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Direct radiative recombination of core-hole highly excited states in CsCl

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The $Cs^+ 3d$ spectra in CsCl have been investigated in detail. The $3d$-f transitions are less intense than the $3d$-p transitions both in the emission and absorption spectra. Resonant emissions due to the direct radiative decay of the $Cs^+ 3d^9 4f^1$ excited state have been observed; they are asymmetrical and about fifty times less intense than the symmetrical resonant emissions seen in the La $3d$ spectrum. These differences may be explained in terms of interactions between the Cs^+ excited state and the continuum states. This is the first evidence of a resonant x-ray emission from an autoionizing bound excitation state.

I. INTRODUCTION

The nd absorptions for elements $Z \geq 54$ have been extensively studied[1–7] in the aim of investigating whether these transitions take place towards bound $4f$ levels or towards ϵf levels in the continuum. It has been predicted for $Z < 56$ that the oscillator strength of the $d \rightarrow f$ transitions is entirely taken up by $d \rightarrow \epsilon f$ transitions well above the $4d$ thresholds. For Cs, the $4d$ photoabsorption has been observed in crystalline[8] and molecular CsCl (Ref. 9) and Cs metal[10] and compared to the spectrum of atomic Cs.[11] As expected the four spectra present a marked similarity because they are all dominated by a "giant resonance" approximately 30-eV large peaked above threshold; this peak is interpreted by $4d$-ϵf transitions. Only the features situated immediately under the threshold differ from one material to the other because the solid-state effects are important in this range. These features are dominated by the $4d$-$6p$ transitions. A weak peak which has no corresponding peak in the spectra of atomic Cs is seen at approximately the same energy in the spectra of CsCl and Cs metal: It has been ascribed to transitions to f-like symmetric localized levels.[9]

In contrast with much work done in the Cs $4d$ range, only a few data at relatively low resolution have been reported on the $3d$ photoabsorption. Much less pronounced peaks than expected have been observed in the $3d_{3/2}$ and $3d_{5/2}$ spectra of Cs I.[12] They have been identified as $3d$-ϵf transitions. As for transitions to the p levels, they have been assumed to contribute only by a faint feature situated between the two principal peaks. On the other hand, the $3d$ photoabsorption of Cs^+ in solid CsCl has been interpreted essentially in terms of transitions to discrete $4f$ levels, $3d$-ϵf transitions contributing also weakly to the spectrum.[13]

It appeared of interest to determine the relative contributions of the transitions from Cs $3d$ levels to p levels and to discrete and continuum f levels. Among the various available experimental methods, the resonant x-ray emission spectroscopy[14,15] is the most convenient for determining the discrete or not discrete character associated with excitation states having a core hole. This method consists in studying the direct radiative recombination consecutive to the excitation of an atomic subshell, i.e., here consecutive to the formation of excitation states having a $3d$ hole. With the resonant Auger spectroscopy, which has been used for the first time in solids to study the $nd\,4f^{m+1}$ states of the rare earths[16–18] and which has been largely developed since,[19] the resonant x-ray emission spectroscopy is the only method which makes possible the determination of the "true resonant" character of a state. It can also yield important information regarding configuration interaction effects between discrete states and continuum states.

We present here a detailed analysis of Cs^+ $3d$ electron-stimulated-emission and photoabsorption in the solid halide CsCl. Besides the emissions occuring in the $3d^9$ ion, one expects that resonant $3d$ emissions will be observed whenever bound states of configuration $3d^9nf^1$ having a sufficient radiative decay probability are formed. Only the absorption transitions corresponding to these resonant emissions involve discrete *f* levels, the others involve *f* or *p* levels in the continuum. Then by comparing the 3*d* emissions and 3*p* and 3*d* absorptions, it becomes possible to propose a description of the photoabsorption in terms of discrete or extended levels above the bottom on the conduction band. In Sec. II, we briefly describe the experimental procedure. Our experimental results are presented in Sec. III together with a concise analysis of present data concerning the electronic structure in CsCl. These results are discussed in Sec. IV. In Sec. V we give some concluding remarks.

II. EXPERIMENTAL PROCEDURE

Among the different cesium halides, the chloride is the most stable which accounts for its being chosen generally for spectroscopic studies. The samples have been prepared by dispersion of finely powdered pure CsCl in a solution of formvar in chloroform. The suspension was spread on a thin aluminium foil (about 0.5 μm thick) for obtaining the absorption screen or on a well-cooled copper target to obtain the emissive anode. By this mean, after evaporation of the chloroform a continuous CsCl sheet was obtained. As the grains of the powder were embedded in the formvar both interactions with the substrate and contaminations due especially to hydratation by the residual atmosphere (5×10^{-7} Torr) were avoided. Due to the preparation method, the absorption screen thickness was not precisely known; it is reasonable to suppose that it was several tens of nm thick.

A 50-cm-radius bent crystal KAP (potassium acid phtalate) vacuum spectrometer was used. It was fitted with a thin polypropylene film windowed Ar-CH_4 gas flow proportional counter as a detector. The resolution was better than 1 eV at 750 eV. In this spectral range the experimental widths have been corrected by means of a quadratic relation.[20]

The absorption spectra were recorded using the bremsstrahlung emitted by a W target excited under 1400 V. Several CsCl targets have been used for the emission. The spectra were recorded at 1400 V and 20 to 50 mA/cm^2. No modifications in the spectra have been observed within the electron beam current limits; moreover, we checked that no change of spectra or samples occurred as a function of the irradiation time.

III. EXPERIMENTAL RESULTS

A. Electronic structure

CsCl is an ionic insulator with closed electronic shells which crystallizes in a simple cubic lattice at room temperature. The valence states are formed by the chlorine 3*p* shell broadened into a band of width about 1.8 eV.[21] The outermost electrons of the Cs^+ ion are the 5*p* electrons; their threshold energy relative to the vacuum level as determined by photoelectron spectroscopy is 13.7 eV.[21] The splitting of the Cs^+ 5*p* core levels is about 1.7 eV; it is approximately the same as the spin-orbit splitting of the Cs 5*p* atomic level. The Cs^+ 5*p* levels retain a strong atomic character in the solid as generally observed in ionic, large-gap crystals.

The width of the band gap as determined from optical spectra[22] is 8.3 eV. Exciton peaks have been observed in the optical spectra: The binding energies of the lowest-energy excitons at Γ have been estimated to be 0.8 eV for the Cs^+ 5*p* core exciton and 0.5 eV for the valence-band exciton.[21]

The energy-band structure of simple-cubic CsCl has been computed by means of a pseudopotential approach.[23] From this calculation, the lowest conduction band is *s*-*d*-like and *d*-like conduction bands are present at less than 2 eV above the first band. The first *p* levels are situated about 3 eV above the bottom of the conduction band and are widely spread.

B. M_{III} absorption

Owing to the dipole selection rules, the M_{III} spectrum corresponds to the $3p_{3/2}$-6*s* 5*d* transitions. We have analyzed the Cs M_{III} absorption in CsCl. It presents a discontinuity together with a broad smooth maximum. Taking into account the symmetry of conduction states as indicated in the preceding paragraph, the absorption discontinuity corresponds to the excitation of electrons from the $3p_{3/2}$ inner level towards the bottom of the conduction band. We have determined its position with respect to the $3p_{3/2}$ level to be 998.8 ± 0.3 eV.

Because the oscillator strength of the $l\rightarrow l+1$ transitions is expected to be higher than that of the $l\rightarrow l-1$ transitions, the maximum reflects the presence of 5*d*-like symmetry empty levels situated close to the bottom of the conduction band. It is very difficult to resolve features in the 5*d* density of states or excitonic transitions since the $3p_{3/2}$

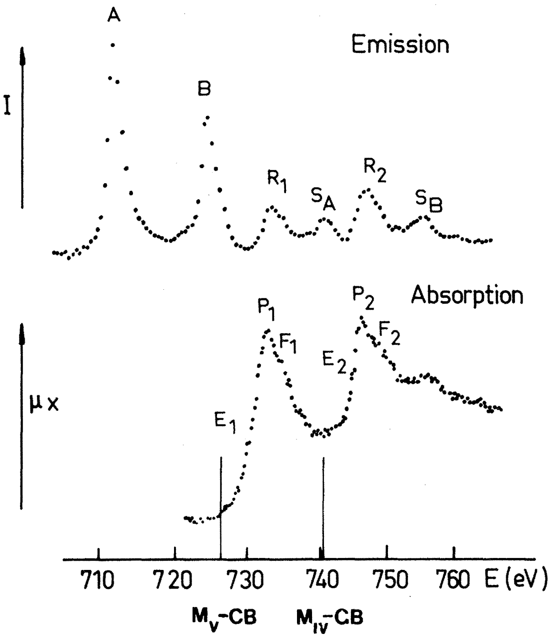

FIG. 1. Cs^+ $3d$ emission and absorption spectra in CsCl.

level has a very short lifetime. Indeed, M_{III}-$M_{\mathrm{IV,V}}N$ and M_{III}-$M_{\mathrm{IV,V}}O$ Coster-Kronig transitions are energetically possible for cesium in the free atom and in solid and, as shown by McGuire[24] for Xe $3p_{3/2}$ level, these transitions are very fast. They contribute to a large extent to the width of the $3p_{3/2}$ level.

C. $M_{\mathrm{IV,V}}$ spectra

The Cs $3d$ emission and absorption spectra in CsCl are plotted in Fig. 1. The bars indicate the position of the bottom of the conduction band with respect to the M_{IV} and M_{V} levels as obtained from the M_{III} discontinuity and the M_{III}-M_{IV} and M_{III}-M_{V} energy differences; the differences were determined from the data of Ref. 25.

1. Emission

In the emission spectrum, three types of transitions are observed: (i) intense lines labeled *A* and *B* situated towards the lower energies; (ii) lines labeled R_1 and R_2 approximately in coincidence with the absorption maxima; (iii) faint lines labeled S_A and S_B towards the higher energies.

The *A* and *B* lines are due to the $5p$-$3d$ transitions. Three lines are expected corresponding to transitions $5p_{3/2}$-$3d_{5/2}$, $5p_{1/2}$-$3d_{3/2}$, and $5p_{3/2}$-$3d_{3/2}$. By taking into account the statistical weights of various subshells, these three lines must be in the ratio 9:5:1. The more intense line situated at 713.4±0.3 eV corresponds to the $5p_{3/2}$-$3d_{5/2}$ emission; it is fitted by a Lorentzian curve of full width at half maximum (FWHM) 2.1 eV. Taking for the $3d_{3/2}$-$3d_{5/2}$ and $5p_{1/2}$-$5p_{3/2}$ splittings 14.0 eV (Refs. 25 and 26) and 1.7 eV,[21] respectively, we have plotted two other Lorentzian curves situated at 725.7 and 727.4 eV, with the same FWHM as the first curve. The three lines are drawn according to the ratios expected. The curve obtained fits the observed emission except between the two lines due to line *A* satellites (Fig. 2). One deduces that the three lines have approximately the same width. Then the $3d_{3/2}$ and $3d_{5/2}$ subshells have similar widths in agreement with the fact that no $3d_{3/2}$-$3d_{5/2}X$ Coster-Kronig transition (*X* is a level of Cs^+) is possible energetically in CsCl. The sum of the widths of $3d_{5/2}$ and $5p_{3/2}$ levels is deduced to be 1.7 eV from the FWHM of line *A* account taken for the instrumental broadening. From photoelec-

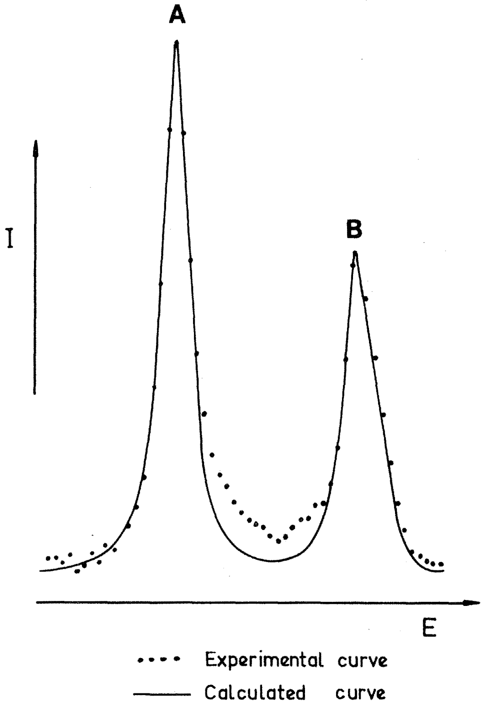

FIG. 2. $5p$-$3d$ emission of Cs^+ in CsCl compared with Lorentzian curves.

tron spectra[21] the width of each $5p$ subshell is found to be less than 0.5 eV. Thus, the width of each $3d$ subshell may be estimated to be about 1.2 – 1.5 eV. To our knowledge no theoretical values of the width of Cs levels are available for comparison. Let us note that the width calculated for the $3d_{3/2}$ subshell in the Xe free atom[24] is 0.68 eV. The discrepancy is larger than the experimental errors.

By analogy with the $3d$ emission spectra of lanthanum and barium, we interpret the lines R_1 and R_2 as $3d^9 4f^1$-$3d^{10}$ resonant emissions.[27,28] This interpretation takes into account the fact that the most intense of the two emissions, labeled R_2, is situated close to the $3d_{3/2}$ threshold, i.e., involves the $3d^9 4f^1\ {}^1P$ excited state. Moreover, the relative intensities of R_1 and R_2 lines are qualitatively in the ratio of the probabilities of dipole transitions between the ground state and the $3d^9 4f^1\ {}^1P$ and ${}^3D$ excited state expected for the Xe-like ions. Contrary to the lines observed for lanthanum[29] the resonance lines R_1 and R_2 do not have a Lorentzian shape; they are asymmetrical and can be fitted by Breit-Wigner-Fano curves[30] having both the same width $\Gamma = 3.1$ eV and the same shape parameter $q = 3$ and the heights in the ration 1:1.3 (Fig. 3). The shape of the resonance lines suggests that the bound state $3d^9 4f^1$ cannot be regarded as isolated but interchannel interactions are present between the state and the conduction states of same energy. Then, the excitation strength might transfer by autoionization from the bound state to the extended states. Consequently, the resonant processes are clearly less intense here than for elements of higher atomic number. Indeed, from the Cs and La emission spectra, we find that the intensity of the resonance line associated with the ${}^3D$ excited state is about 50 times weaker in Cs than in La when normalizing the two spectra with respect to the $3d_{5/2}$-$5p_{3/2}$ transition. From the observation of the asymmetrical resonance lines, one deduces that, in the presence of a $3d$ inner hole, a Cs^+ $4f$ autoionizing bound level lies widely above the bottom of the conduction band in CsCl, at about 7.7 eV from it.

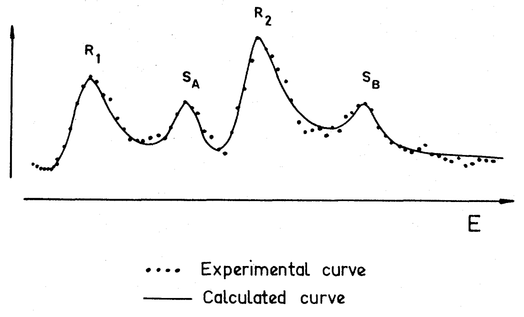

FIG. 3. $3d$-$4f$ emission of Cs^+ in CsCl compared with Fano curves and $5p$-$3d$ satellite emissions compared with Lorentizian curves.

Lines S_A and S_B are situated on the high-energy side of each resonant emission. Whereas R_1 is less intense than R_2, S_A is more intense than S_B and the ratio of the intensities, S_A:S_B, is approximately as for A and B lines. Similarly, the widths of S_A and S_B are narrower than those of R lines and similar to those of A and B. S_A and S_B may be fitted by two Lorentzian curves having a FWHM of 2.4 eV and intensities about 10% of the $5p$-$3d$ transitions (Fig. 3). As a consequence we interpret them as satellites of the $5p$-$3d$ emissions. The probabilities for electron shake-off in Xe have been calculated for the various subshells as the result of a sudden vacancy in the $3d$ level.[31] The higher probability is for $5p$ subshell; it is 10.5%. This suggests that the satellite emissions are of the type $3d^9 5p^5 \rightarrow 3d^{10} 5p^4$. However, let us note that the $3p$-$3d$ N and $3p$-$3d$ O Coster-Kronig processes are possible in our experimental conditions and that the splitting between the $5p$-$3d$ lines and the satellites is relatively large. Calculations of the energy of various possible emissions processes should be necessary to conclude on this point. It is important to underline that, in contrast with the Ba and La $3d$ spectra, the Cs $3d$ emission spectrum shows a predominance of p-d transitions with respect to f-d transitions.

2. Absorption

The Cs^+ $3d$ absorption spectrum presents two strong variations of the photoabsorption coefficient. Each onset corresponds, in principle, with the excitation threshold of the $3d_{5/2}$, or $3d_{3/2}$, subshell to the first empty levels of appropriate symmetry. Their middle points noted E_1 and E_2 on the figure are situated, respectively, at 4.5 and 5.0 eV above the bottom of the conduction band. They are followed by two structured maxima spreading over about 5 eV and two absorption edges are clearly visible. A very faint shoulder is observed on M_V, and not on M_{IV}, at the position of the bottom of the conduction band. Because of the dipole selection rules, the main features of the spectrum must correspond to transitions to the p

or f symmetry empty levels. As for the faint structure at the $3d_{5/2}$ threshold, it presumably corresponds to the $3d_{5/2}$-$6s$ transitions whose probability is weak.

The presence of f-d resonant transitions has been revealed by the analysis of the Cs^+ $3d$ emission spectrum. Two $3d$-$4f$ absorption lines having the heights in the ratio 1:1.3 (see Sec. III C 1) are therefore expected on the high-energy side of the two main absorption peaks P_1 and P_2. Because of the relaxation effects due to the autoionization processes and eventually to the polarization of the neighboring negative ions consecutive to the formation of the core hole in the positive ion (see following paragraph), an electronic rearrangement could be expected in the excited state. This may produce a shift of the resonant absorption with respect to the resonant emission. Then the d-f absorption lines could be assumed to be situated at the position of the features labeled F_1 and F_2 on Fig. 1. So a shift of 0.7 eV should be found between the $3d$-$4f$ emission and absorption lines. It must be noticed that in the lanthanides, no shift is seen between the resonant emissions and absorption lines; but in this case, the excited states are not autoionizing. Supplementary theoretical and experimental data should be necessary to conclude on this point.

On the other hand we have seen in Sec. III A that p levels are expected from about 3 eV above the bottom of the conduction band and on a wide range; this is in agreement with our observation of strong absorptions at about 730 and 744 eV. Because no $3d_{3/2}$-$3d_{5/2}X$ Coster-Kronig transitions are possible for Cs^+ in CsCl, the transitions from $3d_{5/2}$ and $3d_{3/2}$ to the extended p levels are expected to be in the ratio of the statistical weights of the $3d$ subshells, i.e., 3:2. The variations of the absorption coefficient close to the $3d_{5/2}$ and $3d_{3/2}$ thresholds are indeed approximately in the ratio 3:2. Thus, the predominant features in the absorption spectrum can be ascribed to transitions to the p levels. Let us note that at the onset the absorption coefficient rises slowly. This behavior is apparently not excitoniclike; however, because of limitations in the resolution it is not clear whether or not an exciton peak is present under the threshold associated with p bands.

To deduce the transitions to the p levels only, one ought to substract from the experimental curve the d-f transitions, i.e., essentially two absorption lines in the ratio 1:1.3 representing the $3d$-$4f$ transitions. Because the relative intensities of d-f and d-p transitions and the exact position of d-f absorption lines are unknown, we have not undertaken the decomposition of the spectrum. Owing to the presence of transitions involving f-like localized levels, it is difficult to deduce the density of the p conduction-band states from the photoabsorption of Cs^+ in CsCl.

IV. DISCUSSION

While in barium and lanthanum the $3d$ spectra are dominated by the $3d$-$4f$ transitions and very little $3d$-p transitions are visible, a different behavior is observed for Cs^+ in CsCl. Our results show indeed that the $3d$-p transitions are relatively more intense than the $3d$-f transitions simultaneously in emission and in absorption.

From the Cs^+ $3p$ and $3d$ absorptions, we locate the d, then p, then f-like empty levels in succession towards increasing energies. Within the equivalent core approximation the Cs^+ free ion with a supplementary $3d$ inner hole behaves in a similar manner as the Ba^+ ion. The $5p^6 5d$, $5p^6 6p$, and $5p^6 4f$ excited states of Ba II are situated, respectively, at 0.65, 2.6, and 6 eV above the $5p^6 6s$ ground state, the limit $5p^6$ being at 10 eV.[32] Let us note that the excitation levels of Cs^+ in solid CsCl are disposed in the same order than those of the Ba II free ion.

Indeed, when an electron is excited to high-lying levels in a solid, i.e., several eV above the bottom of the conduction band, it is generally strongly influenced by the surrounding ions. As an example, the Cs^+ $6p$ levels form a band in CsCl. These are outer-well levels distributed diffusely outside the region near the Cs^+ core. The corresponding excitation states are not localized and have a negligible probability to decay by resonant radiative process.

On the other hand we have seen that, in the presence of a $3d$ hole, a resonant emission from a Cs^+ f-like localized level is observed in CsCl whereas no strong feature can be ascribed to absorption transitions towards the f continuum levels. In contrast with lanthanum,[27,33] where the excited $4f$ level is close to the bottom of the conduction band, the Cs^+ $4f$ resonant level is situated very high in the continuum of conduction states. Thus the $3d$-$4f$ transition probabilities in Cs are expected to be weaker than for the following atomic number elements. On the other hand, configuration interactions between the bound state $3d^9 4f^1$ and the extended states of same energy become very probable. Indeed, the Cs^+ ion in the bound state $3d^9 4f^1$ can either (i) decay to the $3d^{10}$ ground state by radiative and nonradiative resonant processes analogous to that observed in Ba and rare earths but having a weaker probability, (ii) decay by radiative and nonradiative transitions in the presence of the excited $4f$ electron, or (iii) autoionize to the $3d^9$ ion by interaction with the conduction states. The lines owing to process (ii) are satellites of normal emissions in the $3d^9$ ion and their intensity remains probably weak with respect to the intensities of processes (i) and (iii); they could correspond to the remaining emission at the foot of the lines A and B (Fig. 2). Then essentially two different intershell interactions are present in the $3d^9 4f^1$ excited state: the interaction between the excited electron and the inner hole (which is all the stronger as the wave function of the excited electron is more localized on the atom) and the interactions between the discrete excited state and the continuum states. If the first interaction is predominant, the dipole x-ray resonant emissions are very intense as also the Auger resonant peaks. On the other hand, if the configuration interactions between the discrete state and the extended states are strong, the autoionization process is faster than the direct recombination and the x-ray and Auger resonant transitions are not observed. In the case of Cs^+ $3d$, because autoionizinglike resonance lines are clearly observed, the two processes should have comparable rates.

The resonant emissions are parametrized in terms of the Fano formalism (Fig. 3). In fact, whenever an x-ray discrete state strongly interacts with continuum states one expects the lines to have an asymmetrical Breit-Wigner-Fano shape.[32] But, when an excited atom decays simultaneously by spontaneous emission and by autoionization, the shape parameter q which parametrizes the emission spectrum can be somewhat different from the Fano parameter.[34] The width of the observed profile depends on the widths of the various decay processes of the excited state. Because the presence of competitive interferences, the various processes are not additive and their respective probabilities cannot easily be deduced from spectra.

In summary, although the Cs^+ f-like level is mixed with high-lying conduction states, it forms $3d_{5/2}^{-1}4f^1\,{}^3D$ and $3d_{3/2}^{-1}4f^1\,{}^1P$ resonant states. These states are bound, not quasibound, since during their deexcitation resonant emissions are observed, i.e., photons having a specific energy are emitted. It has been suggested that the f orbit should be a little more contracted near Cs^+ in CsCl than in the free ion due to the potential barrier formed by the electronegative Cl^- ions around the positive ion.[35] Then the f-like level observed in CsCl is referred to an inner-well level having the free-ion character and a slightly different energy. Indeed, it should be necessary to observe the spectrum of the Cs^+ ion in order to ascertain whether or not the $3d^9 4f$ excitation state has different characteristics in the free ion and in CsCl solid. On the other hand, let us note that the $3d$-nf transitions could be weakened, or even absent, in the Cs I neutral atom. Indeed, it has been postulated that the formation of inner-well states is favored in the systems possessing a supplementary charge,[36] i.e., here in Cs^+ with respect to Cs I.

Prominent peaks have been seen in the soft x-ray spectra of other alkali halides, in particular in the Li $1s$ absorption[37,38] and emission[39,40] of LiF. They have been interpreted by transitions between the ground state and excited states localized in the band gap. These bound states have generally been discussed in terms of "highly localized excitons." Indeed, because these excited states have the free-ion character and a "true resonant" character, it seems to be a more natural starting point to consider them as atomiclike excitation states self-trapped on a single site.

V. CONCLUSION

From our experimental results the $3d$-p transitions are predominant in the Cs^+ $3d$ spectra of CsCl. In the photoabsorption these transitions correspond to the transfer of electrons from the inner atomic level to the p-like symmetry conduction levels. Only partial information about the one-particle p band structure can be obtained because the transitions to the f states take place simultaneously. The $3d$-f transitions are relatively weak both in the emission and the absorption; they involve localized excitation states embedded in the continuum largely above the threhold. The presence of localized excitations in the $3d$ spectra can be attributed to an inner-well level which is almost uncoupled from the influence of the solid and analogous to $4f$ excited level in the Cs^+ free ion. These excitation states may decay by autoionization. In spite of the presence of this decay process competitive of the direct radiative decay, we have observed resonance lines in the $3d$ emission spectrum; these lines have a quasi-Breit-Wigner-Fano shape. This is the first evidence of x-ray resonant emissions from autoionizing-bound states. It must be underlined that the Cs$^+$ $3d^9 4f^1$ excited states form an interesting system because spontaneous decay and autoionizing rates are comparable.

In conclusion, deeper insight into the nature of localization processes in the solids may come from investigations by stimulated-electron resonant x-ray emission spectroscopy. This method, together with the resonant Auger spectroscopy, supplies information concerning the decay mechanisms of excited states and therefore the dynamics of these states. An advantage is that the x-ray spectra are generally more easy to interpret than the more complex Auger spectra.

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