

$M_{2,3}$ Emission Band of Copper*D. E. BEDO† AND D. H. TOMBOULIAN
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The copper $M_{2,3}$ band was investigated in connection with a sequential study of the $M_{2,3}$ emission and absorption spectra of the $3d$ transition metals. The characteristic band is superimposed on a continuous spectrum emitted by the target and the paper describes the procedure for removing the effect of this background. Other experimental considerations dealing with such effects as the instrumental window, self-absorption, the presence of contaminants, and the nature of the target layer are included. Where possible, an assessment is made of the distortion produced by such factors in the shape of the band. The photo-metrically determined $M_{2,3}$ intensity contour is compared with recent work based on detection schemes utilizing photon counters. On the basis of certain assumptions the composite $M_{2,3}$ distribution is decomposed into individual M_2 and M_3 curves, whose behavior at the high-energy end of the spectrum is in good agreement with previously available data on the individual absorption edges. Features of the $I(E)/\nu^2$ distribution belonging to the M_3 band are as follows: the band has a maximum at 72.0 eV (172 Å) and excluding satellite structure and tailing effects has a width of 7.8 eV. At the high-energy end, the intensity rises gradually and no sharp structures are noticeable. Except for the satellite structure, no inconsistencies arise when the results on the M_3 band (valence $\rightarrow 3p$) are compared with those on the L_3 band (valence $\rightarrow 2p$).

INTRODUCTION

RECENT experimental evidence¹ from x-ray and neutron diffraction studies and from the measurement of magnetic moments points towards a revised description of the electronic structure of the $3d$ transition metals. It was therefore considered worthwhile to examine the valence spectra of these metals in the light of these developments. A sequential study of the emission bands is now in progress and this paper presents the results on the $M_{2,3}$ emission spectrum of copper. Earlier measurements²⁻⁵ dealing with the valence band spectra of the iron group and neighboring metals have appeared in the literature.⁶

In emission, the L and M bands, which represent electronic transitions from the valence states to an inner p state, should exhibit similar characteristics and reveal the energy spread of the populated levels. In absorption, the measurements are primarily concerned with the photoelectric ejection of a $2p$ or $3p$ electron into a vacant state of the conduction band (L or M spectra), and are expected to yield information concerning the energy of the lowest empty state and other characteristics of the conduction band. The L bands of the metals in question fall in the 10- to 40-Å region while the M bands are observed at longer wavelengths, in the region extending from 150 to 400 Å. In both spectral regions, the instrumentation needed for dispersing and recording the

intensity of the radiation is not highly developed. This fact combined with other technical considerations has made it difficult to attain close correspondence between different sets of results.

To date two sets of measurements have been carried out on the $M_{2,3}$ band of copper. One determination is based on the work of Gyorgy and Harvey⁴ who utilized photomultiplier counting techniques to record the band shape by noting the time rate at which photons arrived at the detector. The second set of measurements are those of Skinner, Bullen, and Johnston³ who detected the radiation photographically and obtained relative intensities by photometric procedures.

The $M_{2,3}$ absorption spectra of the metals belonging to the $3d$ group have already been investigated.⁵ It is hoped that the current systematic examination of the corresponding emission spectra based on accurate photon energy scales will make it possible to discover the reason for existing inconsistencies.

EXPERIMENTAL

The measurements were carried out⁷ by the use of a grazing incidence vacuum spectrograph equipped with a glass grating (radius 1.5 m, 30 000 lines per inch). After outgassing, exposures were attempted only after the running pressures had dropped to the neighborhood of 1×10^{-6} mm of Hg while the power input to the copper target was 300 watts (200 ma at 1500 volts). A freshly deposited target layer was bombarded only for fifteen minutes in an attempt to insure freedom from deterioration. Exposure times of 6 hours were needed for a satisfactory photographic recording of the spectrum.

Unlike the case of Fe, Co, and Ni, no difficulties were

* Research supported in part by the Office of Ordnance Research, U. S. Army.

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¹ W. M. Lomer and W. Marshall, *Phil. Mag.* **3**, 185 (1958).

² Y. Cauchois, *Phil. Mag.* **44**, 173 (1953).

³ Skinner, Bullen, and Johnston, *Phil. Mag.* **45**, 1070 (1954).

⁴ E. M. Gyorgy and G. G. Harvey, *Phys. Rev.* **87**, 861 (1952); **93**, 365 (1954).

⁵ Tombouljian, Bedo, and Neupert, *J. Phys. Chem. Solids* **3**, 282 (1957).

⁶ Papers listed under 2-3 describe investigations on the L emission bands; those under 3-4 give results on the M bands. Reference 2 also contains data on L_2 and L_3 absorption spectra, while reference 5 deals primarily with the $M_{2,3}$ absorption bands.

⁷ For a description of the general procedures followed in soft x-ray emission spectroscopy see H. Niehrs, in *Ergebnisse der exakten Naturwissenschaften* (Springer-Verlag, Berlin, 1950), Vol. 23, p. 359, or the survey article by D. H. Tombouljian, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 30, p. 246.

encountered in depositing the emitting layer of copper by evaporation. Initially the metal was of highest purity and the target layer should have remained free from contamination except for trace impurities such as oxygen, nitrogen, mercury, water, and grease vapors, remaining in the tube. It is possible that the evaporated layer has a granular structure initially, but upon bombardment, structural changes favoring the formation of larger crystalline units should take place.

When the target is cooled, minute amounts of organic materials condense on the target faces not in use. Subsequently, under the action of the electron beam, such organic molecules are broken down. As a result, carbon is deposited on the target which under bombardment emits the K_α radiation (peak at 44.5 Å). The K_α line may appear in several orders and is likely to blend with the spectrum under study. In spite of many precautionary measures adopted to maintain cleanliness, the long exposures and relatively high voltages needed to excite the M bands enhance the appearance of the impurity band. The $M_{2,3}$ band of copper extends from 160 Å to about 190 Å. Thus there is a possibility that the long-wavelength portion of the copper band is distorted somewhat by the fourth order carbon line (178 Å) although records indicate no significant blending because of the weakness of the impurity line. The copper spectrograms were free from other impurity lines such as the K bands of oxygen and nitrogen (at 23.6 Å and 31.4 Å, respectively) and the L bands of sulfur and silicon. Such lines are occasionally observed during long exposures.

The characteristic copper band is superposed on a background consisting of the continuous x-rays emitted from the target. The background intensity observed at a given spectral position is composed of bremsstrahlung diffracted in the first or possibly higher orders⁸ and compares favorably with that of the $M_{2,3}$ band. The continuum shows an absorption structure which appears at 115 Å in the first order and 230 Å in the second order on all spectrograms taken with this spectrograph. This feature is presumed to be brought about by absorption of the incident continuous radiation in the material of the grating. The procedure adopted for removing the background intensity will be described subsequently.

EXCITATION OF THE COPPER M BANDS AND SELF-ABSORPTION IN THE TARGET

A few comments are now offered regarding the choice of incident electron energies used to excite the M bands of copper. The cross section σ_i for the ionization of an inner atomic level may be represented by $\sigma_i = f(E, E_q, n_q)$, where E is the energy of the bombarding electron at the time of interaction with a bound electron of the target atom, E_q is the threshold energy required to eject the bound electron from the particular shell q , and where

⁸ The background may also contain radiation of all wavelengths present in the source and scattered incoherently by the surface of the grating.

n_q denotes the density of electrons which have the binding energy E_q . For incident electrons of low energy (1 to 3 keV), no information is available concerning the functional form of σ_i . Relying on results deduced from atomic spectra⁹ or on the general form¹⁰ of the cross-section curve determined experimentally at higher incident electron energies (15 to 20 keV), we may expect σ_i to rise rapidly with the energy E , to attain a peak at an energy which is four to eight times the threshold energy E_q , and then to drop off gradually as the energy of the electron increases. In the case of copper, $EM_2 = 77.1$ eV, so that the optimum energy for M_2 ionization is expected to be around 450 eV. However the energy of bombarding electrons is dissipated as they penetrate the target and ionizing impacts take place at gradually diminishing values of the electron energy with the result that the efficiency of photon production varies with the depth. For 1- to 3-keV electrons, no retardation formula has been developed. However, an estimate of the penetration range of low-voltage electrons may be obtained by utilizing the observations of Davis¹¹ who, for protein molecules, has measured the "range" or that thickness which reduces the number of emergent electrons to zero. At $E = 1500$ eV, corresponding to the target voltage used in exciting the copper band, the electron range in protein is 460 Å. Considering the relative densities (8.94/1.30) of copper and protein matter, the range in copper is expected to be considerably smaller. Thus, at low energies, ionizing collisions are confined to a shallow depth of the target and the volume effective in producing photons is correspondingly small. When the electron energy is raised so as to enhance the penetration and increase the effective volume, σ_i attains its optimum value at greater depths, since near the surface $E \gg E_q$ and the value of σ_i is less than that at the peak.

Upon raising the target voltage, there results an increase in the electron range. Hence the radiation originating in the contaminated surface layers becomes relatively less consequential. This is a desirable feature since it insures that the bulk of the emitted radiation is typical of the material under study. But with an indefinite increase in the incident energy and the attendant increase in the penetration, more efficient excitation of the L levels and the possibility of self-absorption in the target assume importance. The threshold for L_2 ionization is at 955 eV and the value of σ_{L_2} is much less at 1500 volts than the optimum value requisite for L ionization, which value is presumably in the neighborhood of 6000 eV. With the bulk of the photon emission taking place at greater depths, self-absorption may no longer be negligible.¹² In the case of the valence band

⁹ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, Oxford, 1952).

¹⁰ A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. van Nostrand Company, Inc., New York, 1935), second edition.

¹¹ M. Davis, *Nature* **175**, 427 (1955).

¹² At energies higher than that of the emission edge, the continuum does not suffer from order overlap. Hence if the effects

its influence would be to distort the observed band shape at the short wavelength region.

Advisedly the comments regarding electron interactions have dealt only with one process which results in depopulation of states and gives rise to the production of the characteristic spectrum. Other primary processes involve collisions with electrons and nuclei resulting in bremsstrahlung and secondary electron emission.

TREATMENT OF OBSERVATIONS

To arrive at the intensity distribution of the characteristic valence band alone, the observed composite intensity curve, as obtained from the spectrogram by the application of photometric procedures, must be corrected for several effects. In principle these include the following effects:

1. The modification of the source distribution brought about by the spectral window of the dispersing instrument. Information regarding the instrumental window was obtained by measuring the half-widths of isolated atomic lines as found on the comparison spark spectrum. Over the range of photon energies covered by the band, the observed line widths varied from 0.12 eV to at the low-energy end to 0.20 at the high-energy limit of the band. This means that it will not be possible to resolve structures spaced more closely than about 0.15 eV and that abrupt intensity changes in the emitted spectrum will appear to possess finite widths of about the same amount. In view of the narrowness of the spectral transmission curve, it was not considered worthwhile to carry out a formal "unfolding" operation.

2. The effect of self-absorption of the characteristic and continuous radiation in the anode. All photons generated within the target are subject to absorption by valence electrons. In addition, in copper, the M_2 emission band straddles the M_3 absorption discontinuity. Hence, photons whose energy is in excess of the binding energy of the M_3 state will be subject to the extra absorption by $3p_{3/2}$ electrons. An estimate of the attenuation expected was presented in reference 12. The over-all distortion, if significant, is such that the recorded intensity is relatively too low at the high-energy side of the M_3 emission edge.

of self-absorption are serious, the intensity distribution of the continuum should be modified as the radiation passes through the target layers. From independent measurements⁵ of the absorption coefficient μ on the high-energy side of the edge, it is expected that such a modification might have been noticed as a series of dips at $\lambda=147$ Å, 138 Å, 131 Å, etc., corresponding to positions of maxima observed in the secondary absorption structure. No evidence of this kind could be located in the observations. Now, the changes in μ associated with the structures referred to are about half as large as the jump in μ at the main edge. The effect of fine-structure fluctuations is not detectable within the sensitivity of our measurements. The self-absorption associated with the characteristic band at the M_2 edge is expected to be of comparable magnitude and hence may be regarded as insignificant. This consideration ignores the influence of a possible difference in the effective depths at which the characteristic and the continuous radiation are produced.

3. The distortion of the emission band produced by the underlying continuum and by satellite and impurity lines. Studies of the spectral distribution of the x-ray continuum have not been carried out in the 100-Å region. Investigations by Stephenson and Mason¹³ seem to indicate that in the 10-Å region, the spectral distribution $I(\lambda)$ for 1.4- to 1.6-keV electrons resembles the shape assumed to be valid for thin targets, i.e., $I(\lambda) \propto 1/\lambda^2$, for wavelengths λ far removed from λ_0 , the Duane-Hunt limit. In the present experiment the bombarding voltage was 1.5 keV and, in the region of the copper M band (edge at 164 Å), one might expect to find the $1/\lambda^2$ dependence since for this voltage $\lambda_0=8.26$ Å.

Actually the situation is more complex. There is evidence that the response of the grazing incidence instrument is such that wavelengths shorter than 40 Å are not diffracted with appreciable intensity. Then, the observed background underlying the copper $M_{2,3}$ bands, will contain contributions from radiations appearing in

TABLE I. Values of the relative intensity distribution as a function of the wavelength of the emitted radiation and the associated energy distribution (divided by the square of the radiated frequency). The energy in eV of the emitted photon was obtained from $E=12397.43/\lambda$, with λ in Å.

| λ (Å) | $I(\lambda)$ | E (eV) | $I(E)/\nu^2$ |
|---------------|--------------|----------|--------------|
| 196.0 | 0.95 | 63.25 | 2.31 |
| 194.0 | 1.90 | 63.90 | 4.45 |
| 192.0 | 2.87 | 64.57 | 6.42 |
| 190.0 | 3.84 | 65.25 | 8.23 |
| 188.0 | 5.30 | 65.94 | 9.88 |
| 186.0 | 6.28 | 66.65 | 12.4 |
| 184.0 | 7.78 | 67.38 | 14.7 |
| 183.0 | 10.2 | 67.74 | 18.8 |
| 182.0 | 13.7 | 68.12 | 24.7 |
| 181.0 | 15.6 | 68.49 | 27.7 |
| 180.0 | 22.5 | 68.87 | 39.0 |
| 179.0 | 26.0 | 69.26 | 44.1 |
| 178.0 | 32.5 | 69.65 | 53.5 |
| 177.0 | 40.9 | 70.04 | 65.7 |
| 175.0 | 53.9 | 70.84 | 82.7 |
| 174.0 | 59.6 | 71.25 | 89.3 |
| 173.0 | 65.2 | 71.66 | 95.5 |
| 172.0 | 69.8 | 72.08 | 100.0 |
| 171.0 | 67.4 | 72.50 | 94.4 |
| 170.0 | 65.5 | 72.93 | 90.1 |
| 169.0 | 61.2 | 73.36 | 81.4 |
| 168.0 | 56.8 | 73.79 | 74.3 |
| 167.0 | 44.3 | 74.24 | 56.6 |
| 165.0 | 32.4 | 75.14 | 39.4 |
| 164.0 | 27.9 | 75.59 | 33.3 |
| 163.0 | 19.8 | 76.06 | 22.9 |
| 161.0 | 13.3 | 77.00 | 14.5 |
| 160.0 | 11.8 | 77.48 | 12.6 |
| 159.0 | 12.3 | 77.97 | 12.8 |
| 158.0 | 14.4 | 78.46 | 14.5 |
| 157.0 | 15.0 | 78.96 | 14.6 |
| 156.0 | 15.5 | 79.47 | 14.9 |
| 155.0 | 15.0 | 79.98 | 14.2 |
| 154.0 | 10.4 | 80.50 | 9.50 |
| 152.0 | 5.22 | 81.56 | 4.54 |
| 151.0 | 4.19 | 82.10 | 3.56 |
| 149.0 | 4.74 | 83.20 | 3.80 |
| 148.0 | 5.28 | 83.77 | 4.15 |
| 147.0 | 0.0 | 84.34 | 0.0 |

¹³ S. T. Stephenson and F. D. Mason, Phys. Rev. **75**, 1711 (1949).

the first, and possibly in the second order. If the wavelength response of the grating and detector is known and if the $1/\lambda^2$ dependence is taken as valid, then one may predict the expected shape of the continuous spectrum as contaminated by order overlap. One may then remove from the observed spectrum the background calculated on this basis. The almost hopeless procedure contemplated above for the evaluation of the continuum becomes even less feasible when it is recalled that the continuous radiation is further modified by absorption in the grating surface and by distortions arising from impurity bands.

In the absence of detailed knowledge concerning the over-all instrumental response and the law governing the bremsstrahlung intensity, we resorted to the following procedure for sorting out the continuum. Exposures of the continuum were obtained with two neighboring elements (Cr and Mn) as target metals. In making these exposures, the target potential and current were kept at the standardized values of 1500 volts and 200 ma.

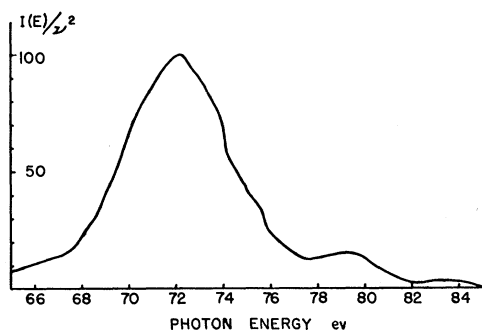


FIG. 1. The $M_{2,3}$ emission band of copper. The ordinate represents the relative energy distribution divided by the square of the radiated frequency.

In such runs λ_0 is the same; furthermore the strictly continuous distributions should have the same shape, the absolute intensity in each case being governed by the atomic number and exposure time. Therefore, such a scheme should make it possible to differentiate between features which are associated with the instrument and those which are characteristic of the particular target metal. The characteristic M_3 emission edges of Cr and Mn lie at 295 Å and 260 Å. Hence the continuous radiation from Cr and Mn was suitable in revealing the behavior of the background at the shorter wavelength region covered by the copper band. After ignoring obvious characteristic features, the intensity of the background in the spectrum of Cr was compared with that of the Mn spectrum at a large number of corresponding wavelengths. This comparison yielded a consistent intensity ratio. The observed shape of the background as deduced from the Cr and Mn runs was matched with the continuum belonging to the Cu spectrum on the short-wavelength side of the Cu $M_{2,3}$ band. The empirically established continuum was then extended to longer

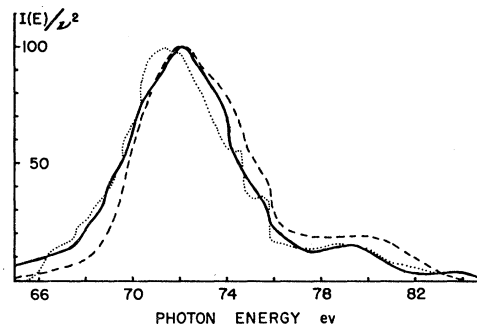


FIG. 2. A comparison of the existing measurements on the $M_{2,3}$ band of copper. Present data are represented by the solid curve. Earlier results of Gyorgy and Harvey and those of Skinner *et al.* are indicated by the dotted and dashed curves, respectively.

wavelengths and was made use of in removing the background from the composite Cu spectrum.

RESULTS AND DISCUSSION

After removal of the background intensity, the measurements on the composite $M_{2,3}$ band were transformed so as to obtain the quantity¹⁴ $I(E)/\nu^2$ as a function of E , the energy of the emitted photon. The numerical data are given in Table I and a plot of the results is shown in Fig. 1. The spectral distribution represents a superposition of individual M_2 and M_3 emission bands. The peak of the composite spectrum falls at 72.1 eV. A low-energy tail in the region below 67 eV and a high-energy satellite at 79 eV are observable. The intensity drops gradually near the high-energy limit of the band. Certain other characteristic features will be mentioned when the curve in Fig. 1 is resolved into components.

The copper $M_{2,3}$ band has been examined by Gyorgy and Harvey⁴ who recorded rates of photon emission from a target on which the metal was deposited continuously and bombarded by 700-volt electrons with a beam current of 3 ma. A photometric determination of the band was also carried out by Skinner *et al.*³ under conditions approximating those found in the present experiment. The measurements just alluded to were presented in graphical form. Hence it was necessary to transcribe them and make the appropriate conversions for comparison with the results of the present experiment. As shown by the curves in Fig. 2, there is a certain over-all correspondence in the band shapes as described by the three sets of measurements. It has already been indicated that distortions in the observed shape of a band may arise from such factors as the presence of impurities, contamination during exposure, the underlying background, self-absorption, and other instrumental effects. It is gratifying that measurements carried out with dissimilar instrumentation and under

¹⁴ The quantity $I(E)/\nu^2$, which represents the spectral distribution divided by the square of the radiated frequency, is proportional to the product of the density of states function $N(E)$ and an average value of $|M_{ik}|^2$, the square of the matrix element between a bound state i and a valence state k .

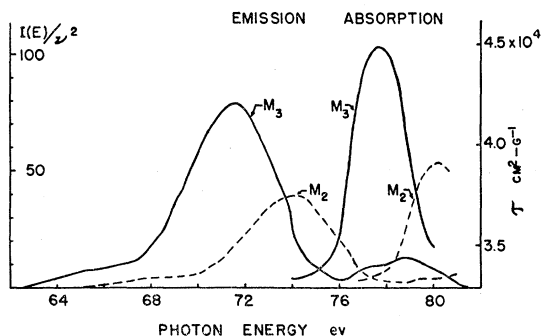


FIG. 3. The solid curves show the individual M_3 emission and absorption spectra of copper. Corresponding data for the M_2 spectra are shown by the dashed curves.

different experimental conditions agree to this extent with regard to such features as the band width, position of the peak, and satellites.

However, there are several differences. The curve obtained by the photon-counting techniques shows a sudden rise toward the peak and the peak itself is displaced towards lower energy relative to the peak of the other two curves. Over the high-energy region of this curve there appear two sharp intensity drops which have been identified as M_3 and M_2 edges. The drop located at 74.7 eV is not reproduced by the photometric measurements, but that at 75.8 eV seems to find its counterpart in both of the other curves, though the corresponding intensity changes are less abrupt. We have no information regarding the width of the instrumental window used in the course of the photomultiplier recordings, but one would normally expect that because of the finite width of the instrumental window, a somewhat greater width should be associated with the observed structures. It is not clear just why the intensity seems to rise to the peak prematurely while approaching the peak from the low-energy side.

More recently, Fisher, Crisp, and Williams¹⁵ have repeated the measurements on the copper $M_{2,3}$ band using the photomultiplier detection scheme. The shape of the band as determined by these experimenters is in agreement with our results and does not reveal the sharp structures present in the dotted curve of Fig. 2. We may therefore conclude that the discrepancies concerning the structure of this important spectrum may now be regarded as resolved.

The observed differences between the $I(E)/\nu^2$ plots deduced from photographic photometry may have come about from the process followed for removing the background. The experimentally determined shape of the characteristic band is sensitive to this correction.

The measured $M_{2,3}$ intensity complex appearing in Fig. 1 may be decomposed into individual M_2 and M_3 emission bands if one knows the magnitude of the (M_2-M_3) energy separation and the intensity ratio between the two bands. Evidence presented in connec-

¹⁵ Fisher, Crisp, and Williams (private communication).

tion with absorption studies of the $3d$ metals,⁵ leads us to select the value of 2.5 eV for the M_2-M_3 interval. For the intensity ratio we take the value of 2 as predicted on the basis of statistical weights of the levels concerned.¹⁶ Assuming that the observed composite curve is free from overlap over a 2.5-eV interval at the low-energy end, one can construct the initial portion of the M_2 emission band taking into account the assumed intensity ratio. By subtracting the portion of the M_2 curve from the resultant, it becomes possible to extend the M_3 curve which extension may in turn be used to lengthen the M_2 curve. The curves shown in Fig. 3 were constructed in this manner from the experimentally determined curve. It is realized that such a resolution is not sensitive to small changes in the value of the (M_2-M_3) interval and to the intensity ratio. On the other hand, unrealistic results are obtained if the inner level interval is raised to 3.0 eV or if the intensity ratio is increased to 4.

The characteristic band may be isolated approximately from the effect of the low-energy tail and the satellite structure by extrapolating the curve until it meets the energy axis. On this basis the M_3 and M_2 emission edges are located at 74.9 eV and 77.4 eV, respectively, and the band width is 7.8 eV.

The energy dependence of the mass absorption coefficient of thin copper foils in the region of the $M_{2,3}$ edge is also plotted in Fig. 3. The individual absorption curves were arrived at by a procedure identical to the one used in decomposing the composite emission curve. The absorption experiments were carried out with the same instrumentation and with the same energy calibration as used in the emission measurements. It is seen that the onset of the absorption at 74.4 eV agrees very well with the M_3 emission edge at 74.6 eV. Similar consistency is found in the case of the M_2 emission and absorption edges. Nilsson¹⁷ has calculated the position of the $M_{2,3}$ absorption edge from precise measurements of the K excitation potential. His result is 75.8 eV and compares favorably with the mean edge energy of 76.3 eV as determined from absorption data.⁵

The shape of the M_3 band should resemble that of the L_3 band (valence $\rightarrow L_3$). Emission studies on the L bands have been carried out by many investigators as indicated in the references cited by van den Berg.¹⁸ For comparison (see Fig. 4), we have chosen the L_3 emission profile (for 6600-eV electrons) as determined by van den Berg using a cylindrical crystal spectrometer and photon counter techniques. (The ordinates of the L_3 curve are not divided by ν^2 , which correction would alter the shape of the curve somewhat.) The bands are similar in width and shape and the inflections and satellites appearing in the M_3 band are also present in the L_3 band.

¹⁶ Actually because of the greater relative de-ionization of the M_2 level by an Auger process, the value of 2 adopted here for the M_3/M_2 intensity ratio may be somewhat low.

¹⁷ A. Nilsson, Arkiv. Fysik 6, 514 (1953).

¹⁸ C. B. van den Berg, thesis, Groningen, 1957 (unpublished).

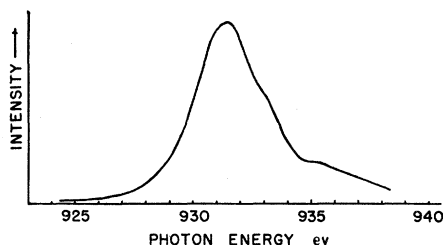


FIG. 4. The intensity contour of the L_3 emission spectrum of copper after van den Berg.

Data on the $K\beta_5$ line of copper corresponding to the nondipole valence $\rightarrow K$ transition $[(3d+4s) \rightarrow 1s]$ has been presented by Beeman and Friedman.¹⁹ The K emission band has a width of about 8 eV at half-maximum. The K and M bands cannot be compared directly, mainly because of differences in transition probabilities and in the widths of the inner states. However, except for possible effects arising from the admixture of p states in the valence band, the energy spread of the K band should be of the same order as that of the M bands, since in both cases transitions originate from initial states having $3d$ and $4s$ character. The K band seems to be wider, in harmony with the expectation that there may be dipole transitions ($4p \rightarrow 1s$) from populated valence states having p character.

Various attempts have been made to calculate the band width and the density of states of copper using the cellular method. The main features of Krutter's²⁰ early calculations were reproduced somewhat later by Rudberg and Slater²¹ and by Tibbs.²² More recently, Howarth²³ has re-examined the band structure of copper. These studies predict a split-up $3d$ band of high level density and an underlying $4s$ band of greater width but much smaller level density. Howarth's results indicate that the $3d$ band has a width of 3.5 eV and that the top of the band lies 3.7 eV below the Fermi level. These deductions prescribe a width of 7.2 eV for the populated levels. Earlier work²¹ yielded widths of approximately 5.5 eV and 9.5 eV, respectively, for the $3d$ and $4s$ bands. The present experimental observations suggest a width of 7.8 eV for the individual M_2 or M_3 bands, but again there is no indication of a split in the observed band. The kink at 74 eV may signal the end of the transitions from the $3d$ band. Beyond this energy, we may assume the emission to originate from states having a mixed $4s$ and $4p$ character of much lower density. The lack of sharpness at the high-energy end is in part brought about by the blurring effect of the $3p$ level. In a round-about manner the spreading due to this cause is estimated⁵ to be of the order of a few tenths of an eV. (Nilsson¹⁷ quotes the values 0.9 and 1.3 eV for the widths

of the L_3 and K levels, respectively; the M_3 is expected to be narrower.)

We have seen how trace impurities, the unavoidable bremsstrahlung, and possibly self-absorption may play a part in distorting the observations. There are other circumstances which may lead to other inherent differences in the spectral distribution emitted at the source. In the actual observation, the target layer is an agglomerate of crystallites which because of size and internal deformations does not meet the conditions postulated in theoretical models. Even if each crystal domain represents a periodic arrangement of sufficiently large dimensions, the energy band structure of the surface layer will not be the same as that of the bulk material.

It is also necessary to assess the effect of the incident electrons which hasten or hinder the formation of contaminants during exposure, alter the structure of the deposited layer, and raise its temperature. Such a rise causes an increase of the lattice constant and in the mean amplitude of the thermal vibrations. As pointed out by van den Berg,¹⁸ an increase in the mean amplitude brings about a statistical variation in the hybridization of the $4s$ and $4p$ bands with a net effect resulting in a weaker binding of $3d$ electrons and a shifting of the emission peak towards higher energies. The broadening resulting from fluctuations in the interatomic distances predominates over the narrowing of the band expected on the basis of an increase in the mean interatomic distance. In the case of the copper L_3 band, measurements of the half-width and the peak wavelength position confirm the changes predicted.

Measurements on the L_3 spectrum by van den Berg suggest a correspondence between the positions of secondary maxima in emission and the positions of the peaks in the fine structure in absorption. It is likely that most of the incident electrons lose their energy gradually by giving rise to interband transitions which transfer electrons into normally unoccupied levels. The coincidence between secondary structures mentioned above might lead one to believe that in emission, such structures or "satellites", are associated with radiative transitions from valence levels which become populated by virtue of cathode-ray bombardment. This view implies that a number of copper atoms may possess the $3d^9$ configuration instead of the normal $3d^{10}$ structure. An additional observation seems to fit in with the model. This concerns the broadening and the shifting of the L_3 band with an increase in the energy of the bombarding electrons. If the energy of the latter is only slightly greater than the energy requisite for L ionization, there will be a high probability that, when an L vacancy is created in a copper ion already having the $3d^9$ configuration, such an ion will revert to the normal $3d^{10}$. In this circumstance the L emission band will be characteristic of an atom in which the $3d$ shell is complete. However, with an increase in the energy of the incident electrons, the emission will increasingly become characteristic of

¹⁹ W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).

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ions which possess the $3d^9$ configuration; that is, the band will become wider and its peak will shift toward higher frequencies. Hence, when the energy of the incident electrons is high, the observed band will reflect the combined emission from $3d^9$ and $3d^{10}$ configurations.

Similar effects might be expected in the case of the M_2 or M_3 band. Our study of the M bands shows one "satellite" peak whose spectral position cannot be correlated with a peak in the secondary structure of the M_3 absorption curve for which reliable measurements are available. In the present experiment it was not convenient to study the possible variation in the shape of the M_3 band as a function of the incident electron energy; so that we cannot state whether the effect noted in the case of the L_3 band is also present in the M_3 band.

Under our experimental conditions, a calculation indicates there are about 60 incident electrons for every copper atom located in the volume effective in the production of photons. Unquestionably, "holes" are created by the incident electrons in the filled states of the valence band, but the equilibrium concentration of such vacancies depends not only on high production rates but also on the rate at which vacancies disappear. Owing to the highly mixed character of the valence states, it would be naive to expect that the lifetime of a $3d$ hole is long, though on the basis of atomic selection rules alone, such an expectation may be regarded as reasonable since the l value of a $4s$ electron must change by two units to bring about the contemplated $4s \rightarrow 3d$ transition.

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X-Ray K -Absorption Spectra of Solid Argon and Krypton*

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The x-ray K -absorption edge structures of argon (at 3.86 Å) and of krypton (at 0.86 Å) have been measured in the gaseous and solid states. The spectra of the gases confirm previous work. The spectra of the solids exhibit pronounced structure extending far to the short-wavelength side of the absorption edge. The broad absorption maxima observed can be correlated with the valence bands in the crystal, but the extremely sharp initial rise requires an unusual density of states in the bands, perhaps offering evidence for the existence of excitation states.

IN the region of an absorption edge, the x-ray absorption spectrum of a given element in the solid state is inherently different from that of the same element in the gaseous state. The difference arises from the perturbation of the outer (unfilled) electronic states in the solid by the fields of neighboring atoms. The discrete atomic levels of the isolated atom are replaced by broad bands, overlapping one another and extending several hundred electron volts toward higher energies. Kronig¹ was able to explain the rather faint structure in the spectrum well to the high-energy side of the edge by considering the scattering of the de Broglie waves of the ejected electron by the absorbing crystal. Observed spectra agree well with his theory, especially for energies greater than some 30 electron volts from the edge. Such intensity structure is characteristic of the crystal structure of the absorber, rather than of the particular element of which it is composed. For energies near the absorption edge, on the other hand, one might expect that the spectrum would reveal the density of states in the conduction bands. It is the purpose of the

work reported here to examine the absorption edge structure of gaseous and solid argon and of gaseous and solid krypton to gather some information on the influence of the crystal lattice on the electronic states and transition probabilities of these atoms.

The absorption spectra were obtained with a two-crystal vacuum x-ray spectrometer fitted with a cryostat for maintaining the absorption cell at low temperature.

The source of continuous radiation for the argon experiment was a gold-plated copper-target x-ray tube operated at 8.8 kv and 40 ma. The electron gun cathode arrangement permitted independent stabilization of voltage and current to within a few tenths of 1%. The target focal spot was about 3 mm in diameter.

Calcite crystals were used after preliminary experiments indicated that reflection of the continuous x-ray

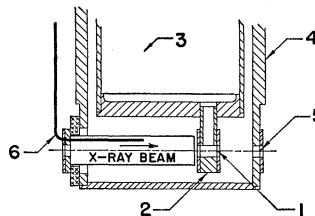


FIG. 1. Section through the low-temperature absorption cell.

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