small compared with that from any of the states within the range of $\kappa \gtrsim 1$, which alone contribute significantly to crystal electron density [cf., e.g., Eq. (40)]. Therefore, the errors in calculations of very small quantum parameters κ are completely negligible when a large number of electrons is considered.

[15] See Refs. 12 and 1(c).

[16] Table II shows that κ_i^λ are clearly larger for the sc lattice—the limiting value of $|\vec{k}|$ in the first Brillouin zone being $\sqrt{3}\,\pi$—than for fcc with the same approximation for $A^{\Gamma_1,\lambda}$. The convergence of the sc solutions is accordingly poorer.

[17] Another interpretation of the maximum value of κ, or $|\vec{k}|$, can refer to the energy at the top of the band in the almost-free-electron approximation; see Sec. VII.

[18] See, e.g., Ref. 1(a).

[19] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. 1, Appendix 7.

[20] This implies that greatly developed $A^{\Gamma_1,\lambda}$ have only a small admixture of j_0 and are dominated by the components with $l > 0$ which can enter $A^{\Gamma_1,\lambda}$ with large weights. These weights may cause the contributions of individual $A^{\Gamma_1,\lambda}$ to be small at $\vec{0}$ but important at other sites.

[21] This limitation on κ holds not only at $\vec{0}$ but seems to exist at any site not too close to the crystal boundary (cf. the end of Sec. VII).

[22] For the less accurate approximation in Table IV [with $\kappa_m^1 = 3.8$, $\kappa_m^2 = 3.9$, $\kappa_m^3 = 4.9$, and $\kappa_m^4 = 5.0$, which are not too far from the corresponding κ_i^λ in Table II and still provide more than 97% of $Q(\vec{0})$ (cf. Tables III and IV)] we have the same band limits: all $E^\lambda = 1$ at $\kappa = 0$ and the minimum value of E^λ inside $(0, \kappa_m^\lambda)$ is $E^4 = -0.33$ at $\kappa = 3.2$.

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K X-Ray Emission from KCl[†]

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Details of the *K* x-ray emission spectra of K^+ and Cl^- in KCl are discussed. It is shown that the valence hole is effectively localized to one atomic site during the lifetimes of both the potassium and chloride 1*s* holes. This localization is found to be an appreciable factor in the processes contributing to the emission. Calculations of the relative intensity of the cross-transition lines, of the type $1s_K^{-1} \rightarrow 3p_{Cl}^{-1}$, $K\beta_5$, are reported. The results of the calculations agree, to within 40%, with the observed values. The widths of the valence emission lines, due to the transitions $1s_K^{-1} \rightarrow 3p_{Cl}^{-1}$ and $1s_{Cl}^{-1} \rightarrow 3p_{Cl}^{-1}$, $K\beta_{1,3}$ are considered. Because of the localization of the final hole state, both initial and final hole states of the $K\beta_{1,3}$ transition see the same crystal potential, and thus there is no first-order broadening due to spatial variation of that potential. This is not the case for the cross-transition line $K\beta_5$. A model due to Dexter is then used to show that the corrected width of the $K\beta_5$ line should be about 0.5 eV greater than that for $K\beta_{1,3}$. This corresponds to the observations made by Deslattes.

INTRODUCTION

The *K* x-ray emission from the constituents of KCl have been among the most studied spectra in the field. One of the prime reasons for this is the ready accessibility of these spectra to present experimental techniques. Also playing a part in the motivation for these studies is the fact that KCl is a typical ionic crystal; understanding the emission processes from KCl is almost a prerequisite for unraveling the spectra from more complicated ionic crystals. In the interpretations, it has been helpful that the constituent ions are isoelectronic with argon, the most studied by x rays of the rare gases.

The room-temperature experimental data from KCl are reproducible and do not warrant further investigation at this time.[1-3] Also, the interpretation of the main features of the spectra are well substantiated. The present discussion uses that interpretation as a starting point for considering some details of the spectra.

The most intense line in each spectrum is $K\beta_{1,3}$, which is due to transitions $1s^{-1} \rightarrow 3p^{-1}$ essentially within each ion.[1,3-5] This line in the chlorine spectrum has a full width at half-maximum, referred to hereafter simply as width, of 0.4 ± 0.1 eV after instrumental, *K*-state, and spin-orbit contributions are unfolded from the recorded data.[1–3, 5] This width is attributed to solid-state effects on the final hole state $3p_{\mathrm{Cl}}^{-1}$. About 2–4 eV above $K\beta_{1,3}$ in each spectrum, and about 0.2 times as intense, is a complex of satellites that have been identified to be of the type $1s^{-1}3p^{-1} \rightarrow 3p^{-2}$.[6] This satellite structure is quite well resolved from $K\beta_{1,3}$. In the potassium spectrum is an additional line $K\beta_5$, lying 11.9 ± 0.2 eV above $K\beta_{1,3}$ and about 0.015 as intense. This line has been identified as being due to the cross transition $1s_{\mathrm{K}}^{-1} \rightarrow 3p_{\mathrm{Cl}}^{-1}$.[3, 4]

The details considered here are mostly ones which are affected by the localization of the valence hole. They include the widths of the valence emission lines, and the relative intensities of the cross-transition lines.

RELATIVE INTENSITIES OF CROSS-TRANSITION LINES

The term "cross transition" refers to a spectral feature which is due to transitions in which electrons predominantly of one atom fill an inner vacancy of a different atom. The particular assignment of $K\beta_5$ as being due to $1s_{\mathrm{K}}^{-1} \rightarrow 3p_{\mathrm{Cl}}^{-1}$ was first made by Valasek.[4] The arguments for this assignment were strengthened by Deslattes,[3] who also estimated the intensity of $K\beta_5$, relative to $K\beta_{1,3}$, from the overlap of $3p_{\mathrm{Cl}}$ and $3p_{\mathrm{K}}$ orbitals. Interpretation of x-ray spectral features in terms of cross transitions have now been made for many compounds.[7–10]

In a linear combination of atomic orbitals (LCAO) model there is no difference in the formal description of the transition probability for valence emission from either ionically or covalently bonded species.[10] As noted in the literature,[7,8] for many cases the relative intensity of a line is a measure of the covalent bonding in the outer orbital involved in the transition. This is not the case in KCl.

It is shown here that the calculations of the relative intensity depend quite critically on the localization of the hole state. It is the degree of localization of the final hole during the characteristic time of the experiment which is of interest here. This is essentially the same definition used by Spicer,[11] although the term localized has been applied also to the atomic hole model. As will be seen below, in that context the term refers to the time a hole is localized at one site, relative to the response time of the valence electrons. Returning to the experimental definition, if the velocity of the hole is such that it moves less than a lattice vector during the characteristic time for the experiment, it will be referred to as being localized. Excluding temperature effects, the width of the hole is a measure of the time it spends at one site T_s, being inversely proportional to the probability that the hole will tunnel to a neighboring chlorine. This definition is equivalent to one based on the average velocity of a Bloch valence-band hole. For KCl, T_s deduced from the width of the chlorine $K\beta_{1,3}$ line is about 1.7×10^{-15} sec, longer than the lifetime of both the potassium and chlorine $1s$ hole states.[1] It is shown below that the $3p_{\mathrm{Cl}}$ hole width deduced from the x-ray data is probably an upper limit. To a good approximation, the hole is localized in the experiments considered here.

The details of the calculations are reported in the Appendix. The observation that, for transitions involving delocalized outermost orbitals, relative intensities in the K x-ray spectra contain information directly related to the covalent mixing parameters is of general interest.[7,8] This is not so for transitions involving localized orbitals, where the charge-transfer part of the dipole moment must be considered. The calculated intensities, relative to $K\beta_{1,3}$ in the same spectrum, are shown in Table I. For $K\beta_5$, 0.19 is in reasonable agreement with the observed value 0.15.[3] The low-intensity line due to the transition $1s_{\mathrm{K}}^{-1} \rightarrow 3s_{\mathrm{Cl}}^{-1}$ would not be observed on the steeply sloping side of the potassium $K\beta_{1,3}$ line, as the final hole states for both transitions have almost the same energies.[12,13]

Because of its low relative intensity, the line due to the $1s_{\mathrm{Cl}}^{-1} \rightarrow 3s_{\mathrm{Cl}}^{-1}$ transitions would not be observed. On the other hand, the relative intensity of $1s_{\mathrm{Cl}}^{-1} \rightarrow 3p_{\mathrm{K}}^{-1}$ should be just large enough to be observed, if sufficiently long counting times were employed in a state-of-the-art experiment. Deslattes has reported observing a very weak line at the appropriate energy,[14] and it seems likely that this line is due to the $1s_{\mathrm{Cl}}^{-1} \rightarrow 3p_{\mathrm{K}}^{-1}$ cross transition. This cross-transition line is unusual in that it is the first to be recognized in the anion, rather than in the cation, spectrum. Such lines will generally be of lower intensity because in most cases the outer orbitals of the cation are less extended and more tightly bound than those of anions. The former condition leads to a reduced charge-transfer term, the latter to negligible covalent effects for most ionic crystals (see Appendix).

WIDTH OF POTASSIUM $K\beta_5$ LINE

A difficulty associated with the interpretation of the emission spectra from KCl is that the width of the $3p_{\mathrm{Cl}}$ hole state deduced from the chlorine $K\beta_{1,3}$

TABLE I. Calculated intensities of cross-emission lines, relative to $K\beta_{1,3}$ in the same spectrum (see Appendix).

$1s_{\mathrm{K}}^{-1} \rightarrow \phi_A^{-1}(3p_{\mathrm{Cl}}^{-1})$	0.019
$1s_{\mathrm{K}}^{-1} \rightarrow 3s_{\mathrm{Cl}}^{-1}$	0.014
$1s_{\mathrm{Cl}}^{-1} \rightarrow 3s_{\mathrm{Cl}}^{-1}$	0.00005
$1s_{\mathrm{Cl}}^{-1} \rightarrow 3p_{\mathrm{K}}^{-1}$	0.0012

emission line (0.4 eV) is appreciably smaller than that deduced from the $K\beta_5$ cross-transition line in the potassium spectrum (0.9 eV).[3] As discussed by Deslattes,[3] this difficulty exists independently of the model used for the final hole state.

Dexter has put forward a theory to describe uv line broadening in ionic crystals.[15] It is shown here that this theory can adequately account for the extra width of the cross-transition line. Because of lattice dilations Δ, there are deviations in the local crystal potential. To lowest order, these deviations will not affect the energy of a transition within a chloride ion since both initial and final states see the same potential. However, in the region of a positive dilation, the energies of all chloride levels will be raised, and those of all potassium levels lowered, by an amount $\frac{1}{2}W=\frac{1}{2}E\Delta$. The energy of a photon from a cross transition in this region of the crystal will differ by $E\Delta$ from that from a region with normal lattice spacing. The superposition of a large number of such energies will constitute a line broadening.

Dexter showed that the probability for the occurrence of a particular value of W is given by

$$P(W)=\left(\frac{C_{ii}}{2\pi E^2kT}\right)^{1/2}\exp\left(\frac{-W^2C_{ii}}{2E^2kT}\right)\quad,\qquad(1)$$

where, in this case, C_{ii} is C_{11} and $E=\frac{2}{3}\,\alpha e^2/d$, where α is the Madelung constant appropriate to the interionic distance d. From Eq. (1), a width of 1.7 eV is deduced for this broadening mechanism at just above room temperature. However, the effect of short-wavelength phonons is overestimated by a factor of 2 in the above expression. Within the approximations represented by (1), this extra breadth can satisfactorily account for the observation that the corrected width of $K\beta_5$ is greater than that of the chloride $K\beta_{1,3}$ line.[3] It is noted that Overhauser has reported a more accurate expression for this type of broadening, based on the same effect.[16] His expression predicts a room-temperature broadening of about 0.4 eV. As the $3p_{\text{Cl}}$ hole becomes more delocalized, as in other chlorides, for example,[17] this form of broadening in the cross-transition line should decrease.

Another possible temperature-independent mechanism of broadening of $K\beta_5$ will be mentioned, but not estimated. That is the breadth expected from the Franck-Condon principle for this case where the transition involves nonequivalent hole sites.

WIDTH OF CHLORINE $K\beta_{1,3}$ AND NATURE OF FINAL HOLE STATE

In discussing the width of the chlorine $K\beta_{1,3}$ line, some aspects of previous interpretations will first be considered. For a long time after Valasek's measurement of the width of $K\beta_{1,3}$,[4] the solid-state broadening of the line was considerably less than that expected from the results of band-structure calculations. In trying to reconcile the two, Parratt and Jossem[1] introduced the concept of a transition probability that varied across the band, although they did not try to justify this suggestion in other ways, and later concluded it was not necessary.[18] Deslattes[3] used the band-structure calculation of Howland[19] to show that there was no significant change of symmetry across the valence band, and from this point of view the experimentally observed width was significant as a measure of the width of the valence-band density of states. Deslattes's argument is sufficient, although this has not been recognized by workers in adjacent fields. His argument holds no matter what the nature of the final hole state is.

However, Deslattes still found that the valence-band width deduced from the chlorine $K\beta_{1,3}$ line was considerably less than that indicated by the then current band-structure calculations of Howland.[19] Agreement between experiment and theory did not come until later, when DeCicco[13] found a width of 0.4 eV from an augmented-plane-wave (APW) band-structure calculation, a value supported by the results of the orthogonalized-plane-wave (OPW) calculations of Kunz.[20] So, now there is agreement between the observed and calculated widths. The question addressed here concerns the significance of the agreement.

The question arises because the traditional model of a hole in the valence band of KCl is a Heitler-London, or atomic, model, which appears to be quite distinct from the band model used in the calculations. The Heitler-London model for a hole is well described by Mott and Gurney[21] and others. An electron is removed from a chloride ion in the solid, the remaining five $3p_{\text{Cl}}$ electrons behaving just as if the ion were free; they contract to a reduced radius at the hole site.[22] Next, the effect of the hole on the environment is considered, a step which includes the electronic polarization of the medium.[23,24] The interaction of the polarized medium with the remaining five $3p_{\text{Cl}}$ electrons at the hole site must then be taken into account. The resulting hole moves through the lattice with wave vector $\vec{k}$, and has all the band structure implied by the crystal symmetry. However, Koopmans's theorem does not give a good description of these processes.[25,26]

At the other end of the scale is the hole described by Koopmans's theorem. To obtain this description it is merely necessary to apply Koopmans's theorem to the removal of a valence electron from any good description of the ground-state electronic structure of KCl.[25,26] The wave functions of the remaining electrons do not change; the hole and the electron properties are essentially identical. There is no sharp distinction between these two types of holes. Two questions can be asked about the valence hole in KCl: Can we say which model best describes the nature of the hole, and do the *properties* of the hole critically reflect its nature? Spicer has been concerned with similar questions in the interpretation of photoemission,[11] although the distinction between the atomiclike hole and experimental localization was not made explicitly in that work.

An attempt is now made to answer these questions from the point of view of the x-ray data. For an atomic-type contraction to occur, there are two criteria to be met. First, it must be energetically favorable for the contraction to occur, and second, the time that the hole occupies any one site must be long enough for the other electrons to react to the hole. For KCl, the contraction is favored energetically for two reasons: This is the stable configuration in the isolated ion, and, the net effect of the interaction of the remaining five electrons at the hole site with the surroundings is repulsive. As discussed above, the time of the hole at a site T_s is about 1.7×10^{-15} sec. This corresponds to a frequency much less than the classical Bohr frequency of the $3p$ valence electron in its potential in the lattice, essentially measured by the energy gap.[27] Thus, it is argued that the most appropriate concept with which to describe the valence hole is that of the Heitler-London model. This model is the one traditionally used to describe the valence hole in alkali halides,[11,21,27,28] essentially for the same reasons as those used here, which are related to the small overlaps.

The next question is, does it matter which model is used to describe the hole, i.e., do the predicted properties of a hole described by Koopmans's theorem differ significantly from those of a Heitler-London hole; or, more practically, do the predicted properties of the hole described by Koopmans's theorem differ from those that can be deduced from the observed solid-state effects on the final hole state of chlorine $K\beta_{1,3}$?

This question has been tackled before, with somewhat conflicting results. The calculations of Nettel point in the direction of a narrower valence band than that predicted by Koopmans's theorem.[29] On the other hand, the work of Phillips and Van Vechten[30] suggests that, to zero order, the valence-band width is not sensitive to the nature of the hole. Presumably, this would be because the effects of contraction of orbitals at the hole site are largely offset by the polarization of the surrounding orbitals towards the hole. It will be seen that the x-ray data do not resolve the problem; nevertheless, it is instructive to continue with the question, particularly as an investigation of temperature effects on x-ray spectra.

The properties of the hole that can be measured from the x-ray data are the energy required to form the hole, and its width. It is the width that is considered in most detail below.

The agreement between the observed width and that calculated by band structure has already been noted.[13,20] The question before us now is whether or not there is a considerable temperature effect in the measured width of the chlorine $K\beta_{1,3}$ line. Some possible temperature effects will be considered below. This discussion is confined to the width of the valence band as deduced from the chlorine $K\beta_{1,3}$ line and need not apply to the width observed by other techniques.

The phonon field in KCl introduces different average interionic distances, which will affect the valence-band emission in a number of ways. First, the electrostatic potential at a chlorine site will vary throughout the lattice. Because the hole is localized, however, both initial and final hole states in the Cl $K\beta_{1,3}$ transition see the same potential, so no broadening will result from this effect. Indeed, there is the possibility that electrostatic effects *reduce* the valence-band width. If the change of electrostatic potential at adjacent chlorides is comparable to the broadening, it is possible that, in the time scale of the problem,[24] tunneling of the hole to adjacent sites is energetically unfavorable, and the lifetime broadening is thus reduced.[31]

While the phonon field will probably not affect the $K\beta_{1,3}$ width due to electrostatic effects, it may affect it through overlaps. Varying overlaps will have two effects. The breadth of the line from one small region will depend on the average interionic distance in that region. It appears that superposition of a large number of lines of slightly varying width[19] will not appreciably increase the observed width. Perhaps more important will be the variation of potential energy of the $3p_{\text{Cl}}$ electrons due to variation of overlaps. That is, the energy of an emitted photon will depend on the repulsive overlap experienced by the electrons of the emitting atom. The superposition of a large number of photons coming from atoms in different environments will contribute width to the line.

Using Koopmans's theorem, this broadening can be estimated to be quite small, < 0.05 eV. However, to be consistent, this temperature effect should be described on an atomic model. The difficulties of estimating the effect of overlaps on the energy of $K\beta_{1,3}$ using this model are formidable, even at low temperatures. These difficulties have been anticipated by Parratt and Jossem,[1] and will not be considered further here.

The outcome of this discussion is that a semiquantitative estimate of the broadening due to this temperature effect cannot be made (using an atomic model) at this time. A calculation of the effect, or a low-temperature measurement of chlorine $K\beta_{1,3}$, would be required to settle the issue from this point of view.

Energy separations within the x-ray spectra are relatively insensitive to the nature of the hole state. For example, the observed separation between $3p_{\mathrm{Cl}}$ and $3p_{\mathrm{K}}$ (11.9 ± 0.2 eV) is accounted for by an atomic model[4,7,32] which includes the effect of polarization[23] and by Koopmans's theorem.[13]

SUMMARY AND CONCLUSIONS

The most continuous theme in the above discussions is the localization of the final hole state and the effects of this on the spectra. This localization is an important feature in the calculation of the dipole moments of the cross-transition lines, and in the discussion of the temperature broadening of $K\beta_{1,3}$ and $K\beta_5$.

The localization of the hole states is also a factor in the existence of Wentzel-Druyvesteyn satellites,[6] when the spectator hole is in the valence band. The relative intensity of the satellite will decrease rapidly as the initial valence hole lifetime becomes smaller than that of the inner hole.

For valence emission spectra involving localized holes, such as the ones observed for KCl, the different zero-order temperature effects on linewidths can be estimated. This is no longer the case when the valence hole becomes partially delocalized. For even greater delocalization, however, temperature broadening would be the same for both anion and cation valence spectra.

It remains to be shown quantitatively whether Koopmans's theorem accurately describes the properties of the valence hole state. In this regard, a low-temperature measurement of the x-ray spectra in conjunction with the accepted band-structure calculations would be useful. Such a measurement could put an upper limit of ± 0.1 eV on the agreement between the observed width and that calculated using Koopmans's theorem.

While the relatively small solid-state effects on the x-ray spectra may reasonably well be described by either the Heitler-London model or Koopmans's theorem, it is believed that the gross structure of the x-ray emission spectra, particularly the satellite structure, is most naturally described by the atomic model and the whole spectra by a slightly perturbed atomic model.[6]

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APPENDIX: RELATIVE INTENSITIES OF CROSS-TRANSITION LINES

The main features of the calculation of the relative intensities can be represented in a very simple model. Consider a pair of ions in KCl, and let the $3p_{z\mathrm{K}}$ interact with the $3p_{z\mathrm{Cl}}$ orbital along the interionic axis z. These will form bonding and antibonding orbitals, given by[33]

$$\phi_B = 3p_{\mathrm{K}} \ , \quad \phi_A = N(3p_{\mathrm{Cl}} - S\,3p_{\mathrm{K}}) \ ,$$

where S is the overlap, and N a normalization factor not very different from unity. In this closed-shell system, all the repulsive energy appears in the antibonding orbitals.[33] Of course, there are other overlaps between orbitals of these ions, but it can be shown that the above ones are the only significant ones so far as the $1s_{\mathrm{K}}^{-1} \rightarrow \phi_A^{-1}$ transition is concerned.

The dipole moments for K x-ray emission involving these orbitals can be written (in the active electron approximation)[10]:

$$\langle 1s_{\mathrm{Cl}} | z | \phi_A \rangle = N \langle 1s_{\mathrm{Cl}} | z | 3p_{\mathrm{Cl}} \rangle - SN \langle 1s_{\mathrm{Cl}} | z | 3p_{\mathrm{K}} \rangle \ ,$$

$$\langle 1s_{\mathrm{Cl}} | z | \phi_B \rangle = \langle 1s_{\mathrm{Cl}} | z | 3p_{\mathrm{K}} \rangle \ ,$$

$$\langle 1s_{\mathrm{K}} | z | \phi_A \rangle = N \langle 1s_{\mathrm{K}} | z | 3p_{\mathrm{Cl}} \rangle - SN \langle 1s_{\mathrm{K}} | z | 3p_{\mathrm{K}} \rangle \ ,$$

$$\langle 1s_{\mathrm{K}} | z | \phi_B \rangle = \langle 1s_{\mathrm{K}} | z | 3p_{\mathrm{K}} \rangle \ .$$

The charge-transfer terms depend on the extension of the outer orbitals of one ion into the region of the 1s orbitals of the other.[10] Neglecting these terms, it can be seen that the above expressions predict that the K x-ray emission from Cl^- in KCl would consist of just one line, $K\beta_{1,3}$, due to $1s_{\mathrm{Cl}}^{-1} \rightarrow 3p_{\mathrm{Cl}}^{-1}$. The emission from K^+ would consist of two lines, separated by the energy difference between the two outermost levels in KCl, and in the intensity ratio $S^2:1$. This is the model implied by Deslattes when he discussed the intensity of the $K\beta_5$ cross-emission line in the K^+ spectrum from KCl.[3] Unfortunately, in general, the charge-transfer terms cannot be neglected[10]: In the present case they are about twice as large and of opposite sign to the overlap term in the above expressions. Because of the radial node structure of the p orbitals, the charge-transfer and overlap terms will always oppose each other for cations with valence 3p electrons.

Using the free-ion functions for Cl^- and K^+ calculated by Bagus,[22] the intensities of the lines $1s_{\mathrm{K}}^{-1} \rightarrow 3s_{\mathrm{Cl}}^{-1}$ and $\rightarrow \phi_A^{-1}$, and $1s_{\mathrm{Cl}}^{-1} \rightarrow 3s_{\mathrm{Cl}}^{-1}$ and $3p_{\mathrm{K}}^{-1}$ (ϕ_B^{-1}) were calculated, all relative to the appropriate $K\beta_{1,3}$ line. To find the intensity of $1s_{\mathrm{K}}^{-1} \rightarrow \phi_A^{-1}$ relative to $1s_{\mathrm{K}}^{-1} \rightarrow \phi_B^{-1}$ in solid KCl, the above expressions are squared and the appropriate ratio multiplied by two to account for symmetry. The results are shown in Table I. Despite the many approximations made, including use of the active electron approximation for calculating both the cross transitions and $K\beta_{1,3}$ and the use of orbitals neglecting the polarization effects, it seems probable that the predicted relative intensities should be accurate to within 40%.

A simple and accurate approximation to the charge-transfer terms in the above expressions has been given by Michels,[34] who pointed out that the amplitude of the tail of the wave function is virtually constant over the whole extent of the $1s$ orbital of the other atom: z, also, can be considered a constant in this calculation.

An interesting result of this work is the effect of localization on the calculation of the charge-transfer term. The above calculation is correct for a localized hole; the *intensities* due to the individual chloride ions are added. If the holes were delocalized, then the amplitude of the wave functions from different chlorides would be added before squaring. For the symmetry under consideration, there would be nearly complete cancellation of $3p_{\mathrm{Cl}}$ tails over the whole $1s_{\mathrm{K}}$ orbital. In this case, there would be effectively no charge-transfer term to worry about, and the relative intensities would give a good measure of covalency, which is just the overlap in this case. This result should be valid for K, but not L, spectra, involving delocalized orbitals of atoms in sites with inversion symmetry, or approximate inversion symmetry.

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