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The X-Ray *K* Absorption Edges of the Elements Fe (26) to Ge (32)

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The structures of the x-ray K absorption edges of the elements Fe to Ge have been measured with a double crystal spectrometer. Measurements were extended about 20 volts beyond the main edge in each case. In the regions of secondary structure, new maxima and minima have been resolved, and their intensities compared with results obtained photographically. The two sets of measurements are found to disagree much more than could be expected from the estimated precisions. Wave-length positions of the first empty levels above the Fermi distribution have been assigned with a probable error of less than 0.1 X.U., and widths of K states have been determined to within half a volt by matching theoretical arctangent curves to the experimental edges. Previously measured $K\beta_{2,5}$ emission lines have been plotted with the corresponding absorption edges and the shapes of both lines and edges explained on the basis of distributions of states in the electronic energy bands of these metals. The $K\beta_5$ line is interpreted as a dipole transition arising from the mixture of p function in the $3d$ bands. Quantitative agreement is obtained in a correlation of the observed Cu emission and absorption structures with the recently calculated electronic bands of this metal.

INTRODUCTION

PREVIOUS experimental work[1] on the x-ray K absorption limits of Fe, Co, Ni, and Cu, has resolved considerable structure in the absorption edges themselves, but no satisfactory explanation of these structures of even a qualitative nature has been proposed, although it has been pointed out that the observed effects might be associated with the presence of an incomplete $3d$ shell.

For the very light elements, some success has been achieved by Mott, Jones, and Skinner and their co-workers[2–4] in interpreting observed shapes of soft x-ray emission lines and absorption jumps, through consideration of densities of states in filled and unfilled portions of the conduction bands. Since calculations have been carried out in recent years on the band structure of copper[5] with extrapolations to nickel,[6] we have attempted to correlate the results of these band calculations with experimental data on K absorption limits and $K\beta_{2,5}$ emission lines. The available emission data are very complete and reliable, but a lack of sufficiently complete and accurate data on the absorption limits has led us to repeat and extend older measurements, with greater resolving power, an improved technique for intensity measurement, and accurate wave-length determinations. The results of the present work on absorption limits from Fe (26) to Ge (32) differ considerably from those of past investigations. When taken together with the data on emission lines, the present measurements offer a semi-quantitative verification of the theoretical band calculations.

The material presented here may be divided into four sections, (1) a description of experimental technique, (2) intensities of secondary structures, (3) K and L level widths, and (4) a discussion of shapes of absorption limits and $K\beta_{2,5}$ emission lines in their relation to the electronic energy bands in the elements from Fe to Ge. The last-mentioned section constitutes the major portion of this paper. It offers an explanation of the large asymmetries of $K\beta_{2,5}$ emission lines and interprets their weak intensities as dipole transitions from bands of mixed states, rather than quadrupole transitions from discrete atomic levels, in Fe to Cu. In a similar manner, the shapes of the experimental absorption edges in these same elements are all qualitatively explained, as resulting from the variation in densities of unfilled states in the conduction and higher energy bands.

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[1] A. H. Barnes, Phys. Rev. **44**, 141 (1933).
[2] H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).
[3] Jones, Mott and Skinner, Phys. Rev. **45**, 379 (1934).
[4] H. Jones and N. F. Mott, Proc. Roy. Soc. **162**, 49 (1937).
[5] H. Krutter, Phys. Rev. **48**, 664 (1935).
[6] J. C. Slater, Phys. Rev. **49**, 537 (1936).

EXPERIMENTAL

The high precision double crystal spectrometer and high voltage supply with which the data here presented have been obtained is described in detail in a paper by Bearden and Shaw.[7] To determine the diffraction angles, angular settings in the $(1+1)$ and $(1-1)$ positions were read by the four-microscope method. Since no calibration correction greater than 0.3 sec. is anywhere necessary,[7] no such corrections have been applied in these measurements. Angular settings were determined to the nearest second, one second of arc in the wave-length region between one and two angstroms, being always less than 0.02 X.U. Temperature corrections and wave-lengths have been calculated with values of calcite expansion coefficient and grating space as given in reference 7.

The calcite crystals used in this work had been previously selected and treated in the usual way by Dr. C. H. Shaw. Table I gives the $(1-1)$ widths for various wave-lengths for the crystals, as measured by the authors in this work. These widths fall close to the theoretical widths of perfect crystals.[8] Most of the measurements have been carried out with a $(1+1)$ width of 39.5 seconds for Cu $K_{\alpha 1}$. The crystals compare favorably with any yet reported in double crystal work.

The gold-plated copper target was cut at an angle of 25 degrees with the horizontal, making the vertical projection of the focal spot 1.5 mm, which may be taken as the height of the first limiting slit for the spectrometer. The second slit, measuring 7 mm high, was separated by a distance of 55 cm from the first, giving a geometrical resolving power over 30,000.

All intensity measurements have been made with Geiger counters of the high pressure argon-alcohol type. The Getting type of multivibrator circuit[9] with a scale-of-sixteen Thyratron circuit[10] and a Cenco mechanical counter were used for recording pulses. In general, counts were taken over two-minute periods, alternately on incident and transmitted intensity at a given wave-length setting. Counting intervals were timed by a synchronous motor-driven switch. With an average counting rate of 2000 per minute in the Geiger counter, it was necessary to take a total of about twenty minutes of readings on incident intensity and an equivalent amount on transmitted intensity to obtain the desired precision per point. Aluminum foils were inserted for the measurement of incident intensity to bring the counting rate below the maximum of 8000 per minute. With this spectrometer it is possible to reset on any given point to 0.1 second, so that portions of curves can be repeated a number of times and corresponding points averaged. In most previous work of this type, such accurate resetting has not been possible, making it necessary to average a number of superposed curves, or publish only one of a set as a typical curve. The probable error per point in the curves shown here does not exceed one percent.

Absorbers were supported between the x-ray tube and the first crystal. To facilitate moving the foils in and out of the beam, they were mounted on a rotating sector, by means of which they could always be returned accurately to the same position in the beam. It was found unnecessary to oscillate the foils, direct tests showing that the curves obtained were independent of the position of the absorber. The x-ray beam was sufficiently wide, so that enough of the absorber was covered to average out small inhomogeneities.

TABLE I. $(1-1)$ *widths of crystals.*

WAVE-LENGTH IN A	EXP. WIDTH IN SEC.	THEORETICAL WIDTHS* FOR PERFECT CRYSTALS
1.12	8.2	7.9
1.19	8.8	8.4
1.54	10.3	9.9
1.61	10.4	10.2
1.78	12.1	11.5

* R. K. Richtmyer and S. W. Barnes, Phys. Rev. **45**, 745(A) (1934).

In the region of secondary structure, occurring on the high frequency side of the edge, tests have been carried out with rolled, electroplated, and powder absorbers of the same element with no observable differences in the amount and position of such structure. Evidently, the effects of crystal orientation due to rolling, and energies involved in strains are very small. The electroplated foils, Fe, Co, Ni, and Cu were obtained by plating onto stainless steel from which the foils were after-

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[7] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935).

[8] S. K. Allison, Phys. Rev. **41**, 1 (1932); L. G. Parratt, Phys. Rev. **41**, 561 (1932).

[9] I. A. Getting, Phys. Rev. **53**, 103 (1938).

[10] J. Giarratana, Rev. Sci. Inst. **8**, 390 (1937).

wards easily stripped. Zn and Pt foils were rolled. The foils ranged from 5μ to 10μ in thickness. Ge was used in powder form, and Ga was run at room temperature in the liquid state. Very homogeneous absorbing sheets of Ga were obtained by making an emulsion with castor oil on filter paper. Once melted, Ga remains supercooled to temperatures considerably below the melting point.

Since only the absorption coefficient has a physical meaning independent of the thickness of the absorber, all the curves given here are plotted with logarithmic ordinates. Most double crystal work on absorption limits has been published in the form of curves of I/I_0 or simply transmitted intensity against wave-length. It has been pointed out[11] that the appearance of such curves is determined largely by the thickness of the absorber. When $\log I/I_0$ rather than I/I_0 is plotted against wave-length the scattering of points on the high transmission side appears considerably reduced, while the contrast in the secondary structure is greatly enhanced relative to the total absorption jump. In double crystal measurements, where intensities of secondary structures have been reported from I/I_0 data, the values given ought not to be confused with the actual absorption coefficient variations.

In this investigation, much of the work has been done with second-order radiation being recorded. Second-order radiation reduces the top to bottom contrast in the absorption curves, affecting them mainly in the high absorption portion. Cobalt and gallium were run at voltages too low to excite second order. Other curves were checked for the effect of second-order radiation. For germanium and zinc, the effect was to reduce the top to bottom contrast by four percent and six percent, respectively. The effect on the intensity of secondary structure relative to the total jump is a much smaller percent. The curves for Ge, Zn, and Pt as presented here are uncorrected. Cu, Ni, and Fe have been rechecked and corrected for second-order radiation. In Fe, the largest correction was necessary, amounting to a 25-percent stretching of the entire curve and an increase in secondary structure intensity of 15 percent. Other corrections were all much smaller. The smallness of these corrections is in part due to the weak absorption of the short wave-length second-order radiation in the argon counter.

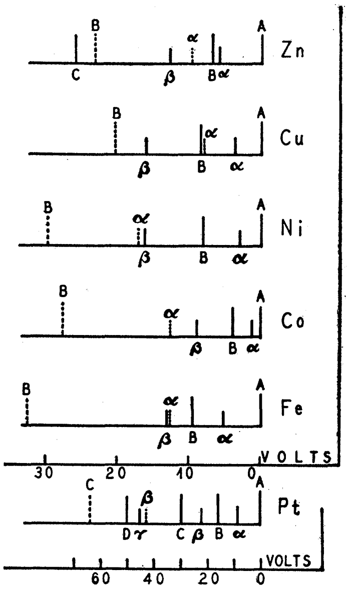

FIG. 1. Positions of secondary structures measured in volts from highest point in main absorption jump, A (See Figs. 3–10). Tall lines refer to maxima of absorption, short lines to minima. In each plot, results of the present work are drawn in solid lines, with letters below, while photographic results (reference 15, and Coster and Smoluchowski, Physica 2, 1 (1935)) are plotted in dotted lines, lettered above. The platinum results are for the L_{III} edge. All others are K edges.

SECONDARY STRUCTURES

That the double crystal spectrometer is well suited to measurements of secondary structure occurring on the high frequency side of an absorption limit has been demonstrated in a number of cases.[12–14] Extensive photographic work on all the metals worked with here, with the exception of germanium, may be used for comparison with our measurements, which have generally been carried out to 15 to 25 volts on the high frequency side. As is apparent from Fig. 1, the higher resolving power of the double crystal spectrometer has revealed, in each case, structure not detected photographically. In some cases, the first minimum in absorption, α, obtained photographically, may be fitted to our second minimum, β.

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[11] R. K. Richtmyer and S. W. Barnes, Phys. Rev. **45**, 745(A) (1934).

[12] P. A. Ross, Phys. Rev. **44**, 977 (1933).

[13] W. H. Zinn, Phys. Rev. **46**, 659 (1934).

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

In reports of secondary structure intensities from photographic measurements, two different definitions have been used for intensity. In some cases, the intensity of a given structure is defined as the ratio of the change in absorption coefficient from maximum to minimum in the structure, to the average absorption coefficient on the high frequency side of the limit. We shall call this definition (a). In other cases, the intensity of the structure is defined as the ratio of the change in absorption coefficient from maximum to minimum, to the total increase in absorption coefficient from the low to the high frequency side of the limit. We shall call this definition (b). Under "single crystal, photographic" in Table II are listed the results of measurements by Coster and Veldkamp,[15] and under "double crystal," the authors' results. The superscript (a) or (b), in each case, indicates the definition of intensity according to which the listed values have been calculated from the data. Structures referred to are indicated with the conventional letters used in labeling the curves in Figs. 2–10. Since the two sets of measurements do not refer to the same structures, no direct comparison of results can be made. However, it is apparent from the microphometer traces redrawn in Fig. 2, that we should expect the structures in Fe, Cu, and Pt, close to the edges, to be much weaker in intensity than the $D-\delta$ structures to which the photographic results in Table II refer. On the contrary, the present measurements show intensities close to the edges as great as or greater than that found far from the edges in single crystal work. For Zn and Pt, intensities measured with the double crystal spectrometer are considerably greater than anywhere in the photographically measured structures. Coster and Veldkamp's measured intensity for AuL_{III} was one-fifth that for Cu *K*, and only slightly less than for PtL_{III}. Our results on PtL_{III} would therefore lead us to expect intensities in AuL_{III} much closer to what we find in Cu *K*. All these discrepancies are far greater than one would be led to expect from the experimental errors, since both types of measurements claim precisions of much smaller order of magnitude than the differences observed. The inherently poor resolution in single crystal technique may be largely responsible for the lack of agreement between the two sets of observations. In PtL_{III} (see Figs. 1 and 2), the first clearly resolved photographic structure is β, which falls close to our γ. On the microphotometer trace, the structure A, α, B, is very uncertain and almost washed out, as would be expected in overlapping, poorly resolved absorption peaks. In Fig. 10, our A, α, B, β, C, and γ structures are easily resolved with consequently large intensities. From Fig. 1, and a comparison of the Fe curve in Fig. 2, with that in Fig. 3, it seems that our $A-\beta$ corresponds to photographic $A-\alpha$. Similarly, for Zn, our $A-\beta$ structure (Fig. 7) again must correspond to photographic $A-\alpha$, and for Cu (Fig. 6) our $\alpha-B$ structure is apparently unresolved and

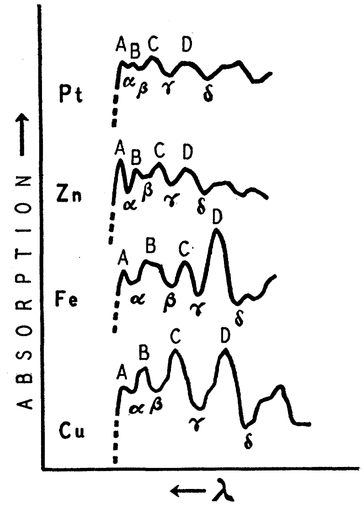

FIG. 2. Secondary structures for Fe, Cu, and Zn *K* edges, and for Pt L_{III}, copied from photographic microphotometer traces (reference 15). The $D-\delta$ intensities are much greater than the $A-\alpha$ in Fe, Cu, and Pt. The Zn structure is fairly uniform.

TABLE II. *Comparisons of secondary structure intensities.*

	Single Crystal Photographic		Double Crystal	
Edge	Intensity (percent)	Structure Referred to	Intensity (percent)	Structure Referred to
Fe *K*	19(a)	$D-\delta$	14(a)	$A-\alpha$
Cu *K*	13(a)	$D-\delta$	13(a)	$B-\beta$
Zn *K*	7(a)	$D-\delta$	17(a)	$A-\beta$
Co			5(a)	$B-\beta$
Ni			9(a)	$B-\beta$
Ga			11(a)	$A-\alpha$
Ge			19(a)	$A-\alpha$
AuL_{III}	2.8(b)	$D-\delta$		
PtL_{III}	4.6(b)	$D-\delta$	14(b)	$A-\alpha$

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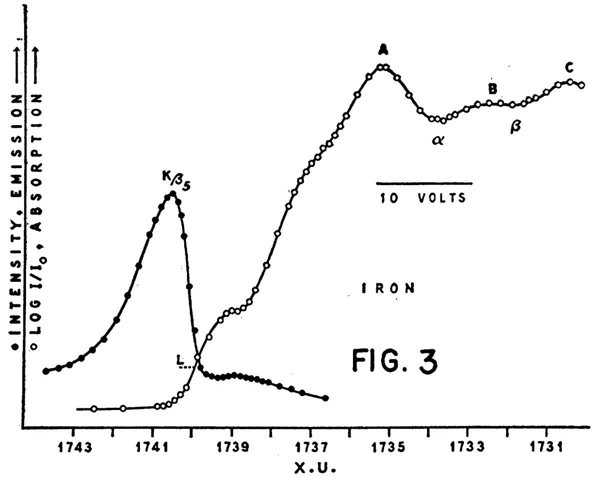
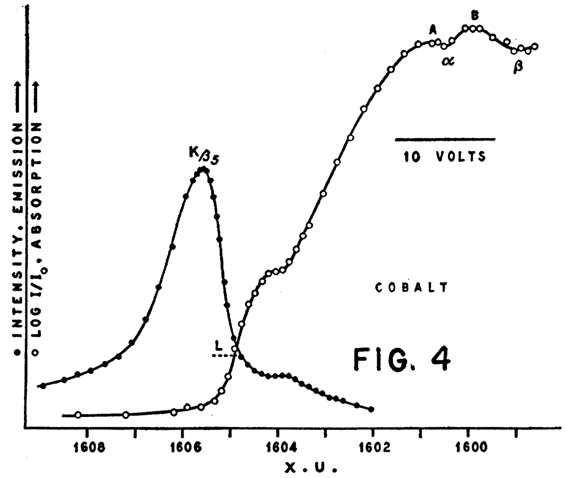
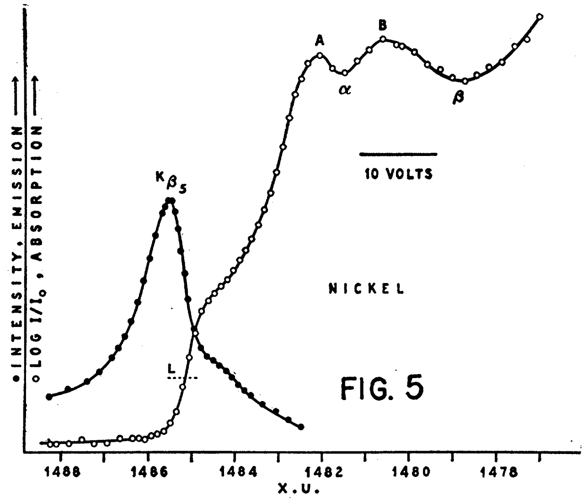
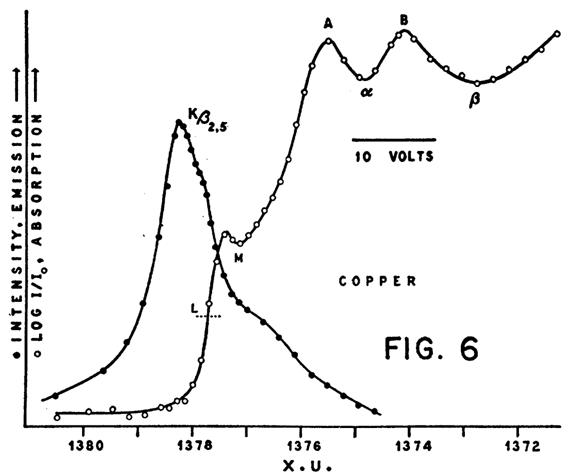
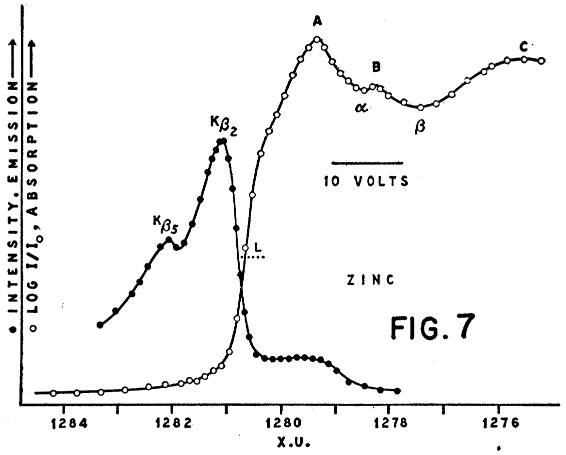
[15] D. Coster and J. Veldkamp, Zeits. f. Physik **70**, 306 (1931); D. Coster and J. Veldkamp, Zeits. f. Physik **74**, 191 (1932).











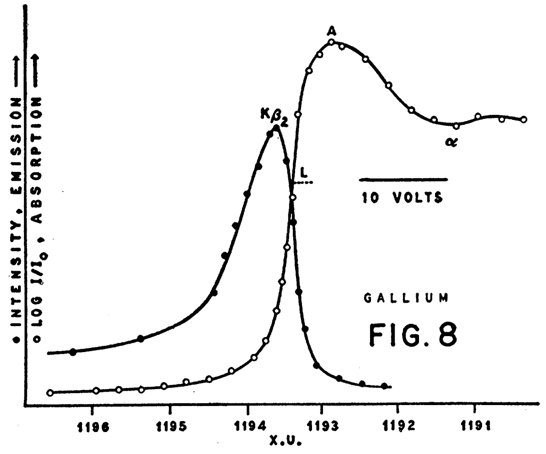


FIG. 3. $K\beta_5$ line and K absorption limit of Fe. All emission lines in Figs. 3–10 are plotted to arbitrary intensity scales.

FIG. 5. $K\beta_5$ line and K absorption limit of Ni.

FIG. 7. $K\beta_{2,5}$ line and K absorption limit of Zn.

FIG. 4. $K\beta_5$ line and K absorption limit of Co.

FIG. 6. $K\beta_{2,5}$ line and K absorption limit of Cu.

FIG. 8. $K\beta_2$ line and K absorption limit of Ga.

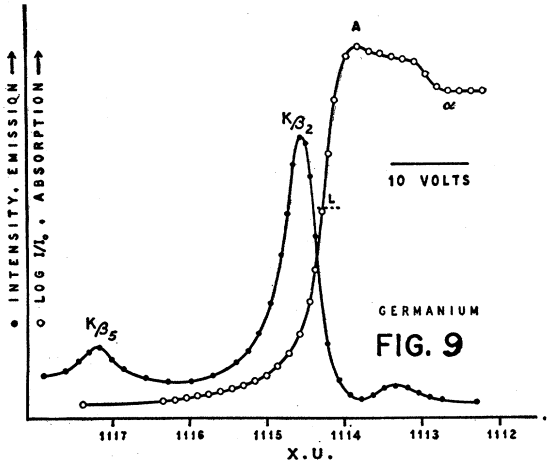


Fig. 9. $K\beta_2$ and $K\beta_5$ lines and K absorption limit of Ge.

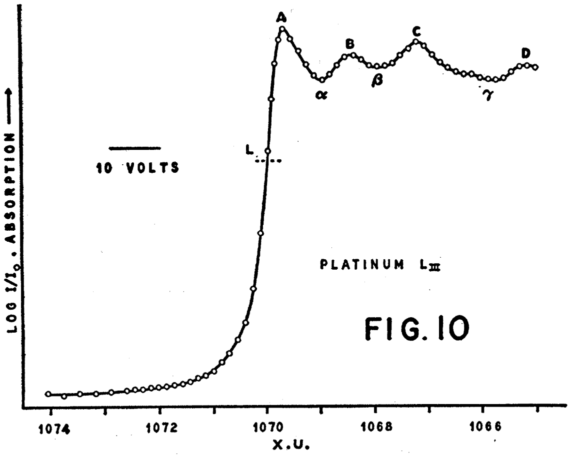


Fig. 10. L_{III} absorption limit of Pt.

lumped into photographic A. Whether poor single crystal resolution is entirely responsible for all the differences observed cannot be determined until the double crystal measurements are extended to the more widely spaced structures 50 to 100 volts from the edges.

The general rule proposed by Coster and Veldkamp,[15] from their results on Fe, Cu, and Zn, that intensities of structures in different elements vary approximately in the same way as the melting points, has not been borne out by more recent measurements on other elements,[13] nor by the results of the present investigation as far as it has gone.

Reference to Fig. 1 and to Figs. 5 and 6 shows that even near the edge, Cu and Ni, elements of adjacent atomic number, both with same lattice structure and only slightly different lattice spacings, have very similar structures, $A-\alpha-B-\beta$, as measured by the double crystal method. However, Co and Zn, Figs. 4 and 7, both with close-packed hexagonal crystal structures, are entirely different in absorption structure near the edge. The secondary absorption in Co resembles that in Ni, the element of adjacent atomic number but different lattice type, much more than the structure in Zn. It therefore seems that the atomic potential fields within 15 volts of the edges are still most important in determining observed absorption structures, and that the electrons cannot yet be considered entirely free.

Widths of Energy Levels

Richtmyer, Barnes and Ramberg[16] have applied the quantum-mechanical radiation theory of Weisskopf and Wigner[17] to the absorption process in such a way as to make possible a calculation of level widths from experimental data on absorption limits.

The quantum-mechanical derivation of the intensity distribution in a spectral line, according to Weisskopf and Wigner, yields the result,

$$I_{AB}(\nu)d\nu=\frac{\Gamma_A+\Gamma_B}{2\pi}\times\frac{d\nu}{(\nu_{AB}-\nu)^2+[(\Gamma_A+\Gamma_B)/2]^2},\tag{1}$$

where Γ and Γ_B are the widths of the initial and final levels A and B between which the electronic transition takes place. The state A has a spectral distribution of the form,

$$I_A(\nu)d\nu=\frac{\Gamma_A}{2\pi}\frac{d\nu}{(\nu_A-\nu)^2+(\Gamma_A/2)^2}\tag{2}$$

and likewise for state B.

Equation (1), with $\Gamma=\Gamma_A+\Gamma_B$ and Eq. (2) are of the same form as the classical equation for the radiation from a damped harmonic oscillator,

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[16] Richtmyer, Barnes and Ramberg, Phys. Rev. **46**, 843 (1934).

[17] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930); V. Weisskopf, Physik. Zeits. **34**, 1 (1933).

TABLE IIIa. *Widths in volts of K_{α_1} and K_{α_2} lines.*[7]

ELEMENT	$K\alpha_1$, $K\rightarrow L_{III}$	$K\alpha_2$, $K\rightarrow L_{II}$
Fe	3.0	3.5
Co	2.8	3.6
Ni	2.6	3.6
Cu	2.7	3.7
Zn	2.9	3.5
Ga	3.1	3.3
Ge	3.2	3.5

TABLE IIIb. *Widths of energy levels in volts.*

ELEMENT	K LEVEL	L_{II}	L_{III}
Fe	1.8±0.5	1.7	1.2
Co	1.5±0.5	2.1	1.3
Ni	1.9±0.5	1.7	0.7
Cu	1.3±0.5	2.4	1.4
Zn	1.5±0.5	2.0	1.4
Ga	1.9±0.5	1.4	1.2

where $2\pi\Gamma$ would be the damping factor, or the reciprocal mean life of the excited atom. Γ gives the half-maximum width of the radiated line. If one of the widths in Eq. (1), say Γ_A, is zero, the distribution in line intensity is of the same form as the energy distribution of the level B.

In the process of a K absorption, an electron from the K shell of an atom in state A, is raised to some level above the Fermi distribution leaving the system in one of a continuum of states of energy E, greater than E_0 (state with the electron from the K shell in the first level above the Fermi surface). Richtmyer, Barnes and Ramberg have shown that the absorption curve for the edge may be taken as the sum of successive absorption lines to the discrete states E, the shape of each absorption line being given by (1). The width of the absorption limit from $\frac{1}{4}$ to $\frac{3}{4}$ maximum of absorption coefficient, calculated with a distribution of excited levels uniform to higher energies, is then exactly equal to the width at half-maximum of one of the absorption lines. If Γ_A is zero, this is the width of the excited state, or K level.

In mathematical form[16] the partial absorption coefficient is given by

$$K(\nu)=C\sum_{\nu_{EA}=\nu_{E_0A}}^{\nu_{EA}=\infty}(E)\gamma_{EA}\times\left(\frac{\Gamma_E/2\pi}{(\nu_{EA}-\nu)^2+(\Gamma_E/2)^2}\right),\qquad(3)$$

in which Γ_A, the width of the normal state, is neglected in comparison to Γ_E. C is a constant. $2\pi\gamma_{EA}$ is the transition probability from state E to the normal state A. By making a number of reasonable assumptions, the summation can be replaced by an integral, which yields the simple result,

$$K(\nu)=C'\left\{\frac{1}{2}-\frac{1}{\pi}\arctan\left(\frac{\nu_{E_0A}-\nu}{\Gamma_E/2}\right)\right\}.\qquad(4)$$

If instead of a uniform density of states E, assumed in deriving this expression, some more complicated distribution is chosen, the results on the low frequency side of the absorption limit are only slightly changed.[16]

By matching curves of the form (4), having different values of the parameters Γ_E and C', with the experimental curves, it is possible to find an arctangent curve, which up to the inflection point, closely fits the measured absorption curve. The value of Γ_E for the arctangent curve then, gives the width of the K energy level. The widths obtained by this method are listed in the first column of Table IIIb. The widths of the K levels within the probable errors indicated are about the same throughout the series measured. Table IIIa gives the widths of the K_{α_1} and K_{α_2} lines of the elements Fe to Ga,[7] from which the widths of the L_{II} and L_{III} levels can be obtained by means of the relation,

$$W_{\text{Line}}=\Gamma_A+\Gamma_B,\qquad(5)$$

if the width of the K state is known. The widths calculated in this way are given in the last two columns of Table IIIb. The L_{II} level in each case is much wider than the L_{III}. The doublets $K_{\beta_{1,3}}$ in this series are not resolved, so that the M_{II} and M_{III} level widths cannot be calculated from the data.

The L_{III} edge for platinum gives a value of 4.1±0.5 volts, which is in good agreement with the value of 4.4 volts obtained for Au L_{III}.[16]

In the case of germanium, a powder absorber has been used and it has not been possible to fit the curve well with any arctangent curve. It is obvious that radiation transmitted through such an absorber does not all pass through a uniform thickness, and while it will show all the structure that would be found with a foil, the logarithmic plot cannot be expected to vary in direct proportion to absorption coefficient. The arctangent curve which most nearly fits the germanium absorption curve would give a width for the edge almost as great as obtained for Pt L_{III}, but such a width for the Ge K state cannot be correct because it is greater than the width of several Ge lines in the K series. In contrast to Ge, the Pt curve fits almost perfectly with its arctangent curve.

To all these widths, corrections[18] for the $(1-1)$ rocking curve widths have been applied. For the region covered the corrections run from 0.6 to 0.7 electron volt.

Wave-Lengths

With the poor resolution obtainable photographically, it has been customary to pick the midpoint of the apparently sharp increase in absorption as the wave-length position of the absorption edge. Since the double crystal spectrometer has revealed considerable width and structure in the edge itself, the question arises as to whether any meaning can be given a wave-length position for the edge. The inflection point of the arctangent curve fitted to an absorption edge gives the wave-length position of E_0, the energy of the first empty levels. It seems logical to pick this position then as the wave-length of the absorption edge. Table IV gives these positions as indicated by the letter L on each absorption curve, and for comparison, the wave-lengths given by other investigators. For the edges from Fe to Cu, as is apparent from Figs. (3–7), we should expect our values to be of shorter wave-length. For Zn, Ga, Ge, and Pt, our values should agree with the others to within at most 0.3 X.U. Since the measurements in the present work are good to 0.02 X.U., our uncertainties lie only in the assignment of the positions L by the arctangent fits. The results, therefore, indicate comparatively large errors in some of the previously reported wave-lengths.

TABLE IV. *Wave-lengths in X.U. of absorption limits.*

EDGE	AUTHORS' MEASUREMENTS	PREVIOUS MEASUREMENTS
Fe K	1739.9	1739.4[1]
Co K	1604.9	1604.0[1]
Ni K	1485.2	1483.9[1]
Cu K	1377.7	1377.4[1]
Zn K	1280.7	1280.5[1]
Ga K	1193.4	1190.2,[2] 1192.5[3] 1192.9[4]
Ge K	1114.3	1114.6[2]
Pt L_{III}	1070.0	1071.0[5]

[1] Ase, reported in Siegbahn, *Spektroskopie der Rontgenstrahlen* (1931).

[2] Duane, Blake and Hu, from W. Duane, Bull. Nat. Res. Counc. U. S. A. **1**, 6 (1920).

[3] W. W. Mutch, Phys. Rev. **50**, 197 (1936).

[4] B. Kievit and G. A. Lindsay, Phys. Rev. **36**, 648 (1930).

[5] A. Sandström, Zeits. f. Physik **54**, 632 (1930).

Discussion

I. Calculation of band structure

The problem of calculating energy levels and wave functions for electrons in a metallic lattice has been approached from two different directions. If the electron is moving with an average kinetic energy large when compared with the maximum variation of potential energy in the lattice, one may say that its wave function will not be very different from that of a free electron. The actual problem can be approximately solved by starting with the solution of the constant potential case and calculating the effects of a perturbing periodic potential. It is found that the perturbation separates the allowed energy ranges into zones whose boundaries are determined by the possibility of reflection of the electron wave by the lattice. The propagation of an electron with such a direction and energy that the associated wave would suffer Bragg reflection from the lattice is not permitted.

Kronig,[19] using the free electron approximation, calculated the distribution of allowed levels and found some energy ranges where the level density was low and others where the levels tended to cluster. These regions agree well in position with the regions of low and high absorption coefficient, observed[15] on the high frequency sides of the K and L absorption edges of several metals.

The second method of calculating, instead of starting with free electron wave functions, uses atomic wave functions as the zero-order approximation. This approach is most applicable to the low-lying bands, where the overlapping of the electron clouds of adjacent atoms and therefore the splitting of the band is not too great. Except

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[18] L. G. Parratt, Phys. Rev. **46**, 749 (1934).

[19] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931); **75**, 191 (1932).

for the work of Jones, Mott and Skinner[3] on the interpretation of shapes of emission lines in the very soft x-ray region, there has been no attempt to apply results of this second method to problems of x-ray spectroscopy.

The most careful calculations with the atomic approximation have been made by Krutter[5] and Slater[6, 20] following the general procedure developed by Wigner and Seitz[21] and Slater.[22] We will give a short description of these calculations since they furnish quite a convincing explanation of the observed shapes of the Cu K edge and $K_{\beta_{2,5}}$ emission line. Calculations have been carried out only for Cu but all the plausible extrapolations made to nearby elements are borne out by the observations.

Bloch has shown that the wave functions of an electron in a periodic field must always be of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \exp [2\pi i(\mathbf{k}\cdot\mathbf{r})],$$

where $\mathbf{k}$ is the wave vector and $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. For electrons with large kinetic energies, $u_{\mathbf{k}}(\mathbf{r})$ is almost a constant and the wave function approximates that of a free electron. In the lower bands, $u_{\mathbf{k}}(\mathbf{r})$ may be a rapidly changing function of position and near the lattice points will behave much like an atomic wave function, as one would expect if an atomic approximation is to be valid.

From the form of the wave function it is seen to be determined everywhere if known in the neighborhood of one arbitrary lattice point. Its value around any other lattice point can be obtained by multiplying by $\exp [2\pi i(\mathbf{k}\cdot\mathbf{R}_0)]$ where $\mathbf{R}_0$ is the displacement vector from the first to the second nucleus. Krutter[5] chose as neighborhood a symmetrical twelve-sided polyhedral cell at whose center was a Cu nucleus. The cell was of such a size and shape that if one cell were placed about each point of the lattice, the set would pack together tightly and completely fill the space. It was assumed that within each cell the potential field is that of an isolated singly charged Cu ion and the radial part of Schrödinger's equation was solved for such a field. However, the boundary conditions are no longer the same as in the case of the isolated ion. Instead of the disappearance of the wave function at infinity, we now have the requirements that in going from one side of the polyhedral cell to the diametrically opposite side the wave function be multiplied by $\exp [2\pi i(\mathbf{k}\cdot\mathbf{R}_0)]$ where $\mathbf{R}_0$ is again the displacement vector involved. This is equivalent to requiring that the solution in one cell be joined onto the solution in an adjacent cell in such a way that when extended through the lattice the wave function is modulated as required by Bloch's theorem.

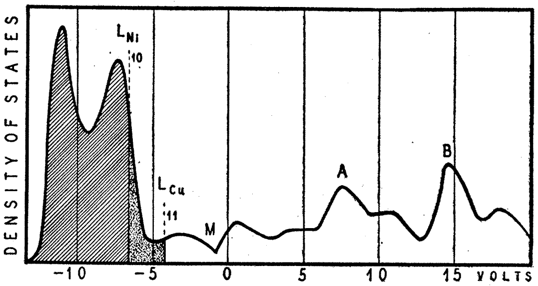

FIG. 11. Density of states as a function of energy in Cu (redrawn from a paper by Rudberg and Slater (reference 20), with some additional markings). Lines labeled L_{Ni} and L_{Cu} give the energies to which the bands are filled in Ni (assuming same energy levels as for copper) and in Cu by 10 and 11 band electrons per atom, respectively.

Krutter expresses the wave function in the cell as a linear combination of twelve independent functions whose angular parts are the twelve lowest spherical harmonics and whose radial parts are the above-mentioned solutions of Schrödinger's equation. The coefficients in the linear combination are determined by satisfying the boundary conditions at the midpoints of the twelve faces. The equations contain as supposedly known parameters, the energy entering through the Schrödinger equation and the direction of the wave vector $\mathbf{k}$ which enters through the boundary conditions. If values are assumed for these parameters, the magnitude of $\mathbf{k}$ can be calculated. It will sometimes be real, corresponding to an allowed choice of the energy for the assumed direction of propagation, and sometimes imaginary, corresponding to a forbidden energy.

Krutter was mainly interested in the splitting of the $3d$ band and actually solved his equations for only three directions in the lattice. The calculations were extended to higher bands by

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[20] E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936).

[21] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[22] J. C. Slater, Phys. Rev. **45**, 794 (1934).

Slater[6, 20] and the results averaged over all directions of propagation. It was then possible to give a curve of density of allowed states against energy such as is here reproduced in Fig. 11 taken from reference 20.

The accuracy of this curve is difficult to estimate since there have previously been few comparisons with experiment and the calculations give little hint of their own reliability. There may be errors of volts in the position of the structure and possibly some change in the nature of band splitting, but our experimental results seem to indicate that the results of the calculations are better than one would generally expect from the approximations involved.

A knowledge of the density of states is not in itself sufficient to give a prediction of the shape of an emission line or of structure close to an absorption edge since the transition probability to those states will also be a function of energy. Jones and Mott[4] write the intensity of x-ray absorption or emission as $I(E)=N(E)\cdot p(E)$ where $N(E)$ is the density of states and $p(E)$ the transition probability. We are dealing with transitions to and from the K state, so $p(E)$ will be assumed directly proportional to the amount of p function used in the description of the band level. The variation of this quantity with energy is not made explicit in the calculations of Krutter and Slater, but enough can be determined about it to permit a comparison with experiment.

There is no great difference in the physical reasons for Kronig structure and structure in the absorption edge itself, inasmuch as the function $I(E)$ determines the intensity of absorption in both cases. Methods of calculating $I(E)$ will change depending upon the distance from the edge, which is equivalent to saying that the relative importance of the various factors, upon which $I(E)$ depends, will change. The crystal structure is decisive for the Kronig structure. Near the edge, the atomic field is more important. The energy regions in which the atomic and free electron approximations are useful do not quite overlap, and between about fifteen and forty volts beyond the main edge, no good calculations exist.

II. The $K\beta_{2,\,5}$ emission lines

We have plotted the $K\beta_{2,\,5}$ emission lines of the transition elements as measured by Bearden and Shaw[7] on the same wave-length scale as the K absorption edges. There are several reasons for believing that these lines should be interpreted in terms of transitions of electrons from the filled bands of the metal to the empty K state. In each case, the high frequency side of the line matches closely the beginning of absorption in the edge. While no other K series lines of these elements have half-widths in excess of four volts, these lines have half-widths of from five to ten volts. The latter widths are about what one would expect for filled bands. The band origin is also suggested by the asymmetries of the $K\beta_{2,\,5}$ lines. Bearden and Shaw[7] report values of indices of asymmetry between two and three for all the elements measured except Ni and Ge. Other K series lines of the same elements have asymmetries considerably less than two. The index of asymmetry is defined as the ratio of the part of the half-maximum width of the line on the low frequency side of the peak to the part on the high frequency side. A value greater than one indicates that the line falls off more steeply on the high frequency side of the maximum. This is just the behavior to be expected in lines arising from transitions from filled bands. The decrease in intensity on the high frequency side comes about because beyond a certain point the bands are no longer filled, and the sharpness of the decrease is limited only by the width of the K state. On the low frequency side, the falling off in intensity is determined by the function $I(E)$ and will generally be much more gradual.

It is not believed that reabsorption in the target of the high frequency side of the line, where the K absorption begins, had any part in producing the high asymmetries. The penetrating power of electrons is much less than that of the x-rays, so the x-rays are produced near enough to the surface of the target so that they will not be appreciably absorbed.

It is customary to classify $K\beta_5$ as a $K-M_{IV,\,V}$ transition, and $K\beta_2$ as a $K-N_{II,\,III}$ transition. This is undoubtedly correct for those elements of which these levels do not take part in band formation in the solid. In Zn, however, the lines are clearly separated, although there are still no electrons in the $N_{II,\,III}$ levels.

If one considers the ratio of the intensity of the line next to the edge (whether it be $K\beta_2$ or $K\beta_5$) to

$K\alpha_1$, as a function of atomic number, a further anomaly appears. It would be expected for the free atom that this intensity ratio should be very low for atomic numbers less than 31, since then, the outermost electrons are either *3d* or *4s* and the transition is from an even state to an even state which is not allowed as a dipole transition. At Ga the first *4p* electron is added and the dipole transition becomes allowed. We would expect a sudden increase in the intensity ratio at Ga, but this is not found experimentally. H. T. Meyer[23] has made measurements extending from atomic number 23 to 49, and reports values of the relative intensity $\beta_{2,5}/\alpha_1$ of roughly 0.0020 for the elements Fe to Zn. Ga is not given but Ge is 0.0046 and As 0.0069. Williams[24] gives values of 0.0036 for Zn and 0.0132 for Ge. Beyond Ge both authors report a roughly linear increase of the ratio with atomic number, i.e., with added *4p* electrons. Thus, in going from transitions which in the atomic picture are forbidden to those which are allowed, the probability increases by a factor of only three.

This behavior is understandable in transitions from filled bands. The radiation is probably always dipole, the necessary *p* function being furnished in the case of elements below Ga by the extensive mixing of states of different angular momentum which occurs when atoms are brought close together as in the metallic lattice. This constitutes a quantum-mechanical description of the breakdown of the conservation of angular momentum about an atomic center, which occurs when interaction with neighboring atoms becomes important.

That there is considerable mixing of *p* function in the *3d* and *4s* bands of Cu was shown by Krutter's calculations. The amount of this admixture will increase gradually as the *4p* band is approached causing a gradual rather than a sudden increase in the intensity ratio. The magnitude of the initial *K* absorption jump as a function of atomic number in this series of elements varies in much the same manner.

III. Correlation of Cu and Ni data with the calculations

It is proposed to try to explain the shapes of the $K\beta_{2,5}$ emission lines and the *K* absorption edges by comparison with the $I(E)$ function, but because of the width of the *K* state, the comparison is not direct in certain cases. If $I(E)$ has a high or low value for some range of levels in the band, its effect on the intensity of absorption is felt not just at the corresponding wave-length but over a range of about the half-width of the *K* state on each side. Conversely, the intensity of absorption or emission at a given wave-length is determined by an average of $I(E)$ over a range extending a volt or two to each side of the corresponding energy level. Most of the comparisons are concerned with the distances between maxima and minima of absorption, and these will not be greatly altered by the width of the *K* state provided that $I(E)$ varies approximately symmetrically on each side of the maximum or minimum.

As has been pointed out, the beginning of each absorption curve can be closely fitted to an arctangent and from this can be obtained the width of the *K* state and the height to which the levels in the band are filled. The latter position is particularly important in making comparisons with the theory.

The calculated density of states for Cu (Fig. 11) shows the *3d* atomic wave functions drawn into a band with a high density of states (really five overlapping bands) extending from -13 to -5.5 volts. This high density of states is to be expected because the overlap of the *3d* functions is relatively small. The *4s* band extends from -13 to about -0.5 volt with a considerably lower density of states. At *M* the *4s* and *4p* bands barely overlap. Above this point, the density of states varies in a rather complicated manner. The intensity of absorption will be great in this region, since the band arises from the splitting of *p* atomic functions and will be largely described by such functions.

In the lower bands it is necessary to know something about $p(E)$. From Krutter's work, it can be found that of the five *3d* bands which combine to give the double-peaked structure below -5 volts in Fig. 11, those which are split least contain no *p* function. It is these bands which give rise to the lower energy maximum in the density of states curve. The remaining bands do contain *p* function, and they combine to give

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[23] Quoted in Compton and Allison, *X-rays in Theory and Experiment*, page 641.

[24] J. H. Williams, Phys. Rev. **44**, 146 (1933).

TABLE V. *Comparison of the calculated and observed structure of copper bands.*

STRUCTURE (FIG. 6)	THEORY (EV)	EXPERIMENT (EV)
$K_{\beta_5}-L$	3.1	3.4
$L-M$	3.4	4.0
$M-A$	8.3	10.7
$A-B$	7.2	9.4

the higher energy maximum. $I(E)$ for the 3*d* band will then have a maximum at about the position of the higher energy maximum of $N(E)$. It will decrease gradually to zero at -13 volts and rapidly to zero at -5.5 volts.

In the 4*s* band, the admixture of *p* function is greater than in the 3*d*, so much greater, in fact, that $I(E)$ assumes higher values there, in spite of the lower $N(E)$. Tibbs[25] has shown that for the (111) direction, the top and bottom state of the *s* band is a pure *s* function. In between, the admixture of *p* function has a maximum, and there seems to be no experimental evidence for more than a single maximum.

In the 4*p* band, nothing has been published about the variation of $p(E)$ except that the lowest state for the (111) direction is a pure *p* state.[25] For higher states the contribution of the *p* function will fall off, perhaps fast enough so that $I(E)$ will not exhibit the maximum at about one volt which $N(E)$ has and which fails to appear experimentally. Good agreement may be obtained between the higher calculated levels and experiment, by identifying the maxima of $N(E)$ labelled *A* and *B* in Fig. 11 with the absorption maxima *A* and *B* in the Cu *K* edge, Fig. 6.

According to the theory, the copper bands are filled to the point marked L_{Cu} in the curve (Fig. 11). With this information, a comparison with experiment can be made. The main peak in the emission line (Fig. 6) corresponds to the maximum of $I(E)$ in the 3*d* band. There is a further slight hump on the high frequency side of the line probably due to emission from the filled part of the 4*s* band beyond the high frequency limit of the 3*d* band.[26] Beyond the filled levels, the theoretical curve for $I(E)$ is to be correlated with the experimental absorption curve. In Fig. 6, there is an initial absorption into the 4*s* band and then a decrease in the absorption at *M* which is due to the small overlap between the 4*s* and 4*p* bands. Beyond *M* the absorption increases steadily to *A* with no suggestion of intermediate structure as has already been mentioned. The numerical comparison is given in Table V. The agreement is within the uncertainty to be expected from the calculations.

Nickel has the same crystal structure as Cu and not too close to the edge one would expect the same band structure. The experimental curves have very similar shapes in the region of high absorption. Near the filled levels the different atomic fields will alter the level distribution somewhat, but if we assume as a first approximation that the Cu levels apply also to Ni, as suggested by Slater,[6] then the ten band electrons of Ni will fill the levels to the height indicated L_{Ni} in Fig. 11. It would be expected from this that the structure on the high frequency side of the Cu K_{β_5} due to emission from the filled 4*s* levels would be missing in Ni. This is experimentally verified by the smooth emission curve in Fig. 5.

We do not obtain in Ni the absorption minimum *M* resulting from the small overlap of the 4*s* and 4*p* bands. This seems to indicate the inadequacy of the assumption that the Ni and Cu bands are identical. The failure is probably due to the smaller nuclear charge and slightly smaller lattice distance of Ni, both of which would cause a greater overlapping of the *s* and *p* bands in Ni.

If one identifies the absorption maxima *A* in Cu and Ni as arising from the same peak in $N(E)$, it is possible to measure the difference in the heights to which the bands are filled in the two metals. This is just the difference between the voltage separations of *A* and *L* in Cu and Ni, Figs. 5 and 6, which give an experimental 2.6 volts against the theoretical 2.4. At first sight, it would seem just as reasonable to match the peaks of the two K_{β_5} lines in emission. The distance from the peak of K_{β_5} to *L* is 3.4 volts in Cu and 2.0 volts in Ni, making an experimental 1.4 volts between the tops of the two Fermi distributions. This discrepancy comes about because in Ni the filled levels extend but a short distance beyond the position of maximum $I(E)$ in the 3*d* band. The width of the *K* state spreads

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[25] S. R. Tibbs, Proc. Camb. Phil. Soc. **34**, 89 (1938).

[26] The small peak at the bottom of this line, on the high frequency side, is a satellite. Such satellites are also present in the $K_{\beta_{2,5}}$ lines of the other elements.

the contribution of each level of the band over an energy range of about two volts, and there results a shift of the peak toward lower frequencies, essentially because at a frequency slightly less than that of $I(E)_{\text{Max}}$ contributions toward the measured intensity are received from states on both sides of the state for which the spectrometer is set, while at $I(E)_{\text{Max}}$ contributions are received only from the low frequency side.

TABLE VI. *Voltage separation $K\beta_5$ to A (from Figs. 2–9).*

ELEMENT	Fe	Co	Ni	Cu	Zn	Ge
$K\beta_5$ to A (ev)	22.2	23.6	19.3	18.1	21.0	33.5

An approximate calculation of the same type as that carried out to yield the arctangent curve for an absorption limit gives a shift of $\frac{3}{4}$ the width of the Ni K state, or 1.4 ev, if $I(E)$ is assumed to be a maximum at the high frequency limit of filled states, falling off to zero with lower frequencies in a distance of eight volts. This again gives agreement with the theoretical separation.

IV. Other elements

A. Identification of the 1st maximum of absorption.—For the other elements no quantitative comparison can be made with the present experimental results because changes in crystal structure make impossible even an approximate extrapolation of the theoretical results in Cu. However, certain general remarks may be made. The point A marking the first maximum of absorption beyond the edge itself is believed to be an absorption into the $4p$ band for each of the elements observed. This has already been shown for Cu and Ni and the extension to other elements can be seen by reference to Table VI where the voltage distance from K_{β_5} to A is given. It is seen that until one begins to add $4p$ electrons at Ge, the voltage separation remains about constant so that A must correspond to the same band in each element. It is known that K_{β_5} is the same emission line for each because the lines fall on the same Moseley diagram. At Ge, of course, the absorption is pushed to higher levels because of the filling of the $4p$ band. No comparison is possible with Ga since K_{β_5} could not be measured in the emission work, perhaps due to the fact that Ga was used on the target in the liquid state.

B. High density of states in 3d band.—All the theories of the transition elements agree in assigning a high density of states to the $3d$ band irrespective of the crystal structure and also agree that this band is in the process of being filled through Fe, Co, and Ni, and is full at Cu. One would expect that in the d band the addition of an extra electron would not raise the top of the filled levels nearly as much as the addition of an electron into the s or p band where the density of states is considerably lower.

Table VII gives the distances from L to A for each element.

Since A is an absorption into the same band for each, the differences in the above figures for the successive elements are a rough measure of how much the top of the Fermi distribution is raised by the addition of an electron. From Fe to Ni the levels are within three volts of each other indicating a high density of states. Co appears misplaced, but no better agreement can be expected when the crystal structure varies. The Cu electron completes the filling of the $3d$ band and overlaps partially into the $4s$ raising the filled levels 2.6 ev. However, at Zn and Ga, the electrons raise the top of the distribution 4.6 and 5.7 volts, respectively, giving direct evidence for the lesser density of states in the $4s$ and $4p$ bands. It is to be noted that this method of treating the data gives directly $N(E)$ and not $I(E)$. Ge and Pt are included in the table to indicate what edge widths are to be expected when there is strong absorption into the first empty levels.

C. Magnitude of initial absorption.—It is possible also to obtain approximately the ratio of $I(E)$ for the lowest empty levels to $I(E)$ for the $4p$ band at the point A. The point L (Figs. 3–10), marking the top of the filled levels, occurs just halfway up the absorption curve which would

TABLE VII. *Voltage distance from top of filled levels to first maximum absorption.*

ELEMENT	L TO A (EV) (FROM FIGS. (3–10))	ELEMENT	L TO A (EV) (FROM FIGS. (3–10))
Fe	19.8	Zn	10.1
Co	20.5	Ga	4.4
Ni	17.3	Ge	4.3
Cu	14.7	Pt	3.3

result if $I(E)$ were a constant for all the empty levels. Therefore, if double the ordinate of L is divided by the ordinate of A, the desired ratio is obtained. The results are given in Table VIII.

TABLE VIII. *Percentage of the total absorption jump accounted for by absorption into the first empty levels.*

ELEMENTS	PERCENTAGE	ELEMENTS	PERCENTAGE
Fe	23.0	Zn	78
Co	29.0	Ga	100
Ni	37.0	Ge	100
Cu	53.0	Pt	100

Table VIII indicates that $I(E)$ at the edge increases continuously from Fe to Ga as would be expected from the gradually increasing admixture of p function in going from the $3d$ and $4s$ to the $4p$ band. It is also clear that $I(E)$ is larger for the $4s$ than for the $3d$ band.

Checks have been made to determine how much the shape of the absorption curve up to the inflection point L was affected by absorption into levels some distance beyond the first empty ones. This was done by cutting off the summation at various distances past ν_{E_0A} in Eq. (3) instead of continuing to infinity. The results indicate that levels removed from highest filled level by more than twice the width of the K state may be neglected. The magnitude of the initial absorption jump is determined then by an average value of $I(E)$ for the states within four volts of the edge, the states closest to the edge being the most heavily weighted in the average.

D. Platinum.—The Pt L_{III} edge, Fig. 10, is an interesting example of the influence of the selection rules on the shape of the edge. It has the same crystal structure and the same number of band electrons as Ni. Results[27] on the paramagnetic susceptibility of Pt alloys indicate that the d band lacks completion by about the same amount as in Ni. However, the shape of the edge is entirely different because in Ni the absorption process involves excitation of an s electron into the d and s band while in Pt a p electron is excited into the same bands. The fact that in Pt the inflection point L occurs more than halfway up the edge, indicates that $I(E)$ has its greatest value for the lowest empty levels, and for slightly higher levels, takes on considerably smaller values. This is to be expected since absorption into the p band will be weak.

E. Asymmetries of lines.—It is possible to understand the asymmetries of the $K_{\beta_{2,5}}$ lines in emission a little more completely by a more careful consideration of the band structure. It has been stated that the asymmetry of the line arises from the asymmetry of $I(E)$ where we assume while discussing emission lines that $I(E)=0$ for unfilled levels. Generally, the discontinuous drop to zero at the top of the filled levels is the decisive factor in giving the line its high asymmetry. If, however, the highest filled level is in a region of very small $I(E)$ then both sides of the line are determined by how $I(E)$ varies in the filled levels, and the line may or may not have high asymmetry. The best example of this is Ge which is a semi-conductor, so that there must be a gap between the top of the filled bands and the bottom of the first unfilled bands. Its K_{β_2} line (Fig. 9) is therefore not expected to be abnormally steepened on the high frequency side. Zinc, on the other hand, is a good conductor; there will be considerable overlap of the $4s$ and $4p$ bands and $I(E)$ at the top of the filled levels will be large. The $4p$ band of Ga is only half-full which again gives a large $I(E)$ at the cut-off. The indices of asymmetry for the K_{β_2} lines are Ge 1.21, Ga 2.93, and Zn 3.02, as reported by Bearden and Shaw.[7]

A somewhat similar situation occurs with the K_{β_5} lines of Ni, Co, and Fe, whose indices of asymmetry are 1.75, 2.06, and 2.44, respectively.[7] Calculations indicate that Ni is filled to slightly beyond the maximum density of states so that $I(E)$ has begun to drop at the top of the filled levels. Co and Fe with fewer electrons would have their highest filled levels in a region of maximum $I(E)$, and this probably explains their greater asymmetries.

We are indebted to Professor J. A. Bearden under whose direction this work was carried out; to Dr. C. H. Shaw for the Geiger counter technique used in recording the intensities; to Dr. M. Goeppert-Mayer for discussions on the theories involved; and to Dr. David R. Inglis for theoretical discussions and criticism of the manuscript. It is also a pleasure to acknowledge the financial assistance granted Professor J. A. Bearden from the Penrose Fund by the American Philosophical Society.

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[27] N. F. Mott and H. Jones, *Properties of Metals and Alloys*, page 199.