REVIEWS OF MODERN PHYSICS VOLUME 31, NUMBER 3 JULY, 1959

Electronic Band Structure of Solids by X-Ray Spectroscopy

L. G. PARRATT*

Cornell University, Ithaca, New York

CONTENTS

I. INTRODUCTION

X-RAY spectroscopy provides the most precise and reliable information about the general electronic structure of atoms. This method is likewise powerful in elucidating certain features of the general electronic structure of solids. Metals, semiconductors, and insulators may all be studied alike.

In principle, x-ray emission spectra give a more or less direct view of the outer occupied electronic levels or, rather, of the corresponding energy states of the solid, e.g., the valence band of states; and absorption spectra provide a similar view of the states corresponding to the unoccupied levels. With a combination of emission and absorption spectra, one hopes to see the forbidden energy gap characterizing nonmetals, and to see the Fermi energy for metals. However, what one actually sees is often dominated by the local discrete states set up as a consequence of the inner electron vacancy. The most difficult feature of this x-ray method is that the unperturbed or normal solid-state band spectra and the local discrete state spectra are superimposed, and careful experimental measurements and a careful interpretation are required. The interpretation is much more difficult than has been generally recognized, but also offers greater possibilities.

Another feature of the method is that, in interpreting emission or absorption spectra, due account must be taken of the relative transition probabilities. These probabilities involve the wave-function characters (symmetries) of the initial and final states, in accord with the well-known selection rules. Although it is commonly supposed that the admixture of the various wave-function symmetries is rather great in the valence and conduction bands of solids, it is still not complete. However, with a combination of spectra characterized by two or more different high-energy states, for example with the $K(1s)$ and the $L_{III}(2p)$ spectra, we can determine (again in principle since the interpretation is very difficult) the energy positions, widths, and shapes of the energy levels or bands, and the degree of occupancy of the corresponding outer electronic levels or bands, of any amenable solid.

For the investigation of its x-ray emission spectra the solid specimen is prepared as an anode of the x-ray tube, or as a secondary radiator for fluorescence radiation. For absorption spectral measurements it is prepared as a thin x-ray absorber. All the elements in the periodic table (except hydrogen and helium) can be studied by this method, although for many of them the variety of practical high-energy states is restricted.

Wavelengths employed in this work range from about 0.5 A ($\sim$25 000 ev) to about 800 A ($\sim$15 ev). There is thus brought into play a wide variety of both old and new experimental techniques, techniques involving the radiation source, diffraction of the beam for monochromatization, dispersion and resolving power, and devices for precise measurement of the x-ray relative intensity.

It is to be understood that this brief review is not intended to be exhaustive; it is intended to introduce and to orient the fundamental aspects of the subject in its present state of development for those physicists, chemists, metallurgists, etc., who have not had time to keep up with it. Other reviews of the subject have recently appeared[1–6] emphasizing the historical de-

---

* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF18(600)-300.

[1] A. E. Sandström, "Experimental methods of x-ray spectroscopy: ordinary wavelengths," in *Handbuch der Physik*, S. Flügge and Marburg, editors (Springer-Verlag, Berlin, 1957), Vol. 30, pp. 78–245.

[2] D. H. Tomboulian, "The experimental methods of soft x-ray spectroscopy and the valence band of the light elements," in

velopment and most of the experimental techniques, so we place our greatest emphasis upon current (and perhaps future) problems of interpretation.

Before launching into typical x-ray spectra and the interpretational problems, we first (a) mention the more general aspects of the method, (b) emphasize some experimental factors that must be appreciated before interpretation should be undertaken, and (c) point out certain essential features of the x-ray energy level diagram that have so far received inadequate attention.

II. GENERAL ASPECTS

Advantages and Disadvantages

As compared with other methods for studying the electronic structure of solids, the x-ray spectroscopic method has five significant general advantages:

(1) All types of solids can be studied (metals, semiconductors, insulators, pure elements, compounds, alloy systems, etc.).

(2) Details of the structure are obtained by the use of a relatively narrow high-energy state as a scanning probe.

(3) A wide energy range of the structure is covered giving widths, shapes, and energy positions of many states and bands of states.

(4) The degree of admixture or hybridization of wave-function symmetries is revealed by the use of two different types of inner electron vacancies.

(5) The spectra are relatively insensitive to the chemical impurities, surface states, or other types of lattice defects (except the defect due to the inner electron vacancy itself) which are so troublesome in most solid-state work.[7,8] Two important general disadvantages of the method are (a) the theoretical and experimental techniques for quantitative work are rather exacting, and (b) the problems of separating the two superimposed types of spectra, *viz.*, the unperturbed solid-state band spectra and the local discrete state spectra, have not been generally solved.

The theoretical aspect deserving special mention is the atrocious many-electron nature of x-ray transitions. Numerous simplifying approximations must be adopted for reasons of expediency and the final effects of these approximations remain unknown. Comment must also be made on the very short times involved in x-ray transitions,[9] of the order of 10^{-12} to 10^{-16} sec, making it important in most instances to take time-dependencies into account in the theoretical descriptions of the pertinent states and transitions. On the experimental side, the measurements must be made with the best techniques and with the highest accuracy in order to allow the necessary corrections to be applied with reasonable conviction. These corrections are listed later. Many spectra have been recorded in the literature for which the appropriate corrections are very large and have not been made.

With regard to the second disadvantage, studies of the local discrete states themselves (which we shall call "excitation" states[10]) provide valuable information about the perturbation due to the inner vacancy; such a perturbation becomes an additional tool in solid-state analysis. The excitation states are most easily recognized in absorption spectra with semiconductors and with insulators, although they are probably present also in some emission spectra. They are very much akin to those commercially-important states (in optical fluorescence) associated with an impurity atom.[11]

Handbuch der Physik, S. Flügge/Marburg, editors (Springer-Verlag, Berlin, 1957), Vol. 30, pp. 246–304.

[3] C. H. Shaw, "The x-ray spectroscopy of solids," in *Theory of Alloy Phases* (American Society of Metals, Cleveland, 1956), pp. 13–62.

[4] Y. Cauchois, *Les Spectres de Rayons X et La Structure Electronique de la Matière* (Gauthier-Villars, Paris, 1948).

[5] H. Niehrs, Ergeb. exakt. Naturw. **23**, 359 (1950).

[6] Landolt-Börnstein Tables (Springer-Verlag, Berlin, 1955), sixth edition, Vol. 1, Part 4, pp. 769–867. Many experimental curves are reproduced without any critical comment.

[7] Since the inner electron vacancy (the essential vacancy for an x-ray transition) involves a relatively high energy, its production is not much affected by the low energies that characterize the bonds in the crystal lattice. It is most improbable that an appreciable fraction of the observed x-ray transitions takes place in the immediate neighborhood of a chemical impurity or other lattice defect (exclusive of the defect due to the inner vacancy itself) unless these defects are present in an *unusually* high concentration.

[8] Another type of impurity, however, is a serious problem. This is the matter of being sure that the material under study is really of the crystalline form desired and is really free of volume and surface contaminants. In emission from an x-ray tube anode, only the first hundred or thousand angstroms of material is sampled, a sampling depth that depends upon the material, geometry and voltage of the anode. The effective temperature of the emitting volume of the anode is difficult to know or to control, especially with a nonmetallic anode, and some physical or chemical change may be unwittingly induced. A thin layer of oxide or sulfide, or a time-dependent layer of tungsten or of a carbonaceous deposit on the anode surface, is often a trial. In x-ray emission in fluorescence, the sampling depth is somewhat greater, the temperature is much easier to know and to control, and generally the physical and chemical state is much better known.

[9] An initial x-ray state may decay either radiatively or nonradiatively. If it decays nonradiatively, an Auger electron, rather than an x-ray photon, is emitted. The probability for radiative decay is called the fluorescence yield (it should be called the "radiative" yield). Values and discussion of this yield are given by Broyles, Thomas, and Haynes, Phys. Rev. **89**, 715 (1953); E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, London, 1952). For any state of energy less than about 15 kev, the Auger process is the more probable one and, hence, dominates the state lifetime; and for states of even smaller energy, the radiative probability becomes rapidly less, being less than 0.1 for states of energy less than about 4 kev.

[10] The term "exciton" is commonly used in reference to one type of excitation states in absorption spectra, especially in ultraviolet absorption. "Exciton" is a theoretical term that refers specifically to a coupled electron and positive hole that, as originally proposed by Frenkel, travel as a unit more or less freely around in the lattice. This term has acquired so much of the aura of the theoretical one-electron model that its use is apt to be misleading in practice, especially in the interpretation of x-ray spectra. Further comments on the one-electron model are made later.

[11] The "impurity atom" in the present case is commonly spoken of as one of atomic number $Z+1$ in a lattice site normally containing an atom of atomic number Z. Actually it is somewhere

Excitation states are discussed further in connection with the energy level diagrams.

Two Energy Regions

Requiring high resolving power (an energy resolution of about 0.1 ev) and accurate measurements of relative intensity (of the order of one percent), this spectroscopic method divides experimentally into two energy regions, with a strong tendency for a corresponding dichotomy of the subject as it appears in the literature.

The division is essentially according to the type of monochromator: For the region roughly 0.5 to 18 A, reasonably perfect crystals (calcite, quartz, mica, etc.) are used either on a two-crystal spectrometer (sometimes called a double crystal spectrometer) or on a focusing instrument in which a single crystal is carefully bent to focus the diffracted beam. For the region roughly 15 to 800 A, ruled concave gratings are used at grazing incidence in a Rowland mount. Vacuum instruments, or instruments whose x-ray path (including any transmission windows) is otherwise made easily penetrable, are employed for wavelengths greater than about 2.8 A.

Another difference between the two regions has to do with the method of measuring the x-ray relative intensity: The precise and reliable photon-counting techniques, especially with the proportional counter,[12] are used most advantageously in the 0.5 to 18 A range. The less accurate photographic techniques are used in the longer wavelength range. However, much work in the former range, especially pioneering work, has been photographic, and some success has been achieved with photon counters in emission work in the latter range. In either range, the photographic method is far better suited for quick surveys of wide spectral regions since only a single exposure is required. It is well known, of course, that the photographic method is well adapted to precise determinations of wavelengths of *well-resolved symmetrical* lines in either range, but a difficult and often impractical procedure must be set up for each exposure in order to translate the photographic blackening to a reliable intensity (or absorption) scale. This fact seriously hampers accurate photographic studies of such spectral properties as widths, shapes and relative intensities. Indeed, reports of such properties, if a reliable scale has not been established, are of very little or no quantitative value.

A third difference between the two regions is in the type of radiation used in absorption work. Continuous x-radiation from a conventional type x-ray tube is evidently too feeble to be practical at the longer wavelengths. Work to date, with one exception, has been done with optical spark lines. An excellent source of continuous radiation is now available from high-energy centripetally accelerated electrons in the orbit in a synchrotron.[13,14] This type of orbit radiation may soon replace the radiation from conventional x-ray tubes in x-ray spectroscopy in *both* wavelength regions, the beam being used directly in absorption work and being used to produce by fluorescence the characteristic emission spectra of any material placed in the beam.

Incidentally, the availability of the continuous radiation from the synchrotron "x-ray tube" will no doubt further stimulate the development of photon or electrical counters for the long wavelength region since this type of measurement system now becomes useful in absorption work as well as in emission. Because of the short pulses of radiation from the synchrotron, such counters will probably have to be arranged to measure an average number of photons per second by means of some integrating device.

III. RESOLVING POWER AND CORRECTIONS

In either energy region, two kinds of resolving power are involved: first, that due to the so-called "spectral window" of the instrument,[15] and, second, that due to the effective width and shape of the high-energy state in the x-ray transition. The central region of the spectral window, in the case of the two-crystal spectrometer, is determined essentially by the lattice type and degree of perfection of the monochromator crystals.[16] The tail regions of the window are usually

---

between Z and $Z+1$, depending upon the particular inner vacancy, because the screening of an inner electron on an outer electron is less than unity.

[12] The proportional counter, if designed to have a very stable and narrow pulse-height distribution, may be used with a single-channel discriminator to reduce the background intensity and also the intensity of any higher order spectra.

[13] D. H. Tomboulian and P. L. Hartman, Phys. Rev. **102**, 1423 (1956); D. H. Tomboulian and D. Bedo, J. Appl. Phys. **29**, 804 (1958).

[14] L. G. Parratt, Rev. Sci. Instr. **30**, 297(L) (1959).

[15] "Spectral window" refers to the effective *over-all* spectral response of the instrument. If the beam incident upon the spectrometer has a flat spectrum, the spectral window may be interpreted as the function which gives the probability that a photon of energy $h\nu$ will be counted when the spectrometer is set at energy $h\nu_s$. For example, the spectral window of a two-crystal spectrometer includes the effects of (a) the geometry of the horizontal and vertical collimating slits, (b) fluorescent radiation and the diffuse or Compton or other spurious scattering (especially from the second crystal), (c) any higher order spectra, (d) any frequency-dependent attenuation of intensity in the x-ray path in the spectrometer, (e) the relative wavelength sensitivity of the intensity-measurement system, as well as (f) the diffraction pattern of the two crystals in the $(n_A, \pm n_B)$ position of operation. The true spectrum is distorted by the spectral window by an amount that depends upon the window's width *and shape*—the somewhat remote tails of the window's shape cannot be ignored.

The dispersion of the instrument, *viz.*, the spread of an x unit or of an ev in Bragg angular measure or in linear measure along a photographic plate, should not be confused with resolving power, although with some types of instruments dispersion and resolving power are closely related.

[16] Calcite crystals are the traditional favorites, but recently quartz crystals have been shown to have higher resolving power and comparable percent reflection. [Adell, Brogren, and Haeggblom, Arkiv Fysik **7**, 197 (1954)]. Practical attainment of the higher resolving power requires skillful operation of a well-designed instrument. For example, with the two-crystal spectrometer with good quartz crystals, angular increments as small as 0.1 sec of arc must be measured accurately and the axes of the two crystals must be maintained parallel to within a few seconds of arc for *all* angular settings including both the parallel and the antiparallel positions of the instrument.

determined by a combination of the so-called thermal diffuse scattering and the slit geometry. In the grating spectrograph, the window is usually dominated by the width of the slit. In the case of the focusing bent-crystal instrument, the window is due to some combination of the crystal, slit, scattering, and focusing imperfections.

In the 0.5 to 18 A range, the over-all effective resolving power is usually determined, not by the spectral window, but by the width of the high-energy state. This state width in the 0.5 to 18 A range is of the order of 0.2 to 8 ev at half-maximum, depending upon the particular state and atomic number. On the other hand, in the 40 to 800 A range, the slit is usually the more important; and it is of the order of 0.01 to 0.5 ev wide. In the longer wavelength range, the "smearing" due to the over-all resolving power is often negligibly small, but this is never so in the 0.5 to 18 A range.

The rather large width of the high-energy state in the shorter wavelength range has been considered by many investigators to be a serious disadvantage, often over-compensating for (a) the ease and efficiency of producing the x-rays, (b) the convenience of the more penetrating x-rays, and (c) the precise measuring techniques of the photon counters. Recently, however, methods have been developed[17] for correcting the observed spectra for both kinds of resolving power if (a) the experimental curves are very accurately recorded, and (b) if the width and shape of both the spectral window and the high-energy state are accurately known. With the two-crystal spectrometer the window shape (exclusive of the remote tails) is usually intermediate between Gaussian and Lorentzian; with the ruled grating it is usually more nearly Gaussian. The shape of the high-energy state is commonly taken to be Lorentzian, as due to lifetime, but it also contains a Gaussian component due to lattice vibrations and often a width due to unresolved multiplet states as well.

Corrections to Observed Spectra

In general, several different corrections must be made to the directly observed spectra in order to obtain a reasonably reliable view of the energy level structure of the solid. The most important corrections in the 0.5 to 18 A range are commonly those for resolving power, both for the spectral window and for the high-energy state. In the 15 to 800 A range, often the conversion from photographic blackening to x-ray intensity is the most important correction. In either range, other corrections are also involved. Briefly, the effects for which corrections must be made, and in the order of procedure for making them, are (a) nonlinearity of the intensity scale, (b) instrumental resolving power (spectral window), (c) self-absorption by the material emitting the x-rays, both of the emission line or lines and of the ubiquitous continuous radiation, (d) background under the particular emission contour being studied, (e) satellites (or other "spurious" lines) in emission, and (f) width and shape of the high-energy state either in emission or in absorption. It is presumed that the material emitting or absorbing the x-rays is clean and of known physical and chemical state. In case of mixed materials, correction for the foreign material must also be included in (c), (d), and (e).

The relative importance of each of these six corrections, as well as the details of the correction procedures, depends upon the particular spectrometer or spectrograph used and upon the particular spectra under study. Unfortunately, even a reasonably adequate discussion of these corrections has not been attempted in most of the published work in this subject to date, and this fact has greatly impeded progress in interpretations.

It is significant that now it is possible, in either wavelength range, albeit difficult in some instances, to obtain "experimental" curves in which essentially the product $N_a(E)T(E)$ is plotted *vs* the energy E. In this product, $N_a(E)$ is the density of those states, including the excitation states, having the appropriate wave-function symmetry for the particular transition according to the radiative selection rules, and $T(E)$ is the transition probability. [Logically, $T(E)$ includes the effects of wave-function symmetry, but it is customary, because of the use of the energy level diagram, to place the subscript s or p, etc., on $N(E)$.] If one desires a view of the normal energy band structure of the solid, $N(E)$, unperturbed by the inner electron vacancy and regardless of the wave-function symmetries of the states, corrections for two additional effects must be made: (g) excitation spectra and (h) variations in the transition probabilities, with due regard for wave-function symmetries,[18] for the pertinent transitions

---

[17] J. O. Porteus and L. G. Parratt (to be published). Preliminary reports appear in Bull. Am. Phys. Soc., Ser. II, 2, 55 (1957); *ibid.* 3, 263 (1958).

[18] For a free atom, the transition probability is proportional to $\nu|M_{i,f}|^2$ in emission and to $1/\nu|M_{i,f}|^2$ in absorption, where $M_{i,f}=\int\Psi_f^*(\partial/\partial x)\Psi_i d\tau$, ν is the radiation frequency, Ψ_i and Ψ_f are the wave functions of the initial and final states, and the integration is over all space. For a solid, a similar expression applies but now the wave functions, especially for a state which contains an outer vacancy (e.g., the final state in emission) or an extra outer electron (e.g., the final state in absorption), are not at all well known, and, in particular, they cannot be assumed to have one-electron properties or even a convenient symmetry for purposes of integration.

As a part of the wave function of the final state in an absorption transition, the wave function of the ejected electron, if it is ejected completely free of the positive hole it leaves behind, is commonly assumed to be that of a plane wave in the lattice. If this assumption is valid, then in the transition probability, the linear momentum of this plane wave electron must be expressed as an angular momentum about the atom from which the electron is ejected.

In emission, the transition probability is proportional to ν, and, hence, the emitted intensity is proportional to ν^2. Some authors have partially corrected for the transition probabilities by dividing the observed intensity by ν^2 (the division by ν^3 by a few authors is evidently in error).[2] By the same argument, the from (or to) each and all states in the bands. With these eight corrections (a) through (h), one would obtain the density of states curve $N(E)$ *vs* E. But we do not yet know how to make corrections (g) and (h) satisfactorily. For example, each solid-state energy level or band contains an admixture of several different symmetries, and correction (h) presumes knowledge of this admixture. At present the most reliable method of obtaining this knowledge is from experimental x-ray spectroscopy with two or more high-energy states of different symmetries. However, in many respects, the degree of admixture is as interesting as the fully corrected $N(E)$ *vs* E curve itself.

Before discussing a few typical experimental spectral curves, let us prepare generally for some of the problems of interpretation. We devote considerable time to the qualitative details of the energy level diagram since it is here that confusion is most apt to arise.

IV. ENERGY LEVEL DIAGRAM

Terminology

At least to the uninitiated there seems always to be confusion among the terms "state," "energy level," "energy level diagram," "energy band," "electronic shell," "orbital," "ordinary x-ray state," "x-ray satellite state," "ionization state," "excitation state," and "electronic level." Let us first try to clarify these terms. This is a major step in the understanding of an energy level diagram.

"State" refers to an assemblage of particles in a particular configuration in a system. The system may be a gaseous atom, a polyatomic molecule, or a localized part of a large piece of liquid or solid material. In a liquid or solid, the degree of localization is determined by the lifetime of the state in question and by the Franck-Condon principle. The energy of a state is also called the energy level in implicit or explicit reference to an energy level diagram. Such a diagram is discussed in detail later. An energy band in a solid (or in a liquid or in a polyatomic molecule) refers to a band of energy levels extremely closely spaced.

Those electrons that are described by the same wave-function characteristics (except for the direction of electron spin) are said to make up, or to be in, one "electronic shell" or "orbital." For example, the $2p_{\frac{1}{2}}$ electrons (called L_{II} or sometimes L_2 electrons) comprise one electronic shell or orbital (called the L_{II} or L_2); so do the $3d_{\frac{3}{2}}$ electrons (called M_{IV} or M_4); etc. The term shell or shells is used especially for the appropriate group or groups of electrons or orbitals in a monatomic gaseous atom and for the inner electrons in a polyatomic molecule, a liquid or a solid, but not very often in reference to the outer electrons in a nonmonatomic system.

It follows that each state of a many-electron assemblage—a gas, liquid, or solid—refers to a configuration of *many* constituent electronic orbitals. It also follows that only an electronic shell or orbital (but *not* a state or band of states or an energy level) can be said to be occupied or unoccupied, i.e., by one or more electrons.

An ordinary x-ray state always refers to an electron configuration in the system in which there is one and only one inner electron vacancy. For this reckoning, any bound electron in the system, except a valence electron,[19] is an inner electron. This definition of an ordinary x-ray state unfortunately excludes the state corresponding to a vacancy in the valence orbitals. In spite of this exclusion, the valence state is, for obvious reasons, always included in the x-ray energy level diagram of ordinary levels.

Two or more inner vacancies correspond to a second- or higher x-ray state, sometimes called an x-ray satellite state.[20] Higher order or satellite states are usually emphasized only in the emission of satellite lines, but they are also of direct interest in absorption spectra.

Any ordinary x-ray state may be an ionization state or it may be one of various types of excitation states. It is an ionization state if the ejected electron is completely free from the Coulomb field of the atom (or ion) in question, and if there is no abnormal configuration of the valence electrons. If the inner electron is ejected from its shell but is not completely free, it remains bound in an orbital outside of the occupied valence orbitals. In this event the system is in one type of excitation state. Excitation states are discussed in detail later.

In this terminology, we refer to the type of many-electron assemblages actually encountered in the interpretation of any and all x-ray spectra. Insofar as the gross features of the *inner* part of the atom are concerned, an x-ray state may be thought of as a "one-electron vacancy state." One of the theorems in atomic spectroscopy says that a one-vacancy system behaves in many respects like a hydrogenic or one-electron system. In hydrogen, it suffices to treat the energy of the system as being the same as the energy of the one electron, and no distinction is made between the electron energy and the system energy. Because of the difficulty of theoretical calculations of a many-electron

---

observed absorption spectra (properly plotted as absorption coefficients) should be multiplied by ν. These partial corrections are of little importance in the short wavelength range but often change considerably the general shape of either emission or absorption curves in the long wavelength range.

[19] We use the term "valence electron" to refer to any electron in the *outermost* band of electronic orbitals that is normally partially or fully occupied. In this use, we do not separately distinguish a conduction electron in a metal, nor heed the special role of certain valence electrons in the physical or chemical bond in molecules or solids.

[20] This is the conventional definition of an x-ray satellite state, but the exclusion of a valence vacancy as the second vacancy does not mean that the energy of the state is not affected thereby. In fact, if the second vacancy is in what we later call an excitation valence orbital, especially if it has s-type symmetry, it produces a very significant change in the energy of an inner-vacancy state. We shall later refer to such an altered state as one type of x-ray excitation state.

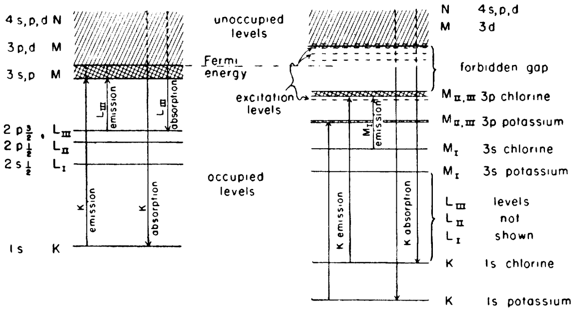
system, the theory of the one-electron approximation is used as the basis of the theory for the many-electron atoms and for the solid state. It is common in solid-state lore to refer to a change in a single electronic level as being simply the change in the energy of the system. This, of course, would be valid if, as *the* electron shifts in its momentum or energy position, there is no shift of any other electron in the system. Actually, in most physical phenomena when examined in some detail, including x-ray spectra, the interaction between electrons is so great as to invalidate this one-electron approximation.

The symbol terminology of the one-electron model, *viz.*, *s*, *p*, *d*, etc. (lower-case letters) to indicate electrons, electronic orbitals, bands of orbitals, states, energy levels, and energy bands, is usually retained in x-ray spectroscopy in spite of the intrinsic many-electron nature of the problems.[21] These one-electron symbols are retained with the implicit understandings that (1) they refer to the *principal* jumping electron in the x-ray transition, (2) they do not indicate an absence of interaction between this principal electron and other electrons in the system, and (3) in applying the radiative selection rules to determine the allowed transitions, the assumption or approximation is made that the change in the angular momentum of the entire system is given by the angular momentum change of just the principal jumping electron, i.e., that no other electron changes its angular momentum. It must be realized that retention of the one-electron symbols carries along a tendency to confuse the many-electron system energy levels with the one-electron system energy levels; *every effort must be made to avoid this confusion.*

"One-Electron-Jump" Diagram

Figure 1 presents a rough sketch of a conventional so-called energy level diagram (a) for a metal and (b) for an insulator. Although this type of diagram contains some confusion and is inherently inadequate, as implied generally above and as pointed out specifically below, it is the one that has been most used in this subject to date and therefore deserves discussion.

By definition, each level in the diagram is supposed to denote the energy of the entire system when one electron is missing from the particular electronic shell or orbital specified in the energy level terminology. It is supposedly a diagram of x-ray ionization states. A few so-called excitation levels are sketched in for the case of the insulator although, as we shall see, inclusion of these states in this type of diagram is somewhat abortive. The principal feature intended, of course, is that the transition arrow give the energy of the photon emitted or absorbed. With a linear energy scale, this energy is interpreted as being the length of the arrow; however, for convenience in x-ray spectroscopy where a wide range of energies is involved, a logarithmic scale is usually used.



(a) Al metal (b) KCl insulator

FIG. 1. Conventional x-ray "energy level" diagram (arbitrary scale) for each of two solids. This type of diagram was devised for a combination of a one-electron-vacancy model and a one-electron model; it is incomplete and misleading (see text).

The confusion in this diagram appears in both atomic and solid-state work, but it is in solid-state work that it becomes especially serious.[22] We shall presently propose another type of diagram, one that is more complex but that, we believe, has the necessary features to avoid the pitfalls of misinterpretation inherent in the diagram of Fig. 1.

One type of confusion is the following. The lower part of the "occupied" region of the diagram is just an inversion[23] of the diagram conventionally used as a satisfactory approximation in interpreting the gross features of x-ray spectroscopy of the "inner" or high-energy levels. But, in the "occupied" and "unoccupied" regions near the valence and conduction bands, we have deviated from the one-vacancy system and have drawn in the normal or unperturbed solid-state bands in which the effect of the vacancy is ignored. In fact, we usually treat the upper or solid-state part of the diagram as a one-electron system instead of as a one-vacancy system. This composite leads to difficulties when transitions between the lower and upper parts are considered. One difficulty becomes readily apparent

---

[21] Upper case letters are often used in referring to theoretical x-ray satellite states corresponding to multiple inner vacancies. In this case the electron configuration is presumed to be completely known and to behave as a monatomic many-electron system.

[22] It may be argued that, in a general sense, any diagram is merely a shorthand aid to memory, and if someone finds a particular scheme useful as a memory aid, it cannot be properly called inadequate or inconsistent for him. But diagrams somehow have a penchant for becoming pedagogical and interpretational aids as well as memory aids, and a poor diagram is often definitely harmful.

[23] All the bound stationary states of a hydrogenic or one-electron system are of negative energy, and all unbound or continuum states are positive. In the case of a one-vacancy system, the bound states are properly reckoned as positive. Accordingly, several years ago, before "solid-state spectroscopy," the x-ray diagram was drawn with the *K* state at the top instead of at the bottom. The arrangement with the *K* state at the top is conceptually better for "atomic" x-rays but it does not allow conveniently for the continuum of states. The inverted arrangement of Fig. 1 has been used in deference to the convention in solid state work.

when it is realized that the initial state for x-ray absorption is actually one for which the system is in its normal unexcited state, i.e., in its "single-valued" ground state,[24] whereas in the diagram the energy of this initial state is drawn as some one of *many different* energy levels in the unoccupied part. This is evidently a confusion of the energy level idea with a part of the electron configuration in the system.

As just implied, the diagram of Fig. 1, with the direction of the transition arrow reversed, is better used to indicate the initial and final positions of the principal jumping electron. Such a one-electron-jump diagram *could* purport to give the energy values of the initial and final states on the argument that each electron configuration, when completely specified, corresponds to a definite energy of the system. The difficulty in this use of the diagram is that there are generally many different electron configurations associated with each inner vacancy, and there may be several different electrons jumping in each transition. For example, it is clear that an excitation energy level exists only because of, and during the lifetime of, the inner electron vacancy. Consequently, when an electron jumps from any occupied orbital to fill the inner vacancy, the excitation level ceases to exist (or changes to a different excitation level), and any electron in the excitation orbital must also jump to some new orbital. In the special event that the inner vacancy is filled by the excitation electron, i.e., by the electron in the excitation orbital, the final vacancy is in no sense in the excitation energy level as this level appears in the diagram. Energy-wise, where did the electron jump from? No transition arrow can be drawn in the conventional diagram to indicate this jump.

X-Ray Excitation States: BEE and VEC Types

A proper x-ray energy level diagram should have a single energy level corresponding to the ground state (which is conveniently called zero energy) as the initial state for each and every x-ray absorption transition; and the final state, being one in which the ejected electron is in any one of many otherwise unoccupied outer electronic orbitals or in the continuum, should be represented as one of *many* high-energy levels. For example, for K absorption, the diagram should show the variety of final-state energies as a type of splitting of the conventional K state, including the continuum of K levels as well as the several discrete K levels. Any one of these many K levels may be the terminus of the head of the arrow representing a K-absorption transition. Similarly, each one of the other conventional x-ray energy levels (L_{I}, L_{II}, L_{III}, M_{I}, M_{II}, etc.) should be split into several discrete levels and a continuum. An x-ray state in which the ejected electron resides in one of the bound orbitals is one type of excitation state. To the many possible states of this sort, we assign the descriptive name "bound-ejected-electron" (BEE) excitation states.

Bound-ejected-electron excitation states are commonly produced in x-ray and ultraviolet absorption but are believed to be only rarely produced by bombardment with cathode electrons in an x-ray tube anode. Such states probably dominate the irregular structure observed near the absorption edges, e.g., see Fig. 2 for a curve for a monatomic gas,[25] Fig. 3 for a polyatomic gas, and Fig. 4 for a solid. But, especially in solids, other types of excitation states may also be involved. Since 1920, any observed structure near the "main" absorption edge has been known as Kossel structure.[1,26]

Another type of excitation state was implied earlier, *viz.*, a state in which the system has some abnormal configuration of the valence electrons. For many materials, it is highly probable that only the so-called normal configuration of valence electrons is significantly involved. But for some materials, e.g., solids having s-type valence electrons and perhaps an incomplete inner shell (transition metals), the "abnormal" con-

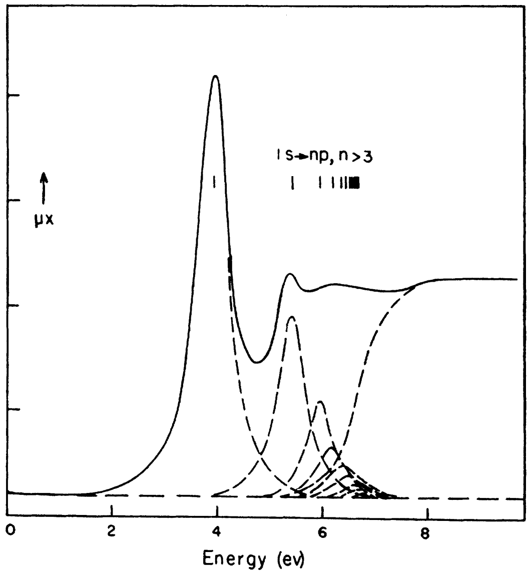


FIG. 2. K-absorption spectra (uncorrected) for gaseous argon [L. G. Parratt, Phys. Rev. **56**, 295 (1939)]. The structure is dominated by bound-ejected-electron excitation states; the "main" absorption edge occurs at the series limit of these states.

---

[24] The energy of this ground state is conveniently taken as the zero energy for all kinds of systems—gases, liquids, or solids.

[25] The correction for instrumental resolving power as reported by L. G. Parratt [Phys. Rev. **56**, 295 (1939)] is not quite right as judged by the results of the new correction procedure. The curve in Fig. 2 is not corrected for resolving power.

J. A. Soules and C. H. Shaw [Phys. Rev. **43**, 470 (1959)] also report this absorption spectrum but they evidently have an inadvertent "thickness effect" in their curve. Indeed, many or most of the x-ray absorption curves reported in the literature suffer from this effect. For a discussion of the thickness effect, see Parratt, Hempstead, and Jossem [Phys. Rev. **105**, 1228 (1957)].

[26] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935), pp. 662–671.

figurations are believed to be important. Let us look at the valence electrons more closely.

As the inner vacancy is being produced, a change occurs in the Coulomb field in which all the electrons of the system find themselves. No doubt, the final configuration of all the electrons would be essentially unique (i.e., only the normal configuration) for a given inner vacancy *if* the inner vacancy were formed very slowly and if the electrons were granted a long time in which to readjust to the altered field. But such deliberation is not allowed. The change in the Hamiltonian of the system occurs in less than about 10^{-18} sec, and in consequence of this change all the electrons are forced to change their wave functions. They do so as rapidly as they are able. Generally, it may be presumed that the inner electrons shift rather quickly to the respective new orbitals closer to the nucleus of the atom in question, but the slow-moving valence electrons may require more time. The alloted time is about the lifetime of the inner vacancy, of the order of 10^{-16} sec for K states. At the termination of this allotted time some of the valence electrons may have succeeded in following the new orbitals and the others may have been obliged to go to an unoccupied excitation orbital[27] or to the unoccupied part of the continuum. The energy of the system depends upon the particular configuration of these electrons, and different configurations yield different energies. Without commenting further about their relative production probabilities,[28] we shall call these possible different states "valence-electron-configuration" (VEC) excitation states. They are reckoned as excitation states whether or not the inner electron is ejected completely free of the atomic field, although of course the energy depends also upon the particular final position of the ejected electron.

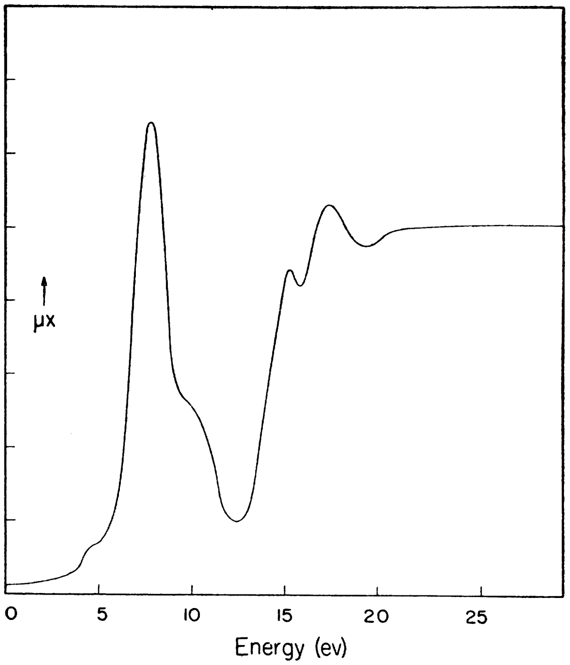


FIG. 3. K-absorption spectra (uncorrected) for gaseous chlorine [Stephenson, Krogstad, and Nelson, Phys. Rev. **84**, 806 (1951)].

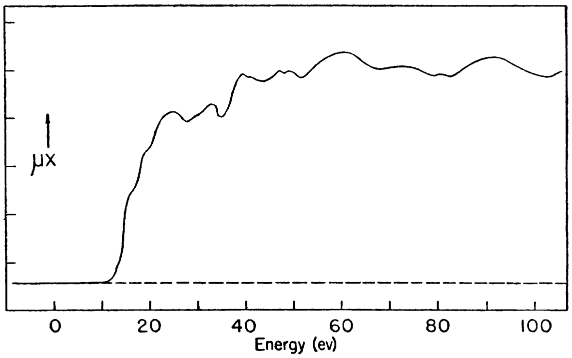


FIG. 4. L_{III} absorption spectra (uncorrected) for metallic silver [L. G. Parratt, Phys. Rev. **54**, 99 (1938)].

Figure 5 is a rough sketch which symbolizes in simple fashion the type of different electron configurations involved in the bound-ejected-electron and valence-electron-configuration excitation states for a solid. The

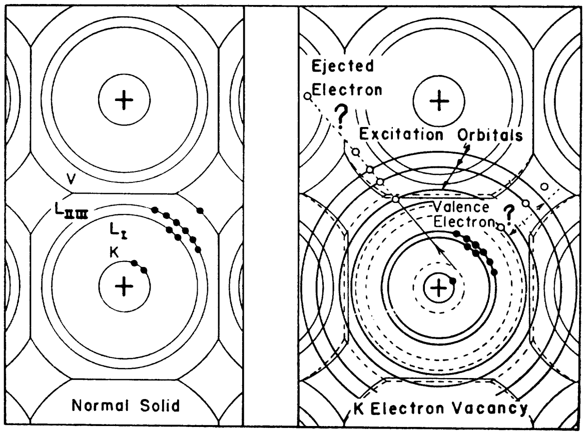


FIG. 5. Symbolic representation of different electron configurations in x-ray excitation states. For clarity, a restricted number of electron orbitals is shown: More than one valence electron and more than one ejected electron may be involved.

---

[27] To illustrate, the 4s valence electron of monatomic gaseous potassium may go, upon production of the 1s hole, to the 5s orbital of the *new* system (i.e., according to the new Hamiltonian) leaving a vacancy in the new 4s orbital.

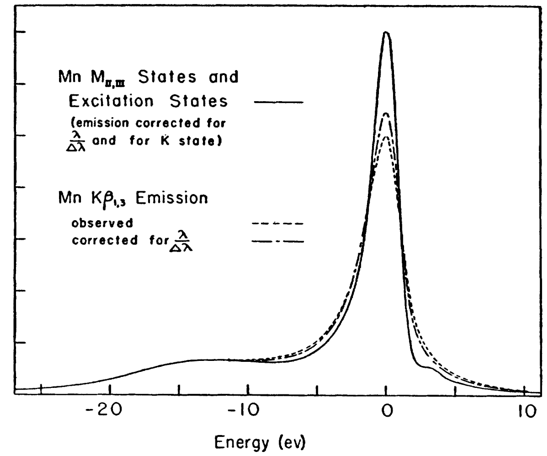
[28] There are many eigenvalues in the solution of Schrödinger's equation for a many-electron system following an abrupt change in the Hamiltonian, and we have mentioned only a few of them. This is done with the implied assumption that only a few have significant probabilities of production.

Also, we have chosen to use a semiclassical description of the states (in terms of specific electrons), rather than a general quantum mechanical description; the latter, although formulated exactly in equations, does not have much practical meaning without solution of the as-yet-unsolved many-body problem. Partial solutions of the quantum mechanical problem, using the best-known wave functions, are nevertheless very much needed.

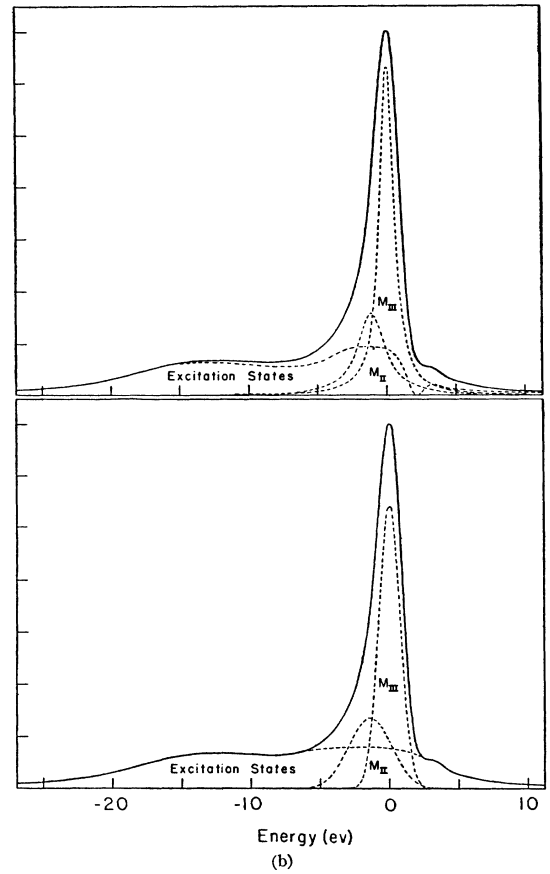
open circles indicate alternative possible positions of the electron in question, although more than one electron in each case may be involved.

As this discussion is intended to apply to all kinds of materials (gases, liquids, and solids) we must distinguish between the valence electrons associated with the particular atom in question and the other valence electrons of the system as a whole. In addition to the possible shift of the atomic valence electrons to orbitals closer to the nucleus, many of the system's other valence electrons may also move in a little closer. This feature for a solid is included symbolically in Fig. 5. The two types of shifts are in competition and they interact with each other since the objective of each is to shield the charge of the positive hole and thus to destroy the shift motivation. For example, insofar as the far-out excitation orbitals are concerned (corresponding to discrete energy levels in, or near the bottom of, the continuum), the in-flow of system electrons in a metal is expected to be much more important than in an insulator. The shielding thus effected by the system's electrons in a good metal is expected to inhibit especially the relative importance of the bound-ejected-electron excitation states in absorption,[29–31] as well as to alter the relative importance of the valence-electron-configuration excitation states in both absorption and emission.

But whether the system's valence electrons are thus effective or not, the new valence orbitals may be present though unoccupied. In this event, it is possible that an outer electron may change its mind, so to speak, after the formation of the inner vacancy and drop into the unoccupied orbital before the allotted lifetime of the inner vacancy has expired. The likelihood of such a change of mind may be negligibly small unless it involves an Auger-type transition in which another electron in the system is shifted farther away from the nucleus. Good metals are especially interesting in this regard because of the ease with which Auger transitions of small energy may take place, the Auger electron being merely moved the necessary amount across the Fermi surface.[32]



(a)



(b)

FIG. 6(a). The observed $K\beta_{1,3}$ emission and the $M_{II,III}$ states for metallic manganese. The observed contour is corrected first for the instrumental resolving power and then for the K state to give the M density-of-states contour.

FIG. 6(b). The M density-of-states contour of Fig. 6(a) resolved arbitrarily into conventional M_{II} and M_{III} components, the residue being indicated as excitation states. In the upper figure the M_{II} and M_{III} components are Lorentzian in shape; in the lower figure they are Gaussian.

An emission spectrum in which valence-electron-configuration excitation states may be involved is shown in Fig. 6, a spectrum studied by Schnopper[33] with a two-crystal spectrometer. This spectrum is the $K\beta_{1,3}$ region for metallic manganese, the transitions supposedly being $K \rightarrow M_{II,III}$ where the $M_{II,III}$ electrans occupy the shells just inside the partially complete $M_{IV,V}$, N_I shells and the valence electrons in this metal. The directly observed spectral contour (dashed curve) has been corrected for the instrumental

---

[29] Y. Cauchois and N. F. Mott, Phil. Mag. **40**, 1260 (1949); and R. Landshoff, Phys. Rev. **55**, 631 (1939).

[30] J. Friedel, Phil. Mag. **43**, 153, 1115 (1952), Proc. Phys. Soc. (London) **B45**, 769 (1952); Advances in Phys. **3**, 446 (1954); J. C. Slater, Phys. Rev. **98**, 1039 (1955).

[31] L. G. Parratt and E. L. Jossem, Phys. Rev. **84**, 362 (1951), Phys. Rev. **97**, 916 (1955); J. Phys. Chem. Solids **2**, 67 (1957).

[32] Small-energy Auger transitions in a metal are discussed by P. T. Landsberg [Proc. Phys. Soc. (London) **A62**, 806 (1949)].

[33] H. W. Schnopper, M.S. thesis, Cornell University (1958).

resolving power,[34] and then corrected for the "resolving power" due to the K state[35] by the method of Porteus and Parratt.[17] The solid curve thus represents the product of the density of p-type states and the transition probability, *viz.*, $N_p(E)T(E)$. The $N_p(E)T(E)$ curve is then shown in the lower two parts of the figure as resolved into three components, M_{II} and M_{III}, and the remaining broad low-energy component indicated as excitation states. This resolution has been carried out first with the assumption that the $M_{II,III}$ states each has a Lorentzian shape, and, then, a Gaussian shape.[36] The excitation states are commonly referred to as the final state for the β_1 line.

The wavelength of a so-called $K\beta'$ component has been reported from photographic measurements by several investigators as near the low-energy side of the low broad component, and this component is commonly known as the β' line. Three possible explanations of the origin of this β' line have been proposed but none of them seems able to account for its rather large relative intensity, about 1.4 times the integrated intensity under the β_1 line as shown in Fig. 6. The first explanation takes it to be a complex satellite corresponding to the double-electron-jump transitions $KL_{II,III} \rightarrow L_I M_{IV,V}$.[37,38] No calculations of the expected relative intensity according to these transitions have been made, but it is generally expected that, in general, double-jump transitions are far less probable than single-jump transitions. For manganese, the single-jump satellites $KL_{II,III} \rightarrow L_{II,III}L_{II,III}$, *viz.*, the $K\alpha_{3,4}$ satellites, are only one percent as intense as the parent $K\alpha_1$ line.[39] The second explanation assigns the β' component to Compton and Raman scattering of the $\beta_{1,3}$ doublet as this radiation attempts to emerge from the x-ray tube anode in which it is generated.[40,41] This requires far more self-absorption in the anode than is reasonable, and, anyway, such a scattered component is not observed accompanying x-ray lines in general, e.g., the $K\alpha_{1,2}$ lines. The third explanation is that splitting of an x-ray state may occur as a result of interaction (angular momentum coupling) between the inner vacancy and an incomplete outer shell of electrons, e.g., the M_{IV} or M_V shell for the transition elements scandium through nickel.[39,42] In general, this type of splitting is expected to be very small and to contribute at most only to the width and asymmetry of the level or of an emission line involving the corresponding state.

It seems that most if not all of the broad low-energy component in Fig. 6 arises from valence-electron-configuration excitation states. Preliminary calculations have shown[43] that, according to this interpretation, the energy intervals and the relative intensity may be of the correct order of magnitude. It is suggested that the observed relative smoothness of this component, i.e., the absence of much obvious structure, is due to the profusion of very closely spaced excitation states and to the continuum of energies of Auger electrons in a metal.

A similar low-energy satellite, $K\beta''$, is observed accompanying the $K\beta_{2,5}$ lines for elements near manganese.[38,44,45] Both the $K\beta'$ and the $K\beta''$ satellites seem to depend somewhat alike on the chemical bonds of the emitting material. It is quite possible that most or all of this $K\beta''$ component should also be assigned to the role of excitation states of the valence-electron-configuration type. Later, it is proposed that most if not all of the asymmetry of the $K\alpha_{1,2}$ lines for these materials is also due to this type of excitation state.

It may be pointed out in our general discussion of excitation states that, in principle at least, another type of excitation state may arise due to the capture of a stray electron that may be just passing through the region, or of an electron from a neighboring atom. Stray capture is very improbable, but it might be considered under certain circumstances, especially for a metal. Capture of another atom's electron, called a cross-transition, has been discussed by several investigators, especially for insulators, but its relative probability has not been well evaluated. Finally, further comment should be made on the state in which there are two or more inner electron vacancies. As stated earlier, such a multiple-inner-vacancy state is the initial state for satellite emission and is of interest in absorption spectra. According to our terminology, these states are not excitation states unless one or more of the

---

[34] This correction presumes that the central part of the instrumental spectral window is given by the experimental $(1, -1)$ curve which has a full width at half-maximum of 0.6 ev and which has a shape between a Lorentzian and a Gaussian, and that the remote tails (the "flat" component) of the window are a little higher than the Lorentzian. The flat component is best obtained from an analysis of the thickness effect in an absorption curve.

[35] The K state is assumed to be of Lorentzian shape having a full width at half-maximum of 1.05 ev.

[36] In each case, the resolution was made on the assumptions (a) that the full widths at half-maximum of the M_{II} and M_{III} states are 1.2 and 2.4 ev, respectively, and (b) that the relative "intensity," or state-density, at the maximum ordinate is 4 to 1. The two M widths are estimated from the radiative and Auger transition probabilities, and from a sort of "best fit" criterion in effecting the actual resolution. The relative density follows from the ratio of quantum weights, *viz.*, 2 to 1, and from the ratio of widths.

[37] According to this transition, which Sawada[38] interprets as $(K \rightarrow L_I)+(L_{II,III} \rightarrow M_{IV,V})$, this satellite has no obvious "parent" line. Nevertheless, it is customarily called a *low-energy* satellite of $K\beta_{1,3}$.

[38] M. Sawada, Sci. Mem. Kyoto Imper. Univ. **A15**, 43 (1932).

[39] L. G. Parratt, Phys. Rev. **50**, 1 (1936).

[40] H. P. Hanson and J. Herrera, Phys. Rev. **105**, 1483 (1957).

[41] F. Bloch, Phys. Rev. **48**, 187 (1935).

[42] G. Coster and J. M. Dryvesteyn, Z. f. Physik **40**, 765 (1927); G. Ortner, Wien. Sitzungsber. IIa, **136**, 369 (1927).

[43] M. H. Skolnick, M.S. thesis, Cornell University (1959).

[44] Vainshtein, Staryi, and Bril', Bull. Acad. Sci. USSR, Phys. Ser. No. 7, **20**, 1956; E. E. Vainshtein and Iu. N. Vasil'ev, Soviet Phys. "Doklady" **2**, 207 and 251 (1957); Vainshtein, Bril', and Staryi, Soviet Physics "Doklady" **2**, 518 (1957).

[45] Unfortunately, studies to date of the shape and relative intensity of the $K\beta''$ and $K\beta_{2,5}$ lines are not reliably quantitative because the corrections as listed earlier have not been made. Careful corrections are imperative for these faint lines that straddle the absorption edge of the emitting material and that appear on a relatively intense sloping background that has absorption-edge structure in it.

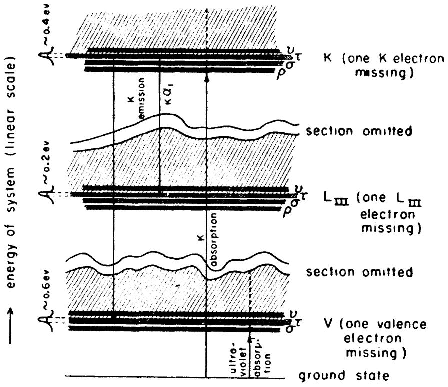


FIG. 7. Part of an x-ray energy level diagram (qualitative) for an insulator. Only a few (of many) discrete states are shown for each type of inner vacancy; each K state, for example, corresponds to a particular electron configuration of *all* the electrons in the system. All the many discrete levels in a given group, e.g., the K group, are involved in absorption spectra, but only one or a few are ordinarily involved significantly in emission spectra (see text). A different continuum of states is shown for *each* type of inner vacancy.

The Ritz-combination principle, according to which the energy of an emission line is the simple difference between two absorption-edge energies, has only qualitative validity; it is not generally valid in detail.

vacancies gives rise to an abnormal configuration of the valence electrons.

Three other phenomena could also be mentioned in this section, all of them of interest in absorption spectra only. These are the interactions of the ejected electron with the other atoms and electrons in a polyatomic system. These interactions—plasma oscillations, and scattering or diffraction—are better discussed later as factors in the transition probabilities, rather than treated as giving rise to separate states.

X-Ray Energy Level Diagram

Figure 7 presents a part of a qualitative energy level diagram which, it is believed, has provisions for the necessary and sufficient complexity to interpret ordinary x-ray spectra. It is designed to avoid the more obvious difficulties encountered with the conventional one-electron-jump type of diagram which is shown in Fig. 1. Figure 7 is drawn for a solid, specifically for an insulator; a similar diagram may be drawn for a metal—the zero energy would appear at or near the bottom of the V (valence) continuum; i.e., near the top of the V_τ band as this band appears in the figure. As compared with Fig. 1, the level arrangement has been inverted; the K group of levels, having the greatest energy, and the energy being positive, appears at the top.

Since the range of spectral energies of primary interest in solid-state work is about the same for all x-ray spectral regions, the diagram is drawn on a linear energy scale. For purposes of illustration, scale sections for only the K, L_{III} and V (valence) groups of levels are shown in Fig. 7, and only a few (four) of the *many* possible discrete levels in each case (except the V case, see later) are shown. A logarithmic scale would again be convenient if the relative energies of many groups of levels of a solid containing an atom of high atomic number were to be indicated coherently in the diagram, but, then, to show the multiplicity of discrete levels due to the splitting, a magnified insert of each group of high-energy levels (e.g., the K group or the L_{III} group) would be required.

The actual separations of the peak positions, the degree of overlap of adjacent states, as well as the relative prominence of the individual members of a split group, are generally not yet known. The diagram of Fig. 7 must be recognized as being merely qualitative in these regards. And a sensible terminology for the various levels in each group must await further knowledge.

Both emission and absorption transitions are indicated. The energy of the system in emission does not include the energy of the ejected electron if it has escaped completely from the system, i.e., escaped from the local region of interest in the solid. But if it has not escaped, it and its energy must be included as part of the system. Although, in principle, all of the discrete states and a few of the continuum states are potentially significant as initial states in emission, it turns out that, in ordinary practice with a conventional x-ray tube, the probability is generally high for a transition from only *one* initial state of a split group (i.e., from only one K state or from only one L_{III} state, etc.). However, this high probability for the involvement of only *one* state in each of the two complex groups of states in emission is *not* correct when the state in question is of low energy, i.e., of energy less than perhaps 20 ev. This point arises again in reference 70.

Let the K level marked "K_τ" refer to the electron configuration in which, conventionally, the K electron has been removed to "infinity" in the solid and left there with zero kinetic energy. (The condition of zero kinetic energy is of interest in absorption transitions only.) It is suggested that this is the significant K level in the ordinary K-emission spectra, whatever is the configuration of electrons appropriate to this level. ("Ordinary K emission spectra" refers to spectra from K states of single inner-vacancy produced by high-energy cathode electron bombardment as in a conventional x-ray tube.) In this sense, we may call K_τ the "unexcited K level."[46] All of the other discrete K levels refer to K states in which a different electron configuration obtains. This different configuration, as already pointed out, may be one in which the ejected K electron is still bound, albeit lightly, to the positive hole it left behind, and/or in which a different number of outer

---

[46] The terminology here becomes a trifle subtle: This particular K state, K_τ, is an ionization state by definition; all other discrete K states are excitation states, some being excited (but not ionized) on each of two or more counts and some being excited ionization states.

electrons failed to jump down closer to the atomic nucleus as the electric field changed upon the production of, or subsequent to the production of, the K-electron vacancy.[47] The continuum of levels indicated by the diagonal lines above K_τ in Fig. 7 represent the theoretical normal density-of-states in the so-called unoccupied continuum, but also in this region are some unmarked discrete levels.[48] In the case of a solid, "normal" refers to the theoretical model in which there is no perturbation due to the inner vacancy; any perturbation effects are presumed to be included in the discrete levels or bands. The theoretical normal continuum has maxima and minima in it, and these are supposed to correspond to "Kronig structure" in x-ray absorption spectra, as discussed later.

One measurement of the difference between the energy of K_τ and about the lowest of the bound-ejected-electron excitation states is afforded by a comparison of the energy required to produce the K state when (1) a large excess energy is available in the process and (2) when no excess energy is available. In the case of metallic copper, the former energy is 8985.5 ev[59] and the latter is 8980.7 ev[1].

Again, what has been said about K states also applies in general to states in which the vacancy is in some other shell or orbital, including those states in which the vacancy is in one of the valence orbitals. But the valence states are significantly different.

By definition, the ordinary x-ray energy level diagram gives the energy of the system when one and only one electron has been lost from the shell or orbital designated in the level terminology. This means, in a strict sense, that the ***normal*** unperturbed valence band of the solid should not be included in the diagram. But the assumption is often made that a vacancy in a normal valence orbital does not significantly perturb the pertinent region of the solid, and hence that it does not significantly perturb the energy or shape of the normal valence band. So, with this assumption, we include the normal valence band in the diagram. This is the band labeled "V_τ" for which the ejected electron is at "infinity" with zero kinetic energy.

By identifying V_τ with the normal valence band, we have pre-empted excitation states, or bands of states, of the valence-electron-configuration type. Unless the perturbation, which is assumed in the previous paragraph to be negligible, is not negligible (or does not remain negligible as the number of valence vacancies increases slightly), all excitation bands are degenerate and are the same as V_τ. The other V bands indicated in Fig. 7—V_σ, V_ν—are representative of the various kinds of bound-ejected-electron excitation bands.

The width and shape of the valence band refer to the density of states regardless of admixed wave-function symmetries and regardless of the probability of position of the positive hole in the band. But, in particular, it may be that in some cases in absorption the position probability is sharply peaked near the top of the band, whereas in emission the vacancy may be more likely near the bottom.[49,30,31] Even if it were preferentially at the bottom initially, e.g., after the jump of a valence excitation electron (from an excitation orbital inside the normal valence orbitals) to an inner vacancy, the hole may tend to "move up" in the band as a consequence of a second valence electron jump, in this instance within the band. Such a double-jump radiative transition is perhaps not very probable.[50] However, it is conceivable that the effective position of the final valence hole may depend upon the particular solid and in some instances may even be time dependent. If such differences in the position probability are real, they are not properly a feature of the diagram ***per se***, but rather are part of the transition probability correction (h) as listed earlier.

Another time-dependency feature in the relative transition probabilities has to do with radiationless (Auger) transitions or with the interaction with lattice vibrations, i.e., with phonons. If an inner vacancy state lives long enough for significant Auger or phonon interaction to take place, readjustment of the configuration of the outer electrons may occur in such a way as (a) to quench or partially quench some of the excitation states in favor of others or of the unexcited ionization state, and (b) to alter the wave-function symmetry of an outer bound electron and thus to introduce somewhat different excitation states. These changes in relative transition probabilities are in addition to the Auger broadening of states owing to reduction of lifetime, and also to broadening due directly to lattice vibrations as discussed later.

Of course, if the readjustment of the outer electrons is not part of the radiative transition, the angular momentum of the system must be conserved in the radiative transition itself. The angular momentum, which in absorption includes the angular momentum of any ejected electron *no matter where it is*, must be

---

[47] For example, the proposed states involved in Mn$K\beta'$ emission are among those symbolically represented as ρ and σ states, i.e., $K_{\rho,\sigma} \rightarrow (M_{II,III})_{\rho,\sigma}$, although these states are not intended to be interpretated so specifically in this generalized diagram.

[48] In a more general sense, when our concepts include the interactions among *all* the electrons and nuclei in the solid, no distinction ***in kind*** need be made between the continuum states and the discrete states either below or in the continuum.

[49] It is common practice in ultraviolet absorption spectroscopy with insulators to depict the first valence excitation band (called an "exciton") as a narrow level instead of as a band. This practice presumes that the position probability of the positive hole in the band is sharply peaked, usually taken as at the top of the band because of the calculated theoretical shapes of the bands or energy *vs* wave vector (one-electron model calculations) and by an application of the principle of conservation of the momentum of the system.

[50] However, Landsberg[32] calculated that the up-movement of the valence positive hole by an Auger or radiationless process in certain metals might take place in less than 10^{-16} sec, a very short time. If the desire for the hole to move up is this great, the double-jump radiative transition may not be so improbable.

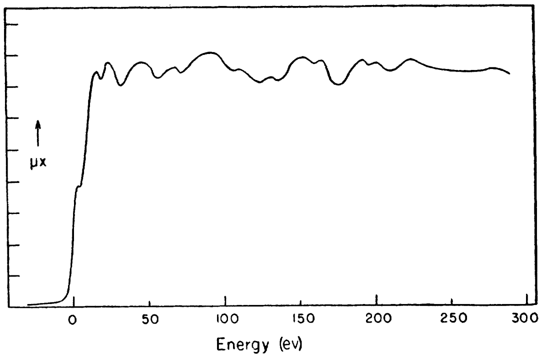


FIG. 8. Extended K-absorption structure (uncorrected) for metallic copper.

reckoned with respect to a reference axis passing through the local atom.

In the case of atoms in an electrically polarized environment, e.g., in a complex ion in a solution or in a solid, many or all of the orbitals of the bound-ejected-electron may be significantly compressed in radii and constrained within a region bounded by a strong localized potential barrier (perhaps by an electrical double-layer). For such atoms, the close-in structure in the absorption spectra are likewise appreciably altered and made much less sensitive to the more remote atomic environment.

Finally, it must be recognized that the diagram of Fig. 7 refers to ordinary x-ray states, and that different but similar diagrams must be drawn for x-ray states involving two (or more) inner electron vacancies. Of course, both emission (satellite) and absorption transitions may be indicated on such diagrams for the multiple-inner-vacancies.

Absorption Spectra: Extended Structure

To recapitulate, the important x-ray states in absorption spectra are (a) bound-ejected-electron excitation states, (b) valence-electron-configuration excitation states, (c) multiple-inner-vacancy states, and (d) the continuum states, including the effects of plasma oscillations and of scattering or diffraction of the ejected electron in the x-ray system. But, generally, the unexcited ionization state, *viz.*, K_τ or L_τ, etc., is *not* significantly involved in absorption spectra close (within say +20 ev) to an absorption discontinuity, notwithstanding widespread elementary notions of the contrary. For the final state in absorption, the geometrical extent of the x-ray system always includes the ejected electron and is therefore usually much larger than is the extent for a state in emission. All the high-up continuum levels are in the diagram for absorption interests only. For emission all these continuum levels become simply K_τ or L_τ, etc., since for them the ejected electron is reckoned simply as having escaped from the system; the energy with which it escaped is of no interest in the energy of the state.

For a monatomic gaseous absorber (e.g., see Fig. 2) *all* K-excitation states of the bound-ejected-electron type appear as levels below the K-ionization level when these levels are presented in a diagram of the type of Fig. 7. In a solid, the K_τ level is proposed as the closest equivalent to the atomic K ionization level. In Fig. 7, one excitation level is drawn above K_τ (or L_τ, etc.); this is partly arbitrary and partly due to the fact that, in a solid, K_τ does not have the simple "series limit" meaning that it has in a monatomic gaseous atom.[51]

In absorption, the relative prominence of the different types of excitation states, compared with the continuum of states, depends upon the particular absorbing material and the particular inner vacancy. For example, for crystalline potassium chloride, discussed later, the excitation states dominate in the region near the "main" K-absorption edge, whereas for metals the excitation states are less prominent. Extended absorption structure, due to scattering or diffraction of the ejected electron, is observed for all polyatomic systems,[52] and, for solids, it seems to be more prominent for metals than for insulators.

Figure 8 illustrates the extended structure typical of crystalline metals. Numerous irregular undulations are observed on the high-energy side of the apparent edge. Although very important in the first 20 ev, the excitation states cannot be responsible for much of the structure 50 or more ev beyond this region. The observed irregularities beyond about 20 ev are commonly referred to as Kronig structure in honor of the first investigator to propose their interpretation (in 1931).[26] According to Kronig, zero absorption is predicted if the ejected electron has such a combination of speed and direction in the crystal lattice that it suffers Bragg reflection[53] from the lattice planes; and a maximum in absorption is predicted if the ejected electron does not have such a combination and does not undergo Bragg reflection. The predicted abrupt changes in absorption become smoothed into mere undulations when various directions in the crystal lattice are simultaneously taken into account. In the band theory of solids, as it developed subsequent to about 1928, a "forbidden" region of energy corresponds to just those values of vector momenta of the electron that allow Bragg reflection (the boundary of a Brillouin zone). An allowed energy

---

[51] There is a strong tendency in the literature for the assumption that a similar or identical series-limit meaning holds in all kinds of absorption spectra. See reference 1 and G. H. Wannier, Phys. Rev. **52**, 191 (1937). Also, Vainshtein, Barinskii, and Narbutt, Zhur. Eksptl. i Teoret. Fiz. **23**, 593 (1952). For a solid, a series-limit for bound ejected-electron excitation states no doubt exists but it is not, in general, coincident with or very near to the bottom of the conventional solid-state unoccupied continuum, nor is it the same limit for different inner vacancies or for different atom species in the solid. This lack of coincidence is due mostly to the respective wave-function extents and symmetries, but partly to the time factors.

[52] H. Peterson, Z. Physik **80**, 258 (1933).

[53] The general scattering or diffraction of the ejected electron becomes Bragg reflection in a crystal if the electron is presumed to be a plane wave in the lattice.

band is that for which the electron can travel freely through the lattice without reflection. Thus, after the spectra have been corrected for the various effects (a) through (h) listed earlier, and if the entire intensity pattern is considered, instead of merely the positions of the maxima and minima, the observed Kronig structure is just the x-ray absorption view of the theoretical normal density of states in the overlapping unoccupied bands of the solid.

In Kronig theory, the inner vacancy is presumed not to perturb the normal bands in any way. It is probable that the influence of this perturbation is such as to complicate seriously any Kronig interpretation of observed structure within 30 or so ev of the apparent edge, and to be a significant factor as far out as 75 or 100 ev. Also, in Kronig theory, the ejected electron is presumed to be a plane wave, i.e., an electron rather far removed from the vacancy site. Actually, for an x-ray state of short lifetime, the ejected electron does not have time enough to travel very far from the vacancy site (a 50-ev electron of normal effective mass would have time to travel a total distance of only about 4 A in 10^{-16} sec), and the plane wave presumption is perhaps not very good except for the very extended absorption structure.[54]

An extension of Kronig's interpretation has been offered by Hayasi.[55] According to Hayasi, if the Bragg reflection occurs at a Bragg angle near 90°, the ejected electron remains in the vicinity of the inner vacancy as in a type of standing wave pattern. An increase in the absorption probability results because of the greater overlap of the wave functions of the initial and final states. Thus, Hayasi predicts an absorption maximum for some of the energies at which Kronig predicts a minimum, or at least an increased absorption at some of Kronig's minima. In the final state, a "quasi-stationary" state as Hayasi calls it, the ejected electron is, in a sense, bound to the positive hole it left behind, and, in another sense, the electron is in a forbidden energy region in the solid. Insofar as the electron is bound to the positive hole, the final state is one form of what we have called an excitation state. Hayasi, like Kronig, ignores the lattice perturbation due to the inner vacancy. Moreover, for a short-lived inner-vacancy state, the ejected electron does not have time to establish itself as a very respectable standing wave.[56] For comparison with experiment we need more detailed and quantitative calculations on the basis of Hayasi's proposal, with inclusion of the vacancy perturbation, the time-dependencies, and all directions of ejection in the lattice.

Efforts to explain the observed details of absorption curves on the basis of Kronig's interpretation have resulted in some but not complete success. Hayasi's modifications may possibly help. The excitation states will probably account for most of the structure in the close-in regions. But it is quite likely that additional processes are involved in the complete explanation. It has been suggested that a correlation exists between the x-ray absorption structure and the discrete loss of energy of electrons as they penetrate thin solid foils.[57] We may distinguish two types of discrete energy loss. The first is in the production of multiple inner-vacancy states. In any type of absorber, the interaction of the electromagnetic field with the system may result in the ejection of two (or more) electrons from an atom instead of just one electron. One or both ejected electrons may come to rest in an orbital or orbitals still bound to the *two* positive holes left behind. Or the second electron may come from a different atom in the system. In any of these cases, the secondary electron-jump absorbs a discrete amount, or at least a minimum amount, of energy and provides an additional way in which the system can absorb the energy of the incident x-ray photon. (The minimum amount of energy absorbed by the secondary jump is essentially zero only for the special case of an electron at the Fermi surface in a metal.) When the photon energy and system are such that the probability for the secondary jump is reasonably high, the absorption should exhibit an increase.[58] There are many potential secondary electrons in a solid, and the discrete amounts of energy become very numerous when more than one secondary electron and more than one atom are considered. The absorption structure due to the production of multiple-vacancy states may indeed show only one or two maxima and an accompanying broad absorption tail of unresolved components.

The second process for a discrete loss of energy is by the induction of plasma oscillations. The ejected electron as it traverses the crystal interacts with the loosely bound valence electrons in such a way that the electrons oscillate collectively. The energy of the oscillation is taken from the absorbed photon via the kinetic energy of the ejected electron. If more than one mode of oscillation is induced, the electron loses more than one discrete unit of loss energy, and if more than one oscillation of a given mode is induced, the electron loses a multiple of a discrete unit. As in the case of

---

[54] In a recent paper, Shiraiwa, Ishimura, and Sawada [J. Phys. Soc. Japan **13**, 847 (1958)], discuss a modification of Kronig's theory by allowing the amplitude of the wave of the ejected electron to decrease rapidly with distance from the parent atom.

[55] T. Hayasi, Sci. Repts, Tôhoku Univ. **33**, 123, 183 (1949); **34**, 185 (1951); **36**, 225 (1952).

[56] To the degree that the general position of the Hayasi electron is localized, the uncertainty principle argues further against its being a plane wave with well-defined momentum. The Hayasi reflection at best should be considered as "quasi."

[57] E.g., see Leder, Mendlowitz, and Marton, Phys. Rev. **101**, 1460 (1956); Revs. Modern Phys. **28**, 172 (1956); E. J. Sternglass, Nature **178**, 1387 (1956); D. Pines, Revs. Modern Phys. **28**, 184 (1956); R. H. Ritchie, Phys. Rev. **106**, 874 (1957).

[58] Production of multiple-vacancy states in gaseous absorbers should be about as probable as in, say, ionic crystalline absorbers. Reports indicate very little absorption structure for gases that can be attributed to multiple vacancies. For this reason these states may not play a very significant role in absorption, but the argument is not generally conclusive.

ejection of a second electron, plasma-oscillation production represents an additional way in which the system can divert the energy of the x-ray photon. An increase in the absorption probability results for those particular photon energies properly tuned.

The energy spectrum of x-ray photo-ejected K electrons from metallic copper has been analyzed magnetically[59] and found to consist of a secondary maximum and a long low-energy tail. It is not yet clear which of the two types of inelastic scattering of electrons is primarily responsible for the observed structure.

As implied earlier, these two discrete-loss processes also take place when no primary inner electron vacancy is produced; in fact, this is normally the situation in the experiments of penetration of electrons through thin solid foils.[57] But the probability with which each process takes place is believed to be increased when the primary inner vacancy is made at the same time. For example, in producing the multiple-vacancy state, the primary electron ejection may, by the abrupt change of the Hamiltonian of the system, trigger the secondary electron jump. This may be especially so in case the secondary electron is a valence electron. (In case the second vacancy is in the valence band, the state would be, according to our terminology, a valence-electron-configuration state.)

In each of the aforementioned possible factors in the interpretation of the extended structure in absorption, a reference "zero energy" is involved. It is usually very difficult or impractical to disentangle this zero energy from the observed structure with the requisite accuracy to make definitive correlations between experiment and theory. To date, only the maxima and minima in the structure have been considered. It would be much more informative if complete absorption patterns were correlated. Then we could better see what absorption remains to be accounted for by additional processes such as discrete loss.

Widths and Lifetimes of X-Ray States

With a sufficiently open energy scale, preferably linear, the width (and the gross shape) of at least one member of each group of levels may be conveniently shown on one side of the diagram of Fig. 7. It should be mentioned that the level width and shape in the case of crystalline solid materials should include the effects of lattice vibrations at a particular temperature. These effects are discussed in some detail later in connection with the interpretations of the spectral curves for potassium chloride. Typically, lattice vibrations at a temperature of about 300°K contribute a few tenths of an ev (or less) to the full width at half-maximum, and contribute a Gaussian factor in the shape. The numerical values of widths indicated in Fig. 7 are about right for chlorine in crystalline potassium chloride if the effects of lattice vibrations are neglected.

The widths of the energy levels corresponding to a few inner-vacancy-states, excluding the effects of lattice vibrations, are given in Table I. These widths, deduced from measurements with the two-crystal type of spectrometer whose resolving power is rather well known, are believed to be essentially atomic values, i.e., unperturbed by (or else corrected for) the physical or chemical environment. Corrections have been made for the instrumental spectral window, for the backgrounds, and for the overlapping lines.

Determination of the lifetime of a state follows from the width according to the uncertainty relation $\Delta t \Delta E \simeq h/2\pi$; a full width at half-maximum of $\Delta E = 1$ ev corresponds to a lifetime of $\Delta t \doteq 6.6 \times 10^{-16}$ sec.

The K width for gaseous argon, 0.5±0.05 ev, obtained from the K-absorption transition $K \rightarrow N_{II,III}$ (or $1s \rightarrow 4p$), is perhaps the most reliable value in the table, and this serves as a sort of anchor point in the determinations of some of the other values.[60] This argon K width is reasonably consistent with the combination of (a) experimental values of the fluoresence yield, and (b) a calculation for the sum of the theoretical radiative transition probabilities.[61] The K and L_{III} widths for gold were taken from the width of the respective absorption edge.[62] This is admittedly not a reliable method for obtaining a level width because of the unknown role of component structure due to the excitation states. However, it happens that both of these gold widths are in fairly good agreement with the calculated theoretical values.[62,63] Furthermore, for the gold L_{III} width, the consistency argument of Richtmyer, Barnes, and Ramberg is reasonably persuasive. (This argument considers the widths of *many* different emission lines.) The same type of argument supports the silver values.[64,65] For every element in the table other than argon and gold, the state widths were obtained from the $K\alpha_1$ emission line. All emitters were

TABLE I. Full widths at half-maximum of x-ray atomic energy levels corresponding to the states indicated (in ev).

State \ Atom	$_{16}$S	$_{18}$A	$_{22}$Ti	$_{25}$Mn	$_{29}$Cu	$_{32}$Ge	$_{36}$Kr	$_{42}$Mo	$_{47}$Ag	$_{79}$Au
K	0.35	0.5	0.8	1.05	1.5	2.0	3.0	5.0	7.5	54
L_{III}	0.1	···	0.25	0.35	0.5	0.8	1.1	1.7	2.2	4.4

---

[59] Sokolowski, Nordling, and Siegbahn, Arkiv Fysik 12, 301 (1957).

[60] The argon absorption curve is being restudied (with higher resolving power, quartz crystals instead of calcites) to obtain still more reliable data on the state shape and width, and on the relative transition probabilities of the series $1s \rightarrow np$, $n \geq 4$.

[61] D. L. Dexter and W. W. Beeman, Phys. Rev. 81, 456 (1951).

[62] F. K. Richtmyer, Revs. Modern Phys. 9, 391 (1937); Richtmyer, Barnes, and Ramberg, Phys. Rev. 46, 843 (1934).

[63] L. Pincherle, Physica 2, 596 (1935).

[64] L. G. Parratt, Phys. Rev. 54, 99 (1938).

[65] As judged now with benefit of the new correction procedures,[17] a small over-correction for the instrumental spectral window was reported in reference 64 for most of the silver L series lines. The corrections reported in reference 62 for the gold L lines are also rather dubious, but this is not of great importance now.

solids[39] except krypton which was gaseous.[66] For titanium, manganese, and copper, the $K\alpha_1$ line is markedly asymmetrical and correction for this asymmetry is discussed in the next paragraph. In each case, the corrected line width was divided between the K and L_{III} states, each state being assumed to be a singlet and of Lorentzian shape. In making the division, two criteria were kept in mind: (1) the radiative components of the K widths should be a reasonably simple function of atomic number Z, and (2) the ratio of the width of the K-radiative component divided by the total K width should agree reasonably well for each Z with the experimental value of the fluorescence yield.[67] The K-radiative widths so obtained are listed in Table II. The K fluorescence yields by this method are also listed. It turns out that the dependence of the radiative width on the atomic number is in good accord with the theoretical Z^4 prediction.[68] (The radiative component of the L_{III} width is very small, much less than the uncertainty in the total L_{III} width.)

As stated in the foregoing, the $K\alpha_1$ lines for titanium, manganese, and copper (and, of course, for some other elements not included in the table) are asymmetrical in shape. When the widths and asymmetries of these lines are each plotted *vs* atomic number through the range $Z=16$ to 42, it becomes obvious that the apparent excess width is closely related to the asymmetry.[39] Illustration of the line shape, after correction for everything except asymmetry, is given in Fig. 9. It is proposed that the excess width on the low-energy side is essentially attributable to transitions between excitation states of the valence-electron-configuration type, just as in the case of the β' structure in the Mn$K\beta_{1,3}$ region discussed earlier.[69] Tentative calculations show that the energy separations between K_τ and the pertinent K excitation states, between $(L_{III})_\tau$ and the pertinent L_{III}-excitation states, and between the $(M_{III})_\tau$ and the pertinent M_{III}-excitation states, are such that now we observe mere asymmetry instead of the plateau region observed in the $\beta_{1,3}$ region. The line from the transition $K_\tau \rightarrow (L_{III})_\tau$ is presumed to be symmetrical and to be obtained by subtracting the mirror image of the high-energy side of the maximum ordinate of the corrected observed curve from the low-energy side. It is the width of this symmetrical component that is used in deducing the K and L_{III} level widths.[70]

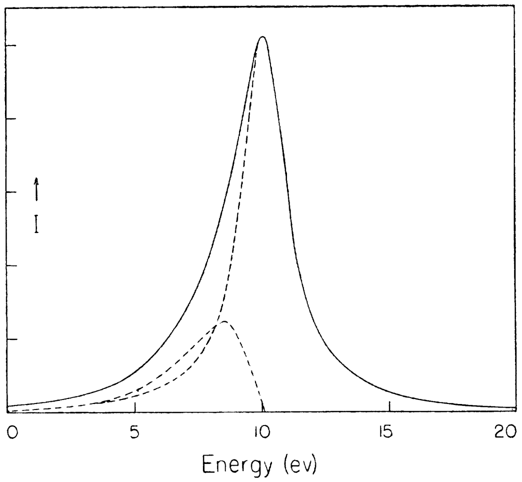


FIG. 9. Asymmetric $K\alpha_1$ "line." The line $K_\tau \rightarrow (L_{III})_\tau$ is presumed to be symmetrical (see text).

TABLE II. K-radiative widths (in ev) and fluorescence yields.

State \ Atom	${}_{16}$S	${}_{18}$A	${}_{22}$Ti	${}_{25}$Mn	${}_{29}$Cu	${}_{32}$Ge	${}_{36}$Kr	${}_{42}$Mo	${}_{47}$Ag	${}_{79}$Au
K_{rad}	0.04	0.07	0.2	0.33	0.65	1.0	1.7	3.6	6.0	50
ω_K	0.1	0.14	0.22	0.31	0.43	0.5	0.57	0.72	0.8	0.93

In support of this analysis of the asymmetry are the facts that the widths so corrected for asymmetry have a fairly smooth dependence on atomic number over a range of Z that includes both symmetrical and asymmetrical lines, and that the radiative component of the K width varies as Z^4. In support of the contention that these widths are essentially atomic, i.e., relatively free

---

[66] E. Wilhelmy, Z. Physik **97**, 312 (1935).

[67] Broyles, Thomas, and Haynes, Phys. Rev. **89**, 715 (1953); E. S. Burhop, *The Auger Effect* (Cambridge University Press, London, 1952).

[68] The report by W. H. Zinn [Phys. Rev. **46**, 659 (1934)] of a Z^4 dependence of the *total* widths is based on measurements of the widths of absorption edges that are evidently replete with excitation structure. These measurements are not reliably interpreted in terms of level widths. Typical of this difficulty, Zinn used the "corrected" K-level width for silver as 25 ev, whereas its actual value is near 7.5 ev. However, the Z^4 prediction is expected to be fairly good for reliable total widths when the Auger contribution is small, as for K widths for $Z \lessgtr 45$.

[69] Some of the asymmetry may be due to the other effects mentioned in connection with the $K_{1,3}$ region, *viz.*, unidentified satellites, Compton and Raman scattering, and interaction between the inner L_{III} vacancy and the incomplete $M_{IV,V}$ electron shells. However, these effects are here presumed to be of negligible importance; but whether they are or not is not relevent to the present argument for obtaining the level width. The pertinent assumption is that all such effects distort the line $K_\tau \rightarrow (L_{III})_\tau$ on only one side.

[70] A final caution may be expressed in regards the numerical widths of x-ray energy levels. If, as is supposed, the excitation states are responsible for asymmetry in an emission line, these states may also contribute to the width of the symmetrical component of the line. In other words, the widths as listed in Tables I and II for single energy levels may be a little too great. If the symmetrical part of an apparently single energy level is itself the sum of several closely spaced narrower components, then, even if each component is of Lorentzian shape, the symmetrical component may be expected to be non-Lorentzian, perhaps more nearly Gaussian. Thus, in the question as to whether the width in Tables I and II is about right for a single state or refers to the width of a composite of excitation states, we find two experimental features of interest: (1) the relative magnitude of the width, and (2) the shape of the state. As judged from present information, the K and L_{III} state widths as listed seem to refer in each case to essentially singlet states, but the evidence is not clear in the cases of M, N, etc., states. E.g., the $M_{II,III}$ states of Fig. 6 are wider than the K state for manganese, and the $M_{II,III}$ states may well be Gaussian in shape. These M states may be wide because of (a) a high probability for Auger transitions, (b) phonon interactions (discussed later), or (c) static interactions of neighboring atoms (solid-state broadening).

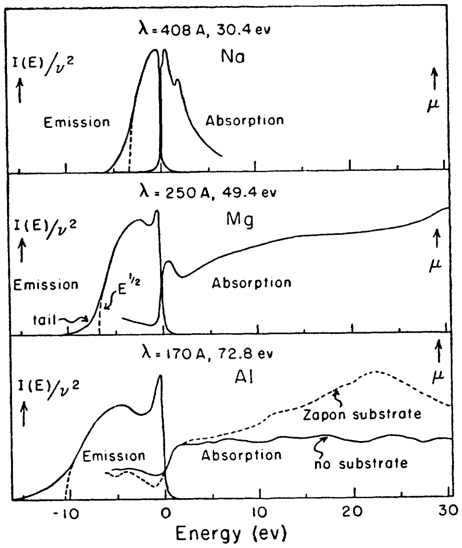


FIG. 10. L_{III} emission and absorption spectra for metallic sodium, magnesium, and aluminum. The same energy-interval scale is used for all the curves; zero is taken as at the estimated position of the Fermi energy. The curves are taken from various authors.[71]

of solid-state effects, is the fact that the gases argon and krypton are included in this atomic number dependence without distinction from the solids.

V. EXPERIMENTAL CURVES AND INTERPRETATIONS

The work in this subject is far too extensive and intensive to be summarized adequately in a few pages. In the preceding sections, only a few topics were selected for discussion; and, in this section, only a few additional curves are selected as illustrative of the experimental results and interpretations.

The interpretations are not clean-cut, in general. For the most part, the corrections listed earlier have not been made to the observed spectral curves; and, in particular, the recognition and use of excitation states is relatively new. A few satisfactory features can be pointed out, but the reader is warned to expect some confusion. An interpretational "break-through," however, may not be far away.

Sodium, Magnesium, and Aluminum

First, we mention briefly the L_{III} spectra of metallic sodium, magnesium, and aluminum. These spectral curves, reproduced in Fig. 10 from various authors,[71] were obtained with sufficiently high resolving power that no correction for this effect need be made. Also, great care was taken (except possibly in the case of sodium absorption) to translate the observed blackening of the photographic plates to an x-ray intensity (or absorption) scale.

There are several features of interest in these curves, but to see them in perspective we first recall the general electronic aspect of these solids. The electron configuration of atomic sodium, atomic number 11, is $1s^22s^22p^63s$ in which the $3s$ electron is nominally in the solid-state valence band, i.e., in the occupied part of the conduction band. For magnesium, atomic number 12, we find two nominal $3s$ electrons; and for aluminum, atomic number 13, we add one more electron, this time in the nominal $3p$ band. It is the combination of $3s$ and $3p$ bands from which the electron comes to fill the inner L_{III} vacancy in the L_{III} emission transition.

The dipole selection rule dictates that only an electron having wave-function symmetry of s type or d type, as viewed from the L_{III} vacancy, may fall radiatively into the L_{III} vacancy (p-type symmetry). Hence, to the extent that the nominal $3p$ band is involved, there must be admixture of s- and/or d-type symmetries in it.[72,73] The selection rule actually applies to the wave functions of the *states*, but, as pointed out earlier, interpretation of this rule in terms of the one-electron model suffices if the primary jumping electron is the only electron in the entire system whose angular momentum changes.

In the electron configuration for sodium, the nominal $3s$ band is half occupied; hence, sodium is a good conductor. The $3s$ band in magnesium is fully occupied and, hence, since magnesium is a good conductor, the $3s$ and $3p$ bands must overlap. Aluminum is a metal because the $3p$ band is only partially occupied. Magnesium has a different crystal structure than sodium and aluminum, but theoretical calculations suggest that the overlap is similar for all three of these metals, the principal difference being in the measure of occupancy. The so-called reduced width of each emission band (i.e., the base width corrected for the "tail" as indicated by the respective dashed curve in the figure) is conventionally taken as a measure of the occupancy of the $3s$, $3p$ bands. The energy widths of the $3s$, $3p$ bands, as obtained directly from the measured bands, are 3.05, 6.4 and 10.6 ev, respectively, and this is interpreted as showing the increase of electron occupancy as we go from sodium to aluminum. It is possible that the role of excitation states is not important in the width and shape of these curves, but, on the other hand, it is conceivable that the valence-electron-configuration type of excitation states do influence the curves in some manner similar to that discussed earlier for the Mn$K\beta_{1,3}$ region. If the excitation states are important, then only the relative magnitudes of the observed widths may be significant in showing relative

---

[71] The emission curves are taken from W. M. Cady and D. H. Tomboulian, Phys. Rev. **59**, 381 (1941); the absorption curves from H. M. O'Bryan, Phys. Rev. **57**, 557, 995 (1940), J. R. Townsend, Phys. Rev. **92**, 556 (1953), and D. H. Tomboulian and E. M. Pell, Phys. Rev. **83**, 1196 (1951).

[72] Although for quadrupole radiation, p to p transitions are allowed, this radiation is very feeble compared with dipole radiation.

[73] It is also important to note that, at least in hydrogenic theory, the transition probability for p to s is much less than (of the order of one-tenth) for p to d.

electron occupancy, not the numerical magnitudes themselves.

The narrow spike observed at the high-energy side of the emission band for both magnesium and aluminum is conventionally explained as a sharp rise in the density of $3p$ states just before the top of the $3s$ band is reached.[74] The spike is markedly higher for aluminum. This explanation requires that there be a *very* large admixture of s- and/or d-type electrons in the bottom part of the $3p$-electronic band. The theoretical density of states, according to the one-electron model, with complete disregard for the wave-function symmetries, i.e., for the transition probabilities, is indeed much like the observed emission curves for all three metals with the Fermi energy appropriately placed. But the calculations have not yet succeeded in giving the degree of admixture of wave-function symmetries of the electrons, or of indicating the role of the possible excitation states. These facts should be taken into account before the explanation of the spike or of the general shape of the curve is considered to be satisfactory.

Next we note that the edge of each of the observed emission bands at the Fermi energy is abrupt, as expected from the degenerate-electron gas theory if the inner electron vacancy causes no perturbation. Indeed, when the small corrections are made for the spectral window of the spectrograph and for the width of the initial L_{III} state, the remaining width of the observed emission edge has been attributed to the effect of the thermal motion of the electrons of the emitting anode.[75,76] Reckoned as between the 5% and 95% points on the edge, the temperature width as deduced from the Fermi distribution formula is 0.06 ev at 110°K, and is 0.45 ev at 670°K. The experimental widths at each of several temperatures in this range are found to be in agreement with these theoretically predicted values.[77,75] However, these three metals are most unusual, apparently unique, in that their L_{III} spectra exhibit this abrupt emission edge, an edge that corresponds so nicely to the Fermi surface predicted theoretically for unperturbed metals. This prediction for metals is based on an assumption that the Fermi surface does not touch a zone boundary.[78]

The long tail on the low-energy side of each of these emission bands (some 8% or more of the total band intensity) is at least partially accounted for, according to Skinner[75] and Landsberg,[32] by Auger transitions that occur as the final-state positive hole "bubbles up" from near the bottom of the occupied part of the valence or conduction band of electronic "levels." In this explanation, the Auger process greatly reduces the lifetime of each of the low-lying levels in the band, and the width of each level is correspondingly increased; the tail is thus simply the lower side of the symmetrical spread of each low-lying level. According to this Auger explanation, the intensity in the tail appears at the expense of intensity in the rest of the band, particularly in the lower half. Hence, if a large part of the tail were to be thus explained, the corresponding redistribution of intensity in the band proper would somewhat invalidate the popular comparison of the reduced band shape with the free-electron parabolic relation $I/(\nu)^2$ *vs* $E^{\frac{1}{2}}$ (or *vs* $E^{\frac{3}{2}}$ in the case of K-band emission). Other proposals to account for this tail, or part of it, have also been made.[79]

In Seitz's proposal[79] the tail may be due to a series of occupied excitation orbitals just below the valence band. Accordingly, a photon of slightly lower energy is emitted if the primary-jumping electron comes from an occupied excitation orbital instead of from the normal valence band. In these two possible types of transitions, the initial states of the system are presumably the same, and the final state in *each* case is one in which the positive hole is in the valence band. Hence, the proposal must be essentially that the energy position

---

[74] For sodium, there is no evidence in the curve of Fig. 10 for the $3s$, $3p$ band overlap according to this interpretation, but a suggestion of such overlap is seen in Skinner's curves [H. W. B. Skinner, Phil. Trans. Roy Soc. London **A239**, 95 (1940)]. Also, this suggestion appears in a recent work by Fisher, Crisp, and Williams (private communication).

[75] H. W. B. Skinner, Phil. Trans. Roy. Soc. London **A239**, 95 (1940).

[76] This is one of the very few cases in the long wavelength region in which correction for either type of resolving power has been attempted.

[77] Incidentally, it is a truly remarkable experimental accomplishment to know the temperature of the local regions of the anode emitting the x-rays, and also to carry out the necessary photographic procedures across such a steep edge to obtain a *reliable* intensity curve.

This interpretation of the edgewidth does not take into account the effects of lattice vibrations, discussed later in connection with the potassium chloride curves, nor of self-absorption in the x-ray tube anode.

[78] It is often said that lithium, sodium, and potassium are our most nearly ideal metals, ideal in the sense of meeting some of the conditions assumed in a theoretical treatment. Lithium K emission does not show an abrupt edge [D. E. Bedo and D. H. Tomboulian, Phys. Rev. **109**, 35 (1958)], and this may possibly be accounted for, according to Dr. V. Heine (private communication), if the Fermi surface touches a zone boundary. Potassium K emission, although recorded [E. L. Jossem and L. G. Parratt, Phys. Rev. **98**, 1151 (1955)], awaits corrections (especially for the resolving power due to the K state, for self-absorption and for the background due to the $K\beta_1$ line) before the answer can be definite. There is a suggestion of the type of distortion observed with lithium. Lack of abruptness in these cases may possibly be attributed, in addition to the distortion due the Fermi surface touching the zone boundary, to the role of excitation states or to the nominal s and d types of symmetry in the conduction band. Since the final state in K emission must have p-type symmetry, the experimental curves tell us the actual (admixed) p-type distribution only.

Dr. S. E. Williams, University of Western Australia, reports (private communication) a new observation that the L_{III} emission of potassium metal may also be abrupt, having a width of "0.22 ev including the instrumental width at 1 A resolution." He estimates that his potassium target was at a temperature near its melting point.

R. H. Kingston [Phys. Rev. **84**, 944 (1951)] reports the M-emission edge of potassium metal to be rather sharp also.

[79] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 436–439; Cady and Tomboulian[71]; S. Raimes, Phil. Mag. **45**, 727 (1954); and D. Pines, *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, pp. 367–450.

of the positive hole is lower in the band when the jump occurs from one of the excitation orbitals than it is when the jump occurs from the normal band.[80] This sort of argument is also discussed (with an indefinite conclusion) in the case of K emission of potassium chloride by Parratt and Jossem[31] where the excitation spectra are presumed to be more intense than the normal band spectra. [As to the expected relative intensity of these two types of spectra, note that the transition probability (independent of relative quantum weights) in each case is proportional to the degree of overlap of the wave functions of the initial and final states, and that the overlap is greater for the excitation spectra simply because the excitation orbital is closer (more tightly bound) to the nucleus.]

If Seitz's proposal were interpreted as implying different initial and final states for the two different radiative transitions, as different valence-electron-configuration excitation states, the explanation of the tail would be essentially the same as is discussed earlier for the $K\beta'$ "tail" in the Mn$K\beta_{1,3}$ region of Fig. 6, and suggested also for the $K\beta''$ satellite accompanying the $K\beta_{2,5}$ lines and for the asymmetry of the $K\alpha_{1,2}$ lines. Indeed, with this interpretation, the significance of the "reduced width" scheme by which the tail is separated from the main emission band, becomes artificial, and we are really talking about the shape of the emission as a whole.

It is conceivable that, if the Skinner-Landsberg explanation of the low-energy tail is even qualitatively correct, the symmetrical Auger-broadening of the states in the band must be sufficient also to produce at least some of the small but definite tail observed on the high-energy side of the band, even though the states in the uppermost part of the band are themselves negligibly broadened. However, Skinner has proposed another explanation,[75] *viz.*, that this high-energy tail is due to the "satellite" band $L_{III}M \rightarrow MM$, i.e., to the transition between an initial state containing both an L_{III} and an M vacancy and a final state containing two M vacancies. According to the usual satellite argument for states of double (or multiple) *inner* vacancy, the unscreened or residual electrical field, which is present as a consequence of the extra inner vacancy, produces a little extra energy in both the initial and final states in such respective amounts that the emitted satellite photon has a slightly greater energy. Note, however, that the extra M vacancy in the case of any of the present three metals is a vacancy in the valence or occupied part of the $3s$, $3p$ electronic bands, and we have presumed above that if the vacancy is in the normal valence band it does not alter the energy of this band. Such a vacancy in the normal valence band also does not alter the energy of the initial L_{III}-vacancy state either. If these presumptions are valid, the $L_{III}M \rightarrow MM$ band is negligibly shifted and is indistinguishable in shape from the parent $L_{III} \rightarrow M$ band.

But, if the extra vacancy in the initial state is in an M-excitation orbital, then, according to our terminology, the state is called an excitation state of the valence-electron-configuration type, and the energy of the state and of the emitted photon is shifted. By the usual satellite argument, the satellite occurs on the high-energy side of the parent line or band, whereas we have discussed the excitation spectra of this type as shifted to the low-energy side. In the latter case, we have presumed that the normal or unexcited $(L_{III})_r$ and V_r states of ionization in the energy level diagram are those for which there exists one (or more) vacancies in the valence excitation orbitals. When less than the normal number of vacancies is found here, the state is an excitation state, and photon emission therefrom is of lower energy than is the normal line or band. In other words, in terms of the earlier discussion of the manganese K-emission spectra, if the definition of a satellite state were to be extended to include a valence orbital vacancy as the second vacancy (instead of another *inner* vacancy), the Mn$K\beta_{1,3}$ lines would be satellites of the $K\beta'$ parent line or lines, and most of the $K\alpha_1$ line would be a satellite of the low-energy "asymmetrical" component. Or, in terms of the present L_{III} spectra, if the excitation orbitals play a role similar to that proposed for manganese, the observed high-energy spike with its abrupt edge may be a satellite of the low-energy part of the emission. It seems better to retain the definition of a satellite state as given earlier.

The relative intensity of the $L_{III}M \rightarrow MM$ band, as proposed by Skinner without excitation orbitals and regardless of its energy position, would be seriously reduced (as suggested by Skinner) by the rapid transfer of the M vacancy in the initial state from the atom in question to a neighbor and then out of the x-ray system. The time for such a transfer depends upon the position of the M vacancy in the valence band, being probably much less than the L_{III} lifetime if the vacancy is at or very near the top of the band. One Auger transition, $L_{II} \rightarrow L_{III}M$, always places the extra M vacancy very near the top; the $L_{II}-L_{III}$ energy difference is very small, e.g., it is 0.3 ev in the case of magnesium,[2] and therefore the M vacancy thus produced occurs within 0.3 ev of the Fermi surface. But there are other

---

[80] The discussion given by Seitz[79] is in terms of the one-electron-jump type of "energy level" diagram. He discusses further whether or not the normal valence band "broadens" as a consequence of the inner electron vacancy enough to "absorb" the excitation levels and thereby to obliterate the excitation spectra. (This is presumably not a question of different energies of the initial state; the initial state is presumed to be of the same energy regardless of whether an excitation electron or a normal valence electron jumps to fill the inner vacancy.) The significant questions are where in the band is the final positive hole, and what is the energy of the final state. The answers are *not* given by the one-electron-jump diagram since the excitation level (and any "broadening" of the valence band proper) ceases to exist with the filling of the inner electron vacancy. This is a typical example, of which there are many in the literature, of the difficulties in interpretation with the one-electron-jump type of diagram in solid-state spectroscopy.

Auger transitions that more frequently place it lower in the band.

Instead of the extra vacancy being in the M band, it may in some cases be in the L_{II} or L_{III} shell, as produced by the Auger transition $K \rightarrow LL$. In this event, the satellites $L_{II}L \rightarrow ML$ or $L_{III}L \rightarrow ML$ are shifted well beyond the Fermi energy and are observed[75] completely separated from the parent band. In shape, these satellites are a small replica of the parent $L_{II,\ III} \rightarrow M$.

The probability for Auger decay of the L_I state is especially very great, and *no* L_I-emission band for any of these metals has ever been reported. Also, the Auger transitions $L_{II} \rightarrow L_{III}M$ and $L_{II} \rightarrow MM$, which "rob" intensity from the L_{II}-emission band, cause the L_{II} band to have only about 1/20 of the intensity of the L_{III} emission for Mg, whereas, on the basis of quantum weights, we would expect an intensity ratio of $\frac{1}{2}$.

As mentioned in the foregoing, some fraction of the intensity thus "robbed" from the L_{II} emission, and likewise some of the intensity "robbed" from the K and L_I emission, reappears as part of the $L_{III}(M)^n \rightarrow M(M)^n$ band where $n \geq 1$; in fact, most of the apparent $L_{III} \rightarrow M$ band is of emission for which one or more extra M vacancies of the normal valence type are present. There is no point in calling most of this emission a satellite or satellites.

Now we turn to the absorption spectra of these three metals. The first point to be made is that the high-energy edge in emission and the low-energy edge in absorption agree in position (at the Fermi energy) as may be theoretically expected of a good metal in the absence of excitation structure. Such agreement is sometimes found for those good metals for which the proper edges can be unambiguously identified, but the proper identification is usually very difficult or impractical. In fact, because of the prospective role of excitation states, the agreement in the present uncorrected experimental curves is perhaps better than we should expect.

Concerning this agreement *vs* disagreement of the emission and absorption edges at the Fermi energy, two effects should be noted in addition to the role of excitation states. First, if the lifetime of the initial state in emission is rather long, significant phonon-interactions may take place and shift the energy of this state before the emission transition occurs. The energy shift is expected to be such as to increase the high-energy side of the emission and, hence, produce disagreement in the positions of the respective edges. Second, if the lifetime of the initial state allows relaxation of the crystal lattice (to relieve the stress set up by the inner vacancy), the energy of both the initial and final states are thereby changed, usually, but not always, reduced.[81] The energy of the inner state is expected to be changed more than that of the outer state, and, hence, such relaxation would also produce disagreement in the respective edges. The lifetime of the MgL_{III} state is probably greater than 10^{-13} sec (Skinner reports[75] the width at 5% maximum to be 0.02 ev), and this is approaching the time required for significant phonon interactions. The lattice relaxation time is a little longer, about 10^{-12} or 10^{-11} sec. These phonon and relaxation effects are not expected to be important when the initial state lifetime is less than about 10^{-13} sec.[82]

There seems to be no obvious explanation of the observed shapes of these three absorption curves beyond the edges. From the conventional interpretation of the emission spectra in terms of the overlapping $3s$, $3p$ bands, we would expect sodium to show strong absorption corresponding to the high-energy emission for magnesium and aluminum. Perhaps it does, but the evidence suggests the presence of additional absorption structure in the range 0 to 5 ev. The magnesium absorption spike, at less than 1 ev from the Fermi energy, seems to be narrower than would be expected on the argument of the aluminum and the $3p$ band, and the aluminum absorption shows no clear maximum in the range 0 to 5 ev.

The fact of *two different* absorption curves in the case of aluminum raises further questions. One of these curves was recorded with the aluminum condensed by evaporation technique onto a Zapon substate; in the other case the aluminum foil was self-supporting. The vacuum-deposited specimen shows a relatively strong broad absorption band beyond about 5 ev above the Fermi energy. There is reason to believe[71] that this strong absorption occurs in a metal-substrate interface region roughly 500 A thick. It is possible that some metal atoms were more or less deeply embedded in the material of the substrate, and that some outer electrons were stripped off the metal atoms in the embedding process. Thus, the neighborhood environment of the boundary aluminum atoms or ions may be quite different than in bulk aluminum metal. There is possibly established, therefore, a wide variety of excitation and ionization states that combine in effect to give the strong but very broad absorption. This type of strong absorption is observed also for celluloid and polystyrene substrates, and indeed for other metals than aluminum.

In general, the interpretation of these spectra, either emission or absorption, is not as yet complete. In this section, we make no effort to present an exhaustive discussion nor a final interpretation. Our purpose is to

---

[81] The dependence of state energy on the lattice spacing is mentioned later in connection with temperature effects in potassium chloride.

[82] Kostarev [A. I. Kostarev, Zhur. Eksptl. i Teoret. Fiz. **22**, 628 (1952); or see M. A. Blokhin, Bull. Acad. Sci. USSR, Phys. Ser. **20**, 701 (1956), English translation] proposed that because of lattice relaxation, *every* valence emission curve should be shifted to higher energies in order better to match the edge positions. Kostarev, however, does not discuss the fact that many x-ray states have a lifetime much less than the relaxation time; for these short-lived states, his arbitrary shift would be out of order.

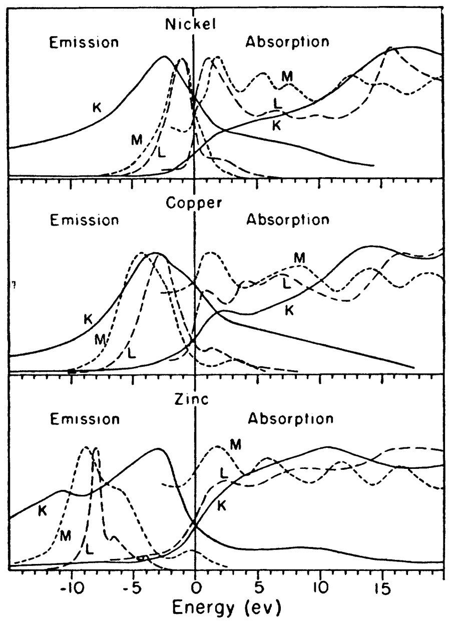


FIG. 11. K, L_{III}, and M_{III} spectra for metallic nickel, copper, and zinc. The curves are taken from various authors.[83]

illustrate typical features of interpretation, and to this end we choose different spectra to emphasize different features.

Nickel, Copper, and Zinc

Figure 11 shows a composite of the K, L_{III}, and M_{III} spectra for three more metals, *viz.* nickel, copper, and zinc.[83] These curves are also normalized and plotted on the same energy-interval scale to facilitate comparison of shapes. The zero of the energy scale is arbitrarily taken in each case as at about the first inflection point of the uncorrected absorption curve[84], the Fermi energy in a good metal is expected to be somewhere near this position. This presumes, as in the case of the sodium, magnesium, and aluminum, (1) sufficient admixture of wave-function symmetries that the different inner vacancies will not, by the selection rule, affect the position of this inflection point, and (2) that excitation states are of negligible importance in this part of these absorption spectra. Neither of these presumptions is generally valid, but there appears now to be no better zero-position criterion. Also, it should be realized that just what is called the first inflection point often depends upon the instrumental resolving power and the precision of the intensity measurements.

The M emission and absorption, as directly observed, consists of overlapping M_{II} and M_{III} bands, but only the M_{III} bands are shown in Fig. 11. In making the necessary resolution, we have taken the energy separation between the M_{II} and M_{III} bands to be small, about 2.5, 2.2, and 2.0 ev for Zn, Cu, and Ni, respectively, in both emission and absorption. Further, we have assumed the relative intensities of the two absorption bands to be 2 to 1 on the basis of quantum weights. In emission, however, the Auger transition $M_{II} \rightarrow M_{III}V$, where V refers to the valence band (admixed $3d$ and $4s$ bands), probably increases this ratio from 2 to 3 or more (and very slightly broadens the M_{II} band); for present purposes, the M_{III}-emission bands in Fig. 11 are deduced from the observed curves with the presumption that the intensity ratio is about 3:1.

None of the experimental curves has been corrected for the corrections (b), (c), (e), (f), (g), and (h) as listed earlier. Although a correction (d) for background intensity has been made in each case by the respective investigators, this correction is often arbitrary. This arbitrariness is probably most pronounced when the background is either changing rapidly with energy (as in the K-emission curves because of the tail of the β_1 line) or is large and somewhat uncertain (as in the M_{III} emission). It is entirely possible that the so-called base width of the K-emission bands in Fig. 11 are too great by 50%, and of the M_{III} bands too narrow by 50%.[85] If the M_{III} bands are as wide and complex as is reported by Bedo and Tomboulian,[85] it seems likely that, in accounting for these features, we must assign a prominent role to the excitation states.

The correction for both kinds of resolving power is large in the K spectra, intermediate in the L spectra, and probably small or negligible in the M spectra. The correction for self-absorption by the anode of the x-ray tube has recently been reported to be very large, at least in certain K-emission spectra.[40] To the extent that an emission band or line, after having been corrected for the instrumental resolving power, straddles an absorption edge, the effect of self-absorption is markedly asymmetrical and causes the emission curve to appear too low on the high-energy side. The self-absorption correction is no doubt important, especially in K spectra for which the jump-ratio at the absorption edge is great.[86] The intensity of the high-energy

---

[83] Curves for this figure were taken as follows: K emission from J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935); K absorption from W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939); L emission from Spielberg, Soules, and Shaw, to be published; L absorption from A. Sandström, Nova Acta Reg. Soc. Sci. Upsaliensis **9**, No. 11 (1935), and C. B. van den Berg, thesis, Gröningen University, 1957; M emission from Skinner, Bullen, and Johnston, Phil. Mag. **45**, 1070 (1954); and M absorption from Tomboulian, Bedo, and Neupert, J. Phys. Chem. Solids, **3**, 282 (1957).

[84] Conventionally, this position in the uncorrected absorption curve is taken as the energy of *the* absorption edge (although the first inflection point in the *transmission* curve is sometimes used, with even less theoretical justification).

[85] D. E. Bedo and D. H. Tomboulian, Bull. Am. Phys. Soc. Ser. II, **3**, 192 (1958); see also Tech. Rept. "The $M_{2,3}$ valence band spectrum of manganese" (July, 1958), Contract DA-30-115-ORD-669.

[86] We are currently in the process of repeating the work of Hanson and Herrera[40] on the K spectra of copper and nickel. The self-absorption correction is not as large as they reported since (1) they did not first correct the observed emission for instrumental resolving power, (2) they used an experimental curve for the absorption edge before it had been corrected for the instrumental resolving power, and (3) their correction for

satellites is very much stronger than is apparent before the correction for self-absorption is made, and careful correction for the satellites becomes imperative.[87] We would expect that, after all the pertinent corrections have been made, any remaining overlap of the emission and absorption spectra (at the Fermi energy) should be accounted for as the effects of thermal motion of the conduction electrons and of lattice vibrations in the emitting anode and in the absorber.

We may remind ourselves that, by application of the selection rule to the principal jumping electron, the K emission refers to transitions to a final state having an electron vacancy of p-type symmetry in valence band. In this application, the wave-function symmetry of the valence vacancy is viewed from the position of the K shell of the emitting atom. The K-absorption process leaves the system with one inner K vacancy and with the ejected electron having p-type symmetry whether it is in an excitation orbital or in some unoccupied part of the conduction continuum. In the L_{III} and M_{III} emission or absorption spectra, the final state vacancy or the ejected electron, respectively, has either s or d symmetry.[88]

As a help in the interpretation of the experimental curves, we may first become acquainted with the theoretical prediction (one-electron model) of the density of states in the solids under study. Such a prediction, which neglects the perturbation of the inner vacancy, is sketched in Fig. 12. This is a "composite" of calculations by several investigators.[89] The double maximum in the $3d$ band is predicted by all the calculations. The base width of the theoretical $3d$ band seems to be about 2.7 ev for nickel (Koster) and about 3.4 ev for copper (Howarth). Extrapolation of these calculated results to zinc is probably not justified because of its different crystal structure. The Fermi energy is indicated for nickel and copper, and it is estimated for zinc. Ten electrons go into the bands for nickel, 11 for copper, and 12 for zinc. In Fig. 12, the Fermi energies are placed for the respective areas to be in this ratio. As drawn, the Fermi energy for copper is about 2 ev above the top of the $3d$ band and also about 2 ev below the bottom of the $4p$ band.

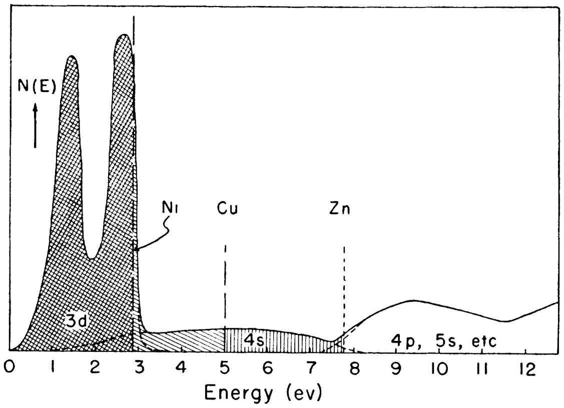


FIG. 12. "Theoretical" density of valence states for metallic nickel and copper, and (questionably) for zinc. This is a composite sketch from several different calculations based on the one-electron model.[89] Estimated Fermi energies are indicated.

Because of the dipole selection rule, we expect quite different shapes in the K emission on one hand and in the L_{III} and M_{III} emission on the other hand, neglecting excitation spectra in each case. Insofar as Fig. 12 applies and insofar as the observed spectra show the normal unperturbed states of the solid, the L_{III} and M_{III} curves should both reflect the s and d band structure of Fig. 12, weighted heavily in favor of d because of the relative transition probabilities and because of the greater density of states, whereas the K curves should show merely the admixed p symmetry in these bands. (In K-quadrupole radiation, the transition of s symmetry to d symmetry is allowed but, as mentioned in the foregoing, the intensity of this radiation is very faint relative to dipole radiation.)

First consider the L_{III} and M_{III} emission. The successive shift of the observed L_{III} and M_{III} emission from the Fermi energy, as we go from nickel to zinc, seems to confirm the $3d$-electronic band as most probably containing the final electron vacancy. On the other hand, it is most disconcerting that there is no (or very little) evidence in these observed curves for the theoretically predicted double maximum in the $3d$ band. The full widths at half-maximum of the observed L_{III}-emission bands are about 2, 3, and 1 ev, respectively, and predicted width at half-maximum of the $3d$ band is about 2 ev for nickel (Koster) and a little wider for copper (Howarth). No theoretical prediction is available for zinc. Even after allowing about 0.5 ev (very rough) in the observed curves for resolving power, etc., the width agreement is fairly good, somewhat unexpected and probably fortuitous in view of the double-peak disparity. The widths at the base are not in agreement. Moreover, the observed M widths at half-maximum are uniformly greater than 2 ev. There is no obvious reason in the one-electron metal why the L_{III}-emission shapes should be different from the M_{III} shapes. And the very wide K bands are not easily explained, even after an estimated 3 ev (very rough)

---

the background radiation (the side of the nearby intense β_1 line and the continuous radiation) was not quite right.

[87] The serious tangle of satellites as often reported in spectral curves recorded photographically [e.g., see Y. Cauchois, Phil. Mag. **44**, 173 (1953), and references cited therein] is frequently a consequence of overexposure of the photographic film and a failure to correct properly to a linear intensity scale. But the correction for satellites is usually not an easy one because of the poorly known background intensity, a background that may contain essential structure itself.

[88] Again note that, at least in hydrogenic theory, the transition probability for p to s is much less than for p to d.

[89] E.g., see E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936); J. C. Slater, Phys. Rev. **49**, 537 (1936); G. F. Koster, Phys. Rev. **98**, 901 (1955); G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952); D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953); C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), Chap. 12.

allowance is made for the correction for resolving power, self-absorption and satellites.

Considerable point is usually made of the apparent coincidence in the energy positions of the abrupt high-energy side of emission and the low-energy side of absorption for the metals sodium, magnesium, and aluminum. This coincidence is always sought for good metals, but it is not so readily seen for most metals. The curves for nickel, copper, and zinc are typical.

In general, we find some spotty agreements in terms of the theoretical predictions based on the one-electron model; but more disagreements. Perhaps some of the apparent difficulties would disappear if proper corrections were made to the observed curves, when more sanitary conditions and materials are used, etc.[90]

In particular, the correction for excitation spectra may be by no means negligible. For example, it is likely that the excitation orbital which forms inside the occupied valence band (see earlier discussion of the $K\beta'$ line for elements in this region of atomic numbers) is not similarly occupied in all K states in the emitting anode of the x-ray tube. If this is the case, then the K emission may be broadened as a result of the energy separations of overlapping excitation states, and also may be accompanied by the $K\beta''$ "satellites."[38,44]

Similar arguments apply to the L_{III} and M_{III} emissions for which the energy separations of the respective excitation states are expected to be somewhat smaller than for the K states. Further, the relative probability of the jump of a normal valence electron, compared with the jump of an excitation valence electron, may possibly be greater in the L_{III} than in the M_{III} emission because of the overlap of the respective wave functions and because the perturbation is stronger in the L_{III} case. If this is so, and if the final-state vacancy following the excitation electron jump is always at a particular favored place in the valence band (as mentioned earlier as a possibility), then we might expect the L_{III} emission to be narrower than the M_{III} emission and to be displaced slightly in energy position. We may continue this speculation: If the favored position of the positive hole in the final state is indeed responsible for the L_{III} emission's being narrower than the M_{III}, and also responsible for the relative energy positions of the L_{III} and M_{III} bands, then perhaps we may conclude that, after the excitation electron has jumped into the L_{III} vacancy, the positive hole is near the top of the $3d$ band. However, in the case of nickel, the L_{III} emission is only a little narrower than the M_{III}, and there is no significant difference in the peak positions. Such speculations are interesting, but very little significance should be attached to their conclusions at this time.

Also contributing to a difference in the energy positions and shapes of the emission bands is the difference in lifetimes of the respective initial states. Thus, in these states, effects of phonon interactions and degrees of lattice relaxation are different.

The L_{III} emission for nickel and copper shows in each case a small bump on the high-energy side of the Fermi energy. It is likely that this bump is a conventional satellite. It is possible, but perhaps not likely, that much of the asymmetry in the L_{III}- and M_{III}-emission bands for copper and zinc is due to high-energy satellites. Satellites, being essentially atomic in character, may generally be identified by observations with elements in a mono-step sequence of atomic numbers. Unfortunately, the necessary identification study of $L\alpha_1$ and $M\gamma$ satellites in this range has not been made.

Now consider the amazingly wide K-emission bands. These are usually identified by x-ray spectroscopists as the $K\beta_{2,5}$ lines or bands, *viz.*, the $K\rightarrow M_{IV,V}$ and $K\rightarrow N_{II,III}$ transitions, the first being nominal quadruple radiation and the second being very improbable because of the small number of $N_{II,III}$ electrons (nominally no such electrons). These bands are very faint, having a peak of only about 1/100 of the peak intensity of the nearby $K\beta_{1,3}$ lines, $K\rightarrow M_{II,III}$, whereas the number of electrons in the nominal $M_{IV,V}$, $N_{II,III}$ (i.e., $3d_{3/5,5/2}$) shells is 10 for copper and in the $M_{II,III}$ (i.e., $3p_{1/2,3/2}$) is only 6. The K-emission bands are obviously severely suppressed but, even so, are more intense than would be expected for normal quadrupole radiation. We conclude that the emission is actually due to an admixture of p-type symmetry in the nominal $3d$, $4s$ energy bands, but that this admixture is not very great or else the K bands would be more intense than they are. The relative feebleness of this $K\beta_{2,5}$ radiation is believed to be an important point in regards the degree of admixture in general.

Mott[91] has suggested that, from an interpretation of the van der Waals forces, an appreciable percentage of

---

[90] The curves reproduced in Fig. 11 are believed to be the most reliable reported to date for these spectral regions. However, the following is illustrative of the experimental situation. The K-emission curves of Bearden and Shaw[83] have been challenged by Hanson and Herrera[40]; the L_{III}-emission band of copper has been reported by several investigators with large disagreements (compare the two curves by Cauchois [Y. Cauchois, Phil. Mag. 44, 173 (1953), and references cited therein] and by Shaw *et al.*[83] as shown in Fig. 24 of reference 3 with the curve in Fig. 8 of van den Berg[83]); and the $M_{II,III}$ emission is in similar trouble (compare Fig. 3 of Skinner *et al.*[83] with Fig. 3 of E. M. Gyorgy and G. G. Harvey [Phys. Rev. 87, 861 (1952); see also Phys. Rev. 93, 365 (1954)] and with Fig. 2 of D. E. Bedo and D. H. Tomboulian [Phys. Rev. 113, 464 (1959)], and see Bedo and Tomboulian[85] who suggest that the assumed background is often highly arbitrary. And the L_{III}-absorption curve of our Fig. 11 has unfortunately a rather vaguely specified ordinate scale.

It is possible that the largest single factor in the experimental disagreements is the unknown intensity scale in much of the photographic work. For example, Cauchois reports that the measured L_{III} band width (and presumably the shape and the apparent structure) for nickel depends upon the exposure time. This dependence is probably not due to a change in materials or structure of the emitting anode of the x-ray tube; rather, the general situation seems to be identical to that in the early work in measuring the relative intensity of satellites {e.g., compare Fig. 1 of F. K. Richtmyer and R. D. Richtmyer [Phys. Rev. 34, 574 (1929)] with Fig. 3(b) of reference[62]} in which discrepancies of a hundred percent were not uncommon.

[91] N. F. Mott, Phil. Mag. 44, 187 (1953).

admixed p symmetry may exist at and just below the Fermi energy in both nickel and copper. This is not believed to be likely because of the low intensity of the K emission, but if it were it would possibly account for the extra bump of intensity observed at -2 ev for copper, and it would presumably give rise to an abrupt edge in the nickel emission somewhat as is observed for, say, aluminum. Such an edge is not found for nickel.

The observed K emission above the Fermi energy may perhaps be relatively too intense to be accounted for as satellites.[92] It is barely possible that there is an appreciable number of stray electrons hovering around in the crystalline anode just above the Fermi surface; if so, and if enough of these hovering electrons drop into the K vacancies, we may be able to explain such a high-energy tail. It is also barely possible that such transitions take place in the case of the L_{III} and/or M_{III} emission. Such transitions, however, would seem to be very improbable.[93]

The large intensity maximum in the K-emission band near the Fermi energy in zinc asks for explanation. As we have stated above, it is likely that the density of states and the Fermi energy as displayed in Fig. 12 are not applicable to zinc. In particular, it may be that the low-energy tail of the $4p$-electronic band is occupied in zinc, and that the observed intensity maximum in question reflects this occupation as dipole radiation. If this is so, and if excitation states do not invalidate the one-electron model, the zinc K emission should exhibit the abrupt high-energy edge expected for metals under these conditions; perhaps it would if the corrections were properly made to the curve. But, even so, it is probable that an energy gap of a few volts would exist between the K emission and absorption edges.

Turning now to the absorption curves, the "jump-ratio" for nickel at the M_{III} edge is about 2 but decreases to about 1.3 for copper and zinc. This may be taken as evidence that the $3d$-electronic band in nickel is not quite fully occupied, but that in both copper and zinc it is fully occupied. Figure 12 is, of course, in accord with this evidence.

Obvious component structure appears in the absorption curves near and above the position of the Fermi energy. It is not clear whether this structure corresponds simply to a variation in the unperturbed $N_a(E)T(E)$ curve or is evidence of excitation states, plasma oscillations and multiple-inner-vacancy states.[94]

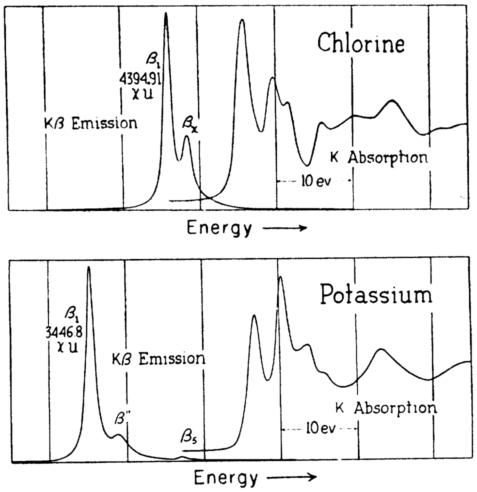


FIG. 13. K emission and absorption spectra (uncorrected) for crystalline potassium chloride.

The band structure of the transition metals is of considerable current interest, primarily because of their electrical and magnetic properties. In this interest, correlations of the results of x-ray measurements have been barely attempted[95] but the possibilities are very promising, especially after the observed curves for selected solid materials have been properly corrected for the various effects (a) through (h) as listed earlier.

Potassium Chloride

Figure 13 shows uncorrected curves for an insulator.[96] Here, the valence band in crystalline potassium chloride, nominally the Cl $3p$ electrons, is probably so far removed from the Fermi energy that the K emission band, designated β_1, is very narrow; the observed full width at half-maximum of β_1 is 1.21 ev. On the high-energy side of β_1, there is observed the line β_x for chlorine and β'' for potassium, and also a rather long faint tail in each case. β_x or β'', and the tail, are probably a complex of satellites and, if so, are of no great interest to us now.

In absorption, the excitation states are no doubt responsible for at least the most prominent maxima—indeed, the overlapping of the excitation spectra and the unperturbed solid-state band spectra is so great that we are at a loss to say where any feature of the unperturbed solid-state spectra may be.

The absorption structure is roughly similar for either the chlorine or the potassium inner vacancy although

---

[92] Stephenson [S. T. Stephenson, Phys. Rev. **58**, 877 (1940)] reports that much of this apparent satellite structure may be an inverse view of the Kronig structure brought out in the self-absorption process. If so, this structure should disappear when proper correction for self-absorption is made.

[93] Many investigators have speculated about this possibility in attempts to explain the apparent satellite structure: e.g., see Y. Cauchois, Compt. rend. **201**, 1359 (1935), T. Hayasi, Sci. Rept. Tôhoku Univ. **25**, 785 (1936), **31**, 1 (1942), and van den Berg.[83]

[94] Photographically recorded CuK absorption curves[65] show in the range 0 to 15 ev four wiggles (component structure) not indicated in Fig. 11. We are currently restudying this region with a two-crystal spectrometer.

[95] E.g., see N. F. Mott and K. W. H. Stevens, Phil. Mag. **2**, 1364 (1957).

[96] These curves are from the paper by Parratt and Jossem.[31] The method used in reference 31 for correcting the emission line widths for the instrumental resolving power is not valid at these wavelengths, as has been shown by the better method of reference 17. An interesting emphasis on the need of a *proper* correction in the absorption curves is demonstrated by Parratt, Hempstead, and Jossem [Phys. Rev. **105**, 1228 (1957)] in the so-called "thickness effect."

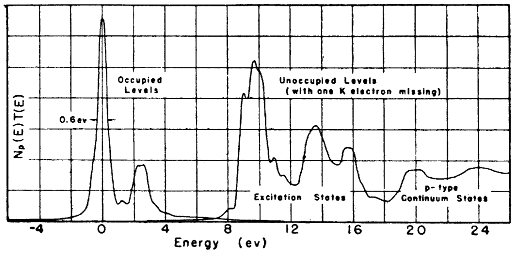


FIG. 14. Density of p-type states (times the transition probability) in crystalline KCl. The occupied electronic levels are those for a crystal having an electron vacancy in the chlorine $3p$ (valence) band; for the unoccupied levels, the vacancy is in a chlorine K shell.

the details and the transition probabilities are considerably different in the two cases. These similarities and differences are expected when we consider the similarities and differences in the immediate neighborhoods of the respective atoms in the crystal.

The chlorine curves for the other alkali chlorides also show[97] different details in the absorption structure, but all of these curves are characterized by pronounced maxima and minima. For LiCl and NaCl, the deep minimum that appears between the first two maxima for KCl and RbCl is effectively filled up, indicating either a smaller energy interval between the most prominent excitation states or else a greater number of such states. The structure for CsCl is again different, but the crystal structure of this chloride is body-centered-cubic whereas the other chlorides are of face-centered-cubic structure. The K-absorption curves for potassium in the potassium halides likewise show both similarities and differences.[98] Similar strong absorption maxima and minima for chlorine are also observed when the chlorine is in a gaseous phase, either in HCl or in free Cl_2[99] (see Fig. 3); this might be expected since the bound-ejected-electron excitation states are vestigial molecular or atomic states.

Figure 14 presents the $N_p(E)T(E)$ graph for potassium chloride. For this graph the chlorine K data shown in Fig. 13 have been fully corrected except for corrections (e), (g) and (h). The corrections for both kinds of resolving power were made by the method of Porteus and Parratt[17]: First, the observed transmission curve was corrected for the instrumental spectral window, and then the absorption curve (the logarithm of the thus-corrected transmission curve) was corrected for a Lorentzian K state.

Now, we see that the chlorine $3p$-valence band is indeed much narrower than has been customarily believed from early theoretical calculations (This problem is discussed in reference 31.) A recent calculation by Howland,[100] however, concludes that the base-width of this band is about 1.5 ev, in sensible agreement with the curve in Fig. 14. But, more recently, Howland has extended his theoretical calculations to predict a shape of this band as well as its width[101]; he predicts a half-maximum width of 1.32 ev, a value much greater than the observed 0.6 ev width, and he predicts a low-energy shoulder in the band which is much more prominent than the slight shoulder seen in Fig. 14.

This feature, just referred to as a slight shoulder, may be evidence of the spin-doublet states $3p_{\frac{1}{2}}$ and $3p_{\frac{3}{2}}$. The separation between these two states in gaseous atomic chlorine is about 0.11 ev and is expected to be about the same in crystalline KCl. It is possible to have two components of identical shape (near Gaussian) and separated by 0.11 ev, each with a width of about 0.5 ev, and with the $3p_{\frac{3}{2}}$ component on the high-energy side being twice as intense as the $3p_{\frac{1}{2}}$ component, such that their sum agrees with the curve of Fig. 14 within the accuracy with which the curve is known. Another interpretation of the slight shoulder would assign it to one or more excitation states of the valence-electron-configuration type, similar to the situation with the transition metals of the manganese group.

From the absorption part of the spectrum, it is significant that the number of evident excitation states is larger than has been previously recognized or theoretically discussed for x-rays. The prominent states here are no doubt of the bound-ejected-electron type.

The question arises as to the meaning of the width of a single component excitation state as it appears in the "unoccupied" part of Fig. 14. This width is the residual width after correction of the true spectrum for the "atomic" K state which is less wide than any K-excitation state. If a full-width K-excitation state had been used in the correction procedure, the result would have been degenerate (a Dirac delta-function[102]). The saving difference between these two K state widths is to be found primarily in the effects of phonons in the lattice. This needs further discussion.

Lattice Spacing and Phonons in KCl

First, we point out an effect due to the average value of the lattice spacing. Then we discuss the effect of statistical time and/or spatial variations in this spacing. The first is relatively easy to discuss insofar as we have knowledge; the second, the effect of the phonons, is a little more involved.

The energy of any x-ray state, i.e., of a system containing an inner electron vacancy, depends upon the total electric field in which the vacancy finds itself. As the lattice expands, e.g., by an increase in temperature, the contribution of electric field due to the presence of neighboring atoms (or ions) is generally altered, and so

---

[97] Parratt, Porteus, and Jossem (to be published).

[98] S. Kiyono, Sci. Repts. Tôhoku Univ. First Ser. **36**, 1 (1952).

[99] Stephenson, Krogstad, and Nelson, Phys. Rev. **84**, 806 (1951).

[100] L. P. Howland, Phys. Rev. **109**, 1927 (1958).

[101] L. P. Howland, Quarterly Progr. Rept. Solid-State and Molecular Theory Group, MIT (January 15, 1958), p. 50.

[102] A Dirac delta-function $\delta(x)$ is zero for $x\neq 0$, infinite for $x=0$, and $\int\delta(x)dx=1$.

is the energy of the x-ray state. The magnitude of the energy shift is probably small but is not easily deduced theoretically. It is believed that the shift is generally to a higher energy for x-ray states in atoms in a metal, and probably also for the anion in an ionic crystal, but to a lower energy for the cation in the ionic crystal.[103]

However, the ground state, i.e., the initial state in any absorption transition, is by definition not altered by the expansion of the lattice. Hence, the energy shift appears directly in the position of the main absorption edge. For a given solid it is expected that the shift is about the same for all states of energy greater than a few hundred ev; it is too difficult to predict the relative shift for states of less energy, e.g., for the valence state. Hence, for an emission line from a transition between states each of energy greater than a few hundred ev, the energy shift caused by the thermal expansion of the lattice, is expected to be small.

In absorption, a lattice spacing effect, in addition to the shift in energy of the main edge, comes into the Kronig and Hayasi structure since the energy positions in this structure depend upon Bragg reflection of the ejected electron in the lattice. The interference conditions in Bragg reflection are temperature sensitive since they depend upon the lattice spacing. The energy dependence of the interference conditions turns out to be an inverse quadratic function of temperature.

Incidentally, the argument may be advanced that a sensitive method for studying the chemical bonds around an atom in a solid, since these bonds affect the lattice spacing, may be in interpretations of the energy positions of (inner-state) → (valence-state) emission (e.g., $K \rightarrow V$), and/or of the inner-state absorption edge, as the chemical composition of the solid is varied. However, in compounds or alloys the role of the excitation states of both the valence-electron-configuration and the bound-ejected-electron types depend upon the chemical composition. It is likely that in a given alloy, even one having a uniform phase, the so-called normal valence configuration may not be the same for all atoms. Alterations in the excitation states probably have a small effect on the peak positions of emission lines but have possibly a large effect on the absorption spectra. In any case in such a chemical-bond study, they must be considered in addition to the effect due to the change in lattice spacing alone.[104,105]

Now consider the broadening of the energy of x-ray states due to phonons or lattice vibrations. (Some authors object to calling this a thermal effect because lattice vibrations are present even at absolute zero of temperature.) It was mentioned earlier that only a localized region of the solid is effectively involved in the energy of each state. This region is, of course, as great as the pertinent electron orbits, including the effective orbit of the ejected electron. The localization is due to the very short lifetime of an x-ray state and to the relatively long time for a phonon (or any other likely energy-bearing agent[106]) to travel through the lattice. This factor in localization is a consequence of the Franck-Condon principle. The x-ray system, therefore, refers to a region that may be only a very few lattice spacings in extent (excluding the ejected electron if it is in the remote part of the continuum).

The energy of a state is affected by the relative positions of all the electrons and nuclei in this localized region, and lattice vibrations give rise to fluctuations in this energy. Of course, the observed spectra represent a statistical average of the spectral energies from all the compressed or expanded regions that are emitting or absorbing the x-rays; the effect generally is to broaden an emission line, an absorption line, or an absorption edge. The statistical vibration broadening in either emission or absorption, considering all vibration frequencies and localized regions, is essentially Gaussian in shape.

For an ionic crystal, there are two kinds of lattice vibrations: (1) the so-called optical branch in which the adjacent positive and negative ions vibrate out of phase,[107] and (2) the acoustic branch in which adjacent ions vibrate approximately in phase. Vibrations frequencies extend from zero to about 10^{13} cps. Hence, after a time greater than about 10^{-12} or 10^{-13} sec, a completely new time and spatial distribution of compressed and expanded regions is expected.

For a metal crystal, the energy smear in an inner-vacancy state due to the vibrations in the electric field may be about a tenth of an ev or so at room temperature, and for an ionic crystal it may be somewhat greater because of the optical phonons. The smear is conveniently expressed as the root mean square of the

---

[103] Interesting studies of the temperature effects in K emission and absorption for ferromagnetic alloys have been reported by V. A. Kazantsev [Bull. Acad. Sci. USSR, Phys. Ser. **20**, 97 (1956), English translation, and Doklady AN SSSR **101**, 477 (1955)]. Although he gives simple interpretations in terms of the one-electron-jump type of diagram, the role of excitation states probably does not invalidate the general conclusions in regards the main trends of energy change.

[104] Nordling, Sokolowski, and Siegbahn report [Arkiv Fysik **13**, 483 (1958)] that the apparent K and L_{III} states for copper change in energy by 4.4 and 2.5 ev, respectively, from metallic Cu to CuO.

[105] Das Gupta reports [Phys. Rev. **80**, 281 (1950)] that the energy shift of the $K \rightarrow V$ or $L_{III} \rightarrow V$ emission peak correlates qualitatively with the heat of formation of a compound or alloy. This is in agreement with our expectations. However, in seeking quantitative agreement, Das Gupta assumes that the heat of formation is due entirely to the energy shift of the valence band alone, there being no shift in the inner state. This assumption does not seem reasonable.

[106] The electron vacancy in the x-ray state has some mobility in the lattice; this feature also extends the local region of interest. Not much is known [T. Takeuchi, Progr. Theoret. Phys. **18**, 421 (1957)] about the transfer of *inner* electron vacancies from one atom to the next, although this mobility is believed to be very small.

[107] The transverse mode of this type of vibration is excitable by an electromagnetic field, such as a light wave; hence the term "optical." We are concerned primarily with the longitudinal modes. The strongest polarization in the crystal occurs when adjacent ions vibrate 180° out of phase.

amplitude of the vibrations of the state energy, and this for a Gaussian shape of the state is a little less than the half-width at half-maximum. For metallic potassium, the smear so expressed is calculated to be 0.15 ev at room temperature; for potassium chloride, the smear is about 0.15 ev at 0°K, about 0.16 ev at 100°K, about 0.19 ev at the Debye temperature, 230°K, and perhaps 0.23 ev at 373°K.[108] Such fluctuations are present in the energy of each x-ray ionization state. The magnitude and phase of the energy fluctuations are about the same for all ionization states in a given atom in the solid for which the effective diameter of the vacancy orbital is small compared with the atomic volume, i.e., for all states whose radiative lifetimes are less than about 10^{-13} sec.

It follows, then, as a prediction, that any emission line arising from a transition between ordinary x-ray states both of which have radiative lifetimes short compared with about 10^{-13} sec has an energy width that is rather insensitive to the lattice vibrations. But each absorption line, band or edge is expected to be broadened, regardless of the lifetime of the final state. Radiative lifetimes less than about 10^{-13} sec are expected for all x-ray states except those for atoms of the lowest atomic numbers and except for those states corresponding to a vacancy in the valence band.

For a singlet state of very short lifetime, shorter than about 10^{-13} sec, the shape is expected to be Lorentzian, as determined by the statistics of random-decay phenomena; and the shape of spectral lines (either emission or absorption) involving such states is also expected to be Lorentzian, and the shape of the *main* absorption edge, if the continuum of "unoccupied" states starts abruptly and is uniformly dense, is expected to be an arctangent. Indeed, within experimental error, the Lorentzian shape is observed for emission lines between *singlet* states both having very short lifetimes. However, in emission involving a longer lived state, e.g., the valence state, there is evidence that the tail on either side of the observed line is less high than Lorentzian, indicating a significant Gaussian contribution in the final state. (For example, the valence state derived from the β_1 line in Fig. 14 shows this effect.) In the longer wavelength range, Bedo and Tomboulian report[78] that the shape of the lithium K state, as interpreted from the K emission, is more nearly Gaussian than Lorentzian; this is to be expected if the K-state lifetime is of the order of, or greater than, about 10^{-13} sec,[109] a lifetime that is reasonable from other arguments.

Now consider a short-lived excitation state of the bound-ejected-electron type. The sensitivity of such a state to lattice vibrations depends upon the diameter of the orbit of the bound-ejected electron. If this electron remained very close to the position of the electron vacancy, its negative charge would effectively cancel the positive charge of the vacancy, and the energy of the state would suffer only minor fluctuations due to vibrations of the electric field. On the other hand, if the excitation orbit were large compared with the lattice spacing, such that the electric fields near a large number of atoms were sampled in the orbit, the lattice vibration sensitivity would be about the same as for an ordinary unexcited x-ray ionization state.[110] It is believed that most excitation orbits are of an intermediate size for which no prediction of the lattice vibration sensitivity is made at this time.

Another broadening effect in each excitation state, of either the valence-electron configuration or the bound-ejected-electron type, is due to the finite lifetime of the electron (or electrons) excitation orbital (or orbitals) as a consequence of all modes of decay other than the filling of the inner vacancy. The most likely types of such decay transitions are those due to Auger or phonon interactions. This type of broadening, Lorentzian in shape, is very small in the present KCl spectra, but the broadening by phonon interactions is possibly important when the inner vacancy has a longer lifetime, e.g., in absorption spectra in the long wavelength region.[111] However, even in the long wavelength

---

[108] These energy fluctuations are calculated from formulas supplied by Professor A. W. Overhauser. For the longitudinal modes in a monovalent metal,

$$[\langle(ev)^2\rangle]^{\frac{1}{2}} \doteq \left(\frac{NC^2k\theta}{6\rho u^2}\right)^{\frac{1}{2}}\left[1+\left(\frac{8T}{3\theta}\right)^2\right]^{1/8},$$

where N = number of atoms/cm³, ρ = density in g/cm³, u = velocity of longitudinal sound in cm/sec, T = absolute temperature, θ = Debye temperature, k = Boltzmann constant, and C = Fermi energy; and for the longitudinal optical modes in an ionic crystal of two types of ions,

$$[\langle(ev)^2\rangle]^{\frac{1}{2}} \doteq 8\frac{(3\pi^2)^{1/6}e^2}{n^2a^{7/2}}\left[\left(\frac{M_2}{M_1}\right)^{\frac{1}{2}}+\left(\frac{M_1}{M_2}\right)^{\frac{1}{2}}\right]\left(\frac{h}{\pi\rho\omega}\right)^{\frac{1}{2}}\left(\frac{2}{\exp(h\omega/\pi kT)-1}+1\right)^{\frac{1}{2}},$$

where e = electronic charge in esu, n = optical index of refraction, a = lattice constant, M_1, M_2 are masses of the two kinds of ions, h = Planck constant, ω = average optical mode frequency, and the other quantities are as defined in the foregoing. The particular type of mode for which the equation is devised is probably the most important one in the respective type of crystal. Inclusion of the other modes, e.g., transverse modes, may increase the total smear somewhat but probably not by more than the uncertainty in the value calculated from the one equation. This uncertainty is estimated to be less than a factor of 2, and the indicated trend with temperature is believed to be very much better than a factor of 2.

[109] Or, if the valence state, i.e., the *final* state in this Li K emission, has a long lifetime, the emission may also be predominantly Gaussian as a consequence of this lifetime and lattice vibrations, independent of the shape of the K state. If the proposal of Skinner-Landsberg[32] for metals is correct, the lifetime of the low-lying valence states for lithium are shortened by Auger transitions and the shape of such a low-lying state in the band becomes essentially Lorentzian.

[110] This presumes that the dynamic phonon-electron interaction is negligible during the short lifetimes of interest; but the statistical static interactions cause a broadening which may increase or decrease the effect in the ordinary unexcited x-ray ionization state.

[111] This broadening has been calculated by A. Radkowsky [Phys. Rev. **73**, 749 (1948)] and found to be appreciable for polar crystals.

region, this broadening effect may be overpowered by the vibration Gaussian contribution which is also a consequence of the longer state lifetime.

Excitation States for KCl in Absorption

Our discussion of the excitation states shown in Fig. 14 may now be completed. The "atomic" K state used in the correction procedure was obtained, as discussed in connection with Table I, from $K\alpha_1$-emission lines and from the strong resonance absorption line in gaseous argon. Because of short lifetimes, this state does not contain the broadening effects of the phonons. So corrected, each component excitation state in Fig. 14 is expected to show phonon width and to be essentially Gaussian in shape, the width being roughly the same for all excitation states. The structure shown in Fig. 14 is consistent with this view. The band of excitation states about 4 ev wide in the center of the figure evidently contains many—at least six—overlapping component states, and the very steep sides of this band indicate component widths of the order of 0.2 ev. Such a width is in agreement with the calculated phonon width given above for KCl at room temperature. The rugged structure extends over a range of about 10 ev, and the total number of excitation states is probably greater than 15. Beyond about 20 ev from the valence band, the density of states has relatively small undulations in it, roughly the sort of undulations expected in the theoretical Kronig structure.

An experimental study of the chlorine K absorption in potassium chloride has been carried out at temperatures from 100°K to 373°K.[112] Two of these curves in Fig. 15, not corrected for resolving power, show: (1) a general shift of the order of 0.2 ev to lower energies, except for the first maximum in the region labeled p-type continuum, (2) broadening of the excitation states, and (3) some alterations in the component structure.[113] It seems reasonable to suppose from these results that the excitation electron in the first excitation state is essentially shared with the near-neighbor potassium ions, in agreement with the usual theoretical model.

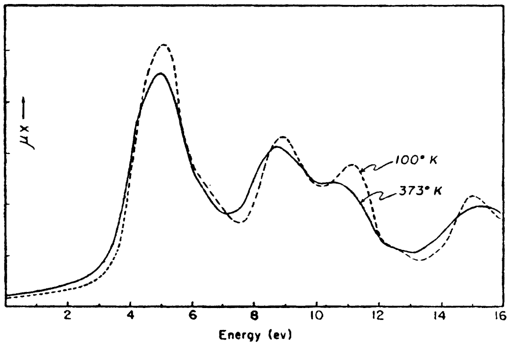


FIG. 15. Temperature dependence in the chlorine K-absorption spectrum of crystalline KCl.

A feature of great solid-state interest in a curve of the type shown in Fig. 14 is the magnitude of the energy gap between the normal valence band and the bottom of the conduction continuum. We discuss this feature now. Nominally, the bottom of the continuum refers to the states of s-type symmetry whereas Fig. 14 gives the density of states of p-type symmetry. Final states of s (or d) symmetry are involved in the ultraviolet absorption, and the desired energy gap has long been interpreted from this absorption as 9.46 ev in crystalline potassium chloride.[114] This interpretation, although the numerical value of 9.46 ev may possibly be changed to about 8.3 ev as a result of recent work,[115] would place the bottom of the s-type continuum at about the position of the central band of excitation states in Fig. 14. Admixture of p type in the nominal s-type states is no doubt present, and some fraction of the density of states in the region labeled excitation states in Fig. 14 should therefore be interpreted as part of the normal continuum. There is no obvious feature of the curve by which we can identify either the bottom of the continuum or even the existence of the continuum as some appropriate fraction under the excitation states. Possibly the deep minimum at about 16 ev above the valence states represents the bottom of the p-type continuum. States to the right of this minimum are designated p-type continuum states in the figure but we do not wish thereby to imply that the continuum necessarily begins here.

In general spectroscopy, it is common to add the energies of two or more selected lines to get the energy of a third; e.g., $(K\rightarrow L_{III})+(L_{III}\rightarrow M_{III})=(K\rightarrow M_{III})$. By a similar argument,[116] in which the energy positions of absorption edges are included, we may possibly derive some help in identifying the gap between the valence states and the bottom of the continuum. In KCl the valence states are the Cl M_{III} states, and we may write the gap-equations as

$$\begin{aligned}\text{gap (to } p\text{-type continuum)}&\\ &=K_{\text{abs}}-(K\rightarrow M_{III})\text{ from Fig. 14}\\ &=M_{I\ \text{abs}}+(L_{III}\rightarrow M_I)\\ &\quad+(K\rightarrow L_{III})-(K\rightarrow M_{III})\qquad(1)\end{aligned}$$

---

[112] Parratt, Hempstead, and Porteus (to be published).

[113] The observed excitation states in ultraviolet absorption in KCl are also temperature sensitive as to both the apparent energy-positions and widths [Hartman, Nelson, and Siegfried, Phys. Rev. **105**, 123 (1957)]. The vibrations in the electric field in the region of a valence orbital are believed to be too complex for even qualitative prediction at this time.

[114] E.g., see N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition, p. 95.

[115] The arguments of E. A. Taft and H. R. Philipp [J. Phys. Chem. Solids **3**, 1 (1957)] may be applied to the experimental curves of Hartman, Nelson, and Siegfried [Phys. Rev. **105**, 123 (1957)] for potassium chloride.

[116] The author is indebted to Professor E. L. Jossem for developing this argument in the present application.
The argument is essentially the Ritz-combination principle mentioned earlier as being valid in a gross description but not valied in detail. Our present interest is gross.

gap (to s-type continuum)

$$=M_{III\ \mathrm{abs}} \text{ from ultraviolet absorption}$$
$$=L_{III\ \mathrm{abs}}+(K\rightarrow L_{III})-(K\rightarrow M_{III}). \quad (2)$$

The only real help to be gained in this type of argument lies in a less ambiguous recognition of the appropriate[117] M_I and L_{III} absorption energies than is the case for K absorption in Fig. 14—the excitation spectra are expected to be somewhat different because of the different positions of the electron vacancy. The M_I state has the same symmetry as the K state, *viz.*, s type, but the L_{III} state has p-type symmetry. The gap-equations (1) and (2) are written separately for the p type and for the s-type continua because it is believed that the experimental values may well be different for these two gaps, and it is alleged theoretically that the admixture of p-type symmetry at the very bottom of the nominal s-type continuum is most unlikely.

The energies of all three chlorine emission lines in the gap-equations have been accurately measured for KCl —$K\rightarrow M_{III}=2815.12$ ev, $L_{III}\rightarrow M_I=182.75$ ev, and $K\rightarrow L_{III}=2622.23$ ev—but the chlorine L- and M-absorption edges for KCl have not been recorded. The Cl $M_{I\ \mathrm{abs}}$ for LiCl has been determined by O'Bryan[118] who remarks that the absorption bands "show a width from 2 to 4.5 ev at the head with less intense continuous absorption extending to shorter wavelengths." The energy at the center of the strong absorption band is 29.7 ev. O'Bryan's description of the absorption curve also fits fairly well the Cl K-absorption curve for LiCl as reported by Parratt *et al.*[97] It is reasonable to conclude that 29 ev is probably a minimum value for the Cl M_I absorption energy for KCl. The Cl L_{III}-absorption energy is also to be deduced indirectly from measurements, and, again, only an approximate value can be obtained. We use the Cl L_{III}-absorption energy for gaseous CCl_4, 200.6 ev, as reported by Prins,[119] and add to this energy about 3.5 ev for the following reasons: 1.5 ev are added as a guess as to the separation between the first strong absorption peak and the appropriate absorption edge. The remaining 2 ev comes from a comparison of the Cl K-absorption spectra for gaseous CCl_4 by Nilsson[120] with the Cl K absorption for KCl by Parratt *et al.*[97]; the K edge shifts by about 2 ev in going from the gaseous CCl_4 to solid KCl. We assume that the L_{III} edge shifts by the same amount. Thus, the approximate energy of the Cl L_{III} absorption is taken to be 204 ev.

Substitution of these numerical values in Eqs. (1) and (2) gives

gap to p-type continuum = 19 ev
gap to s-type continuum = 11 ev.

The uncertainty in the 11-ev value may be 2 or 3 ev, and the 8 or 9 ev previously reported for the s-type case may possibly be a better value than the 11 ev. The 19 ev for the p-type case was deduced as a *minimum* value, and it also may be uncertain by a few ev. The M_I- and L_{III}-absorption edge energies are based on uncorrected curves recorded photographically and, in some instances, with low instrumental resolving power. Nevertheless, the conclusion that there is a difference of several ev between the effective bottoms of the s- and p-type continua is experimentally the best we have to date. This conclusion may easily be altered to say that there is only a very small amount of p admixture in the difference region.

These arguments are interesting and suggest desirable supplementary measurements for the future. At the present time, they are not sufficiently quantitative to provide a convincing basis for the energy-gap interpretation of the curve of Fig. 14; they do however tend to confirm the division of the curve into the general regions labeled excitation states and p-type continuum.

Other Types of X-Ray Curves

There are other ways in x-ray spectroscopy to study the electronic band structure of solids, but these we barely mention.

One way is to record and interpret a curve of the emission intensity of a characteristic line, say the $K\alpha_1$ line, with each of various values of the anode voltage in the neighborhood of the threshold excitation voltage.[121] This method purports to examine the unoccupied levels of the solid by inquiring as to just where and with what probability the inner electron can be ejected to them by cathode-electron impact. It is analogous to the x-ray absorption method except that the radiative selection rules do not apply. When scrutinized more carefully, the correlation between electron energy and the emitted x-ray intensity is as complex as the interpretations in absorption work: Excitation states, plasma oscillations, and multiple-inner-electron vacancy states are all involved as well as the normal unperturbed solid-state bands.

It is interesting to speculate in this method as follows: With the spectrometer initially set at the peak of $K\alpha_1$ for about twice threshold voltage on the x-ray tube, a wavelength scanning (by means of small changes in the Bragg angle) at a constant voltage near threshold may show the peak at a different wavelength. And the line now may be of a different width or asymmetry. Perhaps if both voltage and wavelength were variables, more than one "$K\alpha_1$ line" would be observed near threshold voltage; if so, they would correspond to different radiative combinations of K and L_{III} normal and excitation states. It is believed likely, however, that only one broadened $K\alpha_1$ line would be observed in this fashion because, if more than one were to appear,

---

[117] The difference between the "unexcited" x-ray level (the level referred to earlier with the subscript τ) and the energy of the absorption edge is presumed in this argument to be roughly the same for the various cases.

[118] H. M. O'Bryan, Phys. Rev. **49**, 879, 944 (1936).

[119] J. A. Prins, Physica **1**, 1174 (1934).

[120] A. Nilsson, Arkiv Math. Astron. Fys. **29A**, 4, No. 28 (1943).

[121] A. Nilsson, Arkiv Fysik **6**, 513 (1953).

then, in an appreciable fraction of the emission transitions, (1) the bound-ejected electron would have to jump differently by a few ev or (2) the valence-electron configuration would have to change differently. With regard to the latter possibility, it may be noted that the time required in the formation of the perturbation due to the inner vacancy near threshold voltage is somewhat longer than it is with much excess voltage on the x-ray tube, and consequently the respective probabilities for producing the various excitation states, especially of the valence-electron-configuration type, are perhaps altered.

Another method of studying the electronic band structure of solids is by the spectral details observed near the short-wavelength limit of the continuous x-radiation.[122] The cathode electron comes to rest, or nearly so, wherever it can find an acceptable unoccupied level in the solid. The x-ray intensity pattern gives information concerning the positions of the respective levels and the density of states. In this method, the excitation states are probably not involved, but the plasma oscillations and the multiple-vacancy states are present to complicate the interpretations.

VI. FURTHER READING

For further discussion of the experimental techniques, types and details of observed curves, variety of solids that have been studied to date, theoretical calculations, different speculations in interpretations, etc., the reader is perforce referred to the literature. Only a very few examples have been selected for inclusion in this review. Fortunately, several summaries of the general subject have recently appeared, each giving extensive references.[1–6]

---

[122] S. T. Stephenson, "The continuous x-ray spectrum," in *Handbuch der Physik*, S. Flügge and Marburg, editors (Springer-Verlag, Berlin, 1957), Vol. 30, pp. 368–370, and references cited therein.