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A Theory of the Form of the X-Ray Emission Bands of Metals

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It is shown that the optical transition probabilities for transitions from the conduction levels in metals to the K- and L-levels may vary strongly within the lowest allowed zone, and will also depend on the azimuthal quantum number of the final state. An explanation is given of the form of the x-ray emission bands observed by O'Bryan and Skinner for Li, Be, Mg, Al.

In a recent paper, O'Bryan and Skinner[1] have determined the intensity distribution in the x-ray bands emitted by light metals when electrons make transitions from the conduction levels to the K- or L-levels. To interpret their results, they denote by $n_E\,dE$ the number of conduction electron levels with energy between E and $E+dE$, and by f_E the optical transition probability from a state with energy E (measured from the bottom of the conduction electron band) to the K- or L-level. If the conduction states up to a certain maximum energy $E_{\max}$ are filled, the intensity of the x-ray band is given by

$$\begin{aligned} I_E &= n_E f_E \qquad E<E_{\max} \\ &=0 \qquad E>E_{\max}. \end{aligned} \tag{1}$$

They find a striking difference in the intensity distribution in the bands of beryllium and magnesium, two metals of the same structure which both have two valence electrons per atom. In this paper, we give a theoretical explanation of some of the effects observed, and show that the difference between the bands in Be and Mg is due to the fact that in the former metal a transition to the K-level ($1s$) is observed, in the latter a transition to the L_{II} and L_{III} levels ($2p$). Thus f_E is different in the two cases.

Houston[2] attempted the calculation of f_E using Sommerfeld wave functions and came to the conclusion that f_E should be proportional to E. But he neglected the fact that the important region for transitions into inner shells is that just around the nucleus and that here the wave functions calculated on a free-electron model (which omits the lattice-structure completely) can have no relation to the actual case. A more detailed investigation than his is therefore required.

In the theory developed by Bloch, Brillouin and others, each state of the electron in the metal is denoted by a vector $\mathbf{k}$; the direction of $\mathbf{k}$ is the direction of motion of the electron, and $2\pi/k$ is its de Broglie wave-length. Bloch has shown that the wave function for each individual electron takes the form

$$\psi_k(x,y,z)=u_k(x,y,z)e^{2\pi i(\mathbf{k}\cdot\mathbf{r})}, \tag{2}$$

where $u_k(x, y, z)$ has the periodicity of the lattice. The energy is a function of $\mathbf{k}$; for the values of k_x, k_y, k_z for which Bragg reflection takes place, a discontinuity in the energy occurs. Thus the states of an electron in the metallic lattice may be divided into zones, separated by planes in k-space across which the energy is discontinuous. If we plot n_E for each zone as a function of E, we obtain curves such as those shown in Fig. 1a. If the energy gaps at the surfaces of discontinuity are small enough, the zones will overlap. We know that this must occur in Mg and Be, since the number of states in the first zone is two per atom, and, if there were no overlap, the first zone would be full, and the crystals would be insulators instead of being rather good conductors. We also know that, on account of the similar lattice-structures, these two metals must have (on different energy scales) rather similar n_E curves.

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[1] O'Bryan and Skinner, Phys. Rev. **45**, 370 (1934).

[2] W. V. Houston, Phys. Rev. **38**, 1791 (1931).

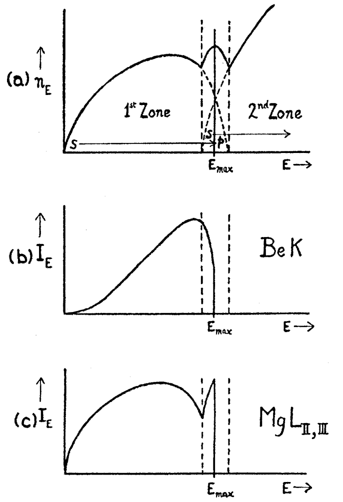

FIG. 1.

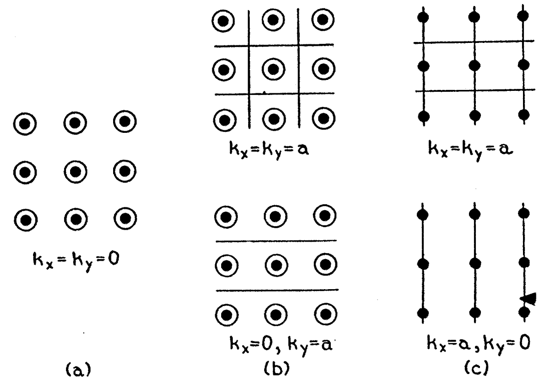

FIG. 2. Wave functions ψ_k for a two dimensional cubic lattice. The dots denote atomic nuclei, the circles and lines denote nodes of the wave function, and a is the lattice constant. (a) shows the lowest state, (b) are the wave functions which, near the nuclei, have the form of a $2s$ electron, and (c) have the form of a $2p$ electron.

§1

We shall now consider the transition probability f_E. If $\Phi(x, y, z)$ denotes the wave function of an electron in the K- or L-state, f_E will be proportional to the quantity

$$\nu^3 \left| \int \Phi^*(x, y, z)[\partial\psi_k(xyz)/\partial x] dx\, dy\, dz \right|^2 \tag{3}$$

where ν is the frequency of the emitted radiation. The factor ν^3 may vary by as much as 2 over an emission band; since, however, we shall use the formula only to obtain the form at the head and tail of the band, the factor ν^3 may be neglected. Thus f_E depends on the form of the wave function of the conduction electron near the nucleus, where Φ is not small.

Let us expand ψ_k, in the region near to one nucleus, as a series

$$\psi_k = \sum_n a_n \phi_n(x, y, z), \tag{4}$$

where the ϕ_n are the wave functions of an electron in the free atom. In this expression, let a_s denote the coefficient of the lowest s-state, a_p that of the lowest p-state ($2s$, $2p$ in Be, $3s$, $3p$ in Mg). Then in Be the transition probability f_E to the K-level will be approximately proportional to a_p^2, whereas in Mg the transition probability to the L_{II}, L_{III} levels will be proportional to a_s^2, since Δl must change by unity.

The nodes of the wave function for the *lowest* state of the first zone are shown in Fig. 2a. In the neighborhood of the nucleus, ψ_k is slightly perturbed from its form ($2s$ in the figure) for the free atom. Nevertheless, it is clear from symmetry that a_p vanishes, for the wave function for a p-state has a node through the origin; thus if a_p did not vanish ψ_k could not reach a maximum value at each nucleus. In the *higher* states, however, a wave of wave-length $2\pi/k$ must be superimposed on a function having the periodicity of the lattice (cf. Eq. (2)). Thus it is no longer true that a_p vanishes. In §2 we show, using a perturbation method, that when the atoms are far apart, then, for small E, $a_p \propto E^{\frac{1}{2}}$. If this result is true in general, we have, for small E

$$f_E \propto E \qquad \text{(Beryllium } K\text{)}$$

$$f_E \propto \text{const.} \qquad \text{(Magnesium } L_{\text{II, III}}\text{)}.$$

Since for any metal, for small E, $n_E \propto E^{\frac{1}{2}}$, we have as shown in Fig. 1 (b and c), for the bottom of the bands

$$I_E \propto E^{\frac{3}{2}} \qquad \text{(Beryllium } K\text{)}$$

$$I_E \propto E^{\frac{1}{2}} \qquad \text{(Magnesium } L_{\text{II, III}}\text{)}.$$

As was pointed out by O'Bryan and Skinner, the tail-forms of the bands of Li and Be metals are certainly different from those of Mg and Al. It can be seen from Fig. 5 of their paper that the first are entirely concave upwards until the maximum is reached, and appear to be increasing about as E^2; while the second pair are concave downward except at the extreme low-energy limit of the bands. Here, it is true, the intensity appears to increase more rapidly than E; but if we can regard this extreme tail (about the last 2 volts) of these bands as incidental (by which is meant that they are due either to spurious spreading of the photographic image perhaps by light-reflection along the acutely inclined plate, or at any rate to some cause not taken into account by the present theory) then a general increase of the intensity proportional to $E^{\frac{1}{2}}$ at the tails of the Mg and Al bands might be taken as correct; and for similar reasons an increase proportional to $E^{\frac{3}{2}}$ (instead of the apparent E^2) for Li and Be might be postulated. Unfortunately it is not feasible at present to make any more exact statement of the facts than this.

We shall now consider the values of f_E near the *head* of the emission band. Figs. 2b and 2c show the type of wave function ψ_k that we shall expect to find in this region. In the type 2b, the form of ψ_k near a nucleus is similar to that of a $2s$ wave function of the free atom; as before, the coefficient a_p vanishes exactly, by symmetry. In the type 2c, the wave function near a nucleus is similar to that of the $2p$ state of the free atom, and a_s vanishes. If, in the free atom, the difference between the energy of the $2s$ and $2p$ states is large compared to the breadth of the allowed zones, it is clear that all wave functions ψ_k in the first zone will be similar to $2s$ functions near the nucleus; in this case the wave functions near the top of the first zone will be of the type 2b, and a_p will rise to a maximum in the middle of the first zone, and be zero at either end. At the bottom of the second zone the wave function will be of the form 2c, and a_p will take a maximum value. If, on the other hand, the energy difference between the $2s$ and $2p$ states is small, wave functions of the type 2c will have *lower* energy than the type 2b. The behavior of the coefficient a_p is discussed from a mathematical point of view in the next section, and it is shown that in this case wave functions of the type 2c occur at the top of the first band, and functions of the type 2b at the bottom of the second band. Thus a_p^2 increases from 0 to 1 in the first band, whereas a_s^2 decreases from 1 to 0. At the bottom of the second band a_s^2 is equal to unity, and a_p^2 vanishes. In order to account for the experimental results we must assume that the wave functions behave in this second way. This is reasonable since the energy separation of the $2s$ and $2p$ states for the Be and Mg atoms is considerably smaller than the energy-spread of their filled conduction-electron bands.

The observed characteristics of the soft x-ray bands of beryllium and magnesium[3] near the heads are: (1) The slow fall of I_E in the Be K-band from a maximum to zero; it appears that I_E has already started to diminish before the sudden drop due to the fact that there are no more conduction electrons. (2) The curious minimum which is found in the Mg, $L_{\text{II, III}}$ band and the very sharp rise just before the sudden drop at the head.

We have seen that Be and Mg, on account of their like lattice-structure must have similar n_E curves of somewhat the type shown in Fig. 1a. Applying the preceding ideas about transition probabilities, we may regard $n_E|a_s(E)|^2$ and $n_E|a_p(E)|^2$ as the numbers of s- and p-electrons respectively corresponding to the energy E. We observe that for Be the introduction, as the energy rises, of electrons from the second zone does not affect I_E, since they are s-electrons and cannot make transitions to the K-level. The shape of the I_E curve therefore depends only on the variation of $n_E|a_p|^2$ in the range of the first zone; and thus, since a_p is steadily increasing, I_E reaches a maximum later than n_E, then begins to diminish till the limit $E_{\max}$ of the filled levels is reached and there are no more transitions. On the other hand, I_E for the Mg $L_{\text{II, III}}$ band depends on the variation of the quantity $n_E|a_s|^2$, which gives the number of transitions into a p-level. Thus with increasing E, since a_s is steadily diminishing, I_E reaches a maximum earlier than n_E and begins to fall. But then the introduction of the overlap with the second zone brings into action a fresh set of s-electrons. So at this point I_E rises rapidly until the value $E_{\max}$ is reached. An attempt is made to show this qualitatively in Fig. 1. It seems that the assumptions made allow one to interpret accurately the characteristic differences of the K- and L-spectra from the same type of n_E curve. From the Mg

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[3] See O'Bryan and Skinner, Phys. Rev. **45**, 370 (1934), Figs. 4 and 5.

curve we may infer that the overlap of the first two zones is of the order of $1\frac{1}{2}$ volts.

When passing finally to Al, the different lattice structure does not allow one to make any precise comparison with Mg, but the x-ray bands are actually very similar. The main difference is that the minimum is considerably further from the edge than is the case with Mg (4 volts instead of 0.7). This difference would certainly be anticipated since, in Al, there are 3 conduction electrons per atom (i.e., more than enough to fill the first zone). The energy range over which we obtain transitions from s-electrons in the second zone is therefore much greater than for Mg.

§2

In this section we consider a three-dimensional cubic lattice of atoms, and calculate the splitting of the energy levels by treating the interaction between the atoms as small, by the method first given by Bloch.[4] Our calculation differs from Bloch's in that we take the ground state of the atom to be an s-state, and consider the next p-state to have nearly the same energy, so that the "zero order" wave function for the lattice will contain both s- and p-states, as explained in the last section. Results obtained for the cubic lattice may be expected to apply qualitatively to more complicated structures, such as the hexagonal close-packed lattices of Be and Mg.

The three independent wave functions associated with the degenerate p-state of an atom may be written $xf(r)$, $yf(r)$, $zf(r)$; r being the distance from the nucleus. We shall denote these functions by $\varphi_1(\mathbf{r})$, $\varphi_2(\mathbf{r})$, $\varphi_3(\mathbf{r})$, respectively, and the single spherically symmetrical wave function belonging to the s-state by $\varphi_0(\mathbf{r})$. If the interaction between the s- and p-states is neglected, the wave functions for the electrons in the lattice can be expressed in the form originally given by Bloch,[4] *viz.*,

$$\psi_{nk}=\sum_{g} e^{2\pi i(\mathbf{g}\cdot\mathbf{k})/G}\varphi_n(\mathbf{r}-a\mathbf{g}), \qquad (5)$$

where a is the lattice constant, G the number of atoms along the side of a unit cube, and each component of $\mathbf{g}$ may have any positive or negative integral value. The components of $\mathbf{k}$ will be written k_1, k_2, k_3.

The question to be answered in this section is how the functions ψ_{nk} derived from s- and p-atomic states combine to form the true 'zero' order wave functions for the electrons in the lattice.

We write in the usual way for the zero-order function Ψ

$$\Psi_{nk}=\sum_{m=0}^{3} a_{mk}\psi_{mk} \quad n=0,\ 1,\ 2,\ 3, \qquad (6)$$

where the coefficients a_m are subject to the normalizing condition

$$\sum_m |a_m|^2=1.$$

The wave equation which these functions must satisfy is

$$(H-E)\Psi=0,$$

where

$$H=-(h^2/8\pi^2 m)\nabla^2+\sum_g v(\mathbf{r}-ag)$$

and $v(\mathbf{r})$ is the self-consistent potential field due to a single atom.

The diagonal elements of the matrix H with respect to the functions of Eq. (5) have been calculated by Wilson[5] and may be denoted by $A_n(\mathbf{k})$. For a simple cubic lattice they take the following values

$$A_0(k)=\alpha_0+2\gamma_0\{\cos(2\pi k_1/G)+\cos(2\pi k_2/G)+\cos(2\pi k_3/G)\}$$

$$A_n(k)=\alpha_n+2\gamma_n\cos(2\pi k_n/G)+2\gamma_n'\{\cos(2\pi k_l/G)+\cos(2\pi k_m/G)\} \qquad n=1,\ 2,\ 3.$$

where l and m are the two remaining numbers other than n, and

$$\alpha_n=\int\phi_n^*(r)H\phi_n(r)d\tau \qquad n=0,\ 1,\ 2,\ 3.$$

$$\gamma_0=\int\phi_0^*(x+a,\ y,\ z)H\phi_0(x,\ y,\ z)d\tau$$

$$\gamma_1=\int\phi_1^*(x+a,\ y,\ z)H\phi_1(x,\ y,\ z)d\tau,$$

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[4] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

[5] A. H. Wilson, Proc. Roy. Soc. **A133**, 458 (1931).

with similar expressions for γ_2 and γ_3. In γ_2 for instance the first term of the integrand is $\phi_2^*(x, y+a, z)$. Finally

$$\gamma_1' = \int \phi_1^*(x, y+a, z) H \varphi_1(x, y, z) d\tau,$$

again with similar expressions for γ_2' and γ_3'. The first term of the integrand in γ_2' is $\varphi_2^*(x, y, z+a)$, and in γ_3', $\varphi_3^*(x+a, y, z)$.

For the nondiagonal elements we have

$$H_{0n} = \int \psi_{0k}^* H \psi_{nk} d\tau$$

$$= \sum_{g,\, g'} e^{2\pi i(\mathbf{g}-\mathbf{g}',\, k)/G} \int \phi_0^*(\mathbf{r}-a\mathbf{g}) H \phi_n(\mathbf{r}-a\mathbf{g}) d\tau.$$

If we restrict ourselves to a simple cubic lattice, and consider only the integrals which correspond to nearest neighbors, then, since

$$\int \phi_0^*(x+a, y, z) H \phi_n(x, y, z) d\tau$$

$$= -\int \phi_0^*(x-a, y, z) H \phi_n(x, y, z) d\tau,$$

we have

$$H_{0n} = 2i\beta \sin(2\pi k_n/G),$$

where

$$\beta = \int \phi_1^*(x+a, y, z) H \phi_0(x, y, z) d\tau.$$

The nondiagonal elements H_{nm} vanish if neither n nor m is zero, for it is clear that a field with cubic symmetry will not raise the degeneracy of the states associated with the wave functions ϕ_1, ϕ_2, ϕ_3.

The secular equation for the energy of an electron in the lattice thus becomes

$$\begin{vmatrix} A_0(k)-E, & 2i\beta \sin(2\pi k_1/G), & 2i\beta \sin(2\pi k_2/G), & 2i\beta \sin(2\pi k_3/G) \\ -2i\beta \sin(2\pi k_1/G), & A_1(k)-E, & 0, & 0 \\ -2i\beta \sin(2\pi k_1/G), & 0, & A_2(k)-E, & 0 \\ -2i\beta \sin(2\pi k_3/G), & 0, & 0, & A_3(k)-E \end{vmatrix} = 0. \qquad (7)$$

In order to calculate the transition probability between a deep lying x-ray level and states described by the wave functions in Eq. (6), it is essential to know the relative amounts of s- and p-atomic states which these functions contain, i.e., we must know the values of a_{nm} as functions of k. It will be sufficient for the present purpose if we consider only the states which lie along a line in the k space from the origin perpendicular to one face of the first cube across which the energy is discontinuous. For such states the functions in Eq. (6) reduce to

$$\Psi_{0k} = a_{00}\psi_{0k} + a_{01}\psi_{1k},$$

$$\Psi_{1k} = a_{10}\psi_{0k} + a_{11}\psi_{1k}.$$

Eq. (7) gives readily

$$|a_{00}| = |a_{11}| = \cos \tfrac{1}{2}\theta,$$

$$|a_{01}| = |a_{10}| = \sin \tfrac{1}{2}\theta,$$

where

$$\cot \theta = [A_1(k) - A_0(k)]/4\beta \sin(2\pi k/G).$$

The wave functions Ψ_{0k} will refer to states lying in the first zone, Ψ_{1k} to states lying in the second zone, and the coefficients a_{00} and a_{01} will then become identical with the coefficients a_s and a_p of the previous section. It follows that we must always have $A_1(0) > A_0(0)$, but when $k = \frac{1}{2}G$ (i.e., the value of k at the surface of energy discontinuity in k space) there are two possibilities.

(a) $A_0(\frac{1}{2}G) > A_1(\frac{1}{2}G)$,

(b) $A_0(\frac{1}{2}G) < A_1(\frac{1}{2}G)$.

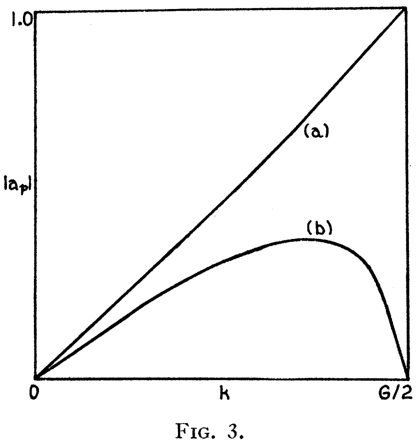

FIG. 3.

In case (a) as k goes from 0 to $\frac{1}{2}G$, θ increases from 0 to π, so that a_p increases steadily from 0 to 1. In case (b), as k goes from 0 to $\frac{1}{2}G$, θ increases from 0 to some maximum value less than π, and then falls again to 0. Hence in this case a_p increases from 0 to some maximum value less than 1 and falls again to zero as k reaches $\frac{1}{2}G$. These two possibilities are illustrated in Fig. 3 where a_p is plotted against k, showing the amount of p-state for each case. Since $|a_{01}|=|a_{10}|$, the curves also show the amount of s-state contained in the functions Ψ_{1k} associated with states in the second zone.

It was shown in §1 that in order to explain the experimental results it is necessary to suppose that for the metals Be and Mg it is the case (a) which actually exists.

For small values of k

$$\tan\theta = 8\beta\pi k/G[A_1(0)-A_0(0)].$$

Hence for small k, a_s is proportional to k, i.e., to $E^{\frac{1}{2}}$ and a_s as approximately constant.