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X-Ray Spectroscopy of the Solid State: Potassium Chloride*

L. G. Parratt and E. L. Jossem
Cornell University, Ithaca, New York

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The experimental K spectral regions of potassium and chlorine in crystalline KCl have a much more complex array of structure, both in emission and in absorption, than can be explained by the conventional energy level diagram for the solid state. The pertinent spectral region is that which involves the valence and conduction bands of the solid. The difficulties seem to arise from a theoretical preoccupation with one-electron transitions.

Consideration of the various probable electron configurations of the many-electron solid system shows several additional initial ($1s$ vacancy) and final (outer vacancy) states. The charge density in the outer electron bands, suddenly confronted with the problem of screening the excess positive charge attending a $1s$ vacancy (or any inner vacancy), redistributes itself, distorting the bands and establishing one or more local discrete levels below each band. With the most probable filled discrete level below the $3p$ band, the narrow intense $K\beta_1$ line is explained but it is necessary to account somehow for the very narrow final state ($3p$ vacancy). An obvious conclusion is that the $3p$ valence band itself is therefore very narrow in energy, only 0.33 ev wide. However, if it is indeed wider than this, as is commonly believed in the lore of solid state physics, the $K\beta_1$ emission must be restricted by some (unknown) mechanism to a small energy region within the band. In this event, x-ray emission involving the entire broad $3p$ band may be part of the observed faint emission on the high-energy side of the $K\beta_1$ line, and, if so, the restricted energy position just mentioned must be at the bottom of the band.

Also a consequence of the $1s$ vacancy are several normally empty discrete levels below and in the conduction band of KCl. With these levels, the narrow intense K absorption lines are explained.

The discussion given is primarily experimental and phenomenological. The qualitative agreements are perhaps compatible with either a narrow or a wide $3p$ band for both potassium and chlorine in KCl, but show a preference for the wide $3p$ band. Either conclusion dictates the need of a new quantitative theoretical treatment.

INTRODUCTION

In x-ray spectroscopy of the solid state it has been generally presumed that the outer "levels" primarily involved are the energy bands characteristic of the unperturbed solid as a whole.[1,2] The emission spectrum near a series limit and the absorption spectrum near an absorption discontinuity are presumed to give directly the energy position and width of the valence and conduction bands, and indirectly the density of states in these bands.

As an example, the pertinent transitions in the K spectra of crystalline potassium chloride are indicated in the conventional energy level diagram sketched in Fig. 1. The $1s$, $2s$, and $2p$ states are narrow in energy. The full width at half maximum of the $1s$ state (width due to the lifetime of the state) is about 0.45 ev for chlorine and about 0.73 ev for potassium.[3] The $3s$ and $3p$ states are presumed to be much broader because of the effect of overlapping electronic wave functions of neighboring atoms in the solid. The $3p$ valence band at half-maximum of the density-of-states curve is estimated theoretically to be about 2-ev wide.[4] The continuum consists of all the overlapping normally empty bands ($4s$, $3d$, $4p$, etc.).

Transition arrows in Fig. 1 are presumed to give directly the energy released or absorbed as the system changes radiatively from the initial to the final state. The width and shape of the $1s\rightarrow 3p$ (or $K\rightarrow M$) emission, when corrected for the resolving power of the spectrometer and for the $1s$ width, are presumed to give essentially the width and shape of the density-of-states curve for the valence band if the transition probability is uniform over the band. The difference in the energy position of the high-energy side of the (corrected) emission, and of the low-energy side of the (corrected) absorption edge, has been presumed to give the energy gap between the $3p$ band and the continuum. And, also, the shape of the absorption discontinuity and the position and shape of any component structure in the absorption spectrum should presumably tell us the

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[1] E.g., see H. W. B. Skinner, Trans. Roy. Soc. (London) **A239**, 95 (1940); H. M. O'Bryan and H. W. B. Skinner, Proc. Roy. Soc. (London) **A176**, 229 (1940); Y. Cauchois, *Les Spectres de Rayons X et la Structure Electronique de la Matiere* (Gauthier-Villars, Paris, 1948); and H. Niehrs, Ergeb. exakt. Naturw. **23**, 359 (1950).

[2] Some exceptions have been made to this general presumption for absorption spectra; e.g., see R. Landshoff, Phys. Rev. **55**, 631 (1939), and Y. Cauchois and N. F. Mott, Phil. Mag. **40**, 1260 (1949).

[3] Direct measurement of the $1s$ width for metallic potassium [J. Platt, Phys. Rev. **69**, 337 (1946)] gives 0.75 ev or 0.73 ev after correction for the resolving power of the spectrometer. The corrected $1s$ width for gaseous argon [L. G. Parratt, Phys. **56**, 295 (1939)] is 0.58 ev. These two $1s$ widths are in excellent agreement with the theoretical prediction of proportionality with the square of the energy of the state. (The metallic potassium absorption discontinuity is apparently free from perturbing unresolved fine structure.) For chlorine we extrapolate and obtain the $1s$ width as 0.45 ev. The width of each of these three $1s$ states is believed to be correct within about 0.05 ev.

[4] The authors do not know of a reliable calculation of the theoretical widths of the $3p$ bands in KCl. However, W. Shockley, Phys. Rev. **50**, 754 (1936), calculated that the chlorine $3p$ band in NaCl is about 4.4 ev wide, and P. Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals* (Almqvist and Wiksells Boktryckeri AB, Uppsala, 1948), calculated the spatial extents of the electronic wave functions for both KCl and NaCl. From these considerations, we tentatively conclude that the chlorine $3p$ and potassium $3p$ bands in KCl are about 4.4 and 3.4 ev wide, respectively. These widths refer to the "base" of the density-of-states curve. The theoretical shape of the density-of-states curve rises perhaps as $E^{\frac{1}{2}}$ near the bottom, reaches a maximum, then descends more steeply on the high-energy side. Hence, the theoretical width at half-maximum of the chlorine and potassium $3p$ bands may be about 2 and 1.5 ev, respectively.

density of energy states (multiplied by the transition probabilities) in the continuum.

In the present paper these relations are studied quantitatively for potassium and chlorine in crystalline KCl. We find that we must add to Fig. 1 (and to the conventional interpretations[1]) "impurity-type" levels (and states) which arise as a consequence of the 1*s* vacancy.[5] We conclude either (a) that the density-of-states curve for the valence band Cl^- 3*p* is very narrow (0.33 ev) at the half-maximum and not greatly different from the classical dispersion or Lorentzian shape, or else (b) that some (unknown) mechanism operates to restrict the energy of the final state in β_1 emission to be localized at the bottom of the 3*p* band. Neither of these two conclusions is in agreement with conventional beliefs about crystalline KCl. Then, we discuss the narrow absorption lines in terms of the discrete normally empty levels below and in the conduction band. From the energy positions of the β_1 emission line, of the first absorption line, and of the absorption peaks in the ultraviolet absorption, evidence favors the (b) conclusion but it does not decisively exclude the (a) conclusion.

EMISSION SPECTRA

The observed emission spectra for chlorine and for potassium in crystalline KCl are shown as part of Fig. 2. The strong emission line in each case is known as the $K\beta_1$ line; the less intense structure on the high-energy side of each β_1 line has been called by the noncommittal name of "satellites".

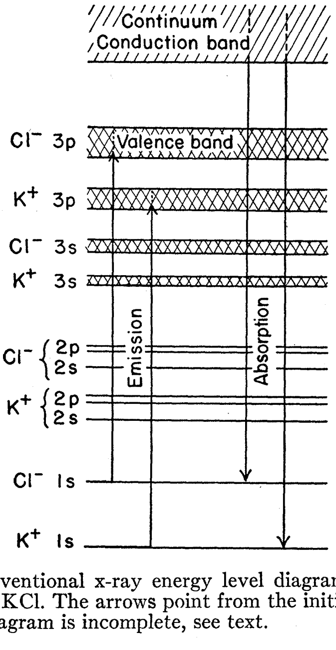

FIG. 1. Conventional x-ray energy level diagram (schematic) for crystalline KCl. The arrows point from the initial to the final states. This diagram is incomplete, see text.

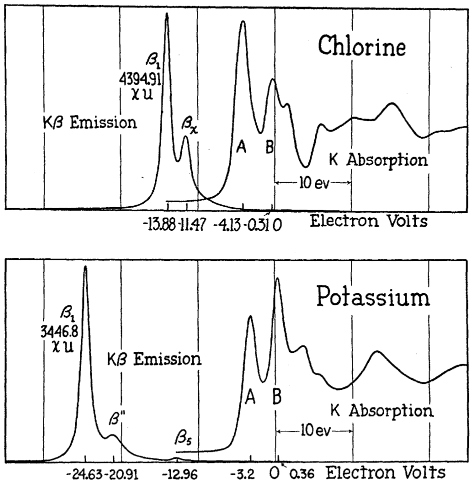

FIG. 2. Experimental emission and absorption spectra in KCl, involving the valence and conduction bands as shown in Fig. 1. The complexity of the spectra requires additional states which are not shown in Fig. 1. The zero of the ev scale is somewhat arbitrary as discussed in the text.

The KCl curves were recorded with a focusing crystal spectrometer[6] and also with a two-crystal spectrometer.[7] Excellent agreement was obtained between the curves recorded with the different x-ray tubes and spectrometers.

With each spectrometer, a proportional counter system including a single channel discriminator, served very satisfactorily for measuring intensity. This system also discriminated effectively against background intensity (higher-order Bragg reflection, scattered photons of appreciably different energy, etc.), a feature of great importance in accurate studies of extremely faint intensities.

With the focusing instrument, a bent mica crystal was used in third order reflection for chlorine and in fifth order for potassium. With the two-crystal instrument, calcite crystals[8] were used in the (1,+1) position.

The x-ray tube target, with each spectrometer, consisted of a layer of KCl condensed by vacuum evaporation on a water-cooled nickel substrate (or copper or aluminum—no effect of the substrate was found). The evaporation and condensation were carried out at a pressure always lower than 10^{-6} mm Hg, in the same vacuum as used in the x-ray generation. Except during this evaporation, the x-ray vacuum was

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[5] L. G. Parratt and E. L. Jossem, Phys. Rev. **84**, 362 (1951); **85**, 729 (1952); and J. Friedel, Phil. Mag. **43**, 153 and 1115 (1952). See also reference 2.

[6] E. L. Jossem and L. G. Parratt, Phys. Rev. **79**, 210 (1950).

[7] L. G. Parratt, Phys. Rev. **54**, 99 (1938), and references. The absorption curves of Fig. 2 are reproduced from J. W. Trischka, Phys. Rev. **67**, 318 (1945), and the wavelength positions and shapes of their essential features have been checked recently with the two-crystal instrument and also with the focusing spectrometer.

[8] These crystals were calibrated as to their reflectivities and designated A_4B_4 by L. G. Parratt, Rev. Sci. Instr. **6**, 387 (1935). After 1935, they deteriorated somewhat upon standing in atmospheric air, and were again ground, polished and etched in 1939. Since 1939, they have again become somewhat imperfect [the (1,−1) widths are a little wider than in 1935] but are still "Class I crystals."

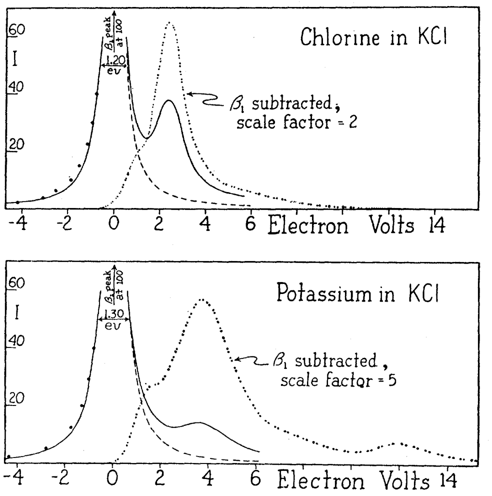

FIG. 3. Emission intensity in the β' region. The components remaining after subtraction of the β_1 line are shown in the dotted curves. β_1 was assumed to be symmetrical about the observed peak intensity. The classical dispersion (Lorentzian) shape, Eq. (1), matched at the peak and at the half-maximum points, is indicated by the solid circles on the low-energy side of β_1. These curves were recorded with the two crystal spectrometer.

always less than 3×10^{-7} mm Hg. With most of these targets, an irregular decrease of intensity with time was observed for both the chlorine and potassium emission, and this time-dependence introduced an uncertainty of a few percent in the relative intensities of various regions of each curve during, say, a two-hour run.[9] To minimize this uncertainty, many curves were recorded and averaged.

With 14 kv across the x-ray tube, and with 5-ma tube current, the counting rate at the peak of the chlorine β_1 line with a fresh thick target was about 500 counts per second with the detector slit of the focusing spectrometer set at 0.0065 mm (0.1 x-units) in width. Under the same conditions (including the absorption path) the counting rate with the two crystal spectrometer was 900.[10]

In Fig. 3 the strong β_1 line has been subtracted from the observed emission contour. The shape of the β_1 line was assumed to be symmetrical about the observed intensity peak.

The shapes of x-ray lines are often compared with the Lorentzian curve

$$I=\frac{P}{1+(\Delta E/W_{\frac{1}{2}})^2}, \tag{1}$$

where ΔE, the incremental energy abscissa, is zero at the peak intensity P and equal to $W_{\frac{1}{2}}$ at half-maximum intensity. The solid circles on the low-energy side of β_1 in Fig. 3 are plotted from Eq. (1). The observed β_1 shape in this region is typical of x-ray lines in general.

Experimental Width of the Final State in β_1 Emission

With the focusing spectrometer, the "observed"[11] full width at half-maximum intensity of the β_1 line is 1.68 ev for chlorine and 1.33 ev for potassium. With the two-crystal spectrometer, the "observed" widths are 1.20 ev and 1.30 ev, respectively. To deduce the width of the final state in this emission, corrections must be made for (a) the resolving power of the spectrometer and (b) the width of the initial 1*s* state.

The "spectral window" of a focusing spectrometer is determined by a combination of the crystal diffraction pattern, the focusing defects, and the width and height of the detector slit. This combination is unknown.

The resolving power of the two-crystal spectrometer is much better understood. With this instrument the width correction is given by the formula

$$W_t=W_0-2.9W_c^{1.7}, \tag{2}$$

where W_c is the width of the $(1,-1)$ curve, W_0 is the observed width of the line whose true width is W_t (all widths in xu).[12,13] For the chlorine β_1 line, corrected for the overlapping β_x, $W_0=1.87$, $W_c=0.414$, and W_t computes to be 1.22 xu or 0.78 ev. Likewise, W_t for the potassium β_1 is 0.95 ev.

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[9] The time-dependence of the intensity, usually a few percent per hour, may have been caused by a target deterioration (stripping of the KCl from the substrate or of Cl from the KCl by electron bombardment and consequent local heating) or by a target contamination layer of either (a) decomposed oil from the diffusion pumps or other "vacuum" residues, or (b) tungsten evaporated from the filament. An effort was made to reduce the oil backstreaming from the pumps, as already described by L. G. Parratt and E. L. Jossem, Rev. Sci. Instr. **23**, 188 (1952), and a liquid-nitrogen-cooled bulb was suspended in the vacuum chamber of the x-ray tube. The x-ray tube filament consisted of a "soda straw" spiral $\frac{3}{4}$ in. long and $\frac{1}{8}$ in. diameter formed from a tungsten ribbon $\frac{1}{16}$ in. wide, 0.002 in. thick and about 3 in. long. The large surface for electron emission allowed operation at a comparatively low temperature to reduce the tungsten contamination on the target. A run with a good metal target (palladium or antimony, whose $L\alpha_1$ line was used as a secondary wavelength reference) gave constant $L\alpha_1$ intensity within 0.5 percent for more than a few hours, so we believe that the irregular decrease with KCl is caused by target deterioration rather than by contamination.

[10] The lower luminosity of the focusing spectrometer is accounted for by the very narrow slit used. The resolving power was only slightly reduced by increasing the slit width from 0.1 xu to 0.35 xu; with the wider slit the counting rate was increased to about 1600. However, the opening at the bent crystal limited the maximum perpendicular cross section of the beam to 1.5×0.4 cm whereas the beam of the two crystal spectrometer was somewhat smaller in cross section, 0.8×0.6 cm. On a basis of equal area and of equal resolving power, the luminosities of the two instruments are comparable.

[11] These widths are measured after the small correction for the β_x or the β'' complex, as illustrated in Figs. 2 and 3 for curves recorded with the two crystal spectrometer.

[12] L. G. Parratt, reference 8. In case $W_c\gtrsim(2/3)W_t$, this formula is not valid.

[13] The numerical resolving power, $\lambda/\Delta\lambda$, of the focusing spectrometer can be approximated as follows: From the observed W_0 for Cl^- β_1 and the known W_t from the two-crystal measurements, W_c is deduced from Eq. (2) as 0.64 xu. Taking $\Delta\lambda=W_c$, we find $\lambda/\Delta\lambda=6870$ for the chlorine β_1 wavelength in third-order reflection. The same procedure gives $\lambda/\Delta\lambda=11\,500$ for the potassium wavelength in fifth order.

With the two-crystal spectrometer, $\lambda/\Delta\lambda=10\,600$ and $12\,200$, respectively, for the chlorine and potassium β_1 wavelengths in first order.

The correction for the width of the initial $1s$ state is easy if we make the assumption that the shape of the β_1 line and the shape of the $1s$ state are each given by a Lorentzian curve, Eq. (1). In this case, the observed line width is the simple sum of the widths of the initial and final states.[14] The observed β_1 line is very nearly Lorentzian in shape on the low-energy side where there is no obvious unresolved structure; on the high-energy side the structure prevents a comparison below near the half-maximum.[15] Theory predicts that any singlet atomic state is Lorentzian in shape. It is believed that no great error is made in taking the width of the final state as the simple difference between W_t and W_{1s}.[16] Then,

$$W_{3p}=0.78-0.45=0.33 \text{ ev for chlorine}$$

$$W_{3p}=0.95-0.73=0.22 \text{ ev for potassium}$$

with an uncertainty of less than 0.1 ev in each case.

The obvious conclusion from these narrow final states is that the $3p$ bands are indeed much narrower than is commonly believed.[4,17]

Perhaps Shockley's calculation[4] is not reliable, and the $3p$ states are essentially atomic in character—narrow and of Lorentzian shape. However, we do not wish to pass this judgment on the calculations without first attempting to reconcile the observed narrow final states with broad $3p$ bands in an unperturbed crystal. In this attempt, we propose that the β_1 emission cannot be represented by the transition arrow in Fig. 1 if the arrow terminus is allowed to range throughout the broad $3p$ band. We therefore re-examine the emission process.

Emission Process: Many-Electron System

In a free gaseous atom, the energy of the ground state is taken to be zero. This, incidentally, is the initial state for x-ray absorption. The ejection of an inner, say, a $1s$, electron causes the atom to shrink—all the outer electrons, now in a stronger electrostatic field, move to positions closer to the nucleus. This is the initial state for emission and is also the final state for absorption. The energy of this $1s$ state must, of course, take into account the new positions of *all* the electrons. Upon emission of an x-ray photon, the inner vacancy is filled and another vacancy is produced farther out in the atom. All the electrons again move to new positions, and the energy of the final state must take into account *all* the new final positions.

When the atom is part of a solid, the wave functions of its electrons interact with those of neighboring atoms. The system which must now be considered includes, in principle, *all* the electrons of *all* the atoms in the solid. Fortunately, interaction between the inner electrons of neighboring atoms is usually negligible, and, for those atoms not suffering the $1s$ vacancy, only the outer electrons are seriously involved.

When an inner vacancy occurs in an atom in a solid, the electrostatic field of the unscreened nuclear charge is felt not only throughout the atom suffering the $1s$ vacancy, but extends a few atomic diameters away from the vacancy site. This field decreases roughly as $e/(\epsilon_e r^2)$ where ϵ_e, the effective dielectric constant, varies with r, the distance from the vacancy, and has a value probably between unity and some bulk "high-frequency" value.[18] This "Coulomb" field is superposed, of course, on the periodic field of the crystal lattice. The radial or energy position of any electron depends upon the net field in its locale.

The theoretical description of the system containing an inner electron vacancy depends upon the model used. The difficulty with almost all treatments to date is that they have been based essentially upon the one-electron approximation. This approximation, invalid in principle even for the treatment of x-ray spectra of gaseous atoms, may be seriously misleading when applied to solids.

Heitler-London Model

One theoretical description is offered by the Heitler-London model. When an inner electron vacancy occurs in an atom, those electrons (and levels) previously contributed to the normal unperturbed solid-state bands by that atom (and by a few neighboring atoms) may be extracted from the normal solid-state bands and occupy local, discrete levels. These new levels are probably just below the "mother" bands.[19] At distances

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[14] E.g., see Richtmyer, Barnes, and Ramberg, Phys. Rev. **46**, 843 (1934), and L. G. Parratt, reference 7.

[15] Confidence is established in the above use of Eq. (2) by the fact that the observed β_1 contour except for the region of overlap is essentially the same as the α_1 shapes for which the formula was specifically devised.

[16] We cannot safely conclude, however, that the shape of the $3p$ final state in β_1 emission is also Lorentzian by this argument.

[17] Previous measurements of the β_1 line (e.g., J. Valasek, Phys. Rev. **53**, 274 (1938)], with lower resolving power and with the less accurate photographic method of intensity measurement, have also implied a similar width discrepancy. O'Bryan and Skinner, reference 1, give a calculated "Sommerfeld band width" of 4.2 ev for the chorine $3s$ band in KCl (expected to be much less wide than the $3p$ band, see reference 4) and discuss an observed $2p\rightarrow 3s$ chlorine line of width 0.65 ev. No particular point, however, has been made of this discrepancy heretofore, perhaps because of unsatisfactory accuracy in the width measurements.

[18] The constant ϵ_e is less than the usual optical or high-frequency value 2.13 [N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford Press, 1948), second edition, p. 85] if the effective electron density within the orbit of the electron under consideration is less than the bulk KCl electron density. The question may be asked whether the usual optical frequency is high enough in view of the extremely short lifetimes of the $1s$ states. For chlorine, this lifetime (reference 20) corresponds to a frequency of about $4/\Delta T \cong 2.7\times 10^{15}$ cps, or to a radiation wavelength of about 1100 A. For potassium the corresponding wavelength is about 680 A. Evidently the optical frequency is not high enough but the proper "high-frequency" value probably differs from the optical value by a negligible amount.

[19] The atom containing the inner vacancy is, so far as the outer electrons and neighbors are concerned, an impurity-type atom of nuclear charge increased by about unity.

Calculations similar to those of B. Kockel, Z. Naturforsch. **7a**, 10 (1952), have been made here with a one-dimensional Kronig-Penny model of the crystal. These calculations show

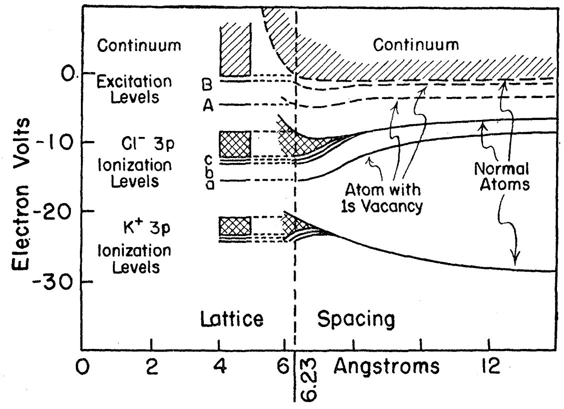

FIG. 4. Outer electron energy levels for normal atoms and for a chlorine atom with a 1*s* vacancy in a KCl crystal. At the equilibrium lattice spacing, 6.23 A, levels *a*,*b*,*c*, . . ., and *A*,*B*, . . . arise when one 1*s* electron has been removed. A different set of *a*,*b*,*c*, . . . and *A*,*B*, . . . levels (not shown) arises if the 1*s* vacancy is in a potassium atom. The energy separations are not intended to be quantitative.

greater than several atomic diameters away from the vacancy site the solid-state bands remain essentially unperturbed.

Some clarification of this model (not without danger of oversimplification, however) may be afforded by the following argument. Consider an otherwise normal KCl crystal to have a very large lattice spacing. In this case, the wave functions of the electrons of neighboring atoms have negligible mutual interactions and the corresponding energy levels of all the like-atoms are of essentially the same energy value. Suppose now that one of the atoms loses a 1*s* electron. All the energy levels of this atom then lie below their previous normal positions. For such a case, if it is a chlorine atom which suffers the 1*s* vacancy, the outer levels are sketched qualitatively in Fig. 4. If now the lattice spacing is reduced[20] to the normal crystal spacing, 6.23 A, the 3*p* ionization level (marked *a* in Fig. 4) persists below the normal 3*p* level, even as the normal level broadens into the solid-state band. And, in addition, new ionization levels (marked *b* and *c* for chlorine) are shown "peeling off" the bottom of the 3*p* bands of both chlorine and potassium.

The *b*, *c* levels may be thought of as near-neighbor levels that arise because the field of the excess positive charge extends to neighboring atoms.

Included in Fig. 4 is a level marked *A* which may be occupied (perhaps by the previous 1*s* electron in an absorption process) or it may be unoccupied.[21] Since the electron in level *A* is still essentially bound to the atom, this level is indicated as an excitation level.[22] In this model, the *A*, *B* levels are actually two of several series of levels, 4*s*, 5*s*, . . ., 4*p*, 5*p*, . . ., 3*d*, 4*d*, . . ., etc.; for simplicity, only two levels are shown, *A* and *B*, presumably the 4*p* and 5*p* if the one-electron transition dipole selection rules apply.[23]

Also, as has already been implied and notwithstanding the suggestion in Fig. 4, the limit or head of the *a*, *b*, . . . series or especially of the *A*, *B*, . . . series may possibly lie within the "mother" band rather than at its bottom edge.

Since the orbital radius of the electron in an *A* level may be of the order of an atomic distance, this level may also be thought of as a near-neighbor level. It is immaterial at this time whether the *A* and *B* levels are thought of as the 4*p* and 5*p* levels, or as near and next-near neighbor levels, or as the first and second "exciton" hydrogenic levels[2] in which the electron is bound simply to the relatively immobile 1*s* hole.

Another rough sketch of these possible electronic configurations is shown in Fig. 5, again not without danger of oversimplification. The regions of large amplitude of the electronic wave functions are presumably those where the heft or darkness of the level or band is large. In positioning the *A* and *B* orbits in Fig. 5, some consideration has been given to the electron attraction and repulsion of the potassium and chlorine atoms, respectively.

Collective Electron Model

The configuration of the outer electrons attending a 1*s* vacancy is probably much more complex than is indicated in the previous section. For example, the Heitler-London model would have six 3*p* electrons in each of the *a*,*b*,*c* levels. In the collective electron model, perhaps one or two electrons drop into the discrete *a* level in the system's effort to screen the bared nuclear charge, with the remaining screening accomplished by a

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unambiguously that local discrete levels do indeed split off the *bottom* of the band as a local square-well potential perturbation is introduced. The discrete levels also return to the *bottom* as the perturbation is removed.

Similar *n*-type impurity levels are discussed by J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936); G. H. Wannier, Phys. Rev. **52**, 191 (1937); J. C. Slater, Phys. Rev. **76**, 1592 (1949); H. W. Leverenz, *An Introduction to Luminescence of Solids* (John Wiley & Sons, New York, 1950); E. N. Adams, II, Phys. Rev. **85**, 41 (1952); G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); and by others, e.g., reference 5.

[20] The lattice spacing must be reduced in a time short compared with the lifetime of the 1*s* vacancy (but with adequate time for the bands to form). The 1*s* lifetime is 1.5×10^{-15} second for chlorine and 9×10^{-16} second for potassium, as deduced from the uncertainty relation $\Delta E\Delta t\approx h/2\pi$.

[21] If the *A* level is occupied, the screening of the excess nuclear charge (bared by the 1*s* vacancy) is slightly altered and all the discrete levels, especially *B*, . . ., are shifted somewhat in position.

[22] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 413, and Wannier, reference 19.

[23] The radiative selection rule, $\Delta L=1$, where L is the angular momentum of the system (assuming Russell-Saunders coupling), is interpreted in x-ray spectra as $\Delta l=1$, where l is the angular momentum of the inner electron vacancy.

Actually, in the x-ray spectra of solids, it is conceivable, since many electrons are involved in the radiative transition, that the angular momentum of the photon can be absorbed by one of the outer electrons rather than as a consequence of the change of parity of the inner vacancy. However, the authors know of no experimental example in which the usual interpretation does not apply.

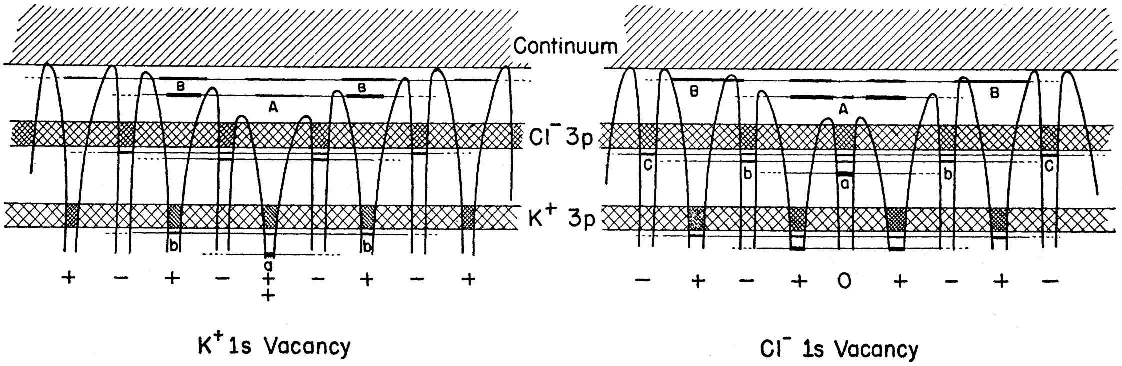

FIG. 5. Rough sketch of generalized electron configuration for crystalline KCl with a 1*s* vacancy in either potassium or chlorine. Possible distortion of the bands is not indicated.

local distortion of the bands themselves. It is possible, for a metal (or any conducting solid), that, for some combinations of atoms and inner vacancy, no electrons drop into the discrete level below the valence band, the screening at this distance from the center of the atom being accomplished entirely by the altered charge density in the valence band.[24,25] Especially, with a good metal, the redistributed charge in the valence band may screen so completely that the *A*,*B* levels do not form.[2]

In the case of an ionic crystal, such as KCl, the charge flow in the bands is probably not very great and at least the *a* and *A*,*B* levels are of real significance. But, it should be pointed out, the wave-function symmetry of these levels is not simple: Each level is some linear combination of all levels or bands near it and has a mixed wave-function symmetry. We are interested now in only the *p*-symmetry part of each level as it interacts radiatively with the 1*s* wave function.[23]

Initial Energy State

It is properly inferred from the above discussion that several different electron configurations are possible with a 1*s* vacancy, and hence the 1*s* state may have several different energy values. For example, the *A* level for chlorine may lie sufficiently close to the valence band that, in the scramble of electrons attending the formation of the 1*s* vacancy, a valence electron may jump to the *A* level with a probability such that the jump may occur for some atoms and not for others. Or the number of electrons dropping into the *a* level may be statistically different. We don't know these relative probabilities. However, it can be definitely concluded experimentally[26] that, if more than one 1*s* energy state exists so far as intense emission is concerned, they are extremely close together. We shall assume that only one 1*s* state is of any importance for emission although we cannot at this time definitely describe its electron configuration.

Figure 6 shows schematically six possible electron configurations, two of which include a 1*s* vacancy. A characteristic energy state exists for each configuration. We have chosen one of the two $K(1s)$ states as the significant 1*s* state for emission.[27]

Final Energy State

We now turn to the final energy state which exists in KCl after a radiative transition in the β spectral region has occurred. Since the 1*s* vacancy is no longer present, the discrete levels, *a*,*b*,*c* and *A*,*B*, no longer exist, and the final electron configuration is one with a vacancy in the 3*p* band.[28] We suggest that the vacancy

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[24] J. Friedel, reference 5.

[25] This may be involved in the success of the conventional interpretations (reference 1) of emission spectra of metals for the very soft x-ray wavelengths, e.g., the $L_{\text{II,III}}$ "bands" of Na, Al, and Mg. However, see reference 29.

[26] The 1*s* vacancy state is the initial state for emission of the $K\alpha_{1,2}$ lines whose structure and widths have been accurately measured. Each of these lines is essentially a singlet whose width is not a very sensitive function of atomic number or physical state of the target of the x-ray tube. (E.g., see L. G. Parratt, Phys. Rev. **50**, 1 (1936), Table VI, and references. Also, see the comparison of the 1*s* width of metallic potassium with gaseous argon, reference 3). The small dependence of width on the chemical or physical state of the target, observed in some instances, is probably caused by effects in the $L_{\text{II,III}}$ final states rather than in the $K(1s)$ state.

[27] The other 1*s* state shown in Fig. 6 might be produced in any of several ways. For example, the electron which was ejected from the 1*s* level might settle down in the *A* level. Alternatively, if the valence and conduction bands were so distorted locally by the 1*s* vacancy that the *A* level in the dip in the conduction band were close to or actually lower than the top of the unperturbed valence band, it is likely that one or more valence electrons would jump into it. We may distinguish between *A* levels having *s*- and *p*-type symmetry, *viz.*, A_s and A_p. In the formation of the 1*s* state, the ejected 1*s* electron may take with it whatever angular momentum is required to allow occupancy of either or both of the A_s or A_p levels. But in the x-ray emission, a transition filling the 1*s* hole, only one unit of angular momentum is taken out of the system by the photon. (The short time involved in the rearrangement of the many-electron system, $\sim 10^{-15}$ second, probably prevents phonon interaction.) Hence, the electron rearrangement may end with an A_s electron in the conduction band, giving a photon energy some 10 ev less than it would have if all the *A* electrons jumped back to the 3*p* band. However, an argument from the widths of the emission and absorption lines allows us to conclude that such a state does not play a significant role in the emission process (see reference 36).

[28] Associated with the hole in the 3*p* band are new *A*,*B* levels, new in the sense that an electron in such a level is bound to the 3*p* hole rather than to the 1*s* hole. The 3*p* hole and its bound electron constitute a Frenkel mobile exciton.

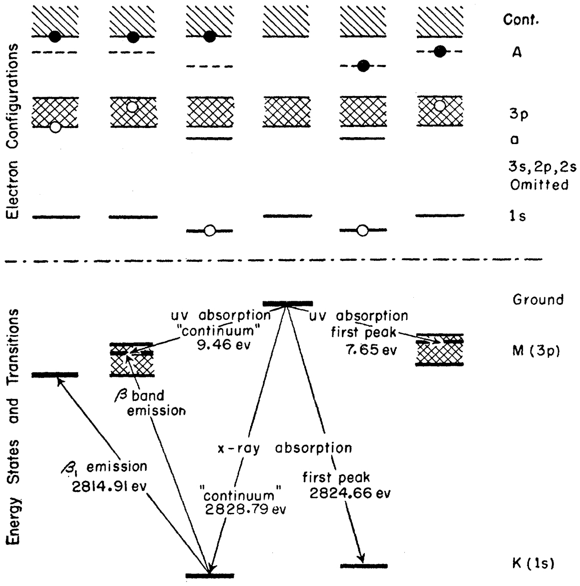

FIG. 6. Emission and absorption for chlorine in KCl. For simplicity, the *B*, . . ., and *b*, . . ., levels (and many others) are omitted. Two 1*s* (or *K*) states are indicated; only one is significantly involved in x-ray emission, but many more than the two shown are involved in absorption. Only two 3*p* (or $M_{\mathrm{II,III}}$) states are shown here in x-ray emission and two in ultra-violet absorption. The energies listed are for chlorine, referred to the β_1 wavelength 4394.91 x-units (Valasek, reference 17). "Continuum" absorption refers to the "bottom of the conduction band," perhaps as indicated by the zero of the energy scale in Fig. 2.

position in the band, and the energy and width of the final state, depend upon whether the electron that jumped to the 1*s* hole came from, say, an *a* level or from the 3*p* band itself.

If the electron came from the *p*-symmetry part of the 3*p* band, the final hole may be anywhere in the band, the statistical position being determined by the product of the transition probability and the density of states in the band. In this event, the β emission should be broad, as discussed earlier, Fig. 1. It is suggested that this transition may give part of the observed faint unresolved structure on the high-energy side of the β_1 line for either chlorine or potassium, Fig. 3, but not the strong β_1 line itself. The 3*p* band emission corresponds to a transition in Fig. 6 from column three to column two.

If the electron came from the *p*-symmetry part of the *a* level, the final hole in the 3*p* band is located at that part of the band (or bands) from which the *p*-type part of the *a* level was extracted during the formation of the initial 1*s* state. The energy represented by the extraction of the *a* level and *a* electron(s) must be essentially the same for all atoms suffering the 1*s* vacancy, since this extraction is an inherent part of the formation of the 1*s* state and since the 1*s* state is known experimentally to be sharp.[3,26] We conclude, therefore, at least phenomenologically, that the final state in "$1s\rightarrow a$" emission must be very narrow.

Suppose that this transition, $1s\rightarrow a$, yields the observed β_1 line. Then, if the band radiation is part of the β_x or β'' complex structure shown in Figs. 2 and 3, the energy position of the final state in β_1 emission is at the lower limit of the broad energy smear corresponding to the 3*p* band. It should be noted that experimentally there is no apparent unresolved structure on the low-energy side of the β_1 line. We conclude that the final 3*p* vacancy in the $1s\rightarrow a$ transition is not only sharp in position but must be at the bottom of the 3*p* band.[29]

The probability that an outer electron will jump into the 1*s* vacancy is proportional to the overlap of the outer electron wave function with the 1*s* wave function. For a photon polarized in the *x*-direction the transition probability $P_{1s\rightarrow a}$ is proportional to

$$e^2\left|\int_\tau \psi_a{}^* x \psi_{1s} d\tau\right|^2.$$

Because the wave function of the *a* level electron is localized about the 1*s* vacancy site, the overlap of ψ_a and ψ_{1s} is relatively large, and perhaps, therefore, $P_{1s\rightarrow a}$ is larger than $P_{1s\rightarrow 3p\ \mathrm{band}}$. If so, it is in agreement with the observed strong β_1 line. (The ratio $P_{1s\rightarrow a}/P_{1s\rightarrow 3p\ \mathrm{band}}$ refers, of course, to areal intensities, not to peak intensities.)

Complex Structure Accompanying β_1

We have already stated that the 3*p* band emission may be part of the high-energy structure accompanying β_1. Perhaps also in this structure is the line arising from a *b* (or *c*) electron jumping to the 1*s* vacancy, but this transition is believed to be relatively improbable and the line to be rather faint at best. It seems likely that one or more "satellite" lines—double inner ionization lines, e.g., $1s3s\rightarrow a3s$—are superposed on the 3*p* band emission and are more intense than the *b*,*c*

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[29] In a metal, the final vacancy in the valence or conduction band, following a transition from the *a* level to the deep inner hole, may "bubble up" toward the top of the band by a series of radiationless transitions in which a conduction electron is raised to an empty conduction level in each transition step. [See P. T. Landsberg, Proc. Phys. Soc. (London) **A62**, 806 (1949)]. In a filled band, however, in either a metal or an insulator, the bubbling is prevented.

If, in a metal, the bubbling process is moderately fast compared with the time of the radiation process itself, it is proposed that the energy of the photon in *a*-type emission may be increased because of the new position of the hole in the band. Such an *a*-type transition, involving an intermediary state, results in the same photon energy as in a conventional band emission but gives a different transition probability and, hence, shape of the emission band. This proposed effect of a bubbling hole is in addition to Landsberg's effect, and the two mutually exclusive effects may be thought of as in competition, both effects changing the shape of the emission for the metal.

If the bubbling is sufficiently fast that the hole arrives at the top of the band before the radiation process is essentially complete, a peak may be observed on the high-energy side of the emission band. Such a peak is actually observed in the $L_{\mathrm{II,III}}$ emission. [E.g., see W. Cady and D. H. Tomboulian, Phys. Rev. **59**, 381 (1941)]. Other explanations of this peak have been proposed by Skinner (reference 1) and by Friedel (reference 5) [see also Y. Cauchois, Acta Cryst. **6**, 352 (1953)].

lines. Satellites in this region have been reported for several neighboring elements, and for various compounds.[30,31] Our knowledge of satellites (at least K-series satellites) is very meager, both experimentally and theoretically.[32] Most $K\beta$ satellite studies for low atomic numbers have been with badly overexposed photographic plates, studies carried out for the purpose of detecting and measuring wavelength positions only.

We cannot yet distinguish clearly between the supposed broad $1s\rightarrow 3p$ band emission and the satellites. However, if we ascribe an appreciable fraction of the observed intensity to the $3p$ band emission, then, to be consistent with our interpretations, we must readjust the background in Fig. 3 to decrease the β_1 component intensity at its peak, shift its peak slightly to lower energy, and thereby leave some $3p$ band intensity to overlap the β_1 peak position by half the width of the $1s$ state. Then, the suggested line very close to β_1 is considerably more pronounced and, if symmetrical, is a narrow component, perhaps a b line or a satellite. This background readjustment, which could leave the width and shape of β_1 unaltered, has not been done because of an unknown relative intensity and shape assignment for the $3p$ band emission.

The potassium β_5 line as shown in Fig. 2 may be a satellite line. This line is found at an energy position 11.68 ev higher than the β_1 peak and -12.96 ev from the continuum as indicated in Fig. 2. Its numerical subscript implies that it is the quadrupole line $1s\rightarrow 3d$ as traced down from elements of higher atomic number. Valasek[17] suggested that this β_5 line may arise from a cross transition $K^+\,1s\rightarrow Cl^-\,3p$, but the transition probability for this is expected to be low. As viewed by the $K^+\,1s$ hole, the $Cl^-\,3p$ wave function has a complicated symmetry.[33] We do not now propose an interpretation of $K^+\,\beta_5$.

Many β_1 "satellite" lines (8 or more for potassium and 12 or more for chlorine) have been reported by various observers using overexposed photographic plates. The interpretation of most if not all of these lines is in some doubt. Many of them may not be double-ionization satellites but, rather, may involve the characteristically solid-state states, both narrow and broad, of which we have mentioned only a few.

ABSORPTION SPECTRA

The experimental absorption curves are shown in Fig. 2. We have already implied an interpretation of the first absorption peak as the transition indicated in Fig. 6, *viz.*, the one in which the $1s$ electron goes to the A level.[34] Also, it appears reasonable that the second strong absorption peak comes about when the $1s$ electron is placed in the B level.

Widths of Final States

To check these assignments, we first examine the final state widths. In each case, if the absorption contour is resolved into two component absorption lines and a complex continuum, the full width at half-maximum of the first line is about 2 ev before correction for the spectrometric resolving power, and about 1.6 ev after correction. This 1.6-ev width, which also includes the $1s$ width (0.45 ev for $Cl^-\,1s$ and 0.73 ev for $K^+\,1s$) in some fashion not presently resolvable,[35] is too narrow for the A level to be just a conventional band in the continuum.[36] The A level, and probably also the B level, must be discrete and localized.

The Continuum

The position of the bottom of the continuum is not recognizable in the observed contour for either chlorine or potassium, Fig. 2, but we would like to know this position in each case.[37] The theoretical calculation of the energy difference between the $1s$ states in which the electron is (1) in the A level or (2) at the bottom of the continuum (i.e., the energy states of the third and fifth columns of Fig. 6) is not an easy one.

In an effort to avoid this calculation, we might consider the $A,B,\ldots$ levels for potassium as the vestiges of the optical $4p,5p,\ldots$ levels.[38] In this

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[30] E.g., H. Tazaki, J. Sci. Hiroshima Univ. **A3**, 321 (1933); **A4**, 185 (1934); **A6**, 299 (1936); and **A10**, 73 (1940); and O. R. Ford, Phys. Rev. **41**, 577 (1932).

[31] E.g., J. Valasek, reference 17.

[32] The current view [e.g., see F. R. Hirsh, Revs. Modern Phys. **14**, 45 (1942)], although only qualitatively substantiated for only some satellites, favors the double inner ionization theory. The competing theory, the Richtmyer "simultaneous double electron jump," is expected to be more favorable as the coupling between inner and outer electrons gets stronger, as with decreasing atomic number. The wavelength position of a "double jump" satellite would seem to be the more sensitive to variations in the solid state, and if the second jump involves a broad band of states (e.g., $1s3s\rightarrow a3p$ or $1s3p\rightarrow a3p'$ where $3p'$ is a hole higher in the band than the initial $3p$ hole) the satellite line should be broad. Satellites as reported appear to be only slightly broader than the parent lines [e.g., see L. G. Parratt, reference 26, and C. A. Randall and L. G. Parratt, Phys. Rev. **57**, 786 (1940)], but this appearance may well be a mere consequence of the arbitrariness in the number of and position of the resolved components.

[33] O'Bryan and Skinner, reference 1, also discuss cross transitions and point out the "symmetry-interchange" effect. However, the emission bands they attribute to cross transitions have an amazingly high relative intensity for such transitions.

[34] The association of the first absorption peak with a discrete exciton-type level is not new; e.g., see reference 2.

[35] We cannot simply subtract the $1s$ width as we would if we were dealing with the integrated product of two Lorentzian curves; here, at best, we are dealing with the sum of two curves, but the situation is more complicated as is indicated later.

[36] Most of the 1.6 ev width of the final state is due to the A level, and this part of the width is so great that it cannot be contained in the width of that $1s$ state which is the initial state for β_1 emission (e.g., column five of Fig. 6).

[37] Identifying the bottom of the continuum is a common problem in x-ray spectroscopy of the solid state, and too often investigators have ignored the difficulty of the task. This problem is also deeply involved in the interpretation of the critical x-ray absorption edges, e.g., in beta-ray spectroscopy. E.g., see Hill, Church, and Mihelich, Rev. Sci. Instr. **23**, 523 (1952).

[38] There is no corresponding optical atomic configuration for the case of a $1s$ vacancy in chlorine in KCl.

event, they may bear some relation to the levels in singly ionized calcium (as in the analysis for gaseous argon, reference 3). From the optical atomic spectroscopic data, the Ca II $4p-5p$ separation is 4.36 ev, $4p-6p$ is 6.08 ev, and $4p-\infty p$ is 8.7 ev. The first three observed separations from the first absorption peak for potassium in KCl are 3.5, 6.9, and 9.0 ev. Although the separations agree within 1 ev in each case, this is probably sheer coincidence; otherwise we might conclude that the dielectric constant is essentially unity and that there are no solid-state effects.

It is clear, however, from the work of Kiyono[39] on the K absorption spectra of potassium in potassium compounds, and from recent (unpublished) data obtained in this laboratory on the K absorption spectra of chlorine in other monovalent chlorides, that the lattice does have an important role in determining the spectrum. Therefore, any such simple "atomic" interpretation which neglects completely the solid-state effects will be quite inadequate.[40]

The simplest, qualitative theoretical calculation may be made from the hydrogenic relation as follows

$$\Delta E^A{}_{n=1} \doteq \frac{m_r}{m_e}\,\frac{R}{n^2\epsilon_0{}^2} \doteq \frac{13.58}{(2.13)^2} = 3 \text{ ev}, \qquad (3)$$

where m_r is the reduced mass of the coupled $1s$ hole and the A electron, m_e the electronic mass, R the Rydberg, $n=1$ for the lowest hydrogenic state, and $\epsilon_0=2.13$ the high-frequency dielectric constant. For the B electron, $n=2$, and then $\Delta E^B{}_{n=2}=0.75$ ev. Each of these calculations presumes the spatial extent of the A or B wave function is large, sufficient to justify using the normal bulk value of the dielectric constant.[18] The wave-function extent, as indicated in Fig. 5, is not this large, especially for the A electron. With a limited A orbital size, the effective ϵ is probably a little closer to unity, and $\Delta E^A{}_{n=1}$ is correspondingly larger than the calculated 3 ev. In this connection, we note that the observed difference between the A and B absorption peaks is 3.9 ev for chlorine and 3.5 ev for potassium, in qualitative agreement with this type of adjustment in ϵ.[41]

The simple treatment of Eq. (3), however, does not distinguish between s- and p-type symmetry and assumes a highly questionable dielectric constant. An attempt was therefore made for potassium to divide the region in which the electron is localized into two parts: (1) the impurity cell and (2) the region outside the impurity cell. In the impurity cell the radial wave functions for the potassium core are used to estimate the phase of the radial function near the edge of the impurity cell. The potassium core is presumed to resemble closely that of Ca^{++} for which the quantum defects can be deduced from the optical spectra of Ca II by the method of Kuhn.[42] Outside the impurity cell an additional field term A/r^2 is used to make the potential continuous at approximately the Goldschmidt radius r from the center of the impurity. With the inner and outer regions thus joined, assuming again that $m_r=m_e$, the calculation gives $\Delta E^A{}_{n=2}=1.5$ ev. But, even with the A/r^2 term, we have probably taken the effective value of ϵ too large.

Morita[43] has reported a similar sort of calculation for KCl. However, he assumes that the second absorption peak represents the bottom of the continuum and he also neglects possible electronic polarization of the crystal. He obtains a value of 2.7 ev for the separation of the A and B peaks as compared with the observed 3.5 ev.

Nevertheless, these calculations, although still inadequate, are believed to be much better than the one of Eq. (3) for the $1s$ hole, and we conclude that the hydrogenic calculation is not to be taken very seriously.

It may also be pertinent to remark that the bottom of the continuum in crystalline KCl is normally thought of as the bottom of the $4s$ chlorine band. The potassium $1s$ electron may go happily (by the selection rules) to the bottom of this band because of the symmetry-interchange effect, but the chlorine $1s$ electron may prefer to go to a higher level having p-type symmetry near chlorine and perhaps s- or d-type near the potassium sites. (In general, the symmetry types in a band become mixed as one progresses up from the bottom, but at and near the bottom of an s-type band, the symmetry remains pure s-type.[44]) Hence, we may expect the $1s$ absorption continuum for potassium to be a little lower than for chlorine, and the shape of the absorption to be different in the two cases. This symmetry effect is believed to be important in accounting for the reversed ratio of intensities of the

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[39] S. Kiyono, Science Repts. Tohoku Univ. First Ser. **36**, 1 and 236 (1952).

[40] Another empirical "atomic" approach to this problem has been reported by Narbutt, Vainshtein, and Barinskii, Doklady Akad. Nauk S.S.S.R. **87**, 381 (1952). They propose that two superposed series of energy levels (one associated with the potassium ion and the other with the chlorine ion) are involved in the absorption spectra of both potassium and chlorine in KCl. The observed separations of the absorption lines arbitrarily resolved are used to calculate quantum defects which allow each series of levels to be described by a simple hydrogenic formula with a common series limit. These authors attach considerable significance to predictions made from these levels and to "confirmations" in the ultraviolet absorption spectrum of KCl, but the method appears to be rather *ad hoc* and to ignore the differences in the wave-function symmetries of the ultraviolet and x-ray absorption transitions.

[41] Equation (3), applied to the case of the A electron coupled with a $3p$ hole (column six in Fig. 6), gives $\Delta E^A{}_{n=1}=1.8$ ev, if the ratio $m_r/m_e=3/5$ which seems reasonable for the mobile exciton (assuming that the same dielectric constant applies). This ΔE agrees with the separation between the peaks observed in ultraviolet absorption for KCl (Mott and Gurney, reference 18, page 97). However, the extent of the A wave function associated with the $3p$ hole is not the same as with the $1s$ hole, and we should not derive much confidence from the simple, qualitative calculation of Eq. (3).

[42] T. S. Kuhn, Phys. Rev. **79**, 515 (1950).

[43] A. Morita, Science Repts. Tohoku Univ. **36**, 256 (1952).

[44] F. von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

A,B absorption lines for potassium as compared with chlorine.

The energy position of the bottom of the continuum is arbitrarily taken as 4.13 ev and 3.2 ev as measured from the first absorption peak for chlorine and for potassium, respectively, as indicated in Fig. 2.

This choice in each case, we might say, also helps make palatable the observed relative intensities of the A and B absorption lines. The relative height of the second line for potassium is reduced, as a component line, when the continuum background is subtracted.

The chosen energy position for the bottom of the continuum does not agree in either case with any previously reported position of the K absorption edge.[45] Although fine structure has been commonly observed near the edge, there have been very few satisfying attempts to interpret it.[37] The usual pragmatic definition of the position of the edge places it about halfway up the first abrupt absorption rise regardless of the kind or amount of fine structure present.

Shape of Absorption Line

A careful look at the shape of the first absorption line for either chlorine or potassium shows it to be very unusual. The low-energy side of the line falls much farther below the Lorentzian shape, matched at P and $W_{\frac{1}{2}}$, Eq. (1), than does any "reasonable" x-ray line. Furthermore, the shape near the peak of the chlorine absorption line is strangely asymmetric and strongly suggests multiplet structure. This asymmetry is not very evident on the scale of Fig. 2, but is very marked when the scale is enlarged.

Three possible causes of multiplet structure are now mentioned:

(1) The A level has p-type symmetry and is therefore split into a spin doublet. It is extremely difficult to calculate the expected spin-doublet separation. For the potassium case, we note from optical spectra for Ca II that $4p_{\frac{1}{2}}-4p_{\frac{3}{2}}=0.03$ ev, a negligible splitting, but the assumption here of optical terms is, of course, not quite valid.

(2) The A level must have p-type symmetry with respect to the $1s$ vacancy, but, as viewed by neighboring atoms, its symmetry is more complicated. Perhaps the interactions with the neighboring atoms cause the A level to be split into several discrete levels.

(3) The thermal vibrations of the lattice result in an apparent splitting of the A (or B) levels. Although the lifetime of the $1s$ vacancy is very short compared with the time of a vibration cycle, each atom having a $1s$ vacancy is caught in a different part of the cycle but most likely at either end of its vibration motion. The amplitude of vibration is different in different directions in the crystal. Hence, the A level is really a band of infinitesimally closed spaced levels. But the band may appear experimentally "flat-topped" or with a minimum in the central region.

Splitting, as mentioned above, may justify an arbitrary resolution of the A and B absorption lines into, say, two components each of which has a reasonable width and shape and whose sum equals the observed contour. Such resolution is not indicated in Fig. 2, however, because of the uncertainty of the appropriate absorption line component structure and the uncertainty of the bottom position and shape of the continuum.

Base Width of the 3*p* Valence Band

In ultraviolet absorption, two peaks are observed with KCl, one at 1620 A (7.65 ev) and the other at 1310 A (9.46 ev). The first peak is interpreted as corresponding to the transition indicated in Fig. 6, the second to the transition in which the $3p$ electron is ejected to the continuum. (It has been assumed that the ultraviolet B level, i.e., associated with a $3p$ hole, is at the exciton series limit (Mott and Gurney, reference 18) and at the bottom of the continuum (Wannier, reference 19). The $3p$ hole in the final state is taken at the maximum of the density of states, a position about $\frac{3}{4}$ of the way along the base width of the band as sketched in Fig. 6.

Then, if the energy contribution of the ultraviolet A level can be taken arbitrarily as about 1 ev less than that of the chlorine x-ray A level, we can deduce an approximate value for the base width of the valence $3p$ band by the following relation, using energies given in Figs. 2 and 6,

$$\frac{3}{4}W_{3p} \doteq 13.88-4.13-7.65+1.0,$$
$$W_{3p} \doteq 4.2 \text{ ev (base width).}$$

This value is in good accord with the expected width[4] although both values contain some rather poorly evaluated guesses.

CONCLUSION

Many points in the interpretation of x-ray emission and absorption curves in the spectroscopy of the solid state have been discussed. Crystalline potassium chloride has been used as an example. The processes of emission and absorption involve discrete local "impurity-type" levels associated with the solid state bands, both filled and unfilled.

Perhaps the most significant conclusion is the following: With curves accurately recorded (with a

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[45] E.g., Y. Cauchois and H. Hulubei, *Longueurs d'Onde des Emissions X et des Discontinuites d'Absorption X* (Hermann & Cie, Paris, 1947), and A. E. Lindh, *Handbuch der Experimental Physik, Rontgenspektroskopie* (Akademische Verlagsgesellschaft m. b. h., Leipzig, 1930), Vol. 24, Part 2.

precision intensity scale and very high, known resolving power), we find that the strong emission line involving the valence band electrons probably does not in general give much information about the normal unperturbed valence band itself. This conclusion, contrary to the most fundamental postulate in x-ray spectroscopy of the solid state, is more or less tentative. If this conclusion is wrong, we seem obliged to believe that the valence band in KCl is only 0.33 ev wide at the half-maximum of the density-of-states curve. Resolution of the question awaits a more precise theoretical treatment than has yet been made.

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Antiferromagnetism*

GEORGE W. PRATT, JR.
Lincoln Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts

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The nature of the spin coupling in MnO is discussed, the details of the discussion being based on a very simplified three-center system. The coupling between magnetic ions whose charge densities interact with an intervening nonmagnetic ion but not directly with each other is described as the result of the polarization of the nonmagnetic ion. The configuration interaction representation of this polarization is treated by non-orthogonal orbitals, orthogonal orbitals, and by a method due to Kramers. These three approaches are applied to a numerical example. It is concluded that a reliable description of the simple three-center problem is more complicated than generally believed due to the importance of highly excited states of the system which have been neglected in previous treatments of the problem.

INTRODUCTION

THE problem of the spin coupling of paramagnetic atoms or ions whose outer charge densities overlap an intervening nonmagnetic atom or ion, but do not directly overlap each other, is of considerable interest in understanding antiferromagnetism. Such a situation is met in MnO, an antiferromagnetic oxide of simple cubic structure. The magnetic ordering has been determined by neutron diffraction.[1] The (111) planes consist alternately of Mn^{++} ions and $\mathrm{O}^{=}$ ions. The spins of the Mn^{++} ions on a given plane are coupled ferromagnetically but the coupling between neighboring planes of Mn^{++} ions is antiferromagnetic as shown in Fig. 1. The distance between Mn^{++} ions on adjacent planes appears to be so large that no important direct overlap, hence interaction, exists. The antiferromagnetic spin coupling between planes seems to arise in part through an interaction involving the $\mathrm{O}^{=}$ ions. A detailed analysis of the actual situation in the crystal would be very difficult. It seems reasonable, however, that an examination of an $\mathrm{Mn}^{++}-\mathrm{O}^{=}-\mathrm{Mn}^{++}$ unit lying on a straight line connecting three planes, as shown by the dotted lines in Fig. 1, may explain the role of the oxygen ions in the spin coupling of the Mn^{++} ions. The energies of various spin orientations of the system must be found and compared. As the energy differences involved will be small, a meaningful result can be obtained only by a fairly complete configuration interaction investigation. Even the $\mathrm{Mn}^{++}-\mathrm{O}^{=}-\mathrm{Mn}^{++}$ problem is a very hard model to treat, and to further simplify the situation we will consider a three-center system containing four electrons. Here we have two magnetic ions A and A' separated by a nonmagnetic atom B as illustrated in Fig. 2. This situation was first investigated by Kramers[2] and more recently by Anderson.[3] It is the purpose of this paper to re-examine the problem in detail and to point out some of the requirements for an adequate description of the spin coupling.

THREE-CENTER SYSTEM

The ground configuration of our three-center system will be taken to be that in which there is one electron in a localized orbital u_A or $u_{A'}$ about the magnetic ions A and A', respectively, and two electrons with opposite spin occupying a single orbital u_B localized about the nonmagnetic center B. We speak of A and A' as being magnetic centers since they have a net spin associated with them in their lowest state. B is called a nonmagnetic center as it has a closed shell structure for its ground state. Clearly the energy of the ground configuration of the system will be independent of the spin orientation of the electrons about A and A' if the localized orbitals about these centers do not directly overlap since an undistorted closed shell ion does not care how the spins of its neighbors are situated. In order to get an energy separation for the states of different spin we must break up the structure of the intervening nonmagnetic ion. We wish, therefore, to find the answers to the following questions: First, when we have included the necessary configurations to describe this

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[1] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

[2] H. A. Kramers, Physica **1**, 182 (1934).

[3] P. W. Anderson, Phys. Rev. **79**, 350 (1950).