

Effect of Chemical Combination on the X-ray Spectra of Copper.

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[PLATE 13.]

The effect of the chemical combination of an element upon its emission and absorption spectra has been the subject of many investigations by different authors.* The results lead to the conclusion that the X-ray spectrum of an element is not a purely atomic phenomenon; it varies according to the state of chemical combination of the element. The effect appears to be more marked, and therefore more easily investigated, in the absorption than in the emission spectrum. Both spectra have, however, been examined and the effect in the K series measured for a number of the lighter elements from phosphorus to potassium; more recently the work has been extended to heavier elements such as iron.

The present investigation deals with the K series spectra of copper, and was undertaken mainly with a view to obtaining, if possible, further information as to the nature of the chemical bond existing between elements in inter-metallic compounds.

It is generally accepted that the metallic elements are able to form compounds among themselves and many such compounds have been found to exist in alloy systems. Their existence is deduced from the form of equilibrium diagrams constructed from thermal, microscopic and other data. Further evidence is gained from a study of the physical properties of alloys, including density, hardness, thermal and electrical conductivity and magnetic susceptibility. When there is no compound present in an alloy series, the physical properties of the alloys vary continuously, but the occurrence of discontinuities indicates, in general, the formation of a compound.

Investigations carried out on inorganic compounds show that valency is an important factor in determining the displacement of the lines in the emission X-ray spectrum or the edge in the absorption spectrum of an element; and one striking feature of intermetallic compounds is that they do not fall in with

* See Siegbahn's "Spectroscopy of X-rays," and later papers by Siegbahn and his colleagues.

the generally accepted rules of valency. It would appear, therefore, that an investigation of the emission and absorption spectra of an element entering into a series of intermetallic compounds might lead to useful information regarding the nature of these compounds.

The first part of the work included measurements on the $K \alpha_1 \alpha_2$ doublet in the emission spectrum of copper in a number of intermetallic compounds, solid solutions and the two oxides of copper. The second part of the work was devoted to the study of the edges of absorption bands in several inorganic compounds and in a few typical intermetallic compounds and solid solutions of copper.

Emission Spectra.

In the investigation of the position of the $K \alpha_1 \alpha_2$ doublet of copper in various compounds, attention was paid not only to the actual position of the doublet but to the separation of the lines, since previous investigations have shown that in addition to the shift of lines in the spectrum, there may be observed a contraction or a resolution of a doublet.

The apparatus employed in the investigation consisted of a porcelain Shearer tube* operated by a Schall transformer capable of a continuous output of 30 m.a. at 100 K.V. The Muller camera used had been carefully calibrated although the method adopted in the actual measurements, as will be seen later, was, more or less, independent of the calibration. But owing to the fact that the method depended for its accuracy on the exact replacement of one target by another in the tube, it was important to know that the special targets made for the purpose of the experiment yielded results which were reliable. As a first step, it was therefore decided to examine the spectrum of an element—tantalum was actually chosen—which had been mounted on the target in the manner it was proposed to adopt with the compounds under investigation. If this experiment yielded results which satisfactorily corroborated well-established data obtained by other observers, the photographs taken in the actual experiment could be relied upon to supply accurate information.

The (111) face of a well-formed carborundum crystal, which had been previously used for the determination of wave-lengths, was set up as reflector.

Several attempts were made at constructing a suitable target to investigate the K lines of tantalum. The body of the target was of copper. As tantalum will not solder, other means of fixing it to the target had to be sought. In the first attempt a recess was made in the face of the target and the tantalum sheet

* See Owen and Preston, 'J. Sci. Instr.,' vol. 4, p. 1 (1926).

inserted and kept in position by burring over the edge of the recess. The exciting potential for the K series spectrum of tantalum is about 67 K.V. When the tube was operated at this voltage excessive local heating took place causing the thin sheet of tantalum—the only specimen of the material available—to crumble and fall off the target; this caused the evolution of gas and an unsteady discharge, with the result that the tube was rendered useless for the purpose.

In the second method a number of holes were made with a hard point in the face of the copper target so that it resembled a rasp. Small pieces of the metal were then inserted in the holes and secured in position by hammering down the irregularities until the surface was again even. This was an improvement on the previous method, but still the tube was unsteady and became excessively hot when operated at the required voltage. The K spectral lines could be obtained, but they were too indistinct for accurate measurement. Attention was therefore diverted to the L series lines which should appear at an operating voltage of about 50 K.V. With a current of 10 to 12 m.a. at this voltage, the L series lines could readily be obtained, an exposure of about 20 minutes being sufficient for the purpose. The K series lines of copper were also registered on the plate; these were used as reference lines, and their wave-lengths were assumed to have the following values:—

$$\alpha_2 = 1541.2; \quad \alpha_1 = 1537.4; \quad \beta_1 = 1389.3 \text{ X.U.}$$

Taking the distance between the planes parallel to the (111) face of carborundum to be 2.49 \AA ., the results shown in Table I were obtained, x being the distance from the line to the centre of the plate. The mean distance of the crystal to the plate, calculated from the position of the K series copper lines and a knowledge of their wave-lengths, was 3.863 cm .

Table I.

x .	θ .			λ .	λ (Siegbahn).	Line.
cm.	°	'	"	X.U.	X.U.	
2.782	17	52	52	1529.1	1529.4	Ta. La_2
2.755	17	45	3	1518.3	1518.25	Ta. La_1
2.628	17	6	53	1465.6	1465.5	Ta. $L\eta$
2.346	15	38	21	1342.5	1342.2	Ta. $L\beta_4$
2.305	15	24	47	1323.6	1323.54	Ta. $L\beta_1$
2.262	15	10	34	1303.7	1303.3	Ta. $L\beta_3$
2.213	14	54	21	1281.1	1281.0	Ta. $L\beta_2$

Siegbahn's values of the wave-lengths are included in the table for comparison; the agreement between the two sets of figures shows that the above method of mounting the material on the target is capable of yielding accurate results, so that there is no reason to doubt that if a flat plate of the material were soldered on the target equally reliable results would be obtained.

A separate target body, made of iron, was constructed for each specimen of intermetallic compound and solid solution, so that once mounted the specimen could be used over and over again for checking purposes. In every case a thin sheet of the material, 1 mm. thick, was prepared; as in most cases the alloys were very hard and brittle, some difficulty was experienced in producing suitable sheets. To fix the material on the target, a groove about 1 mm. deep, with two undercut edges, was machined across the face and filled with solder. A plate of the material cut to size and shape, was introduced into the groove while the solder was hot, and when cold was ground down to the general level of the iron on both sides of the groove. To ensure efficient cooling the soldering process was carefully carried out; in some instances, a hole was, by accident, made right through the target in cutting the groove, in which case the water cooling of the target was as effective as it possibly could be. Care was taken that the face of each target inserted in the tube took up the same position relative to the window. The target was suitably marked to enable this to be done.

To secure an accurate comparison between the $K\alpha$ lines from pure copper and from copper in the materials under examination, it was arranged for both spectra to be registered on the same film. This was done in the following manner. The upper half of the film was covered with lead sheet about 1 mm. thick, and the $K\alpha$ doublet from a copper target photographed on the lower half. The upper half of the film was uncovered and lead sheet placed over the already exposed lower half. A photograph of the doublet from the material mounted on an iron target was then taken on the upper half of the film. This procedure justified the use of films for this part of the work.

The doublet was photographed in the third order spectrum from the (111) face of carborundum, the angle of reflection of the $K\alpha_1$ line in this spectrum being approximately $67^\circ 48'$. The crystal was set at this angle and rotated through about 2.5° on either side of the setting. With all the materials examined, lines of sufficient intensity for accurate measurement were obtained with an exposure of from 5 to 10 minutes at 40 K.V. and 10 m.a. When longer exposures were made, fogging of the plates occurred owing to stray radiation, and the lines became broadened and ill-defined and were difficult

to measure with accuracy. The fogging was also as marked when aluminium was substituted for the lead shield covering half the film. For these reasons all the exposures were made as short as possible.

The width of slit was 0.6 mm. The lines which appeared in the spectra were very fine (see fig. 1, Plate 13), and the position of each could be measured to within 0.02 mm. The distance between the lines of the doublet in the third order was 0.35 mm., which corresponded to a difference of about 23' in angle of reflection, since $\theta K\alpha_1 = 68^\circ 48'$ and $\theta K\alpha_2 = 68^\circ 11'$. The wave-length difference of the doublet taking the values given in Siegbahn's 'Spectroscopy of X-rays' is 3.86 X.U. Hence a difference of 0.01 mm. in the position of a line in this region of the plate is equivalent to a wave-length difference of about 0.15 X.U.

Two or three photographs of the $\text{CuK}\alpha$ lines from each intermetallic compound and alloy were taken and each was measured in two different settings, so that each final result is the mean of eight to twelve measurements. The distance between the $\text{K}\alpha$ lines emitted from the copper target and that between the $\text{K}\alpha$ lines from the material were measured and the corresponding wave-lengths calculated. The separation of the doublet was also measured on both sides of the centre of the film for each spectrum, thus each film when measured in three different positions gave twelve distinct readings for the width of the doublet.

The summary of the results obtained are included in Table II.

Table II.

Material.	Wave-length of $\text{CuK}\alpha_1$.		Δs (separation of $\alpha_1\alpha_2$ lines).	
	From Cu.	From material.	From Cu.	From material.
	X.U.	X.U.	mm.	mm.
* Cu_3As	1537.1	1536.9	0.34 ₇	0.35 ₁
Cu_3Sn	1537.0	1537.3	0.35 ₁	0.34 ₇
Cu_2Sb	1537.5	1537.4	0.34 ₈	0.34 ₆
CuSn	1537.2	1537.4	0.34 ₆	0.34 ₃
† Cu_3P	1537.5	1537.3	0.34 ₉	0.34 ₇
$\text{CuZn } (\alpha + \beta)$	1537.5	1537.4	0.34 ₅	0.35 ₀
‡ $\text{CuZn } (\epsilon)$	1537.2	1537.1	0.34 ₀	0.34 ₃
Mean	1537.3	1537.2	0.34 ₇	0.34 ₇

* Very brittle and found to fracture under the action of the cathode beam, thus causing the tube to become unsteady.

† Particularly brittle, small pieces of the material freely driven from target.

‡ Resembled colour of zinc, but after exposure in the tube for about 10 minutes its colour resembled that of the $\text{CuZn } \alpha$ phase.

All the materials investigated show but slight changes in the wave-length of the $\text{CuK}\alpha_1$ line, changes which are within experimental error, so that it may be definitely concluded that there is no change in the wave-length of the $\text{K}\alpha_1$ line of copper when the copper atom is present in the above materials. Likewise the variations in the width of the $\text{CuK}\alpha_1\alpha_2$ doublet are so small that they may be put down to experimental error.

The two oxides of copper were subsequently studied. These were ground into fine powder and pressed well into scratches or small holes made on the face of an iron target. Every effort was made to get the powder into good contact with the target so as to avoid local heating and consequent decomposition. With each of the compounds definite indication was obtained, however, that the oxide had been reduced to the metallic state during the exposure. This was the case, particularly with cuprous oxide, after short exposures of a few minutes. Ten photographs of each compound were taken with varying times of exposure, the cooling of the target being as vigorous as possible in each case. No photograph showed any broadening of the lines which seems to indicate that decomposition of the powder took place rapidly. The following results are the mean obtained from the 10 films taken with each compound.

Table III.

Material.	Wave-length of $\text{CuK}\alpha_1$.		Δs .	
	From Cu.	From material.	From Cu.	From material.
	X.U.	X.U.	mm.	mm.
CuO	1537·5	1537·2	0·34 ₉	0·34 ₉
Cu_2O	1537·1	1536·9	0·34 ₄	0·34 ₅

There is no definite change in the wave-length corresponding to the copper line in these photographs. It is likely that any change that may occur is masked by the decomposition that takes place. A more definite statement can be made, however, regarding this after the absorption edges have been investigated; in the latter case no discrepancies due to decomposition of the material examined are likely to arise.

Absorption Spectra.

Preparation of the Absorbing Screens.—In obtaining the absorption spectrum of electrolytic copper the absorption screen was a piece of thin foil weighing

0.0073 gms. per square centimetre. It had been found in the laboratory that there was no difference in the observed parameter of copper whether it was examined in foil or in powder form.

The other materials investigated were reduced to fine powder if they were not already in that form. Fine filings of the intermetallic compounds were usually produced and these were subsequently powdered further in a mortar. The powder was thoroughly mixed with a solution of celluloid in amyl acetate and the resulting preparation poured on to a glass plate and allowed to dry. The film thus formed was removed from the glass with a razor blade. By varying the amount of powder used, and controlling the area covered by the mixture, screens of any desired density could be made in this way.

There is an optimum thickness of screen which gives the best contrast on the photographic plate. If μ_1 and μ_2 are the absorption coefficients just above and just below the absorption edge respectively, the optimum thickness is given by $(\log \mu_2 - \log \mu_1)/(\mu_2 - \mu_1)$. It is, however, essential that the absorbing screen should be uniform, otherwise it is difficult to obtain a well-defined edge; for it is clear that a screen, the average thickness of which agrees with the value of the optimum thickness deduced from the above expression, but which has some parts thick and other parts with little or no absorbing material, will not give a good edge, because the radiation is directly transmitted through those parts where there is little or no absorber, and this will tend to mask the edge produced by the thicker parts of the screen. Thus the best screen for the purpose depends on uniformity rather than on average density.

The screens were placed on the slit block system on the side nearer the window of the X-ray tube. When the screens were placed between the slit and the reflecting crystal, secondary radiation emitted by the screen caused undue blackening of the plate.

For the production of "white" radiation, the X-ray tube was fitted with an iron target, into a recess on the surface of which a disc of platinum was soldered.

To obtain a good absorption edge, the maximum of the curve showing the relation between the intensity and the wave-length of the radiation emitted by the tube should be at the wave-length corresponding to that of the absorption edge sought. For the copper K edge the maximum should correspond to the wave-length 1378 X.U., so that the limiting wave-length should be about 1034 X.U. which corresponds to a voltage of 12 K.V.

All the photographs of the CuK absorption edge were taken with a voltage a little over 12 K.V. applied to the tube. The tube seems well suited for this

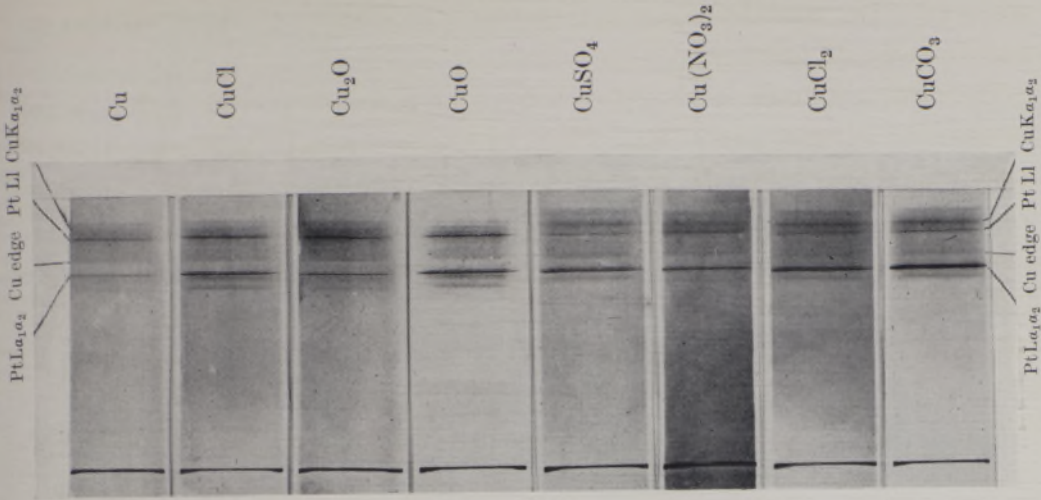


FIG. 3.—The copper K absorption edge in various inorganic copper compounds.

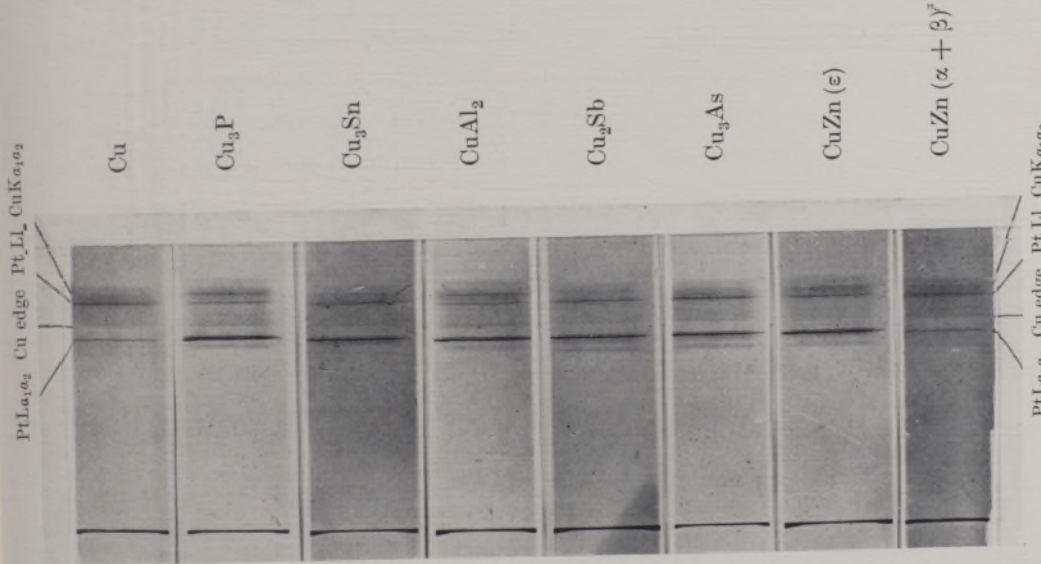


FIG. 2.—The copper K absorption edge in copper and various copper alloys.

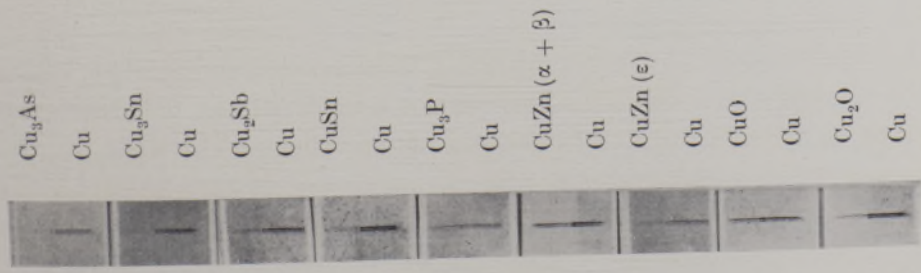


FIG. 1.—K $\alpha_1\alpha_2$ doublet of copper, photographed in the third order spectrum from the (111) face of carborundum.

kind of work; when operated at 12 K.V. and 15 to 20 m.a. it could be left for several hours without needing attention. It was also found to work for about 8 hours daily for several weeks without requiring to be cleaned. When working under these conditions and when once the tube had attained a steady state, the required degree of vacuum could be maintained by the oil pump alone.

In taking photographs of emission lines it is essential to have the tube in good focus, but with absorption edges this is not so important and very sharp edges can be obtained without a well-defined focal spot. If the focus is very bad, however, longer exposures are needed.

The time of exposure depends upon the density of the absorbing screen. With copper foil the edge was obtained in about 4 hours, but with the inter-metallic compounds the time varied from about 5 hours for Cu_3P to about 8 hours for Cu_3Sn . As several of the compounds were very hard and brittle it was difficult to obtain a fine powder; in these cases more material was required to produce a uniform screen, but variations, within limits, in the amount of the material in the screen did not seem to have any effect on the appearance of the absorption edge, so long as the material was uniformly distributed.

It is possible that the absorbing screens undergo a change under prolonged irradiation. To eliminate the possibility of a discrepancy on this account the screens were moved so that the absorption took place in different parts of the screen during each consecutive hour. New screens were made for each exposure.

The absorption spectrum was registered on a straight plate (12 cm. \times 2 cm.), wrapped in a sheet of thin black paper and inserted in the plate holder of the camera.

The L series lines of platinum were used for reference lines. It happens that these lines are very conveniently situated on the plate to serve as reference lines; the La_1 and Ll lines, having wave-lengths of 1310.1 and 1497.2 X.U. respectively, are situated one on either side of the CuK absorption edge which has a wave-length of about 1378 X.U. In view of the positions of these lines very accurate measurements of the wave-length of the edge can be made.

In some previous investigations reference lines have been produced by placing chemical compounds on the target. This is open to serious objection, as the compounds may undergo chemical change with possible changes resulting in the positions of the reference lines.

Measurement of the Plates.

The plates were measured with a Hilger travelling microscope, the readings of which could be estimated to 0.001 mm. The lines and edges were sharply defined and their positions could be measured to within 0.01 mm. Each plate was carefully measured in ten different positions, the lines and edges being approached from two directions; the final result then represents a mean of 20 separate readings each of which differed from the mean by less than 0.02 mm.

The wave-length of any line or absorption edge can readily be calculated if the separation of two lines of known wave-lengths is measured on the plate. If the distance from crystal to plate is s , and the separation of lines of wave-lengths λ_1 and λ_2 is l , then if x is the distance of the line of shortest wave-length from the point where the direct beam meets the plate, we have $x/s = \tan 2\theta_1$, and $l/s = (\tan 2\theta_2 - \tan 2\theta_1)$, where θ_1 and θ_2 are the angles of reflection. Hence we determine x and s which can be used to calculate the wave-length of the copper absorption edge. Each plate was separately calibrated in this way.

The width of the slit was 0.08 mm., and the carborundum crystal was rotated between 14° and 18° with the direction of the X-ray beam.

Before inserting the screen in the X-ray beam a photograph was taken of that part of the spectrum containing the CuK edge. When the screen was in position any additional detail found on the photographic plate was then known to have come from the screen.

Results.

The values of the wave-lengths corresponding to the reference lines Pt $L\alpha_1$ and Pt Ll were respectively 1310.1 and 1497.2 X.U. The spacing of the (111) planes of carborundum was taken to be 2.490 Å. Let us take as an example the copper edge obtained when using copper foil; suppose θ_1 and θ_2 are the glancing angles of Pt $L\alpha_1$ and Pt Ll respectively, then $\theta_1 = 15^\circ 15' 8''$ and $\theta_2 = 17^\circ 29' 36''$. Hence we have $x/s = 0.3892$ and $l/s = 0.1110$. The mean distance (l) between Pt $L\alpha_1$ and Pt Ll on the plates was 4.74 mm., so that $s = 4.276$ cm. and $x = 2.519$ cm. The distance of the Cu edge from the $L\alpha_1$ line is 1.64 $\frac{1}{2}$ mm.; hence the distance of the edge from the point where the direct beam meets the plate is 2.684 cm. If θ_e is the glancing angle corresponding to the wave-length of the Cu edge, then $\tan 2\theta_e = 2.684/4.276$, whence $\theta_e = 16^\circ 3' 23''$, so that $\lambda_e = 1377.4$ X.U.

Table IV contains a summary of the results obtained in the above manner with different materials.

Table IV.

Material.	Time of exposure.	Wave-length of CuK edge.	$\Delta\lambda$ (separation of edge from the edge for pure copper).
	hours	X.U.	X.U.
Cu (foil)	4	1377.4	—
Cu ₂ O	6	1377.3	-0.1
CuO	6	1376.5	-0.9
Cu ₃ P	5	1377.5	0.1
Cu ₃ Sn	8	1377.3	-0.1
CuAl ₂	6	1377.4	0.0
Cu ₂ Sb	8	1377.3	-0.1
Cu ₃ As	6.5	1377.3	-0.1
CuZn (ϵ)	6.5	1377.2	-0.2
CuZn ($\alpha + \beta$)	7	1377.4	0.0

The results show that there is no difference between the position of the edge in pure copper and its position in cuprous oxide, the intermetallic compounds or the two solid solutions investigated. Cupric oxide is unique in that the edge corresponds to a wave-length of 1376.5 X.U. and is thus 0.9 X.U. shorter than the edge in pure copper, which has a wave-length of 1377.4 X.U.

Since the compound CuO was the only material hitherto examined, which showed a definite shift of the copper K edge, it was decided to extend the investigation to cover a number of inorganic compounds of copper. Screens of these substances, powdered, were prepared as already described and placed in the X-ray beam. The results obtained are collected in Table V.

Table V.

Substance.	Time of exposure.	Wave-length of CuK edge.	$\Delta\lambda$ (separation of edge from the edge for pure Cu).
	hours	X.U.	X.U.
Cu	4	1377.4	—
CuCl	7	1377.4	± 0.0
Cu ₂ O	6	1377.3	-0.1
CuO	6	1376.5	-0.9
CuSO ₄	7	1376.3	-1.1
Cu(NO ₃) ₂	8	1376.2	-1.2
CuCO ₃	8	1376.1	-1.3
CuCl ₂	8	1376.5	-0.9

In all the cupric compounds there is a change of about 1 X.U. in the position of the edge, the edge having moved towards the shorter wave-lengths, but in the cuprous compounds no change is indicated. The change is quite definite

and is well outside the limits of experimental error. The actual photographs taken are shown in figs. 2 and 3 (Plate 13). The intermetallic compounds all behave like the cuprous salts—not a single one examined showed the shift in the absorption edge found in the cupric salts.

Discussion of Results.

The fact that the K absorption edge of copper is shifted in cupric oxide, whereas no indication of a shift was observed in the emission spectrum, seems to indicate that chemical changes take place rapidly in materials placed on the anticathode of an X-ray tube. Actually, the emission spectrum from copper in cuprous or cupric oxide examined in the earlier part of the work was not registered owing to the rapid reduction of the oxides under cathodic bombardment. In the particular tube employed the focus was good, and iron, which is a comparatively poor conductor, was used for the target; both of these factors would help to produce intense local heating of the compound resulting in its decomposition. This rapid decomposition of a salt placed on a target is a serious drawback to the examination of emission spectra by this method.

The intermetallic compounds, however, were soldered to and therefore made good contact with the target which was vigorously cooled, thus making an appreciable rise of temperature unlikely. It may reasonably be expected that in these circumstances the intermetallic compounds were not decomposed, and that actually the emission spectra of copper, in the states in which the copper existed in the compounds, were registered. If we may assume this, the information supplied by the emission spectra agrees with that supplied by the absorption spectra, namely, that the energy of the K electrons of the copper atom is not affected when the atom is held in combination with other metallic atoms as in intermetallic compounds.

All the inorganic salts which were examined show that the X-ray line and absorption spectra of copper in free copper and in the cuprous salts are identical, whilst the absorption edge of copper in the cupric salts is shifted on the average by 1.1 X.U. (which corresponds to 7.1 volts) to a lower wave-length. The reason for this is readily obtained from the consideration of the configuration of the copper atom. The electrons in the copper atom are located in the various orbits as follows :—

Group.	K.	L.			M.					N.
Orbits	1 ₁	1 ₁	2 ₁	2 ₂	1 ₁	2 ₁	2 ₂	3 ₂	3 ₃	1 ₁
Number of electrons	2	2	2	4	2	2	4	4	6	1

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There is only one electron in the N group; this electron takes part in the formation of the cuprous compounds. Since copper may be divalent as in cupric oxide, another electron from the interior of the atom takes part in chemical combination.* When this electron is removed a re-arrangement of the remaining electrons takes place, which causes a change in the energy of electrons in all the orbits, including those of the K group. Since the nucleus has now fewer electrons to hold, the intensity of the forces binding the electrons to the nucleus is increased. Thus the energy necessary to eject a K electron is increased, causing the K absorption edge to move to a shorter wave-length.

Turning to the intermetallic compounds, it is found that the wave-length of the absorption edge is the same as in pure copper or in the inorganic cuprous compounds. This indicates that if a chemical bond exists between the elements in the intermetallic compounds considered, not more than one electron is supplied in each case by the copper atom; if two electrons were involved as in inorganic cupric salts a shift in the absorption edge would be expected. Hence the chemical forces called into play in intermetallic compounds are not such as to cause the removal of an electron from the M group.

The intermetallic compounds examined were chosen at random from a collection of specimens which had been submitted at some time or other to X-ray examination. They were typical compounds; for instance, Cu_2Sb had a striking purple colour and was exceedingly brittle; moreover, the actual specimen used to determine the absorption edge was found on analysis to possess a tetragonal structure.* Addition of more antimony revealed the same Cu_2Sb structure with lines of antimony superposed. Similarly, CuAl_2 has been found to possess a definite structure and is a typical intermetallic compound. But there is some ground for stating, in the light of recent work, that some of the other materials examined are not intermetallic compounds, although they are generally regarded as such.

It may happen that an intermetallic compound is in solution in or mixed with one of its constituents. If this were the case in any of the materials used here, the results would not be affected. Taking, for example, Cu_3Sn , the atomic proportions may correspond to the formula Cu_3Sn , but actually the material may be $(\text{CuSn} + \text{Cu})$ or $(\text{Cu}_2\text{Sn} + \text{Cu})$. In either case we should expect to find two edges in the spectrum if the copper in the compound were in the cupric state—one due to the free copper and one at a shorter wave-length due to the copper in the compound. Similarly, if the compound CuSn were dissolved in or mixed with tin, the presence of the tin would not alter the copper spectrum

* This will be published in a separate paper.

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emitted by the copper in CuSn. So that if the formation of an intermetallic compound, either in solution or isolated, involved two copper electrons as in cupric oxide, it would be revealed by a shift in the absorption edge. We therefore conclude that whatever be the nature of the union between copper and other atoms in these intermetallic compounds, the binding forces do not affect the energy of the K electrons of the copper atom as in the formation of inorganic cupric compounds. In other words, the copper atom in intermetallic compounds must be in the cuprous state; this distinguishes a compound from a solid solution in which the copper atom is in the free state.

The above result is in agreement with the work of Padoa,* who concludes from the results of an experimental investigation of the form of combination under which intermetallic compounds are anodically dissolved, that in these compounds only secondary valencies are active.

The result is also in agreement with the theory of the constitution of intermetallic compounds suggested by Hume-Rothery.† The valency rules in ordinary chemical compounds are based on the fact that the whole of the available valency electrons may be used up and bound into stable configurations. Hume-Rothery assumes that in intermetallic compounds all the valency electrons are not used up, and that stable arrangements are possible under these conditions. The evidence now deduced from emission and absorption spectra that the copper atom loses or shares one and only one electron in intermetallic compounds is in harmony with this view.

Summary.

The $K\alpha_1\alpha_2$ doublet of copper in copper and its oxides and in a number of intermetallic compounds and solid solutions has been investigated. In all cases there was no change found in the wave-length of the $K\alpha_1$ line, or in the separation of the lines in the doublet. It is pointed out that whereas these results are probably true for the intermetallic compounds and solid solutions, they do not hold for the oxides of copper owing to the decomposition that takes place when the latter are placed on the target of an X-ray tube.

The positions of the K absorption edges of copper in the same substances together with a number of inorganic compounds of copper were determined. The edge in copper and in the cuprous salts corresponds to the wave-length 1377.4 X.U. and was the same as that obtained with the intermetallic com-

* 'Gazz. Chimica Italiana,' vol. 52, pp. 189-202 (1922).

† 'J. Inst. Metals,' vol. 1, p. 295 (1926).

pounds and solid solutions. But in all the inorganic cupric salts the edge had moved towards the shorter wave-lengths; the shift amounted on the average to 1.1 X.U., which corresponds to 7.1 volts.

The bearing of the results on the constitution of intermetallic compounds is briefly discussed.

We have much pleasure in recording our indebtedness and thanks to the Royal Society for a grant which enabled us to carry out the work.

The Use of Thyratrons for High Speed Automatic Counting of Physical Phenomena.

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Introduction.

It is sometimes necessary to count physical events which are repeated very rapidly. An example of this occurs in problems connected with radio-activity, where it is desired to count the number of α -particles entering a collecting chamber. One method of doing this is to amplify (by means of thermionic valves) the minute ionisation currents produced in the chamber by single α -particles, and to pass the amplified currents—which take the form of impulsive surges of about 10 milliamperes—through telephones, counting the “clicks” by ear. For more rapid working, the currents are passed through an oscillograph, and a photographic record is obtained, which can be analysed at leisure after development. It is often necessary, however, in addition to recording the particles rapidly, to know the result immediately, so that further observations may be made on points of special interest. In a recent paper* it has been shown that it is possible to use a mechanical relay and a counting meter (similar to a cyclometer) in conjunction with a valve amplifier for automatic numerical counting of α -particles. Each 10 milliamperere current surge (corresponding to a particle) passes through the relay windings and closes the contacts momentarily, thus completing a local circuit containing the counting meter. Such a method of counting, while extremely simple and convenient,

* Wynn-Williams and Ward, ‘Proc. Roy. Soc.,’ A, vol. 131, p. 391 (1931).