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The Soft X-Ray Spectroscopy of Solids. I. K- and L-Emission Spectra from Elements of the First Two Groups

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THE SOFT X-RAY SPECTROSCOPY OF SOLIDS

I. *K*- AND *L*-EMISSION SPECTRA FROM ELEMENTS OF THE FIRST TWO GROUPS

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1. An account is given of new experimental investigations on the radiation emitted from solid elements of the first two groups in the periodic table in the wave-length region 40–500 A. As a result, the properties of these soft X-ray bands have been systematized. The effect of variation of the temperature of the material is also described.

2. The bands reflect the properties of the energy levels of the substance dealt with. A characteristic difference between those of metals and non-metals has been established. The temperature effect on the metal bands is shown to be directly connected with the Maxwellian distribution of the conduction electrons, and the influence of thermal expansion is appreciable. A new feature of the levels of a solid, namely, a large broadening of the valence levels of lowest energy is proposed. With the help of this conception, the general interpretation of the bands is almost complete; they can be used for providing detailed information on the level system in specific cases. In determining the precise features of a band, the crystal structure of the material is the most important factor.

1. Introduction

The aim of the group of papers, of which the present is the first, is to describe the results of a systematic examination of the soft X-ray spectra of solid substances. From these results, we shall show that it is possible to determine experimentally the characteristics of the system of energy levels of valence electrons in a particular solid. We thus obtain material analogous to that provided in the case of free atoms by the well-known methods of optical spectroscopy. The level systems of a free atom and of a solid have this fundamental difference: for the atom, the levels of a valence electron have a set of discrete energy values, whereas the levels of a valence electron in a solid form a continuum, which can only be specified by a *density function* $N(E)\,dE$, representing the number of levels in the energy range between E and $E+dE$. It is this function which it is our object to investigate experimentally. It can easily be seen that the continuous character of the level system in a solid drives us into the region of soft X-rays in order to obtain the required information. For it would be hopeless to try to disentangle the structure of the $N(E)$ curve from the radiation emitted or absorbed in the transitions of electrons between pairs of levels, both of which are members of the continuum. On the other hand, if one of the levels between which the electron makes its transition is a discrete level, the structure of the continuum is rather directly reflected in the emitted or absorbed radiation. The required feature of sharpness is provided in the X-ray levels which correspond to electrons bound

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more or less completely to individual atoms. The actual breadth of the X-ray level sets a limit to the *resolution* which can be applied to the determination of the structure of the continuum. For both theoretical and technical reasons, this resolution is greatest if we work in the region of very soft X-rays, say from 40 to 500 A. In this region, it has been found that the X-ray levels are often sharp to within $\frac{1}{10}$ eV or even less, and there is every reason to believe that this is adequate for the resolution of all the features which exist in the $N(E)$ curve. In the region of shorter wave-lengths, the resolution is less good, though useful work can be performed on spectra down to 5 A, or perhaps even farther. A fuller discussion of the use of X-ray spectra in order to determine the level system of the valence electron in a solid is to be found in a recent article (Skinner 1939).

The investigation of the spectra of light elements of the first two groups of the periodic table lies in the foreground of our problem. This is mainly because, for technical reasons, these substances show the spectra which are most suitable for detailed interpretation; in fact, the resolution is greatest. Further, in the first instance, it is better to confine attention to solids made up of single elements; since, although work has been done on chemical compounds, the general interpretation is naturally likely to be more difficult. Therefore, in this first paper, we shall only deal with the element metals and element insulators of the first two groups.

It is true that considerable work has already been done on the soft X-ray emission and absorption bands of these substances. The K-emission bands of elements Li to C in solid form, and the L_{23}-emission bands of Na to Si (lying in the range 40–400 A) were investigated by Siegbahn and Magnusson (1934, 1935) and by O'Bryan and Skinner (1934). The K-absorption bands of Li and the L_{23}-absorption bands of Mg were investigated in detail by Skinner and Johnston (1937), and recently the L_{23}-absorption band of Al has been added by Johnston (1939). The distinction between the information available through the study of emission and absorption bands is the same as in atomic spectra; the emission bands give information relating to those states of the solid which, in the normal state of the lattice, are occupied; while absorption spectra give information to levels normally unoccupied. Since the occupied levels are more closely connected with the ordinary properties of a solid, the investigation of emission bands appears to be of the greater importance. Therefore a very careful reinvestigation of these emission bands of element solids of the first two groups has been undertaken.

As a result, many new features of the bands were brought to light. These may be classed under the headings:

(1) Many new features of the known bands were found. In some cases (as, for example, the form of the bands for element insulators) these are of fundamental importance for the understanding of the results.

(2) Temperature effects on the emission band edges of metals were observed, and the results appear to be a direct confirmation of the Fermi-Dirac statistics as applied

to conduction electrons. Such results, some of which have been obtained by the new technical method of running an X-ray tube with liquid-air cooling of the anode, provide perhaps the most stringent test available of the current theory of the solid state.

2. Experimental technique

(a) *Spectrograph*

The radiations investigated lie in the range between 40 and 500 A. We have already mentioned that there is a *theoretical* limit to the resolution which can be applied to the determination of the $N(E)$ curve. We shall see that this limit appears to lie in the range between a few hundredths and a few tenths of an electron volt in the cases in which we are interested in the present paper. Experience has shown that a practically sufficient *experimental* resolution of these X-ray bands may be obtained using a spectrograph with the radiation incident at 6° on to a grating having a radius of curvature of 1 m. Thus a single spectrograph may be used for the whole range of wave-lengths, without refocusing.

The instrument was the same as that used by Skinner and Johnston (1937) for absorption work, the metal grating of 15,000 lines per inch being replaced by a 30,000 line glass grating ruled by Professor R. W. Wood. The glass grating, apart from its greater dispersion, was found to possess a considerable advantage over the metal grating (slightly tarnished, it is true, during the course of previous work) in the matter of the intensity of diffusely scattered radiation. The width of grating used was limited to about 15 mm., which is close to the theoretically optimum width for best focusing (see, e.g., Siegbahn 1937).

The slit width used in most of the experiments was about $\frac{2}{100}$ mm. Using a line spectrum, the spectrograph was very carefully focused, and a check was made that the actual image width was in approximate agreement with the width to be expected. Table 1 shows the voltage resolution obtained in the first order spectra at different wave-lengths. It is calculated from the widths of sharp spectrum lines at heights on the photometer records corresponding to 5 % of the peak intensities. Thus, except at the shorter wave-lengths, the experimental resolving power is of the same order of magnitude as the theoretical limit. Fortunately, in the case of the short wave-lengths, high-order spectra are particularly intense; thus it is quite possible in the case of a 50 A line to use the 6th order and thus retain a resolution of 0·4 V. It is probably scarcely worth while to narrow the slit further, since we have to use the method of photometric photometry, which, on account of the effect of the grain, involves the use

Table 1

λ (A)	50	100	200	400
ΔV (eV)	1·3	0·39	0·13	0·04

of a finite area of the plate for each single measurement. A further consideration, of course, is the obvious one that in dealing with bands covering a considerable range in wave-length, the exposure needed is proportional inversely to the slit-width.

We do not suggest that the 1 m. grating at 6° is ideal for the whole wave-length range. For example, the angle of incidence is certainly too large for obtaining maximum intensity for the shortest wave-lengths. But this is not of fundamental importance, and, generally speaking, the instrument can be quite conveniently used, giving adequate resolving power, and quite good intensity over the whole range. It can almost certainly be claimed that no essential feature of the soft X-ray bands has been missed through lack of experimental resolution.

The spectrograph included a movable screen in front of the plate so that three (or in some cases five) exposures could be taken during a single evacuation. The height of the single exposures was thus about 8 (or 4) mm.

(*b*) *Photographic method*

The 'Q_1-plates', manufactured by Messrs Ilford Ltd., are extremely suitable for photography in this region, and their use constitutes one of the chief advantages which the present work has over the earlier work of O'Bryan and Skinner (1934), who used ordinary photographic plates smeared with oil. We are greatly indebted to Dr O. Bloch and the research staff of Messrs Ilford for specially coating with this Q_1-emulsion the very thin glass plates (about $\frac{1}{3}$ mm. thick) which are necessary in order that they can be bent on to the Rowland circle of 1 m. diameter.

These Q-plates can be regarded as intermediate between ordinary plates and Schumann plates, in that they have only a very thin layer of gelatine, probably of the order of 10^{-5} cm. thick, covering the silver bromide grains. Over most of our spectrum range, the absorption of this layer of gelatine is small, though towards the long wave-length end it certainly becomes appreciable. Here, perhaps, there may be some loss of speed as compared with Schumann plates. But, if so, this is more than compensated for by the excellent photographic properties of the emulsion, which is very simple to handle, and gives microphotometer records comparable with those obtainable using ordinary commercial emulsions. The one disadvantage of the emulsion is that it gives a rather small maximum density, especially in the region of longer wave-lengths.

The plates were analysed using the recording microphotometer described by Lees (1931), in which the current from a photoelectric cell is amplified. In the usual way, one needs a calibration curve to translate a given photometer deflexion d into intensity of the radiation which caused the blackening of the emulsion. Such curves must be obtained for different wave-lengths. The procedure which was generally used was to assume the photographic reciprocity law, and to expose a band under constant conditions for different times, say, in the ratio of 1 : 2. Since a given band comprises a fairly wide range of intensities within a relatively narrow wave-length region, this is sufficient. In some cases, the current in the X-ray tube was varied instead of the time of exposure. The validity of this method, however, depends on the assumption that the focal spot in the X-ray tube remains constant and there was definite evidence that the area of the spot tends to expand as the current is increased. Nevertheless, the results obtained by the two methods, when translated into actual band forms, were not very different; and there seems little doubt that the assumption of the reciprocity law gives results adequate for our purpose. No correction was applied for the variations of the emulsion sensitivity and of the light-gathering power of the spectrograph with wave-length, since the effect of the first factor is hard to estimate, and, over the width of a single X-ray band, neither can be of much importance.

As will be seen, the X-ray tube was run under quite different conditions of power input, and hence no general rule as to exposures can be given. With an input of $\frac{1}{2}$ kW, the K-band of Be (110 A) may be photographed with an exposure of 15 sec., while 6 hr. was given for the L_3-band of Na with an input of 30 W. These figures indicate the range of the exposures.

(*c*) *X-ray tube*

Since the radiations to be investigated are very absorbable in air, or in any other material, no ‘window’ can be allowed to intervene between the X-ray tube and the slit of the spectrograph. The X-ray tube and spectrograph, therefore, must be evacuated as a unit.

In the matter of the X-ray tube, we have followed the technique of O’Bryan and Skinner (1934). The main essential is that a rather high vacuum must be maintained. If the vacuum is poor, the surface of the anticathode becomes contaminated. This has two results: (1) the band of a substance which is required may be distorted by radiation emitted from a chemical compound of that metal (e.g. oxide or carbide), (2) the deposition of even an invisible layer of, for example, carbon on the anticathode is found to give an appreciable amount of carbon K-radiation, which, diffracted in a high order, is liable to overlie the band of radiation to be investigated. Experience has shown that only by working at a pressure less than about 10^{-6} mm. in the X-ray tube can these effects be avoided.

Since a large number of exposures were to be taken and we were aiming at finishing one exposure, and preparing for the next, during each working day, a fast pumping system was essential. A battery of three diffusion pumps with Apiezon oil, with a speed of about 20 l./sec., was used to evacuate the X-ray tube. Even so, it proved to be essential to use a liquid-air trap (consisting of a container let into the pumping tube), with its enormous pumping speed for condensible vapours; only in this way was contamination by carbon, coming from the grease of the cone-joints, etc., completely avoided. In practice, an ionization gauge was always used, and exposures were delayed until a pressure in the X-ray tube, known by experience to be satisfactory, was reached. The pressure in the spectrograph, which is only connected to the X-ray tube by the narrow aperture of the slit, is less important. Nevertheless, three Apiezon pumps, one of which was shared with the X-ray tube, were used for its evacuation, in view of the desirability of removing quickly any vapours given off by the photographic emulsion.

The second important point in our technique is the method of the evaporated anticathode. Wherever practicable, the material to be investigated was evaporated from an evaporating unit under the above high vacuum conditions on to the copper base of the target of the X-ray tube. In this way, a very clean deposit of the material may be obtained. Further, the surface of this deposit may be easily changed, if any sign of contamination appears, or is thought, from experience, to be liable to exist. In practice, the surface of the target was generally renewed after 15–30 min. running. The method also has the advantage that the surface of the target may be changed without breaking the vacuum, if the evaporating unit can supply two distinct substances.

Since the vacuum available is good, nearly all substances can be evaporated quite simply. The general method adopted has been to suspend small lumps of the material, by means of a tungsten wire, in the neighbourhood of a tungsten filament. In the case of easily evaporated material, the radiation from the filament suffices for heating the lump. In the case of more refractory materials, a voltage of about 1000 V is convenient to heat the lump by electron bombardment. In most cases, evaporation occurs at a sufficient rate before melting. In other cases, e.g. Al and the alkali metals, a container of some sort is required. In the case of the comparatively refractory Al, a tungsten spiral is most suitable; in the case of the alkalis, a very small iron crucible was used. With the exception of carbon all the substances investigated were evaporated. In the case of sulphur and phosphorus, a special technique, to be described later, was used. In the case of carbon, the material was deposited on the copper target, in the case of graphite by means of the colloidal substance known as 'Aquadag', and in the case of diamond from a suspension of commercial diamond dust in carbon tetrachloride; and in the latter case, especial care was taken with the process of degassing the anticathode.

In general, the technique consisted of the following parts:

(1) After putting the plate into the spectrograph, pumping out for several hours (usually overnight).

(2) Heating of the glass bulb of the X-ray tube with a bunsen flame, heating of the tungsten filaments for degassing, heating, by radiation from the filaments, of the copper anode to about 400° C with the water cooling stopped.

(3) Evaporation of the target material and preliminary running of the X-ray tube, until a satisfactory pressure is reached.

(4) The actual exposures made.

A glass bulb was used for the X-ray tube, on account of its advantage in degassing. The anticathode was a square-sectioned copper tube, about $\frac{1}{2}$ mm. in wall thickness, water-cooled, so that a power input of about 1 kW was possible. The anticathode could be rotated on a cone-joint, so that four sides could be placed in position relative to the slit of the spectrograph. The filament was of tungsten (0·4 mm. thick) and was shielded by a focusing box in order to give a focal spot of about 5 × 2 sq. mm. The evaporating unit was placed on the side of the anticathode opposite to the main filament, so that, after the target substance was evaporated, a rotation of about 180° brought the anticathode into the running position. A general diagram of the X-ray tube is shown in figure 1.

The source of power was a set using full-wave rectification with two mercury valve rectifiers, but not smoothed by condensers. The mean voltage employed was about 3500 V. The set could supply currents up to 250 mA, but in most cases the full current was only used in degassing. This was partly because a lower pressure could be attained at a smaller current in the X-ray tube; but mainly because of temperature effects (see below). The normal running currents were from 10 to 100 mA.

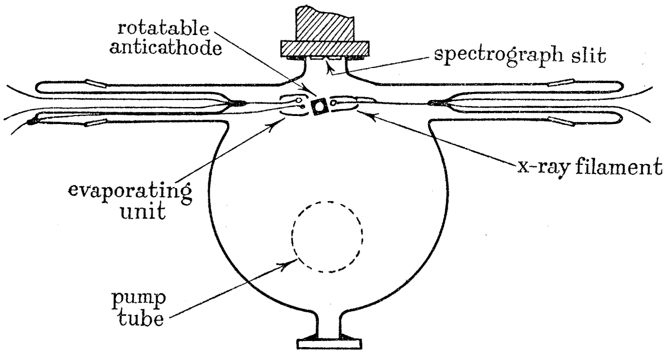

Figure 1. X-ray bulb.

As was mentioned in § 1, one of the innovations of the present work was that frequently the X-ray tube was run with the anode cooled with liquid oxygen, instead of water. From a technical point of view, an important difference between these two cooling substances is that, while water, at room temperatures, is well below the boiling point, liquid oxygen is *at* the boiling point. So that, in the latter case, any input of heat converts it into gas. It follows that, behind the focal spot of the X-ray tube, there will be no liquid. This has an important bearing on the design of the anticathode, as was pointed out by Dr O'Bryan. That is, for cooling, one should rely chiefly on conduction in the copper of the wall of the anticathode, which should therefore be made *thick*. In practice, a wall thickness of about 2 mm. was used. With a current of 10 mA in the X-ray tube, a rough calculation showed that the conductivity of the copper should be adequate to keep the anticathode temperature to within some 20° of the boiling point of liquid oxygen (90° K). The liquid oxygen was simply poured into a funnel over the anticathode which served as a reservoir, and was replenished after every 2 min. running. This rather crude system appeared to work very well, although of course the anticathode temperature was not very accurately known, and no convenient method of improving upon it presented itself.

In other cases, it was desired to run the anticathode at a temperature above the room temperature. Then two methods were available, both of which were used in individual instances:

(1) Water cooling, relying on the temperature drop across the thickness of the anticathode, with a suitable power input. This method sufficed to melt Li (180° C) with a 2 mm. anticathode, using 100 mA.

(2) For higher temperatures, air cooling of the anticathode, employing a blower. In these cases, a thermocouple was inserted into the anticathode. At a suitable current (generally about 10–15 mA) temperatures up to about 600° C are easily reached.

In the case of very volatile substances (P and S), it seemed desirable to work with the liquid air cooled anticathode. Since it was found that these materials evaporated appreciably during preliminary running, thus giving a thick sulphide or phosphide deposit on the anticathode, yellow sulphur and red phosphorus were sealed off in evacuated glass capsules which were only broken when the preliminary running of the X-ray tube was over and then were evaporated by slight heating from a nearby filament on to the anticathode, already cooled with liquid oxygen. Working in this way, a thin deposit (which can be easily renewed) stays on the anticathode for an appreciable time. If the anticathode were raised to room temperature, the loss of material would be rapid, and considerable doubt would be introduced as to whether the resulting radiations from the pure elements were contaminated by radiation from compounds with copper. This method of low-temperature condensation leaves one in doubt as to what allotropic modification of P and S one is using. But comparison with a photograph of the L_{23}-band of sulphur published by Siegbahn and Magnusson (1934) shows that our S appears to have had the usual rhombic structure.

3. General interpretation of soft X-ray spectra

Before proceeding to give the results of our experiments, it will be well to describe the general features of the theoretical background against which they may be understood. The more specialized aspects of the theory will be left over to the detailed interpretation of the results in § 10.

Since the simple theory has been described in a recent article (Skinner 1939), we shall deal with it only shortly here. Suppose that an X-ray level of a certain atom A in a solid has been ionized by electron impact in the X-ray tube. The system is now in an excited state in which it stays long enough for the ejected electron to travel right away from the neighbourhood of the atom A. Since the X-ray level is sharp, the energy of the system (*without* the ejected electron) still has a definite value. If now a transition occurs of one of the valence electrons into the vacancy, the system returns to its original state, except that it is left with a vacancy in one of the normally occupied valence-electron levels. These cover a finite energy range (e.g. 3–40 eV in different cases). Since an electron from *any* of these valence levels may make the transition, the final energy of the system will depend on which valence level is left vacant. Thus, if radiation is emitted during the transition, the quantum of energy emitted will not be a constant for individual elementary processes of ionization of the X-ray level of the atom A. So, if a large number of such ionizations of the atom A and other atoms in the solid occur, a broad band of radiation will be emitted whose energy spread is $(E_m - E_0)$, the energy difference between the lowest and the highest of the normally filled valence-electron levels. In practice, it is convenient to define the zero of E as the energy of valence electrons of lowest energy (that is, $E_0 = 0$).

Let $N(E)\,dE$ be the number of energy levels (per atom) in the solid within the energy range from E to $(E+dE)$. Let $\nu^3 f(E)$ be the probability per unit time that an electron of energy E will make the transition into the vacant X-ray level. Let $I(E)\,dE$ be the intensity, measured as numbers of quanta per second, of the radiation in the emitted band in the range of quantum energies from E to $(E+dE)$. Then

$$\left.\begin{aligned} I(E) &\propto \nu^3 f(E)\,N(E) \qquad & E &\leqslant E_m, \\ &= 0 & E &> E_m, \end{aligned}\right\} \tag{1}$$

where ν is the absolute energy of the transition, and the factor ν^3 is that which is present in all problems of emission intensity. For the sake of completeness, we shall also consider the corresponding absorption process, in which an electron is ejected, by the absorption of a quantum of radiation from the specified X-ray level into one of the vacant valence-electron levels. Let $\mu(E)$ be the partial absorption coefficient of a thin layer of the solid as a function of the quantum energy of the absorbed radiation. Then

$$\left.\begin{aligned} \mu(E) &= 0 \qquad & E &\leqslant E_m, \\ &\propto f(E)\,N(E) & E &> E_m. \end{aligned}\right\} \tag{2}$$

We thus see that emission and absorption experiments are complementary in the information they provide about the $N(E)$ curve of a given substance. It is clear that the two types of results may be expected, when used together, to give a completed $N(E)$ curve.*

These equations are sufficient for the understanding of the most obvious properties of the emission bands (finite band widths; sharp edges in the case of metal bands, and the effect of the temperature of the anticathode on these edges). Other properties depend on the transition probability $f(E)$.

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* Of course, we must sort out from the observed emission spectrum as 'satellites' any parts which are due to initial *double* ionization of an atom core. Also, there is a formal distinction between emission and absorption experiments, since, in the latter, an electron is missing from an inner shell *after* the transition. There may be levels of the particular atom whose existence depends on this electron being away. The 'lines' in the soft X-ray absorption of alkali ions in alkali halides (O'Bryan 1936) probably have this origin, but no such effect occurs for metals.

Owing to the fact that the spread of the wave function for the X-ray levels is small compared with the lattice constant, the determination of $f(E)$ is largely an atomic problem, as was pointed out by Jones, Mott and Skinner (1934). The simplest treatment is to expand the wave function ψ of an electronic level of the lattice in a series of functions ψ_s, ψ_p, ψ_d, ..., having the symmetry of s, p, d, ... atomic wave functions in the neighbourhood of the nuclei. Thus we write

$$\psi = A_s\psi_s + A_p\psi_p + A_d\psi_d + \ldots,$$

where $$|A_s|^2 + |A_p|^2 + |A_d|^2 + \ldots = 1.$$

If we then write $$N_s(E) = N(E)\,|A_s|^2, \text{ etc.},$$

we have $$N(E) = N_s(E) + N_p(E) + N_d(E) + \ldots, \tag{3}$$

and, taking $f_{s\to p}$ as proportional to $|A_s|^2$, $f_{p\to s}$ as proportional to $|A_p|^2$, etc., we may formally retain the atomic selection rules and rewrite equation (1) as

$$I(E) \propto \nu^3 f_{p\to s}(E)\, N_p(E) \tag{4}$$

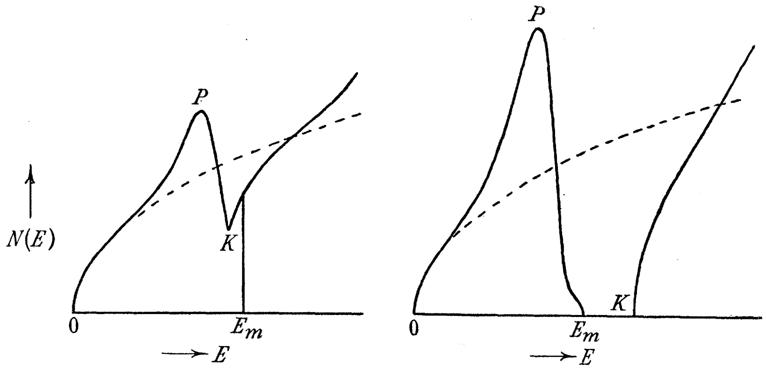
for a K-spectrum, when the excited state is of the type (1s) and

$$I(E) \propto \nu^3 \{f_{s\to p}(E)\, N_s(E) + f_{d\to p}(E)\, N_d(E)\} \tag{5}$$

for an L_2- or L_3-spectrum, with excited state of the type (2p). The advantage of this procedure is that the functions $f_{p\to s}$, $f_{s\to p}$, $f_{d\to p}$, etc., approximating to atomic transition probabilities, are now practically independent of E. Thus the intensity form of a K-spectrum gives us a direct measure of $N_p(E)$, while that of an L_3-spectrum gives us a mixture of $N_s(E)$ and $N_d(E)$, in an undetermined ratio. We shall, somewhat loosely, refer to the results obtained from L_3-spectra as giving $N_{s+d}(E)$. But, at least for fairly small values of E, the contribution of the d-levels may safely be assumed to be negligible. In this case, the addition of the results from K-spectra and from L_2- or L_3-spectra in a certain proportion would give us the $N(E)$ curve in accordance with equation (3).

In order to proceed further, it is necessary to have some idea of what is to be expected from theory as to the general run of the $N(E)$ curves. Two cases present themselves, namely, those of conductors and of insulators. The theoretical conceptions of these two types of solids, simplified as far as possible and partly adapted to the empirical results of the present paper, are shown in figure 2. The $N(E)$ curves follow, on the average, the dotted parabolic curve, which represent the result of Sommerfeld's 'electron-gas' theory, which takes no account of the lattice structure of solids. However, in the regions represented by P and K, there are large variations from the parabolic form. The $N(E)$ curves are filled up to a certain maximum energy E_m by the available valence electrons of the solid. The distinction between conductors and insulators is, as is well known, that for the former $N(E)$ remains finite for all positive values of E, while for the latter $N(E)$ sinks to zero at the value E_m, and remains zero for a certain range of E known as the 'energy gap'.

It has been shown by Jones, Mott and Skinner (1934) and by Jones and Mott (1937) that the two characteristic features of the $N(E)$ curve shown at the points P and K cannot manifest themselves in the same spectrum. Thus if the maxima, such as P, which we shall refer to as 'peaks', are to be seen in a K-spectrum, as is found empirically to be the case, then the discontinuities such as K ('kinks') will occur, not in the K-spectrum, but in the L_2- and L_3-spectra. This conclusion is a simple deduction from the symmetry of the relevant wave functions, when the wave-lengths of the electrons passing through the lattice have the correct energies to be diffracted by a set of crystal planes. In actual practice, various sets of points P, K will appear, according to the crystal structure of the material.



metal insulator

FIGURE 2. Illustrative $N(E)$ curves.

4. SPECTRUM NOTATION

An X-ray line, due to a transition between two inner shells, will be referred to in terms of the nomenclature of these shells (e.g. the KL_3 line). When the state from which the transition takes place is a valence level, giving rise to an 'emission band', the notation of X-ray shells becomes inconvenient, owing to the fact that levels denoted by different symbols co-exist at the same energy value. Hence, we shall use the symbol V for the valence electrons (e.g. the KV band). In cases which are not liable to ambiguity, we shall frequently omit the symbol V altogether (e.g. 'the K-band of Li'). In the case of satellites, due to double ionization of the emitting atom, the shell from which the extra electron is removed can conveniently be put in brackets (e.g. 'The $K(L_2)L_3$ satellite').

For convenience, we shall substitute the symbols L_1, L_2 and L_3 for the previous notation of L_{I}, L_{II} and L_{III}, and similarly for other shells. When the energy separation between two similar spectra is unimportant, we often write, for example, L_{23}, instead of L_2 and L_3.

5. Experimental material

In figures 3–6 are reproduced photometer curves of the emission bands for solid substances of the first two groups of the periodic table. These are arranged as follows: figure 3, metals; figure 4, metals, the effect of the temperature of the anticathode; figure 5, non-metals; and figure 6, satellite bands. For metals, the curves of figure 3 correspond to emission from an anticathode at liquid-air temperatures; figures 5 and 6 correspond to room temperature except that the curves for P and S were obtained at liquid-air temperatures, as described in § 2 (*c*).

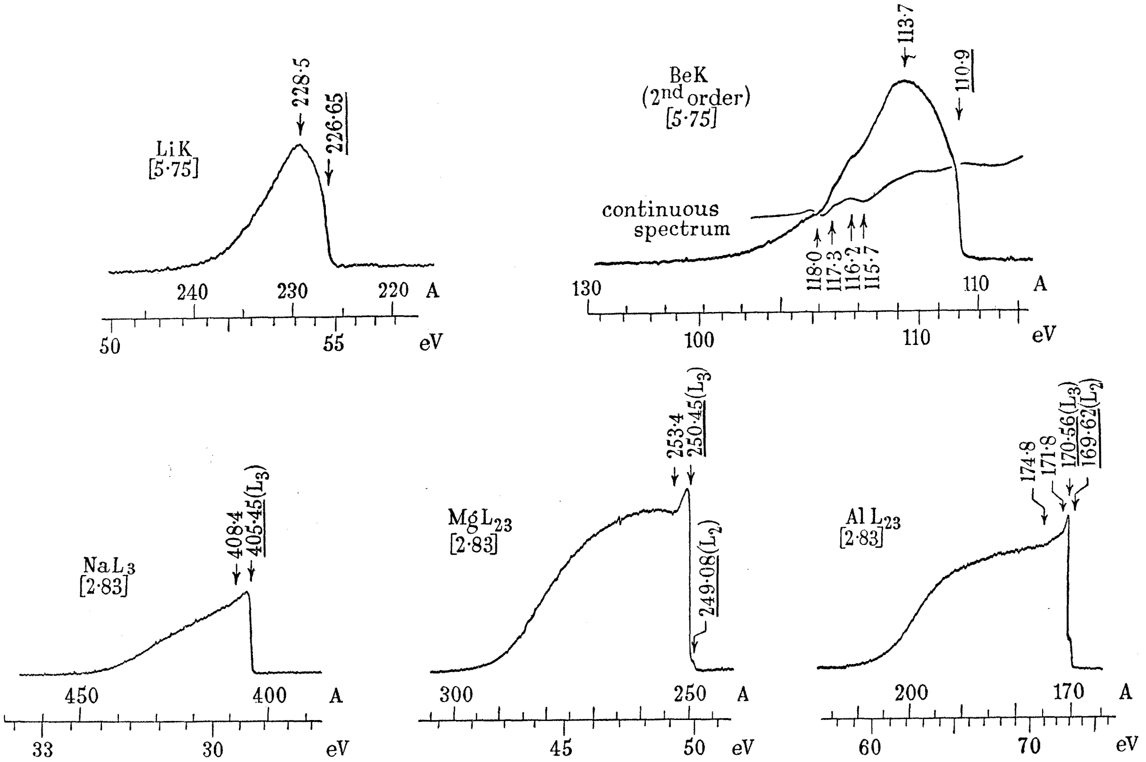


Figure 3. K and L bands of metals. (Square brackets indicate the gearing ratio used in obtaining the photometer curves, reduced 2·0 times in reproduction.)

As has already been noted, to translate from the photometer deflexion into the intensity as a function of wave-length, a calibration curve for the photographic plate is required. We shall not for the moment give the intensity curves for the bands; we may note, however, that the photometer was so adjusted as to give a deflexion proportional approximately to the intensity of the soft X-rays which are responsible for the blackening of the plate. The photometer was used at a constant sensitivity, so that all the results are comparable, except that they were taken with several different batches of Q-plates and the plate characteristics are apt to be somewhat variable. Several gearing ratios for the relative movement of paper and plate in the photometer were available. In the figures the numbers in square brackets indicate the ratio used. The curves are considerably reduced in reproduction, and the proportion is also given. The plate 'background' deflexion was in many cases negligible; where it is not, the 'clear plate' deflexion is indicated by dotted lines at the sides of the diagram. An exception is the case of the satellite bands (figure 6); here the bands are so weak that the background was considerable and is not indicated. For these curves, the differences in deflexion are so small that we may be sure that the band intensity is proportional to this difference; the actual background, consisting of continuous X-radiation together with a certain amount of fogging by visible and ultraviolet radiation, is indicated by the dotted line. This background may be obtained from spectra using an anticathode which gives no characteristic radiation in the relevant region. Although both sources of background would undoubtedly give an intensity increasing continuously with decreasing wave-length, it was found that the apparent background intensity is not a smooth curve. The source of irregularity was shown to be almost entirely connected with the absorption and dispersion of L-electrons of Si in SiO_2, the main constituent of the glass of the grating. A system of apparent background intensity fluctuations could be traced in several orders of the spectrum,

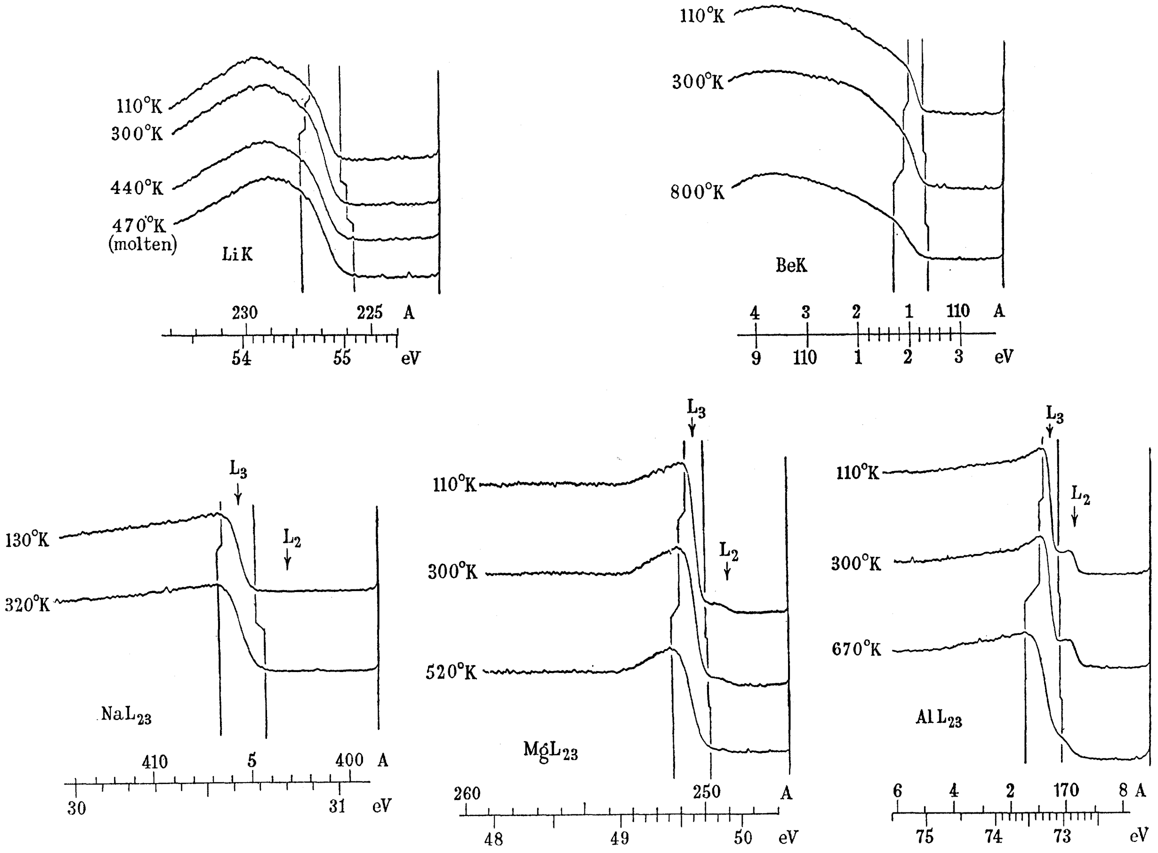


FIGURE 4. Temperature effect on metal emission edges (reduced 2·4 times in reproduction).

showing that in the region of longer wave-lengths, the background is mostly due to high-order diffraction of the continuous X-ray spectrum. Thus at long wave-lengths this irregularity of diffraction merely forms a background which can be subtracted from the observed intensity to give the band form. Exceptions occur when the band investigated lies in the region where this absorption dispersion anomaly occurs in the first order, because then the effect on the radiation in the band is primary. The region in question extends from about 120 A to about 100 A, and cuts across the K-band of Be (figure 3) and the L_3-band of P (figure 5). In these instances, a curve for a continuous spectrum has been added to show what features of the observed band are due

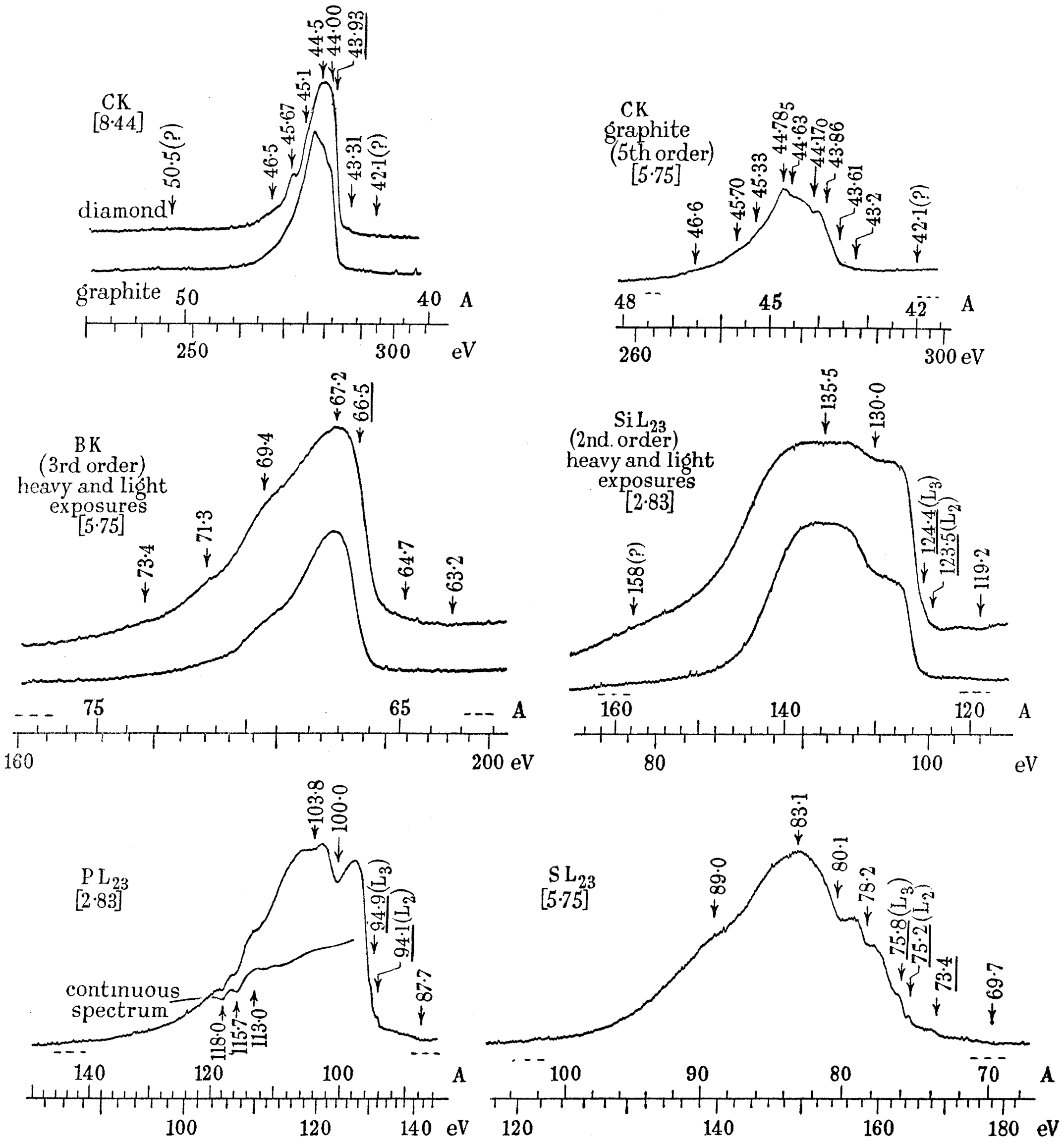


FIGURE 5. K and L bands of non-metals (reduced 2·1 times in reproduction).

to this cause. However, it is not an easy matter to be sure of the exact intensity form of these two bands in this region, although, of course, the main characteristics are clear enough.

It does not seem to serve much purpose to give a table of wave-lengths; the wave-lengths of characteristic points on the curves are indicated on figures 3–6. It is not possible to choose any particular system for the points so marked; in general, the sharpest points demarcating any particular feature on the curves have been used. In a number of cases this point is that at which the intensity has fallen to half value in a steep fall of intensity. Such points are indicated by *underlining* the wave-length figures. The wave-lengths of characteristic points of some of the bands were obtained by direct (photometric) comparison with the wave-lengths of the Al condenser-spark lines, as given by Sonderquist (1934); such are the bands of C (graphite), Mg and Al. The Na L_3-band was measured against Cu spark lines, given by Kruger and Cooper (1933). These features, namely, the 'edges' in the case of the metal bands, should be correctly obtained with a probable error of about 0·05 A. For the remaining bands, a characteristic feature of the K-spectrum of C was used as a secondary standard. The wave-length of this feature was obtained, correct to about 0·005 A, as 44·170 A and, refracted in many orders, formed a convenient comparison. Such wave-lengths are estimated as correct to 0·1 A; in the cases of S and P the error may be somewhat greater. The wave-lengths of satellite bands (figure 6) were not, in the cases of Al and Si, obtained by direct comparison, but were merely inferred from the wave-

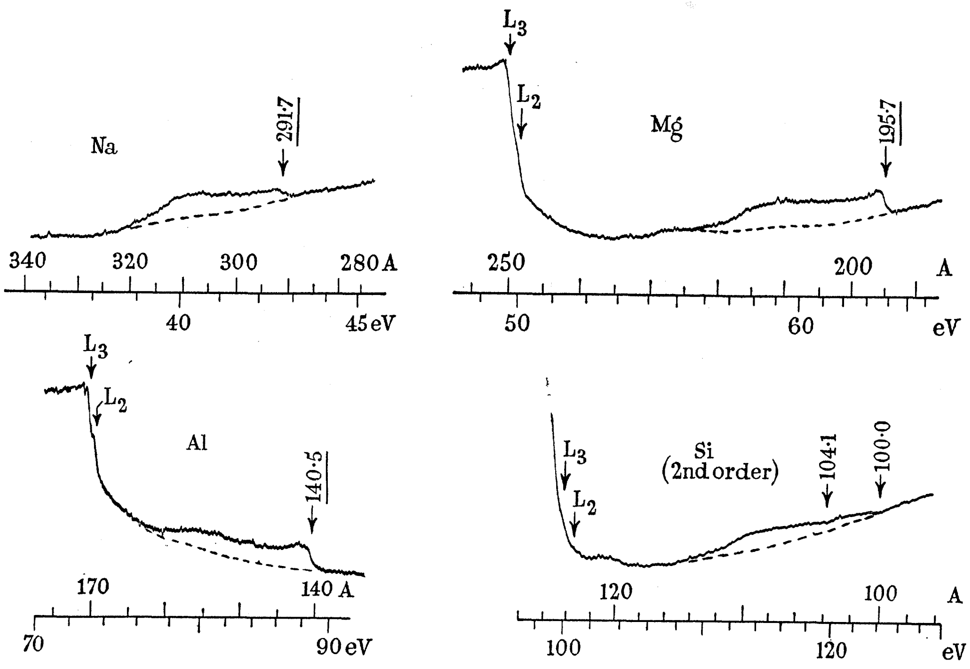


FIGURE 6. Satellite bands (reduced 1·6 times in reproduction).

lengths of the main L_3-edges, using the dispersion curve of the spectrograph. Other wave-lengths in a given diagram were obtained using this same dispersion curve, giving an accuracy of about 1 % for the wave-length differences from the directly determined wave-length. The latter was always the sharpest feature of the curve; exceptionally, in the case of *B*, no really sharp characteristic is available.

In a few cases, characteristic points have been marked with a query. Most of these are so weak that we do not feel absolutely sure of their existence. On the other hand, the long wave-length bumps of the C and Si curves are probably spurious; the first is thought to be a shadow effect in the spectrograph, and the second is almost certainly due to slight contamination by SiO_2.

In the case of comparison with the line spectra, the method of partly overlapping the X-ray band and the lines on the plate was used. In comparisons with the C *K*-spectrum, the breadth of this band makes this practice impossible, and one had to compare two spectra side by side. Since the spectrum lines are somewhat curved in a direction perpendicular to the dispersion, a system of marking the plate was needed. This was provided by cutting out a slip of paper in the form of a circle of the necessary radius and sticking it to the plate parallel to the direction of the spectrum lines. A sharp mark on the photometer-record was thus provided. The curves of figure 4 were assembled together by this method, and experience showed that the errors involved were only of the order of a few hundredths of an A.

The photometer curves of figures 3–6 are the result of a large amount of work. Except in the case of the temperature variations (figure 4) and also the single case of P, at least two plates were taken of every band represented. The spectra were wide enough to allow about three or four independent photometer runs to be taken. The curves to be published were selected from a number so as to be characteristic. The slit of the photometer was so chosen as to contribute only a small amount to the diffuseness of any particular feature. The grain size of the Q_1-plates is very small, but they are liable to occasional defects, mainly in the form of clear spots on the plate. In a few instances, such spots have been removed when they occurred in places on the published curves where they might be misleading. On the whole, it may probably be claimed that the curves given are definitive; namely, that all the features given are genuine, and that no essential features have been missed from faulty resolution or inadequate technique.

It is of interest to consider the question of the thickness of the layer of the anticathode of the X-ray tube which is effective in producing the spectra obtained. There are two factors defining this: (*a*) the absorption of the solid for the radiation emitted, and (*b*) its absorption for the 3500 V electrons which excite the radiation. The first factor would set a limit of between 10^{-4} and 10^{-5} cm., and the limit set by the second factor is of the same order of magnitude. So it seems certain that the effective layer is at least 10^{-5} cm. thick, and this is enough to ensure that the results shall be characteristic of the bulk metal.

6. Metals and non-metals—emission edges, real and false

In all the curves of figures 3 and 5, the most evident feature is a sharp drop in intensity at or near the short wave-length end of the band. This feature will be referred to as an 'emission edge'. In the case of metals, the edge occurs at the short wave-length limit of the band; the amount of radiation emitted of shorter wave-lengths is very small. In the case of L-spectra the edge is doubled; this corresponds obviously to the fact that we are dealing with two L-levels, the L_2- and the L_3-level. Since L_2- and L_3-levels differ only in spin, it is safe to assume that the corresponding band forms are identical; and the weakness of the L_2-spectra makes it a fairly simple matter to separate them out to give the pure L_3-spectra. L_1-levels, as we shall show subsequently, do not provide any observable spectra. In the case of L_{23}-spectra of metals, the intensity in the band drops suddenly from its maximum value; in the case of K-spectra, the intensity falls more or less gradually and then drops suddenly at the emission edge. As is shown in figure 4 the breadth of the emission edge depends on the temperature; at liquid-air temperature it is less than about $\frac{1}{10}$ eV, but rises at room temperature to about $\frac{2}{10}$ eV.

In the case of non-metals, there is a characteristic difference. The sharp fall in intensity occurs, though in the case of sulphur in several stages. This large fall in intensity, however, always occupies an energy range of at least 1 eV; it is not sufficiently sharp to show the (L_3-L_2) doubling. Also, on the short wave-length side of this '*false*' emission edge, other comparatively sharp features of the band are to be found. These are weak, but they are in fact sharper than the false edge already mentioned. Thus, in the case of Si, P and S a drop in intensity occurs sufficiently quickly to show the (L_3-L_2) separation with certainty. This characteristic, which the present work is the first to establish, will be designated as the main 'band end'; further band ends, too weak to show (L_3-L_2) doubling seem always to appear at even shorter wave-lengths. The band ends are by no means as sharp as the metal edges; they never attain a breadth less than about $\frac{1}{2}$ eV. Nor can this peculiarity be ascribed to temperature. It is true that when an insulator is used as anticathode, the effective temperature is somewhat uncertain. Nevertheless, in the cases of P and S, if the temperature had risen up to room temperature, a considerable evaporation of the material would have taken place. Further, in the cases of B and Si, the conductivity is certainly good enough to prevent any appreciable rise in temperature due to the electron bombardment in the X-ray tube, and, in the case of Si, experiments at temperatures between 110 and 700° K failed to show any measurable change in the band form.

Thus, there is no doubt that we are dealing with an *intrinsic difference between metals and non-metals*. The metals show true emission edges, while the non-metals show the phenomena of false edges and band ends. It is very interesting to note that the bad conductors B, C (graphite) and Si, fall very definitely into the latter category, showing that, if a true edge exists, it must be entirely negligible in magnitude. From the spectroscopic point of view, the behaviour of these substances is indistinguishable from that of insulators.

In the case of metals, sharp absorption edges as well as emission edges have been observed. It is easy to see from our interpretation of emission and absorption bands given in § 3 that the two edges of a given metal must fall at exactly the same wave-length. For no energy gap exists between the filled and vacant states. Using the absorption results of Skinner and Johnston (1937) and Johnston (1939), in conjunction with the present emission results, table 2 has been compiled. To take into account the small broadening of the edges due to temperature, and, in the case of absorption, to inadequate resolving power, the mean edge wave-lengths λ_m are compared. The Al L_{23}-absorption edges have not been resolved. The agreement is very good. For insulators, absorption should only begin at a wave-length somewhat shorter than the wave-length end of the emission band, corresponding to the energy gap. We have no data for elements, but the limit of the L_3-absorption of Si in SiO_2 can perhaps be judged, as we have seen, from the absorption of a continuous spectrum by the glass of the grating. The absorption begins at about 118·5 A. The L_3-emission of Si in SiO_2 probably has a weak projection stretching down to 121 A, though the main rise of the curve only begins above 124 A. In any case, an energy gap of several eV seems indicated.

TABLE 2

	Li K	Mg L_3	Mg L_2	Al L_3	Al L_2
Emission edge, λ_m	226·65 ± 0·1	250·45 ± 0·05	249·08 ± 0·1	170·56 ± 0·05	169·62 ± 0·1
Absorption edge, λ_m	226·5 ± 0·2	250·7 ± 0·2	249·3 ± 0·2	170·0 ± 0·2	

7. TEMPERATURE EFFECTS ON THE METAL EMISSION EDGES

In figure 4 are shown photometer traces of the emission edges of Li, Be, Na, Mg and Al, on a large scale. The different curves correspond to different temperatures of the anticathode from which the radiation is emitted. In all cases, except that of Li at the highest temperature, the metal of the anticathode remains solid. It will be seen that the effects of an increased temperature are twofold: (*a*) a broadening out of the edges, which in the case of Al obliterates a feature of the band, and (*b*) a shift of the mean point of the edge which occurs towards longer wave-lengths in all cases, except that of the alkali metals, for which the mean point remains practically stationary.

In the case of liquid lithium (for which the melting-point could be accurately gauged by the flowing of the surface of the anticathode) it will be seen that there is no marked difference in the shape of the curve from that emitted by solid lithium at a slightly lower temperature. However, a very careful study of many photometer traces has convinced us that the slight difference to be observed in figure 4 is genuine. This consists in the fact that the curve for liquid lithium is more smoothly rounded (and that in consequence its maximum occurs at a shorter wave-length) than for solid lithium.

In the case of insulators and semi-conductors, the considerable diffuseness of the false edge, and the low intensity of the sharp short wave-length limit makes the bands relatively insensitive to temperature effects from a practical point of view. In the case of Si, experiments with the anticathode temperature varying between 110 and 600° K failed to show any noticeable difference in the band shape. This does not necessarily apply to very high temperatures. In fact, Hautot and Serpe (1937) report a certain smoothing out of the features of the boron K-band when emitted from an anticathode at a temperature of about 1800° K. For such experiments, boron is probably a suitable element. Farineau (1938) has reported an appreciable change in the shape of the Al K-band when emitted from the liquid metal at about 1100° K. But when we attempted the corresponding experiment with the L_{23}-band, we found that the metal either alloyed with the base metal of the anticathode (in this case tungsten), giving a grey powder deposit which seems to consist partly of Al_2O_3; or if we attempted to keep a considerable mass of Al under the focal spot of the X-ray tube by tying a piece of metal on to the anticathode, it simply flowed away when melted. Thus we are inclined to be doubtful about the interpretation of Farineau's result as due purely to melting.

The two effects due to temperature on the emission edge of a metal, namely, diffuseness and shifting, may be discussed separately and we shall begin with the first. It is well known that at the absolute zero of temperature, all the electrons in a metal are in their lowest states. The number $N(E)$ of electrons per unit energy range therefore jumps discontinuously at a certain energy E_m from a finite value to zero. But at a finite temperature, some of the electrons with energies near to E_m are excited. $N(E)$ is now given as a function of the temperature by the expression

$$N(E) = N_0(E_m)\,\frac{1}{1+e^{(E-E_m+\xi)/kT}}, \tag{6}$$

where $N_0(E_m)$ is the value of $N(E)$ for the value E_m at the absolute zero of temperature. It is assumed that $N_0(E)$ does not vary appreciably within a small energy range near the value E_m. The quantity ξ, related to the 'thermodynamic potential' $(E_m-\xi)$ of the electrons, only causes a shift of the edge, and, as we shall see, may be neglected. Equation (6) clearly gives a curve which fits our curves qualitatively, and which broadens with the temperature in the required way. If we call the 'edge breadth', b, the energy interval in which the $N(E)$ curve rises from 5 % of its final value to 95 %, then b should be very nearly equal to $6kT$, and thus varies, in our temperature range, from about 0·06 to 0·45 eV.

If we wish to consider the broadening effect due to temperature in more detail, we must attempt to separate out the broadening due to the finite instrumental line width characteristic of the spectrograph. This has been experimentally determined by measurements on narrow spectrum lines, and we shall assume it to follow a Gaussian form. We have therefore to consider the effect of such a line broadening on the form of our observed experimental emission edge. $I(E)$, the intensity emitted per unit energy range is, in the absence of a correction, proportional to $N(E)$. Correcting, we have

$$I(E) \propto \int_{-\infty}^{\infty} N(E')\, e^{-\alpha(E-E')^2}\, dE', \tag{7}$$

where α is a constant which can be expressed in terms of the 'line width' w, namely, the energy interval in which the line intensity rises from 5 % of its maximum and falls back to the same value. The integral (7) cannot be evaluated except by quadratures.

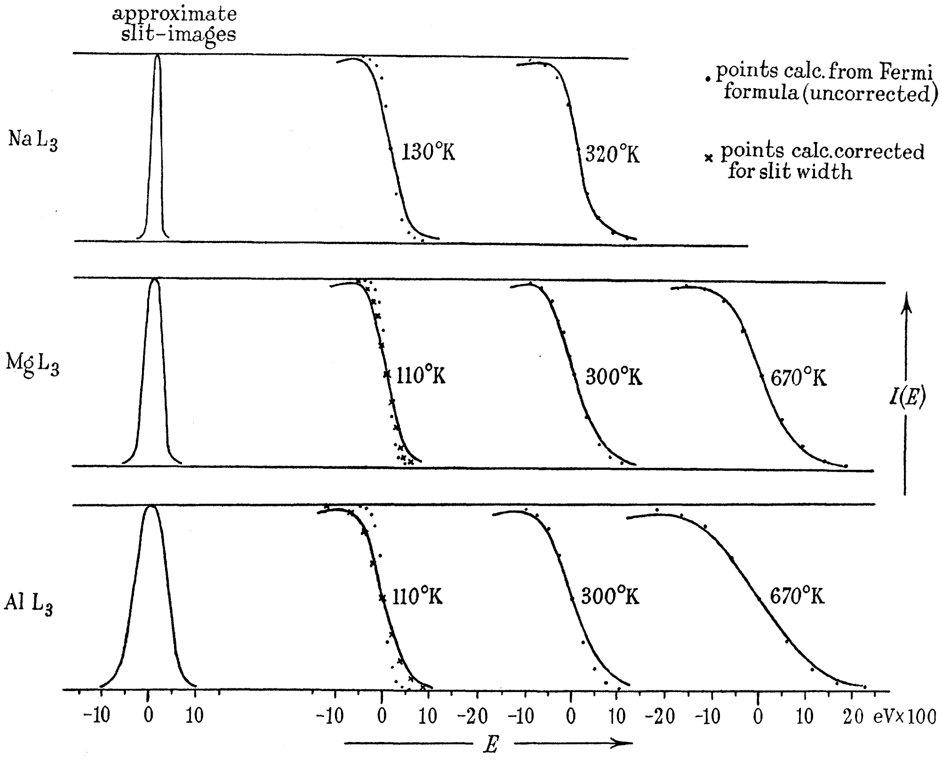


FIGURE 7. Temperature-broadening of emission edges.

In figure 7 we have reduced to intensities $I(E)$ the photometer curves of the L_3-edges of Na, Mg and Al, corresponding to different temperatures. The contribution of the L_2-edges has been eliminated. The instrumental line widths are indicated, and theoretical points from equations (6) and (7) are plotted. It must be remembered that these assume that $N_0(E)$ is constant; in actual fact, it is increasing with increasing E up to the edge, so some slight misfit on the low-energy side is inevitable. The uncorrected points are badly off the curves corresponding to 110° K, especially for Al. But in this case, when the correction for slit width is applied, the discrepancy is nearly accounted for. For Mg, the agreement is not quite so good, while, for Na, the correction is negligible. Perhaps temperature errors, due to the inefficiency of liquid oxygen as a cooling fluid, are involved.* For higher temperatures, the uncorrected points are only slightly off the curves, and, without making an exact calculation of the effect of the slit width, it is clear that correction would bring the agreement within the experimental error. Thus the curves give a direct and convincing proof of the applicability of the Fermi formula (6) for the effect of temperature on the electrons in a metal.

We shall merely summarize the remaining cases by giving the observed edge breadths, b, which are collected in table 3. The data are expressed in hundredths of 1 eV and were obtained with the aid of the plate calibrations, not direct from the photometer curves. The probable errors vary from about $\frac{2}{100}$ eV to about $\frac{4}{100}$ eV for Li, and for Be, Mg, Al at the highest temperatures. The Fermi breadth b_F, calculated from equation (6), is also given, together with the line width, w, of the spectrograph.

Table 3. Observed and calculated values of the edge breadths (eV × 100)

	Li		Be			Na		Mg			Al		
	110°	300°	110°	300°	800°	130°	320°	110°	300°	520°	110°	300°	670°
b	21	30	24	36	60	11	17	12	20	28	14	22	41
b_F	6	16	6	16	42	7	17	6	16	27	6	16	35
βw	3	2	7	6	5	1	1	2·5*	2	2	6·5*	6	5
w	10	10	20	20	20	4	4	8	8	8	16	16	16

* Values actually calculated by numerical integration.

b is the observed edge breadth and b_F that calculated according to equation (6). βw is a quantity correcting b for the effect of the finite image width w of the spectrograph.

b_F and w are not additive, and so we introduce the fraction β such that $(b_F+\beta w)$ represents the width of the corrected edge. If w is much greater than b_F, then it can be shown from equation (7) that β is about $\frac{2}{3}$; if w and b_F are roughly equal, the numerical integrations carried out give β of the order of $\frac{1}{3}$ and increasing with w/b_F. So the values of βw, corresponding to the various cases for which the integration has not been performed, can be roughly estimated and are included in the table. It will be seen that for Na, Mg and Al, the whole of the breadth b is accounted for by $(b_F+\beta w)$ for all temperatures, to within about the probable error. But, for Li and Be, there seems to be a definite difference of about $\frac{1}{10}$ eV between the observed and calculated values.

We think this must be explained as a definite natural edge breadth, analogous to the breadth of spectrum lines, which would exist at the absolute zero of temperature. Owing to the non-additive property of such quantities, it is not easy to estimate this natural breadth exactly. It seems, however, to be between $\frac{1}{10}$ and $\frac{2}{10}$ eV for Li and Be K-edges, and to be not more than a few hundredths of 1 eV for Na, Mg and Al

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* Also, experience in melting Na by electron bombardment on the anode showed that this metal tends to form a non-conducting layer of oxide between itself and the copper. Although a small correction for this effect has been applied, it is naturally unreliable.

L_3-edges. The difference between the two sets of results is probably due to a spectroscopic distinction between K- and L_3-spectra, rather than to properties of the individual metals.

We now turn to the consideration of the shifting of the mean points of the emission edges when the temperature is altered. It is natural to attempt to explain this effect as principally due to thermal expansion. The temperature difference between the highest and lowest temperatures of the curves of figure 4 is responsible for about a 1 % linear expansion in each case. We may assume that the band width is proportional to the square of the lattice constant.* Hence, if the temperature is raised, a decrease in the band width will occur. If we further assume that the *mean* energy of the electrons remains constant, it follows that, owing to the contraction of the band width, the energy of the highest filled level will descend with increasing temperature. In the case of a Sommerfeld gas of electrons, the amount of the descent would be $\frac{2}{5}$ of the alteration in the band width; and in the case of a real metal we may take this value without serious error, since the Sommerfeld band width, as we shall see, always gives a good approximation to the actual band width. In table 4 are given the observed shifts of the mean points of the edges towards lower energies for various metals and the shifts, calculated, as we have described, from the expansion in a given range from 110° K to the value given, and from the observed band width (see § 10). The values are expressed as hundredths of 1 eV. The figures in brackets are somewhat uncertain. The expansion effect has also been observed for a non-metal, Si.

TABLE 4. EDGE SHIFTS (eV × 100) DUE TO RAISING THE ANTICATHODE FROM 110° K TO THE TEMPERATURES GIVEN

Metal	Temp. ° K	Expansion %	Calc. shift $\frac{1}{100}$ eV	Obs. shift	Temp. ° K	Expansion %	Calc. shift $\frac{1}{100}$ eV	Obs. shift
Li	440	(2·0)	(6)	0·5 ± 0·5	300	1·1	(3·5)	0·5 ± 0·5
Na	300	1·2	3·0	−0·5 ± 0·2	—	—	—	—
Be	800	(1·0)	(12·5)	13 ± 1	300	0·3	(3·5)	2·5 ± 1
Mg	520	1·0	5·6	4 ± 0·5	300	0·6	2·5	1·0 ± 0·5
Al	670	1·2	13·0	9 ± 0·7	300	0·4	4·4	2·0 ± 0·7

It will be seen that the shift observed is of the right order of magnitude, but that in general it is smaller than the calculated shift by an amount which, particularly in the case of Na, is well outside the limits of error. Also, the fact that the shift for Na and Li is practically zero, makes it impossible to try to explain this difference by a variation of the factor $\frac{2}{5}$.

Neither does it seem possible to try to explain it by a variation of the *mean* energy of the conduction-electron levels with increasing expansion. It is true that a rise in

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* For example, the elementary formula to be given in § 10 gives the band width for a metal as proportional to $\rho^{\frac{2}{3}}$, where ρ is the number of atoms per c.c. This obviously gives the above result.

this mean energy must occur, but it is merely a second order effect, and can be calculated in terms of the compressibility of the material. The result gives only a displacement of the order of 10^{-3} eV.

Another possibility to be considered is the effect of the quantity ξ of equation (6), which can be approximately evaluated as $\pi^2/6(kT)^2 . d \log N(E)/dE$ (Mott and Jones 1936, p. 178). At the value E_m, our experimental curves show that $N_{s+d}(E)$ is increasing and $N_p(E)$ decreasing with E, and, although probably the former predominates in $N(E)$, this is not certain. But in any case, the slopes of the observed curves at the values E_m give only shifts of the edges of the order of 10^{-3} eV at 300° A.

We think, therefore, that the effect can only be explained as a modification in the form of the $N(E)$ curve for a band when the lattice constant is altered. All the metals dealt with (except possibly Li) have, at liquid oxygen temperature, the property that an overlap of Brillouin zones occurs within a few tenths of an eV of the edge. One possibility is that this overlap might disappear, or become changed in amount, with increasing temperature; and indeed there is a certain amount of evidence, which, though not conclusive, points to the fact that this may be the case, at least for Na and Al. For a reference to figure 4 will show that the kinks in the observed intensity curves which occur near to the edges are obliterated at the highest temperatures, and, though one cannot be quite sure, it seems that this obliteration is more than one could expect from the mere diffuseness of the edge. In the case of Na, the upturned portion near to the edge which represents the Brillouin zone overlap has an area of perhaps $\frac{1}{60}$ of that of the whole band at 110° A. If, therefore, at 300°, the zone overlap has disappeared, the width of the band would be extended towards higher energies by an amount of about $\frac{1}{100}$ of the actual band width, say about 0·03 eV. This would be of the required order of magnitude in order to account for the discrepancies between the observed and calculated values in table 4.

8. $L_1 : L_2 : L_3$ INTENSITY RATIOS—SATELLITE BANDS

With a given electron bombardment of the anticathode, the L_1-, L_2- and L_3-levels must be ionized in practically their statistical ratios, namely 1 : 1 : 2. The spectra, however, are not observed in these intensity ratios. Hence there must be some secondary mechanism which, after the initial ionization, alters the statistical proportions of atoms ionized in the L_1-, L_2- and L_3-shells. This mechanism is found to be the Auger effect.

Let us first consider the case of the L_1-spectra. A set of very weak bands, of intensity of the order of $\frac{1}{100}$ of that of the main L_{23}-bands, is found to their short wave-length side. In the case of Na, Mg and Al metals, these bands show a sharp emission edge (figure 6). It was natural to consider that they might represent L_1-radiations, especially since this interpretation would give an (L_3-L_1) energy separation of the right order of magnitude. But suspicion was cast on this view since the bands of Mg and Al did not agree in intensity form with the K-bands of these metals. Since K- and L_1-radiations both involve transitions of the type $p \rightarrow s$, this would be very difficult to account for. The alternative explanation, kindly pointed out to me by Dr Farineau, is that these short wave-length bands are to be regarded as satellites due to double ionization of the L_{23}-shell, and that the L_1-radiation is *entirely missing*. Dr Farineau, in a private letter, was able to support this view by calculating the exact edge energies of the short wave-length L-bands of Mg and Al from the known energies of the K-satellites of these metals, as determined by Karlsson and Siegbahn (1934). The energy difference between the *line* satellite $K(L_{23})\,L_3$ and the emission edge of the *band* satellite $K(L_{23})\,V$, which can both be unambiguously identified, gives the absolute quantum energy of a postulated $L_3(L_{23})\,V$ satellite; and the agreement with the observed energy of the short wave-length L-bands was found to be very good. This appears to settle definitely the identity of these bands as satellites. We shall not enter here into the question of why such K and L satellites, which represent emission from atoms in abnormal states, show features similar to, though not identical with, those of the K- or L_3-emission bands themselves; thus for metals, the satellite bands show sharp emission edges as we have mentioned, and in general the total band widths are the same as those of the main bands.*

The important fact from the present point of view is that we have established that the L_1-bands are not found in sufficient strength to be observable, and that their intensity is therefore only a fraction of 1 % of that of the L_3-bands. This implies that when an L_1-shell is ionized in the X-ray tube, the vacancy is almost immediately filled by a process which does not provide radiation in our region of the spectrum. Obviously, the most natural process to be considered is the transition L_2 or $L_3 \rightarrow L_1$. If this process occurred with the emission of radiation, this would lie in the region of 1000 A. We have not made any systematic search, but it is almost certain that if this radiation can be found, it must be very weak. Owing to its small quantum energy, a process such as $L_3 \rightarrow L_1$ is much more likely to occur with the emission of an Auger electron. Of course, it is implied that there exists a level into which the Auger electron can make its transition, but this condition is certainly satisfied even for free atoms, provided the energy difference $(L_3 \rightarrow L_1)$ is sufficiently great, and is always likely to be fulfilled for solid materials. The part played by Auger effects of this type in the case of hard X-ray spectra has been discussed by Coster and Kronig (1935). In the case of soft X-ray spectra, it is even more important, as we shall see.

Such an Auger process has two effects on our spectra: (1) it diminishes the probability of a $V \rightarrow L_1$ radiative transition, and (2) it shortens the life of the L_1-excited state, thereby broadening any characteristic discrete features of the L_1-emission or absorption bands. It is interesting that Karlsson and Siegbahn's (1934) observations of the $K(L_1)\,V$ and $K(L_{23})\,V$ satellites of Al give some evidence on these effects. Their photometer curves, corrected for the line width of their spectrographic equipment, give an

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* This matter will be referred to in § 3 of the second paper of the series, by O'Bryan and Skinner.

edge width of about $2{\cdot}5 \pm 0{\cdot}5$ eV for $K(L_1)\ V$, as compared with $0{\cdot}5$ eV for $K(L_{23})\ V$, in the case of Al K-radiation (8 A). It follows that the Auger process $L_3 \rightarrow L_1$ causes an edge width of the order of 2 eV for the Al $K(L_1)\ V$-radiation and hence an equal edge width for the Al $L_1\ V$-radiation. Since the absolute edge width for Al L_3-radiation is certainly less than a few hundredths of 1 eV, it is clear that the intensity of the L_1-emission band of Al should not exceed about 1 % of that of the L_3-band.

In absorption, the L_1-edge should be diffuse, but it should not, of course, be weak. In fact, owing to the greater strength of $s \rightarrow p$ than of $p \rightarrow s$ absorption transitions, its strength should exceed the statistical ratio of 1 : 2 as compared with that of the L_3-absorption edge. Absorption data in the required region have been given by Skinner and Johnston (1937) and by Johnston (1939)* for Mg and Al respectively. Neither show any evidence of a sharp L_1-absorption edge. The approximate position of the absorption can be estimated. Near the required place a diffuse but strong maximum of absorption is observed both for Mg and Al. It seems fairly sure that the L_1 'edge' lies on the slope to the long wave-length side of this maximum, i.e. at 180–190 A for Mg and 130–140 A for Al. The L_1-absorption system is superposed upon the L_{23}-system in this region, and the characteristics of either cannot be deduced without making an assumption about those of the other.

We next come to the discussion of the relative intensities of L_3- and L_2-emission bands of the second group elements. On a simple view, these should be in the ratio of 2 : 1. Actually, in most cases, the ratio is considerably less, as is shown in table 5. Except possibly for Na, the ratios should be correct, certainly to within 20 %. We may also add that, for the metals Ca-Cu, new experiments by Dr Bullen have shown that the L_3/L_2 intensity ratio is of the order of 10 in all cases.† It seems clear therefore that the reduction in the intensity of the L_2-band is much less for non-metals than for metals. Among metals, the reduction increases as the $(L_3 - L_2)$ separation becomes small.

TABLE 5

	Na	Mg	Al	Si	P	S
L_3/L_2 intensity ratio	~ 50	20	9	3	2	2
$(L_3 - L_2)$ separation, eV	$0{\cdot}20 \pm 0{\cdot}02$	$0{\cdot}27 \pm 0{\cdot}01$	$0{\cdot}40 \pm 0{\cdot}01$	$0{\cdot}73 \pm 0{\cdot}05$	$1{\cdot}1 \pm 0{\cdot}1$	$1{\cdot}3 \pm 0{\cdot}1$

This effect can also be accounted for by an Auger process. The number of ionized L_2-levels is effectively reduced by the transition $L_3 \rightarrow L_2$ with the emission of an Auger electron. It is worth noting that in this case, unlike the case of $L_3 \rightarrow L_1$, there can be no question of the emission of radiation, since the radiative transition $2p_{\frac{3}{2}} \rightarrow 2p_{\frac{1}{2}}$ is absolutely forbidden. The observed fact that the filling of the L_2-level from the L_3-level is much less probable than that of the L_1-level is perhaps connected with this selection rule.

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* Unfortunately, Johnston was induced, by our mistaken interpretation of the L satellite bands as L_1-bands, to interpret his results in accordance with this hypothesis, and to look for sharp L_1-absorption edges.

† See the third paper of this series (Bullen, Johnston and Skinner).

Another distinction between the $L_3 \rightarrow L_1$ and $L_2 \rightarrow L_1$ Auger processes is that in the latter case the energies involved are only of the order of 1 eV or less, while in the former they are 10 eV or more. It follows from the smallness of the $(L_3 - L_2)$ differences that this Auger process could not occur for free atoms, since there will be no excited state of the atom with the right energy to receive the Auger electron. For such a process to occur, it is necessary to have a continuum of states, and for free atoms this only exists at energies greater than the ionization energy of the valence electrons. It is the characteristic of a metal, however, that such a continuum of states exists down to indefinitely small energies. But this is not the case with an insulator; the energy gap between the filled valence states and the lowest excited levels is of the order of a few volts, and this is just sufficient to prevent the occurrence of the $L_3 \rightarrow L_2$ Auger process for the cases in which we are interested. For P and S, we therefore obtain the normal L_3/L_2 intensity ratio, for the 'bad conductor' Si, nearly so. The $(L_3 - L_1)$ energy difference for these non-metals is, on the other hand, sufficient to allow the Auger electron to bridge the energy gap, and so the L_1-spectra are missing, just as for the metals.

Unlike the transition $L_3 \rightarrow L_1$, the Auger transition $L_3 \rightarrow L_2$ is not sufficiently probable to produce any measurable extra diffuseness of the L_2-emission edge over that found for the L_3-edge of the second group metals. As we have shown in § 7 the latter have a residual width of not more than a few hundredths of 1 eV, whereas the K-edges of Li and Be appear to have a definite residual width of the order of $\frac{1}{10}$ eV. It may well be that this is due to the rather probable occurrence of an Auger process $V \rightarrow K$, with the emission of an electron. Also, since our experimental limits, even for the L_3-edge breadths, are large compared to the breadth due to radiation-damping, the occurrence of Auger processes $V \rightarrow L_3$, though they must be less frequent than the processes $V \rightarrow K$, cannot be excluded.

In conclusion, it may perhaps be of interest to give the effective widths of different levels of a substance, due to various causes, radiation-damping, Auger effect, and lattice binding. We choose the case of Mg, and the experimental results are given in table 6.

TABLE 6

Level	K	L_1	L_2	L_3	V
Energy, eV	1301	62	49·9	49·6	7·7 to 0
Effective width, eV	0·5	~ 2	$< 0·05$	$< 0·02$	7·7

9. 'TAILING' EFFECTS. BROADENING OF LEVELS IN A BAND

In none of the bands is any sharp *long* wave-length limit observed. The curves fall away gradually towards low energies, and with sufficient exposure can be traced up to at least 20 or 30 eV from the main bands. This 'tailing' is more marked in the case of L_{23}-bands than of K-bands. It also seems to be larger in total amount in the case of many-electron elements (e.g. S) than of one-electron elements (Na).

Since the radiation forming a band is incident on the photographic plate at an acute angle, the possibility arose that the long wave-length tailing might in some way be due to reflexion of the radiation along the surface of the plate. In order to eliminate this possibility, an experiment was done in which the direction of increasing wave-length on the plate was reversed. A slip of plate was put into the spectrograph so that the angle of incidence of the radiation was the same as usual, but the place, instead of lying along the Rowland circle, lay as shown in figure 8; so that, if a spurious effect exists, it should now be seen on the short wave-length end of the band. The experiment was performed with Al. The band, though of course out of focus except at one point, was not so blurred as to spoil the result. It was found that the tailing effect persisted on the long wave-length side of the band and that practically none was to be seen on the short wave-length side. Hence the tail consists genuinely of radiation of longer wave-lengths.

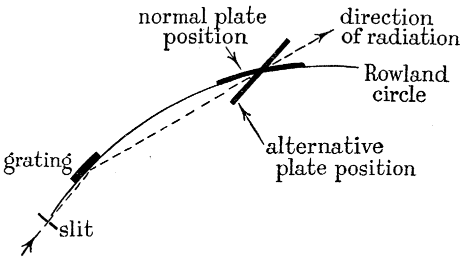

FIGURE 8. Experimental test for 'tailing'.

The short wave-length ends of metal bands are remarkably free from tail. The edges have a certain breadth, mainly due as we have seen to temperature effects. This broadening, however, fades out quickly to short wave-lengths. Beyond it, in cases of great over-exposure of the bands, a very slight tail appears, which can be distinguished from the temperature broadening by the slower rate at which it falls off towards the short wave-lengths. This feature will be described as the 'short wave-length tail'.

These tailing effects are illustrated by a very heavy over-exposure of the Mg L_{23} band which has been translated in terms of intensity. The curve of figure 9 gives $I(E)/\nu^3$, where ν is the absolute energy of the radiation. It is found that the long wave-length tail contains some 4 % of the total intensity, whereas the short wave-length tail contains only $\frac{1}{4}$ %. Another feature is to be seen on figure 9, namely, a very weak 'line' at 31.7 A superposed on the long wave-length tail. Since this is not a general characteristic of the 'tails', from the present point of view it may be ignored.*

* A very similar 'line' is found in the case of Al; it lies at about 290 A and so is at a greater distance from the main L_{23}-band than is the case for Mg. Another 'line' also occurs for Na at 375 A, namely, on the short wave-length side of the band. The origin of such 'lines' is obscure. Since they are by no means as sharp as spectrum lines emitted from the gas phase, the emission must certainly take place from the solid surface of the anticathode. On the other hand, they are quite unlike emission bands from any chemical compounds with which we have had experience. They may possibly (especially in the case of Na) be connected with the evaporation of metal from the surface under the electron bombardment. Or perhaps they are connected with the presence of almost monomolecular surface layers.

The explanation of the long wave-length tails remained for a long time one of the most puzzling features of the soft X-ray spectra. The theory of solids, even in its most general form, gives the result that $N(E)\,dE$, the number of levels between E and $(E+dE)$, varies as $E^{\frac{1}{2}}$ at the low-energy base of a band. Even taking into account the interaction between electrons (Wigner 1938), this relationship does not appear to be effectively altered. It has as consequence (Jones, Mott and Skinner 1934) that near the value $E=0$, the following relationships hold:

$$N_s(E) \propto E^{\frac{1}{2}}, \tag{8}$$

$$N_p(E) \propto E^{\frac{3}{2}}. \tag{9}$$

These properties follow simply from the symmetry of the wave functions. Thus, theoretically, the levels in a solid cease rather suddenly as the energy is diminished.

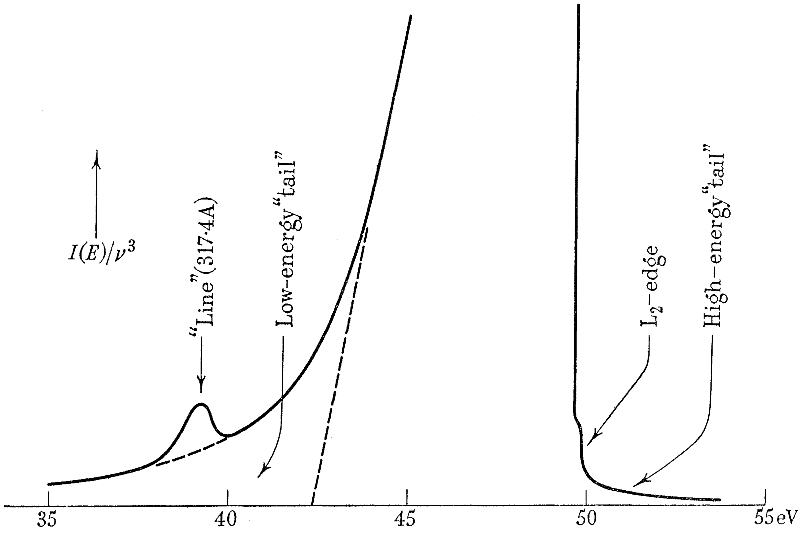

FIGURE 9. Tailing of Mg L_{23} band.

Now, according to § 3, an L_3-spectrum should represent $N_{s+d}(E)$ or, since there are no d-levels near the value $E=0$, $N_s(E)$. Thus, the L_3-spectrum should also break off sharply at the long wave-length end. This is very far from being the case, as we have seen.

There are three possibilities of explanation: (a) to interpret the tails as due to some secondary effect, (b) to give up the identification of $I(E)/\nu^3$ as representing $N(E)$, or (c) to abandon the theory. Attempts at explaining the tails as secondary and still retaining the theory having failed, we have come at last to an explanation of the type (b). The difficulty with such attempts of the type (a) is to explain the marked contrast between the sharpness of features at the high-energy end of a band (e.g. an emission edge) and the extreme diffuseness of the tail. Any mechanism which one may propose to obliterate an $E^{\frac{1}{2}}$ rise in the intensity at low energies also introduces a broadening of the high-energy characteristics of the band. The actual spreading out of the radiation to long wave-lengths could probably be explained by a mechanism in which part of the energy difference involved in the transition of a valence electron into a vacant X-ray level is taken up by the transition of a second valence electron into a vacant valence level. It is quite possible that such a process may account for a fraction of the long wave-length radiation observed in the tails. But if it were sufficiently probable to mask the parabolic rise at the low-energy end of the band, it would also spoil the sharpness of the emission edge. Thus such attempts to explain the tailing would necessitate the abandoning of the $E^{\frac{1}{2}}$ law. This could only be avoided by introducing the effect of the finite grain-size of the material which would preclude the existence of electron waves of above a certain wave-length, but calculation shows that the necessary grain-size would have to be unreasonably small.

Since it seems that any secondary process must apply nearly equally to radiation of all energies in a band, we are led to the conclusion that the tailing effect must be intrinsic. In other words, the $I(E)/\nu^3$ curves for the emission bands represent correctly the function $N^*(E)\,dE$, the number of *electrons* in a given energy range (or rather, more exactly, the associated functions $N^*_{s+d}(E)$ or $N^*_p(E)$). Since, however, we wish to retain the relationship (8) for $N(E)$, the number of *levels* per unit energy range, we must consider whether there may not be some possibility that $N(E)$ and $N^*(E)$ might not be proportional to one another. It is easily seen that the proportionality fails if we have to regard the individual levels as appreciably *broadened*, in the same way that atomic levels are slightly broadened by radiation damping. For then, in defining $N(E)$, we are forced to specify the energy E of a given level as its *mean* energy. $N(E)$, therefore, does not give a complete representation of the states of the valence electrons in a solid. On the other hand, since the theory of the solid state ordinarily takes no account of the broadening of individual levels, it is the quantity to which the theoretical formulae of the type (8) apply. The actual state of the solid is defined by $N^*(E)$, the number of *electrons* per unit energy range. If the levels are sharp, then, owing to the operation of the Pauli principle, $N^*(E)$ is just twice $N(E)$, and we shall see that in practice this relationship holds, except at the low-energy end of a filled band of levels. If we wish strictly to define the quantity $N^*(E)$ for all the valence levels of a solid, filled and unfilled, we may (since the factor 2 is of no importance) describe it as the number of *level elements* per unit energy range.

Let us now consider how this broadening effect can occur. We were actually led to consider it in the following way. We have seen that the L_1-levels of the second group elements are widened out to about 2 eV by the Auger transitions L_2 and $L_3 \rightarrow L_1$ involving an energy of the order of 10 eV. We know therefore that level breadths of the required order of magnitude can actually occur. Suppose now that the (L_3-L_1) energy difference is reduced and that at the same time the L-electrons become the valence electrons. We come thus to the case, for example, of oxygen in oxides, and we shall show in a subsequent paper that the band of $2s$ (L_1) levels, which is only just separated from the band of $2p$ (L_2 and L_3) levels, is very much broadened by Auger transitions $2p \rightarrow 2s$. Proceeding further, we come to the cases of interest in this paper, in which the $2s$ and $2p$ bands have become amalgamated in one band. We have to consider whether, if a vacancy has been created in some way in a level towards the low-energy end of a band, a transition can be made by an electron from a higher level in the band into the empty place. Such a transition could not be radiative owing to the 'k-selection' rule, which forbids such transitions within a band. But this prohibition will not apply if the vacancy is filled by an Auger transition, when the excess energy is taken off by another valence electron. Such a process is illustrated in figure 10; if it can take place with a high probability, the lifetime of a 'hole' in a level near the bottom of a band will be short, and the level itself will be broadened.

Dr Fröhlich and Dr Bouckaert very kindly undertook the calculation of the probability of this process, using a free electron model. As a result, they found that widths of the order of 1 eV could exist for levels near the bottom of a band. It is clear that the levels at the top of a band will not be affected, since there are no electrons which could make the transition into a vacancy in them. Thus there will be a progressive broadening of levels as we pass downwards from the highest filled level. It is evident that this is just what is required to account for the tailing effects.

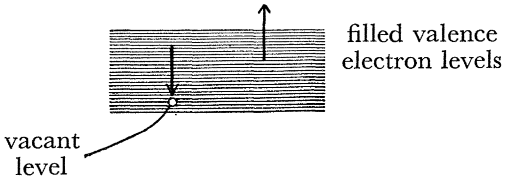

FIGURE 10. Auger process causing broadening of lower levels in a band.

The picture which one makes is therefore that the number of levels $N(E)$ rises as $E^{\frac{1}{2}}$ in the neighbourhood of $E=0$, but that they are individually diffuse. The form of a diffuse level is known; the probability $p(E)$ that it will contain an electron with an energy E is given by

$$p(E) \propto \frac{a^2}{(E-E_0)^2+a^2}, \tag{10}$$

where a is a quantity representing the degree of broadening. As we have seen, a is not really a constant for all the levels in a band, but for the purpose of this calculation we shall take it so.

Thus, for an L_3-band, we shall have, for sufficiently small values of E,

$$N_s^*(E) \propto \int_0^{E_m} E_0^{\frac{1}{2}} \frac{a^2}{(E-E_0)^2+a^2} dE_0. \tag{11}$$

This equation will also give a good approximation for all negative values of E. If the absolute value of E is not too great, we may substitute the limit ∞ for E_m. The integral can then be evaluated, giving

$$N_s^*(E) \propto \frac{a^2}{[\sqrt{(a^2+E^2)}-E]^{\frac{1}{2}}}. \tag{12}$$

A curve representing this function is shown in figure 11, in which the value of a has been taken as unity and the units of E as arbitrary. For negative values of E, the approximation fails and the curve has been adjusted by means of numerical integration taking the limit E_m as $10a^2$; the value of the upper limit makes no appreciable difference for positive values.

It will be seen that, in figures 12 and 13, the curve gives a good approximation to the $I(E)/\nu^3$ curves actually observed for L_3-spectra. The parabolic form, $E^{\frac{1}{2}}$, is very closely retained for values of E greater than about a^2. On the other hand, for negative values of E there is an extended tailing. The diagram also shows that in estimating the end of the band by an extrapolation of the linear part of the curve (shown dotted in the diagram), an error of about $2a^2$ is made. In the case of Mg, a fitting of the experimental tailing curve already given in figure 9 gives a value of a^2 of the order of $\frac{1}{2}$ eV. However, this method cannot give a^2 accurately because, for large negative values of E, the theoretical curve is rather sensitive to the limit E_m, and, owing to the fact that a really decreases with increasing E, it is hard to estimate what value of E_m one should take in equation (11) to obtain the best approximation. A comparison with the actual curves for positive values of E, using a rather naïve extrapolation of that part which seems to conform to the $E^{\frac{1}{2}}$ law, probably gives better values. These are tabulated in table 7. Though only rough, they appear to show a definite increase in a^2 with increasing band width, as might be expected.

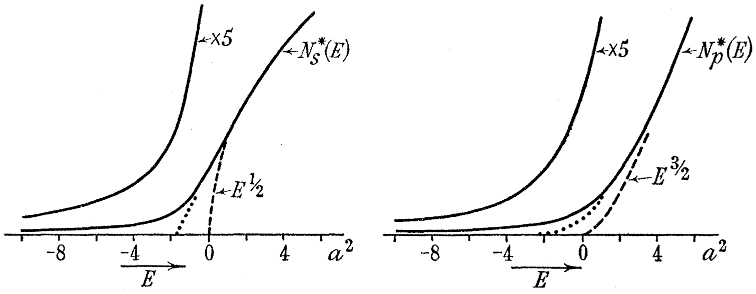

FIGURE 11. Calculated $N^*(E)$ curves. Dotted curves show types of extrapolation found empirically.

TABLE 7

	Na	Mg	Al	Si	P	S
a^2 (eV)	0·2	0·5	0·6	0·7	1·5	2·0

A similar calculation may be carried out for the K-spectra, for which $N_p(E)$ rises as $E^{\frac{3}{2}}$. But the necessary integral does not converge for the infinite limit. Numerical integration, using the value $E_m = 10a^2$, gives the curve also represented in figure 11. This shows the degree of closeness with which the $E^{\frac{3}{2}}$ curve (dashed) is followed. An extrapolation (shown dotted) of the part of the curve above the value $E = 0$ according to an E^2 law gives a definite end-point, as is found experimentally. This, as shown by the dotted line, differs by about $2a^2$ from the theoretical end-point. But the amount of this difference is much more sensitive to the actual value taken for the upper limit E_m than is the corresponding quantity for the L_3-spectra. This fact makes it almost impossible to estimate a^2 from the K-spectra, except as regards order of magnitude. However, the value $10a^2$ for E_m gives the correct form of the L_3-spectra, and we think it may be fairly accurate to assume the same value for the K-spectra and to correct the extrapolated end-point by the value $2a^2$.

To summarize this discussion, it seems that the theory of the broadening of levels of a band accounts adequately for the features of the $I(E)/\nu^3$ curves for negative and small positive values of E. It gives correctly the different peculiarities of the main bands of the K- and L_3-spectra, as well as providing an explanation of their very diffuse tailing-away towards low energies.

A few words may be added with respect to the *short* wave-length tailing of metal bands, already illustrated in figure 9 for the case of Mg. We think that probably this must be ascribed to satellite radiation of the type $L_3(V)\,V$. A condition for the emission of a satellite is that the second ionization must remain in the neighbourhood of the emitting atom while the radiation is actually emitted. In the case of a metal, the average time taken for a hole in the conduction band to move from one atom to the next is of the order of 10^{-15} sec. Since the radiation time is at least 10^{-13}–10^{-12} sec., the probability that a hole will have moved away is great. But there is a certain probability that it will stay during the emission period, and this is increased on account of the fact that if the hole happens to occur near the bottom of the band, it will move relatively slowly. We think that this mechanism is sufficient to account for the very weak short wave-length tails. In the case of insulators, stronger tailing to short wave-lengths is observed, but this radiation seems to end more or less abruptly, and is almost certainly genuine radiation belonging to the band itself.

10. Band widths and band forms

We now give the actual intensity curves of the bands, in figure 12 for metals[†] and in figure 13 for non-metals. In accordance with the theory of § 3 they are plotted in the form of $I(E)/\nu^3$ curves. They represent, therefore, probably with reasonable accuracy, the functions $N^*_{s+d}(E)$ and $N^*_p(E)$ for L_3- and K-bands respectively. In the case of L_3-bands, the effect of the overlapping of L_2-bands has been eliminated. In drawing the curves, other photometer curves besides those given in figures 3 and 5 have been referred to. The low-energy parts of the Be K and P L_3 curves are somewhat doubtful, owing to the effect of the grating absorption already mentioned. In the case of non-metals, where sufficient accuracy is available, we have also drawn the weak high-energy end of the band on an enlarged scale. Since, in passing from wave-

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[†] Owing to a slight distortion of the Mg L_3 curve in reproduction, the curvature just to the left of the highest point is exaggerated, and the suggestion of an inflexion at the top of the down-slope is spurious.

lengths to energy units, we have to divide intensities by ν^2, in comparing the $I(E)/\nu^3$ curves with the photometer records, a factor of ν^5 must be taken into account, and this is often quite large.

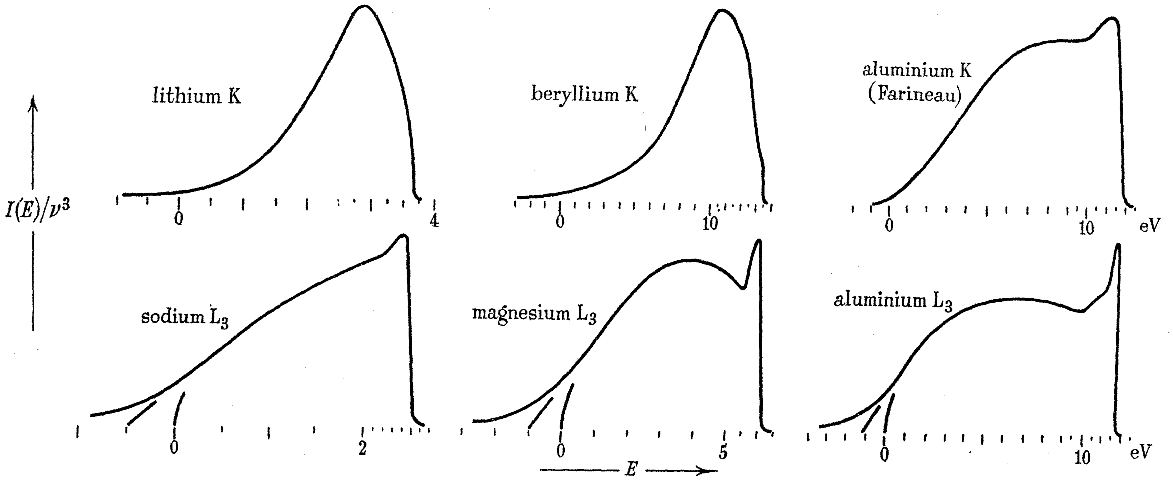

FIGURE 12. K and L_3 bands of metals.

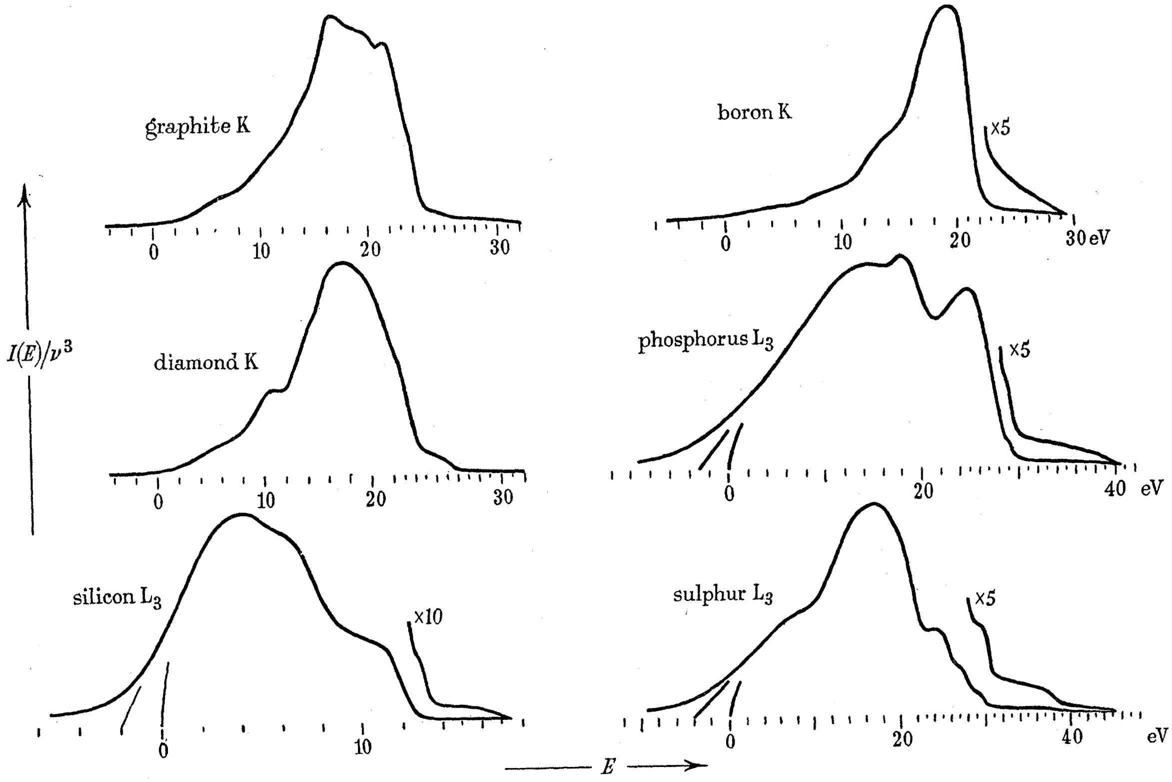

FIGURE 13. K and L_3 bands of non-metals.

One of the most obvious characteristics of the bands is the total energy range which they cover. Unfortunately, it is not an easy matter to define it in any satisfactory way. For, though the short wave-length limits of the bands are very sharp, the long wave-length ends as we have seen are badly marked. Thus an empirical definition of the long wave-length end of a band is desirable. In the case of L_3-spectra, we may use the linear portion of the $I(E)/\nu^3$ curve, extrapolated to zero intensity, as has been indicated in figures 12 and 13. In the case of the K-spectra, one has to attempt a quadratic extrapolation of the curve, assuming that $I(E)/\nu^3$ rises as E^2 over a range of energies near the long wave-length end of the band. This method seems rather unsatisfactory, but, owing to the weaker tailing of the K-bands, it leads to a result not much less exact than those obtainable for the L_3-spectra. One cannot make any precise test of the consistency of the two definitions by comparing band widths of a single substance as obtained from K- and L-spectra. For, though the K-spectra of the second group metals have been investigated by Farineau, he merely estimates the long wave-length limit of the band as the point at which the intensity becomes appreciable. Nevertheless, as we shall see, his K-band widths agree rather well with our L_3-widths.

In this way, we obtain a set of quantities which may be called the *empirical band widths*. These can often be measured to within a fraction of 1 eV. From a theoretical point of view, they are not satisfactory; what one needs is the width of the band, assuming that the tailing effect did not exist. We have already seen that, if our theory of the broadening of individual levels is correct, this theoretical end-point of the band may be approximately obtained from the extrapolated end-point by subtracting the quantity $2a^2$. This can be fairly satisfactorily done in the case of the L_3-spectra, for which the assumed parabolic rises of the curves are indicated in figures 12 and 13. The K-bands are more difficult to deal with and, for these, the a^2 values can only be roughly guessed. By subtracting the energy $2a^2$ from the empirical band width, we obtain a quantity which may be called the *reduced band width*.

In tables 8 and 9 we give the results. In the case of elements of the second group, Farineau's (1938) results obtained from K-spectra are added. The short wave-length ends of the bands are, for metals, unmistakable; we simply take the mean points of the emission-edges. In the case of non-metals, we give the full band width, including the projections of low intensity at the high-energy end.

The calculated band width is obtained using Sommerfeld's 'electron-gas' theory of the metallic state. This gives for the band width

$$E_m = h^2/2m(3\rho n/8\pi)^{\frac{2}{3}}, \tag{13}$$

where ρ is the number of atoms per c.c. of the substance, and n the number of valence electrons per atom. Comparison should be made with the reduced band width and it will be seen that there is, in many cases, a rough agreement. Of course, it may be objected that the electron-gas theory is at best a very poor approximation to the facts, and could scarcely be expected to be applicable. The fact that it gives results which are approximately correct means that the $N(E)$ curves must conform to a certain extent to the parabolic curve of the simple theory. We have seen in § 3 that with increasing E, they actually first rise above it to give 'peaks' and then fall beneath it. Thus we might anticipate that the band widths would be less than the theoretical values for metals with one valence electron. This, in fact, seems to be the case. The good agreement obtained for metals of higher valency means that the effect of those parts of the $N(E)$ curve above and below the parabola just cancel one another.

Table 8. Metals

	Li	Be	Na	Mg	Al
K-band width (empirical), eV	4·2 ± 0·3	14·7 ± 0·5	—	7·4 ± 1*	12·7 ± 1*
L_3-band width (empirical), eV	—	—	3·0 ± 0·2	7·2 ± 0·2	13·2 ± 0·4
Band width (reduced), eV	3·7 ± 0·5	13·8 ± 1	2·5 ± 0·3	6·2 ± 0·3	11·8 ± 0·5
Band width (calculated), eV	4·8	14·6	3·2	7·3	11·9

* Results of Farineau (1938) slightly corrected so that the high-energy end of the band is taken as the mean edge energy.

Table 9. Non-metals

	B	Diamond	Graphite	Si	P	S
Band width (empirical), eV	31 ± 2	33 ± 3	33 ± 2	18·2 ± 0·5	43 ± 3	49 ± 2
Band width (reduced), eV	29·5 ± 3	32 ± 3	32 ± 3	16·7 ± 1	40 ± 4	45 ± 3
Band width (calculated), eV	25·2	29·5	21·9	12·7	(11·5)†	14·3

† Corresponding to 'yellow' phosphorus.

For non-metals, the existence of the high-energy projections of low intensity makes the comparison rather arbitrary. If these had been omitted from band width, a quite good agreement would have been obtained for boron, diamond and Si. This is of interest in that it shows a distinction between these substances and graphite, P, and S. Especially for the two last, the disagreement is very large.

The clue to the understanding of these three substances seems to be that they are all cases of complex crystal structure, whereas the remainder, apart from B whose lattice structure is unknown, are all simple (cubic or close-packed hexagonal). The comparison between diamond and graphite is especially instructive. These allotropic forms, with quite different densities, have the same band width. Diamond has a structure with uniform properties along three cubic axes, whereas graphite consists of planes very tightly packed with C atoms, the planes being separated by a distance three times greater than the distance between the atoms in a given plane. The obvious inference is that the electron density is non-uniform, being very small in the region half-way between two consecutive planes. Thus if we calculate, as we have done, the effective electron density, for insertion in equation (13), from the actual density of the material, we obtain a result considerably too small.

The comparison of the band forms of diamond and graphite presents another interesting feature in the obvious mimicry of the two curves (figure 13). Though entirely different in detail, these are seen to follow one another very closely as regards their general run. Of course, for two allotropic forms to be able to co-exist, it is implied that the mean binding energy of their valence electrons must be nearly the same.

This condition is fulfilled, at least in the case of diamond and graphite, by a close similarity of the $N(E)$ curves for all values of E, and not merely by the approximate equality of the average electron-energies.

We propose finally to give an account of those characteristics of the bands which are of most general interest. We begin with those of the metals, the curves of which have been given in figure 12.

In § 3, we have already referred to the fact that the $N_{s+d}(E)$ and $N_p(E)$ must be considered as components of the $N(E)$ curve, which show different peculiarities. The $I(E)/\nu^3$ curves give, for the L_3-spectra, $N_{s+d}(E)$, and for the K-spectra, $N_p(E)$. From the curves of figure 12, by adding the results of the K- and L_3-spectra of a given metal, it can be seen that an $N(E)$ curve of the general form shown in figure 2 is obtained. But, since our curves unfortunately do not give $N_{s+d}(E)$ and $N_p(E)$ in absolute units, there is no simple way of determining the proportion in which the two sets of experimental results should be added. The individual peculiarities of the K- and L_3-spectra have been mentioned in § 3, where we have seen that the 'peak' of the $N(E)$ curve occurs only in $N_p(E)$, whereas the discontinuous 'kinks' occur in $N_{s+d}(E)$. A general examination of figures 11 and 12 shows this plainly.

These peaks and kinks furnish direct evidence of the Brillouin zones, which are defined by the lattice-structure of the solid. To proceed further, we must make use of the usual k-diagrams of the theory of metals.* k is a vector representing the momentum of electrons in the lattice, and a vector diagram of k has the property of a phase space in which unit volume represents just two electrons. The Brillouin zones are closed polygons in this k-space, bounded by a set (or sets) of planes possessing space symmetry. The energy E, in general, increases regularly as k increases in a given direction; but E jumps discontinuously as k penetrates a set of these planes. When k just touches a set of the planes, we get a peak of the $N(E)$ curve; when the energy is high enough to allow k to pass through, we obtain a kink. The energy difference between a peak of an $N_p(E)$ curve and the corresponding kink on the $N_{s+d}(E)$ curve gives a means of determining experimentally the magnitude of the energy discontinuity.

The number of peaks and kinks observed in the emission spectrum of a given metal depends on two factors: (*a*) the number of independent sets of planes forming the first Brillouin zone, and (*b*) the energy value E_m up to which the levels are filled in the normal state of the lattice by the available conduction electrons. Peaks or kinks which have a higher energy than E_m will appear in the absorption spectrum.

The alkali metals have one electron per atom, and this is enough to fill only half of the volume of the first Brillouin zone. Hence it has often been supposed that the value of k, corresponding to the maximum energy of the conduction electrons, would be too small to touch the bounding planes, the energy contour in k-space therefore remaining approximately spherical. This would imply featureless emission curves. The kink of the $N_{s+d}(E)$ curve for Na, which is certainly observed when the metal is at the

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* See, for example, Mott and Jones (1936).

temperature of liquid oxygen, shows that the k-vector has not only touched, but also penetrated the boundaries of the first zone, before the energy has reached the value E_m. Unfortunately, the K-spectrum of Na has not been published.* If we assume it to be the same as that of Li, a metal which also has body-centred cubic structure, compressing the energy scale to give the correct band width, we may estimate the energy gap across the bounding planes of the first Brillouin zone as about $\frac{1}{10}$ eV.

In the case of Al, we have three electrons per atom, and the first Brillouin zone is certainly full. The face-centred cubic structure has the characteristic that this zone is bounded by two sets of planes, corresponding to slightly different k-values. Two well-defined kinks are to be seen on the $N_{s+d}(E)$ curve. However, the two corresponding peaks of the $N_p(E)$ curve are not resolved, but appear only as a broad hump in the middle of the band. The energy gaps in this case are both about 3 or 4 eV.

Be and Mg metals, with two electrons per atom, have hexagonal close-packed structure, and the first zone is bounded by three sets of planes. Only one kink appears on the Mg L_3 emission curve, and so it would seem that the energy gaps are too great for the others to appear before the edge is reached. An inflexion is found just beyond the edge in the absorption spectrum (see Skinner 1939), and this probably represents the other two kinks unresolved. Energy gaps of the order of 2 eV seem to be indicated.† The peak of the K-emission curve of Be appears to show slight traces of complexity.

It will be observed that the kinks of the L_3-curves are sharp to within about $\frac{1}{10}$ eV, but that the peaks of the K-curves are quite broad. Since the latter lie at comparatively low energies, they are more subject to the 'tailing effect' of § 9; and it is hard to say how sharp they might be, if this did not occur. Beyond a kink, in analogy with equation (8), the contribution from the second Brillouin zone to the $N_{s+d}(E)$ curve should rise as $(E-E_1)^{\frac{1}{2}}$, where E_1 is the energy of the kink. The contribution to the $N_p(E)$ curve, on the other hand, should rise asymptotically as $(E-E_1)^{\frac{3}{2}}$, and this will not show as a discontinuity, since it is superposed upon a contribution from the first zone. In the relevant region, the latter is usually decreasing rapidly with increasing E, and thus it tends to mask the forms of the contributions of the second zone, both in the case of K- and L_3-curves. However, in the case of Al, the metal for which the zone overlap is largest, the asymptotic rise of $N_p(E)$ as the contribution from the second zone begins is easily recognized; while in the case of Be, it can just be detected as a slight upward curvature immediately before the edge. Indications of the parabolic nature of the rise in the contribution to $N_{s+d}(E)$ from the second zone can also be seen on the Al L_3 curve.

It is possible, in a more detailed analysis, to attempt to relate the characteristics of the $N(E)$ curves of a given metal to the actual lattice structure. We shall not describe the results here, but shall proceed to the consideration of the bands of non-metals,

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* It has been described by Dr Farineau in a private letter, and seems to have general characteristics similar to those of the K-spectrum of Li.

† Using a Mg K-spectrum of Farineau (1938), which was not included in figure 11, since, according to a letter of Dr Farineau, it is probably distorted through contamination by MgO.

the curves for which have been given in figure 12. Some of these refer to real insulators and some to bad conductors, but there is no distinction to be seen in the bands. We shall therefore treat all as though referring to insulators, that is, substances with filled Brillouin zones.

The complexity of the curves arises from the fact that, since all the substances dealt with have three or more electrons per atom, the filled Brillouin zone has always sets of planes in k-space within it. These give rise to sets of peaks and kinks; a very good example of the former is seen at 10 eV in the case of diamond, which, with Si, has the simplest lattice structure of all. In this paper, however, we shall ignore such complexity, and deal only with the general features.

The most characteristic properties of the bands for non-metals, namely, 'false edges' and 'band-ends', have already been mentioned in § 6. They occur indiscriminately in K- and L_3-spectra. We shall now try to interpret these features with the aid of a simple model. Suppose that the Brillouin zone holding all the valence electrons is a simple cube. As k increases in the centre of the cube, as long as the contours of constant energy remain approximate spheres, we obtain the relations

$$E = \alpha \frac{h^2}{2m} k^2, \tag{14}$$

$$N(E) = \frac{2\pi}{h^3}\left(\frac{2m}{\alpha}\right)^{\frac{3}{2}} E^{\frac{1}{2}}, \tag{15}$$

where α may be considered as constant. Now let us start from the maximum energy E_m in the band, corresponding to a k-vector, k_m, just reaching into the corners of the cube. It is well known that in this region we must have a relationship of the type

$$(E_m - E) = \beta \frac{h^2}{2m} (k_m - k)^2. \tag{16}$$

The energy contours may be taken as parts of a sphere with centres at the corners of the zone. It is then easily seen that

$$N(E) = \frac{2\pi}{h^3}\left(\frac{2m}{\beta}\right)^{\frac{3}{2}} (E_m - E)^{\frac{1}{2}}. \tag{17}$$

$N(E)$ therefore rises from this end in a parabola similar to that which applies to the low-energy end of the band, but inverted. These parabolas are shown in figure 14 and theoretically must form the two ends of the $N(E)$ band. In between lies the region in which the vector k, in increasing, comes near to, and then touches the boundary planes of the zone. In this region, the energy contours are not spherical, and the $N(E)$ curve rises above the parabolas to a peak, as we have previously mentioned. Consideration of the shape of these contours leads to the conclusion that the $N(E)$ curve will remain on the low-energy parabola for a longer distance than on the high-energy parabola, thus causing an asymmetry of the band. The fall on to the parabola on the high-energy side must be rather sudden, giving a 'false edge', while the parabolic limit of the band is a 'band end'.

We have, however, to consider how this $N(E)$ curve is to be divided up into its $N_{s+d}(E)$ and $N_p(E)$ components. We know the variations of these two quantities for small values of E; we also know that the peak will appear in $N_p(E)$. For values of E near to the end of the band, our experimental curves show very similar features in each case, and thus we shall assume the extreme high-energy ends of the bands to be identical. Dividing up the $N(E)$ curve according to these rules, we obtain the component curves shown in figure 14 which have been drawn for the case of equal numbers of $(s+d)$ electrons and p electrons (e.g. C or Si).

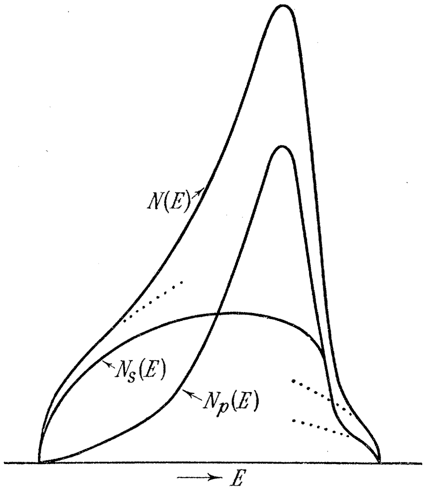

FIGURE 14. Illustrative $N(E)$ curves for non-metals.

In this way, apart from the low-energy tailing, we appear to have built up curves which represent fairly well the general properties of the bands. It will be noted that since only the $N_{s+d}(E)$ curve follows the low-energy parabola, but that both components follow the high-energy parabola, weakness of the observed band ends is partly accounted for. In actual cases, of course, we find considerable complication from the lattice structures. One such complication is of general interest; in practice, for a non-metal, we never find a Brillouin zone which has only one type of corner. For example, the regular dodecahedron of the diamond structure has two sorts, at different distances from the origin, and therefore corresponding to appreciably different energies. One may therefore expect to find more than one band end, and in most cases the experimental curves actually show two, though S has more. The band ends of a given curve must be represented by parabolas with different constants, which are always considerably smaller than that of the parabola representing the low-energy part of the band. If we were dealing with the $N(E)$ curves themselves, instead of with the $N_{s+d}(E)$ curves, we could obtain the values of α and β relating to the different parabolas; and these quantities would be inversely proportional respectively to the 'effective masses' of electrons occupying levels in the main body of the band and levels corresponding to points near the various corners of the zone. Since we have to deal with $N_{s+d}(E)$, we must correct for the fact that the band ends occur also on the $N_p(E)$ curve, as has already been mentioned. In this way, an estimate of the effective mass appropriate to any particular band end may be obtained and it is found that values considerably smaller than the electron mass are obtained in most cases, not only for the extreme band ends, but for the stronger band ends too. Thus, in the case of Si, assuming that half of the electrons of highest energy are to be found in the $N_{s+d}(E)$ band ends, the remainder being *p*-electrons, we obtain values of $\frac{1}{4}m$ for the first, and about $\frac{1}{10}m$ for the extreme band end. Fröhlich and Mott (1939) have recently given evidence for similar low values in the case of polar crystals, and the existence of a low effective mass when the Brillouin zone is very nearly full is in general agreement with the results of the work of Jones on metals such as bismuth.

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