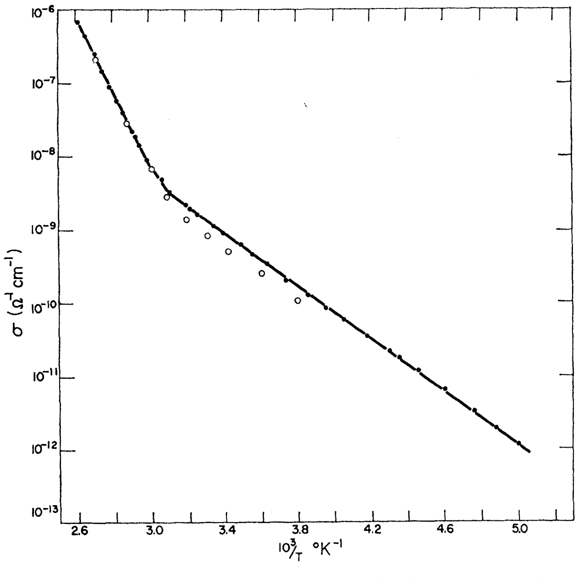

FIG. 4. Dark ionic conductivity (D.C.) of pure AgCl (open circles) and AgCl:I crystals (filled circles). The iodide-ion concentration is about 10^{18} ions/cm^3. The conductivity difference in the extrinsic range is of the order of that observed between different pure crystals. We conclude that the iodide ion has little effect on the ionic disorder.

ion (I^-), one must use the *J-L* coupling scheme[11] to describe the excited state. Thus, we are dealing with an *S* to *P* transition, which is parity-allowed, and therefore the low oscillator strength is apparently not due to a parity-forbidden transition.

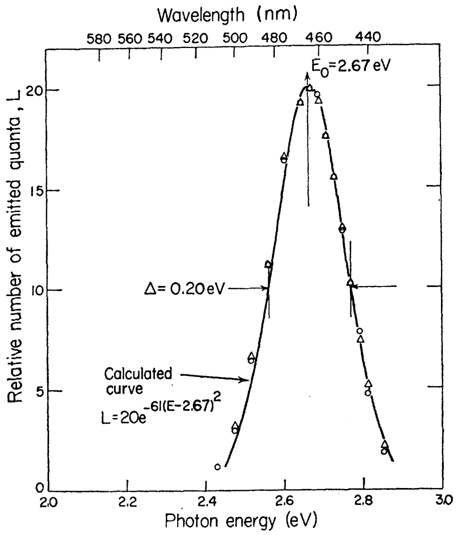

FIG. 5. Steady-state emission band in AgCl:I^- crystals at 77°K produced with excitation in the iodide band only (405 nm; circles) or with excitation in the silver chloride edge (365 nm; triangles). The iodide-ion concentration is about 10^{18} ions/cm^3. Both emission bands fit a curve of the form $L=20e^{-61(E-2.67)^2}$.

B. Steady-State Luminescent Emission

Excitation in the iodide band at low temperatures produces a luminescent emission, shown in Fig. 5. The emission band has a peak near 2.67 eV, and a half-width of about 0.2 eV at 77°K. The energy difference between absorption and emission (Stokes shift) is about 0.46 eV and the width of the emission band is not much greater than that of the absorption band. The Stokes shift of 0.46 eV is about 15% of the absorption energy and is small compared to that observed in the case of other centers in the silver and alkali halides. For example, the absorption and emission bands found for Cu^{+1} ion in AgCl[12] or the *F* center in KCl[13] show a Stokes shift of greater than 50% of the absorption energy. This emission band is distinctly different from that observed in pure AgCl.[14] In that case, ultraviolet excitation produces an intrinsic green emission peaked near 2.5 eV and with a half-width nearly 0.4 eV.

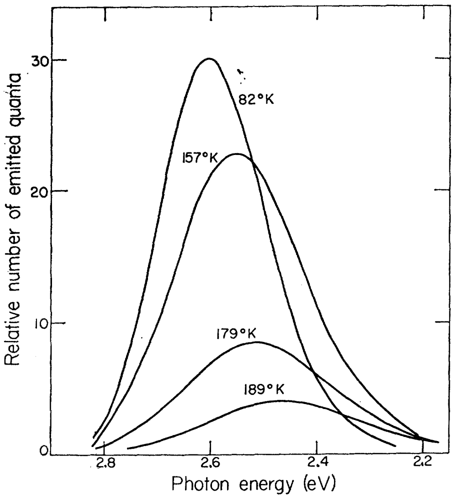

FIG. 6. Steady-state emission band in AgCl:I^- crystals at several different temperatures.

At elevated temperatures, this emission band associated with the iodide ions is thermally quenched, and the band also broadens and shifts somewhat to longer wavelengths as competing nonradiative recombination begins to be important. The emission spectrum at higher temperatures is shown in Fig. 6. The emission is essentially quenched above 200°K.

C. Emission and Photoconductive Response with Pulse Excitation

Pulse-excitation studies of the luminescent emission and photoconductive response were carried out with the apparatus shown schematically in Fig. 7. Light

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[11] G. Racah, Phys. Rev. **61**, 537(L) (1942).

[12] R. S. Van Heyningen and F. Moser, Bull. Am. Phys. Soc. **8**, 230 (1963).

[13] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Macmillan Company, New York, 1962), p. 77.

[14] G. C. Smith, Phys. Rev. **140**, A221 (1965).

from a short-duration (30-nsec) flashlamp was passed through a monochromator, and the selected excitation wavelength imaged on the sample, which was contained in an optical cryostat. The emission was detected at right angles to the excitation, and displayed on an oscilloscope. Appropriate filters in front of the photomultiplier tube excluded any exciting light scattered in that direction.

The luminescent decay following pulse excitation in the iodide band was studied as a function of temperature. The emission showed a decay time which was strongly temperature-dependent. The results of such measurements are shown in Fig. 8, in which we have plotted the radiative lifetime as a function of temperature. Near 4.2°K, the lifetime is about 6 μsec, but drops rapidly in the neighborhood of 25 to 30°K. The sharp drop in the neighborhood of 25°K probably occurs because of thermal ionization of electrons into the conduction band, where they are captured in other electron traps known to be present in high concentration at these temperatures. If this is thermal ionization of the relaxed excited state, one may estimate the depth of this state below the conduction band. Using the expression[15]

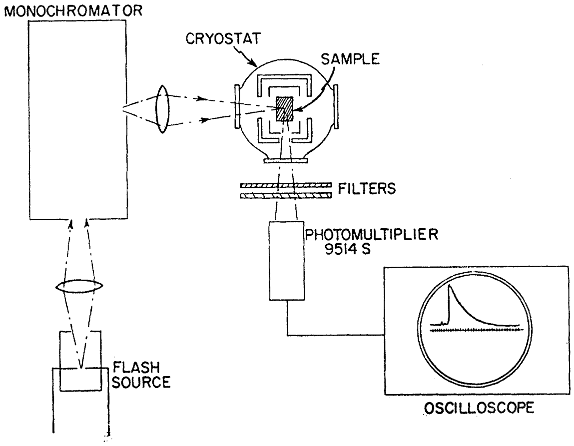

FIG. 7. Schematic diagram of apparatus used in pulse-excitation luminescence studies. The flash source has a duration of about 30 nsec.

$$1/\tau = 1/\tau_R + 1/\tau_0 e^{-E/KT},$$

where τ_R is the radiative lifetime, $1/\tau_0$ is a frequency factor, and E is the depth of the excited state, we can approximately fit the experimental results if the following parameters are chosen:

$$\tau_R = 6\times10^{-6}\ \text{sec},$$

$$\frac{1}{\tau_0} = 1.5\times10^{13}\ \text{sec}^{-1},$$

$$E = 4.2\times10^{-2}\ \text{eV}.$$

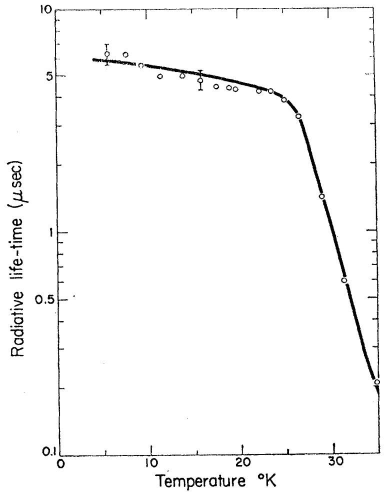

FIG. 8. Radiative lifetime of the excited I^- center as a function of temperature. The lifetime is taken as the $1/e$ value of the luminescent decay curve produced by flash excitation.

Thus, we see that the thermal depth of the relaxed excited state (which is E in the expression) is quite small. This state is even more shallow than that of the relaxed F center in the alkali halides,[15] which is about 12×10^{-2} eV.

So far, the results of the pulse work have been described only for *excitation in the iodide band*. If the pulse excitation is optically filtered so that absorption is in the *AgCl lattice*, then, at temperatures near 10°K, there is no measurable emission. At temperatures near 40°K, prolonged flash excitation or continuous excitation does give an observable emission. This behavior can be understood in terms of competing electron traps, although we do not have any atomic description of these traps. Previous work[16] on electron mobility in silver chloride has led to estimates of the electron-trap concentration at various temperatures. At temperatures of 10°K or below, there are apparently effective electron

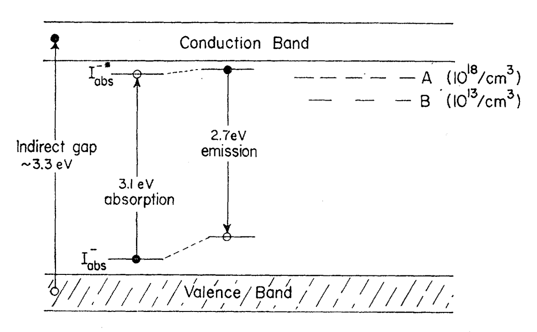

FIG. 9. Schematic energy-level scheme of AgCl:I^- and unidentified A and B trapping centers. The iodide states in absorption differ from those in emission because of lattice relaxation effects.

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[15] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

[16] R. S. Van Heyningen and F. C. Brown, Phys. Rev. **111**, 462 (1958).

traps in concentrations exceeding $10^{18}/\mathrm{cm}^3$. At 80°K, the concentration of effective traps is much less, perhaps about $10^{13}/\mathrm{cm}^3$.

Figure 9 shows these traps very schematically on a simple spatial energy-band diagram. The iodide absorption band at 3.13 eV corresponds to the transition from I^- to I^{-*}. We estimated that I^{-*} lies about 0.04 eV below the conduction band. Below 30°K, pulse excitation in the iodide band measures the radiative lifetime, since no thermal ionization occurs. On the other hand, gap excitation of 3.3 eV, or greater, puts electrons into the conduction band at *any* temperature. Below 10°K, the high-concentration A traps compete very efficiently with the iodide centers for the electrons, and the luminescence is effectively quenched until most of these traps are filled. Since each flash generates only about 10^{10} carriers, we see no luminescence with band-gap excitation at very low temperatures even after many flashes. High-intensity steady excitation does eventually fill these traps, although we observe a considerable inertia, as expected.

At temperatures above 50°K, A traps are no longer effective and only B traps, present in much lower concentration, are effective. These can also quench the flash-induced luminescence with gap excitation. The pulse height of the emission reaches its maximum value after about 1000 flashes. This is in qualitative agreement with the estimate of 10^{13} traps/cm^3 and 10^{10} electrons released per flash.

IV. DISCUSSION

On the basis of the experimental results, we may conclude that iodine substitutionally replaces chlorine in the AgCl lattice and does not segregate even at high concentrations. Also, the I^- ion has a bound excited state in the crystalline environment giving rise to discrete absorption and emission bands. The oscillator strength of the absorption is 4×10^{-3} and the radiative lifetime of the emission is about 6 μsec. Since an allowed dipole transition should occur in about 10^{-8} sec, the relative emission probability is about 1.6×10^{-3}. Thus, we find low but roughly equal transition probabilities for both absorption and emission. We have already pointed out that the Stokes shift is quite small for a center in an ionic crystal. Owing to the usual displacement of adjacent lattice ions when the charge distribution is changed (i.e., an electronic transition occurs), the emission energy is often less than one-half of the absorption energy for centers in ionic solids.

Taglauer and Waidelich[17] studied the properties of thin-film mixtures of AgCl-AgBr. They found that the exciton peaks characteristic of AgCl shifted linearly to those characteristic of AgBr as the concentration of the latter was increased. Joesten and Brown[4] found that bromine in AgCl produced no discrete band such as was found here, but that a continuous shift of the indirect absorption edge to longer wavelengths was produced upon bromine addition. In this case, a virtual-crystal model,[18] which has been successfully applied to Si:Ge mixtures,[19] correctly describes the situation.

The virtual-crystal model is applicable when a potential, which is an average of the two kinds of atoms weighted by their concentrations, gives the correct transition energies. Such is the case when an exciton wave function samples a large number of lattice sites—i.e., is of the Wannier type.[20]

By contrast, the study of mixed KCl:KI and KCl:KBr by Mahr[5,6] showed that the characteristics of the individual components were preserved in the mixture. Baldini and Teegarden[21] found that thin-film mixtures of RbCl:RbI and KCl:KI show structure analogous to the exciton structure of the pure materials. In these cases, the excitons are primarily of the Frenkel or tight-binding type.

Cardona[22] has studied the absorption of thin films of AgI in both the wurtzite and zinc-blende phases. In both phases, absorption peaks occur at about 3.0 and 3.8 eV which may be described as direct excitons associated with the Γ_8 and Γ_6 valence bands, respectively. This is just the familiar spin-doublet which occurs when the iodine atom is left in either a $j=\frac{3}{2}$ or $j=\frac{1}{2}$ state. The position of these peaks is about the same in the two crystalline structures although Γ_8 is split by the crystal field in the wurtzite structure. Corresponding peaks are found in CuI at about 3.1 and 3.7 eV. Also CuCl-CuBr systems behave much the same as AgCl-AgBr mixtures in that the identity of the individual components is destroyed. As Wannier excitons seem to predominate in the silver and cuprous halides, probably due to the high dielectric constants, we might expect the AgCl:AgI system to be described by a virtual-crystal model. However, our experiments show that at least the low-energy component of the iodine spin-doublet forms a discrete band within the gap. We should not be surprised that this absorption band occurs at about the same energy (3.13 eV) as the Γ_8 exciton in AgI and CuI.

We must conclude then that the discrete state formed by I^- in AgCl is related to the first exciton in AgI and can be described as a trapped exciton. This description has also been applied to I^- in KCl and RbCl.[21] It also follows then that this trapped exciton is of the Wannier type. Such a state is consistent with low oscillator strength and small Stokes shift for emission.

A situation giving rise to a small Stokes shift has been

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[18] R. Parmenter, Phys. Rev. **97**, 587 (1955).

[19] R. Braunstein, A. R. Moore, and F. Herman, Phys. Rev. **109**, 695 (1958).

[20] R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1963), Suppl. 5.

[21] G. Baldini and K. Teegarden, J. Phys. Chem. Solids **27**, 943 (1966).

[22] M. Cardona, Phys. Rev. **129**, 69 (1963).

discussed by Fowler and Dexter.[23] In a transition to a very diffuse orbital, the electronic wave function is screened from the ionic rearrangement near the core by the dielectric medium. The excited electron before and after relaxation sees about the same potential; hence, the excited-state wave functions for absorption and emission are quite similar when both are effective-mass states. Also, if the excited-state wave functions are diffuse and the ground-state wave functions are localized in the unit cell, the overlap integral is small. These circumstances would account for a low transition probability in absorption or emission (i.e., low oscillator strength or anomalous radiative lifetime).

Fowler and Dexter[23] have developed a relation between oscillator strength and lifetime in terms of the dipole matrix elements for absorption and emission and certain other parameters of the crystalline environment. They consider the change in the Einstein A and B coefficients of an electronic transition when the atom or center is in a solid, and the local environment of the center is taken into account. They show that, in general, the Einstein A and B coefficients are not equal in an ionic solid, but that the oscillator strength f_{ge} and the radiative lifetime τ_{eg}, are related by the following expression:

$$f_{ge}\tau_{eg}=\left(\frac{\epsilon_0}{\epsilon_{\mathrm{eff}}(E_{eg})}\right)^2\frac{\hbar^2c^3m^*}{2e^2n(E_{eg})}\times\frac{E_{ge}}{(E_{eg})^3}\left\{\frac{\sum_{g,e}|\langle r_{ge}\rangle|^2(2J_e+1)}{\sum_{g,e}|\langle r_{eg}\rangle|^2(2J_g+1)}\right\},$$

where ϵ_{eff} is the effective field at the center, and ϵ_0 is the average field in the medium. E_{ge} and E_{eg} are the absolute values of the absorption and emission energies, respectively; $n(E_{eg})$ is the index of refraction at wavelengths corresponding to the emission band; m^* is the appropriate value of the effective mass of the electron undergoing transition. The last part of the expression is the ratio of matrix elements for absorption ($g\rightarrow e$) and emission ($e\rightarrow g$) multiplied by the degeneracy factors, $(2J+1)$.

The quantities f and τ have been measured experimentally. One can then calculate the ratio of matrix elements using this equation, and taking values for the various parameters consistent with our model that the excited state is diffuse before and after local relaxation. If, then, the ratio of matrix elements is about unity, it means that this assumption is self-consistent. Since we are assuming a diffuse excited state, we let the effective field at the center ϵ_{eff} be equal to the average field ϵ_0 in the medium. The index of refraction is about 2, and the effective mass m^* is taken to be equal to the free-electron mass since it enters the equation as the mass appropriate to the ground state. The lowest energy transition in Xe is $\Delta J=1$ from $J_e=1$ to $J_g=0$, and this is what we use here. Substituting the experimental values of τ, f, E_{ge}, and E_{eg}, we get a value of 1.3 for the ratio of the matrix elements. The choice of m^* is open to some question, and we could change this value by using other possible values. However, we still place limits on the ratio of elements at between 0.8 and 1.6. Thus, our model of diffuse excited-state wave functions which change very little upon lattice relaxation is self-consistent when the experimental parameters are inserted in the Fowler-Dexter formula.

V. CONCLUSION

Our model then pictures the electronic transition at 3.13 eV as occurring between a localized ground state on the I^- ion to an effective-mass or Wannier-type state. The hole state created at the iodine is the $j=\frac{3}{2}$ state which is so energetically removed from the lattice states that it does not mix with them. If this picture is correct, one should be able to detect a larger separation of the chlorine spin-doublet due to the mixing of the $j=\frac{1}{2}$ iodine state with the Γ_6 valence-band states. Further work hopefully will verify this assumption.

ACKNOWLEDGMENTS

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[23] W. B. Fowler and D. L. Dexter, Phys. Rev. 128, 2154 (1962).