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The X-Ray $K\beta_{2,5}$-Emission Lines and K-Absorption Limits of Cu-Zn Alloys*

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The shapes of the $K\beta_{2,5}$ lines of Cu and of Zn and their K-absorption edges in the pure metals and in a series of brasses have been studied with a double crystal spectrometer. Mixing Cu with Zn increases the high energy part of the emission of Cu $K\beta_{2,5}$ and decreases the corresponding part of the intensity of Zn $K\beta_2$. The magnitude of this redistribution of high energy conduction electrons between Cu and Zn is found to agree with theoretical calculations, which predict a maximum positive charge of about 10 percent of an electronic charge on a zinc atom dissolved in a Cu lattice. The present results are offered as further support for that interpretation of Cu $K\beta_{2,5}$ structure which attributes the extra low frequency emission to $3d$ band emission. In every alloy Zn $K\beta_5$ appears with very little change in width or in intensity per Zn atom, and can be definitely assigned to $3d$ quadrupole emission. No shifts of the high energy sides of the emission lines or the corresponding absorption limits greater than the experimental error have been observed with alloying, and there appears to be no evidence of any effect of crystal structure on the emission lines.

INTRODUCTION

IT has been demonstrated in recent work[1] that x-ray solid state spectroscopy in the hard x-ray region between one and two angstroms is capable of yielding considerable information about the nature of the conduction levels and higher lattice levels of metallic solids. In the work referred to, the double crystal spectrometer was applied to the study of the shapes of the $K\beta_2$- and $K\beta_5$-emission lines and the K-absorption limits of the pure elements Fe to Ge. These emission lines correspond to transitions in which electrons fall from $3d$ and $4s$ band levels into vacancies in the atomic K shells. The absorption edges result from the ejection of electrons from atomic K shells into empty levels above the Fermi surface of filled states. If one assumes a very narrow width for the K level compared to the $3d$ and $4s$ band widths, the intensity of emission or absorption at any given energy may be written as a product of density of states in the electronic bands, at the given energy, multiplied by the corresponding transition probability. The width of the emission line, where the K level is sharp, will therefore give directly the width of the electronic band.[1] The shape of the emission line will reflect the variation of density of states in the band, with modifications due to the transition probability factor. The effect of finite width of the K level can be taken into account in the manner described by Richtmyer, Barnes and Ramberg,[2] for absorption edges. In reference 1 most interest was attached to the results obtained for Cu, for which metal extensive theoretical calculations have been made. With the idea of testing some commonly held theories of the nature of binary alloys, and to check further on the correctness of the interpretation of this earlier work on pure metals, similar measurements have been carried out on a number of binary alloys. The substances chosen for study are alloys of Cu with Zn, Cu with Ni, and alloys of Ni with Zn. The selection of these alloys has again been determined by the fact that they have been the subject of much theoretical treatment and that considerable related experimental data are available on their optical constants, resistivities, specific heats, and in the case of Ni alloys, their magnetic properties.

EXPERIMENTAL

The present paper reports the results obtained for the $K\beta_{2,5}$ lines and K-absorption edges of the two component metals in alloys of Cu with Zn. The measurements were made with a Societé Genevoise precision double crystal spectrometer, which was a generous gift of Dr. A. L. Loomis.

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* This research is supported by a grant-in-aid from the American Philosophical Society.

[1] W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).

[2] F. K. Richtmyer, S. W. Barnes and E. Ramberg, Phys. Rev. **46**, 843 (1934).

The constant primary voltage supply, the high voltage plant, x-ray tube and Geiger counter technique of measuring low x-ray intensities is that developed by the senior author together with Dr. C. H. Shaw. For methods employed and technique used in recording the data reference is made to previous publications.[3] During the course of the investigation no change in the properties of the crystals, from those previously reported, has been observed.

The emission measurements have been carried out for a series of four α-brasses, a β-brass, a γ-brass, and an ϵ-brass. All the alloys were made from commercial high grade cathode copper and electrolytic zinc, containing impurities to the extent of not over 0.01 percent lead and 0.01 percent iron in the alpha-alloys, and perhaps 0.02 percent lead in the beta- and gamma-alloys. The alpha- and beta-alloys were annealed repeatedly during rolling from the castings and were given a final annealing at 700°C. The gamma-alloy was sand cast and then annealed for 24 hours at 600°C. The ϵ-brass was prepared in a similar manner. Table I gives the nominal compositions by weight and by atomic number for the various alloys studied. The composition may vary by 0.25 percent from nominal.

The α-brasses have the face-centered cubic structure of pure Cu with lattice constants that increase linearly from 3.62A for the 5 percent Zn to 3.67A for the 30 percent Zn. β-brass, with the approximate composition CuZn, is a body-centered structure, forming a superlattice below about 460°C. The lattice constant is 2.95A and when the superlattice is complete the system may be described as two equivalent simple cubic lattices, one of Cu and one of Zn, with the Zn atoms, say, at the centers of the Cu cubes. The γ-brass structure is a complicated cubic lattice with the unit cell containing 52 atoms. The ϵ-brass has the zinc hexagonal structure.

TABLE I. *Composition of alloys.*

Phase	α	α	α	α	β	γ	ϵ
Zinc weight (%)	5	10	20	30	48.2	67	79.7
Zinc atomic (%)	4.9	9.8	19.7	29.4	47.5	66.4	79.2

For use as targets, the alloy samples were shaped into buttons $\frac{7}{8}''$ in diameter and $\frac{3}{16}''$ thick. These buttons were soldered onto the water-cooled target of the x-ray tube. The foils of α-brasses used in the absorption measurements were rolled from the buttons that had previously been used as targets. At various stages of the rolling the foils were annealed at between 500° and 600°C in an atmosphere of hydrogen.

The $K\beta_2$ and $K\beta_5$ lines in Cu and Zn are the least intense lines in the K series of these elements. H. T. Meyer[4] and J. H. Williams[5] have shown that these lines have only about 1/400 the intensity of the $K\alpha_1$ lines. With the counting technique that we have employed, however, it has been possible to obtain accurate data even with x-ray tube currents of less than 10 ma at 35 kv. In running the γ-brass the power dissipated in the target was kept below 100 watts. At greater powers, because of the poor conductivity of this alloy, there is the possibility of distilling zinc out of the target. With β-brass as the target the x-ray tube was run at 5 ma and 35 kv and careful examination of the target surface after twenty hours of operation showed no change in the surface at the focal spot, which was 4 mm in diameter. It is possible, however, that even at low power the surface of the target may have been heated to a temperature of a couple of hundred degrees during operation of the tube. This would have been sufficient to partially destroy the order of the superlattice.

In all measurements on the Zn lines, correction had to be made for the additional intensity due to the tungsten $L\beta_1$ line appearing about 2 x.u. from the peak of the $K\beta_2$ line. The vacuum conditions during operation of the tube were sufficiently good that very little intensity due to tungsten could be observed. Trouble was experienced only with the 10 percent and 5 percent Zn alloys, where because of the low Zn concentrations it was necessary to use as high as 600 watts to obtain measurable intensities,

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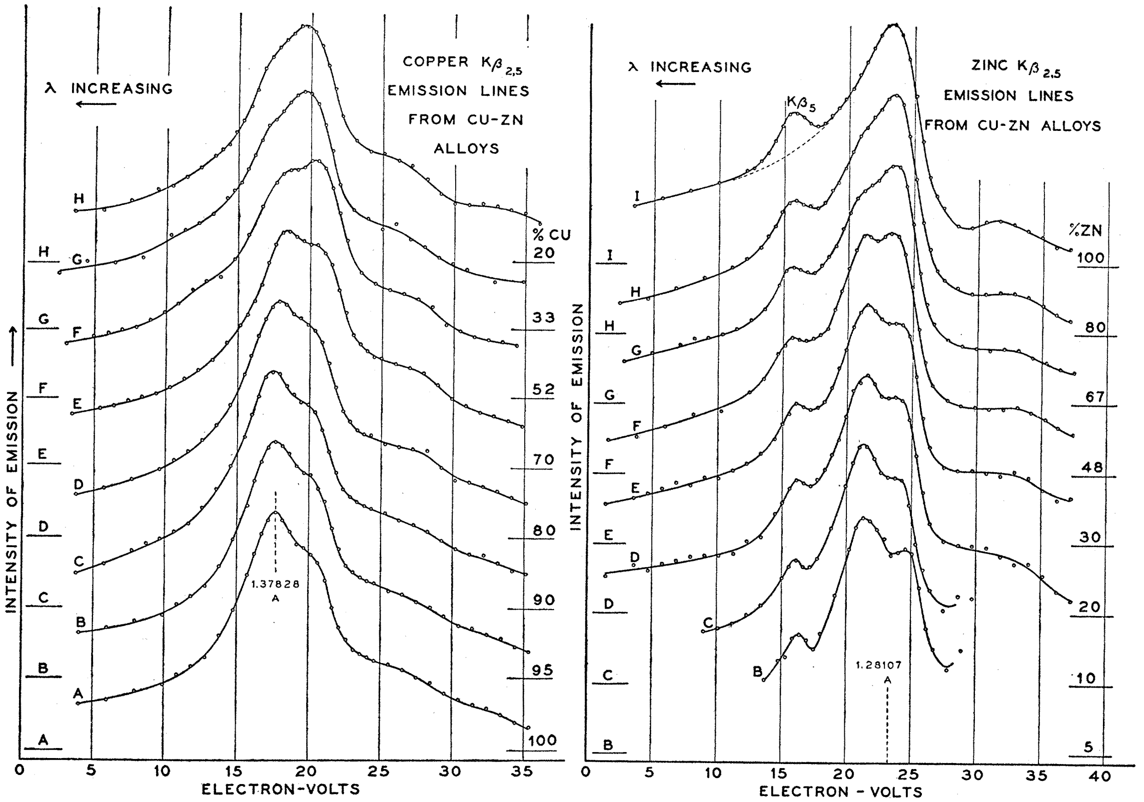
[3] J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935); J. A. Bearden and C. H. Shaw, Rev. Sci. Inst. **5**, 292 (1934); C. H. Shaw, Phys. Rev. **57**, 877 (1940); W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).

[4] Quoted in A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, 1935), p. 641.

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



FIGS. 1 and 2. The base line for each curve is given by horizontal lines on right and left sides of the curve. The base corresponding to each curve is labeled on the left with the same letter found on the low frequency tail of the curve to which it refers, and on the right with the percentage by weight of the emitting element in that alloy target.

and in these cases the tungsten correction was probably large enough to introduce some error into the final results. The correction was determined in the following way. The tube was run overnight at low power with the target covered by a molybdenum shield. With the filament well outgassed by such treatment and with the spectrometer set for the peak of W $L\beta_1$, the first reading taken after removal of the molybdenum shield should give negligible intensity due to tungsten $L\beta_1$ and give a base from which the tungsten intensity in all succeeding runs may be measured. Successive readings on the peak of the $L\beta_1$ line in general indicated a very slow evaporation of tungsten from filament to target.

For the measurement of absorption edges, a gold disk was soldered to the target and both incident and transmitted intensities for various foils were determined over a range of from 30 to 50 volts through the edge. The results on Cu K absorption are more accurate than those on Zn, because of the much greater difficulty of measuring the Zn absorption. Zn gives only a weak absorption at the Cu edge, but Cu gives a strong absorption at the Zn edge. This, combined with the fact that the zinc percentages, in the foils studied, were low, accounts for the difficulty experienced in obtaining good data on the zinc absorption edges.

DISCUSSION

A. Widths of emission lines

From the simple free electron theory of metals, the maximum kinetic energy in the Fermi distribution would be expected to increase as Zn is added to Cu in accordance with the relation

$$E_{\max}=36.1(n_0/\Omega)^{\frac{2}{3}}\text{ ev},\qquad (1)$$

where n_0 is the number of free electrons per atom, and Ω is the atomic volume in cubic angstrom units. If we assume one free electron per atom of Cu and two per atom of Zn, $E_{\max}$ for Cu would be 7.0 ev and for Zn 9.5 ev. Since Ω changes very little in the series of α-brasses, $E_{\max}$ should increase almost linearly with n_0. For a 30-percent alloy the conduction band should contain 1.3 free electrons per atom. With $n_0=1.3$, formula (1) gives $E_{\max}=8.0$ ev for the 30-percent Zn alloy compared to the 7.0 for pure Cu. This would lead one to expect an increase in width of the observed emission band of one volt and a corresponding shift of the high frequency side of the Cu $K\beta_2$ to shorter wave-lengths.

Figures 1 and 2 give the experimentally measured shapes for Cu and Zn $K\beta_{2,5}$ lines in the pure metals and the seven alloys. All curves have been plotted to arbitrary scales of ordinates so that they match at top and bottom. Because of the differences in intensity of satellite structure with respect to $K\beta_2$ intensity, the following arbitrary procedure has been followed in comparing widths of emission bands. The straightest portion of the slope of the high frequency side of each Cu line has been extrapolated and the width at half-maximum intensity is measured from this extrapolated slope. For Zn the high frequency slope has been similarly extrapolated and on the low frequency side, the side of the $K\beta_2$ has been extended (see curve I, Fig. 2) so as to cut off the $K\beta_5$. The widths for Zn have been measured from the high frequency extrapolation to the low frequency side of $K\beta_2$. The widths measured in this way are given in Table II.

The results listed in Table II show approximately the same widths for Cu and Zn emission bands from the same alloys. In the range of α compositions, where the crystal structure is always face-centered cubic, the width of the Cu $K\beta_{2,5}$ increases from 8.2 to 8.8 or 0.6 ev upon addition of 30 percent Zn, with roughly the same increase in width for Zn $K\beta_2$ in the same range.

Experimentally then, the widths of the emission bands attributed to conduction electrons increase with increasing n_0 but not as much as predicted on a free electron theory, nor is there any corresponding shift of the high frequency side of the Cu $K\beta_2$ in the α-brasses to higher energies by any amount greater than the experimental error of about 0.3 ev. Better agreement would be surprising, since the free electron gas model of a metal is only a very rough approximation. Still, it is interesting to see how closely the experimental widths of Cu $K\beta_{2,5}$ and Zn $K\beta_2$ correspond to the predictions of this simple theory. This seems to leave no doubt but that the above-mentioned x-ray bands are actually transitions from conduction electron levels. For no other transitions could the emission lines be expected to be as broad as observed.[6] To attempt to understand the detailed features of the curves of Figs. 1 and 2, it is necessary to resort to a more refined picture of the nature of the band electron levels involved.

TABLE II. *Half-widths of emission bands as defined above.*

Zn	Cu $K\beta_{2,5}$	Zn $K\beta_2$
0.0	8.2±0.2 ev	
5	8.3	8.4±0.3 ev
10	8.5	8.5
20	8.6	9.0
30	8.8	9.0
48	9.8	9.0
67	9.0	9.2
80	9.1	9.2
100		9.4

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[6] It should be pointed out that the above procedure for measuring widths does not yield a reliable measure of the electronic band breadth in cases where the emission shows a complex structure. For example, consider a combination of a band of great breadth and low density of states with a narrow band of a very high density of states, which occupies part of the former's energy range. Such an overlapping band system might yield an emission structure which, measured across half-maximum intensity, would give a width more characteristic of the narrower band than of the wider band.

The wave-length position on the emission line corresponding to the actual limit of the Fermi distribution of a given alloy may be obtained from the wave-length position of the inflection point on its absorption limit (see references 1 and 2). (The half-maximum points in the extrapolation of the high frequency side of our lines correspond fairly closely in wave-lengths to the absorption edge inflection points.) The width of the emission band should then be measured from this point over to a point on the low frequency side of the emission corresponding to the lower limit of filled states. This latter point is more difficult to determine because the density of states on the low energy side of the electronic band is not cut off abruptly as it is at the Fermi surface. Theoretically (H. Jones and N. F. Mott, Proc. Roy. Soc. **2**, 162, 49 (1937)) the density of "*p*" function at the bottom of the conduction band should fall off as exp. 3/2 and reach a zero value at about 7 volts from the Fermi surface for Cu and at about 9.5 for Zn. Actually there seems to be considerable low frequency emission extending much further than given by the widths of Table I. The low frequency tails on the emission lines fall off much less rapidly than would be given by the crystal diffraction patterns or widths of the ground states. The same effect has been found (H. W. B. Skinner, *Reports on Progress in Physics* (1938), Vol. V, p. 269) in soft x-ray emission lines, and has not yet been explained.

B. Correlation of line shapes with electronic band structures

Calculations of the band structure of Cu have been carried out by Slater[7] and Krutter,[8] and an attempt has been made to correlate the observed x-ray emission structure for Cu[1] with these calculations. According to the calculations ten $3d$ electrons per atom of Cu are contained in a $3d$ band of high density of states with a double peaked structure and a spread of about 7 ev. The $4s$ band, containing 1 electron per atom, is a band of low density of states about 13 volts wide, overlapping the $3d$ band. The filled electronic levels in the $4s$ band extend about 2 ev beyond the limit of the filled $3d$ band. On the basis of these calculated results the Cu $K\beta_{2,5}$ doublet has been attributed to transitions in which electrons drop from these $3d$ and $4s$ band levels into holes in the K shells. Part of the low frequency intensity in the emission band has been attributed to electrons in the $3d$ portion of the band system and the high frequency hump has been described as emission from the filled part of the $4s$ band extending beyond the $3d$. The transitions were assumed to take place in accordance with the selection rule allowing only s to p transitions. Krutter's calculations[8] indicate that there is considerable mixing of p function in the $3d$ and $4s$ bands, enough to attribute most of the observed intensities to dipole transitions rather than quadrupole. In the case of Zn with two $4s$ electrons, the $4s$ band would be full, making Zn an insulator, if the $4s$ and $4p$ bands did not overlap slightly. This slight overlap contributes a high density of "p" function at the top of the filled electronic levels, that has been assumed responsible for the maximum intensity of emission at the high frequency side of the $K\beta_2$ line. The $K\beta_5$ line has been associated with emission from the $3d$ band of Zn, which should be expected to lie somewhat lower relative to $4s$ than the $3d$ of Cu relative to Cu $4s$.

A further development of the method of calculation used by Krutter and Slater for Cu has been carried through by Chodorow.[9] In his calculations he has partially taken into account exchange and correlation effects neglected in the earlier calculations. Exchange effects cause a contraction of the "d" wave function and a narrowing of the $3d$ band by about 1.7 ev compared to the calculations of Krutter. Furthermore, the conduction band, although very similar to one containing free electrons, is split into two sections by the perturbations of the other bands. These newer results suggest an alternative interpretation to that which assigns the low frequency extra emission in Cu $K\beta_{2,5}$ to $3d$ band emission. The experimental double structure might be interpreted as emission from a split $4s$ band and the results on the brasses could perhaps be taken as support for such an interpretation. Before attempting to prove the correctness of either one of these two possible explanations of the observed Cu $K\beta_{2,5}$ structure, it is best to consider the Zn $K\beta_5$ emission. The interpretation of this latter x-ray line is straightforward and an examination of its relation to the Zn $K\beta_2$ emission will help in settling the question of the origin of the Cu emission.

The curves in Fig. 2 all show the structure on the low frequency side, called $K\beta_5$, that has been attributed to $3d$ emission in pure Zn. No similar structure ever appears in the Cu curves of Fig. 1. If one starts with pure Zn and increases the percentage of Cu, the intensity of emission per Zn atom is lowered on the high frequency side relative to that on the low frequency side of $K\beta_2$, but there is little effect on the $K\beta_5$ structure. If the long wave-length side of the $K\beta_2$ is extrapolated as shown for the 100-percent Zn in Fig. 2, and the $K\beta_5$ intensity measured from this new base line, the resulting $K\beta_5$ lines are symmetrical lines having the half-widths given in Table III. When subtraction of 0.7 volt for crystal widths is made, the resultant half-widths are very close to the half-width of the K state alone, which has been given as 1.5 ± 0.5 ev.[1] The $3d$ levels of Zn then, in pure Zn and in the alloys, are not appreciably broadened by the lattice and the $K\beta_5$ lines are evidently quadrupole transitions of the $s\rightarrow d$ type. Electrons in the Zn $3d$ levels must remain tightly bound to their parent atoms in the lattice and cannot contribute to conduction. The peak intensities in these quadrupole transitions range from 15 percent to

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[7] J. C. Slater, Phys. Rev. **49**, 537 (1936); E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936).

[8] H. Krutter, Phys. Rev. **48**, 664 (1935).

[9] M. Chodorow, Phys. Rev. **55**, 675A (1939).

11 percent of the peak $K\beta_2$ intensities in going from pure zinc to 10 percent zinc. Integrated intensities due to quadrupole radiation, similar in magnitude to those found for zinc, should also be expected in Cu. However, the larger breadth of copper $3d$ in pure copper would tend to give a broad quadrupole emission with small peak intensity, rather than a narrow prominent structure like Zn $K\beta_5$. In the alloys, increasing dilution of zinc does not appreciably affect the breadth or intensity per atom of the $K\beta_5$ emission, because already in the pure metal, the overlap between $3d$ wave functions of nearest neighbors is so slight as to give no appreciable broadening of the levels. Increasing dilution of copper must be expected to narrow up the copper $3d$ band, but it is improbable that the contraction of the band would progress far enough even with low Cu concentration to ever give a $3d$ quadrupole emission from copper of similar shape and intensity per atom to that found for zinc. Support for this statement is found in the results on Cu-Ni alloys and allows of these two metals with aluminum.[10]

TABLE III. *Half-widths of* Zn $K\beta_5$ *lines in pure* Zn *and brasses.*

Zn	100	80	67	48	30	20	10	percent
Half-width	2.5	2.5	2.4	2.6	2.4	2.2	2.0	ev

Returning to the curves of Figs. 1 and 2, it appears that the $K\beta_{2,5}$ structures for Cu are very similar to the $K\beta_2$ of zinc in the same alloys. As Zn is added to Cu, the high frequency intensity rises relative to the intensity on the low frequency side of the Cu emission band, and vice versa for the Zn $K\beta_2$ as Cu is added to Zn. Certainly, in pure zinc and the alloys, all the Zn emission structure to the high energy side of Zn $K\beta_5$, as well as the tail of the emission extending to low frequencies must be $4s$ band emission. The close similarity between Cu $K\beta_{2,5}$ and Zn $K\beta_2$ would make it appear then that the double structure in both cases is due to $4s$ electrons in support of Chodorow's split Cu $4s$ band. This would require that Cu $3d$ emission be spread out over most of $4s$ and so weak as not to give rise to any pronounced structure superposed on the $4s$ emission. References to Figs. 1 and 2 shows that the zinc $K\beta_2$ structure in the α-alloys has a more distinctly split appearance than the copper $K\beta_{2,5}$. A broad copper $3d$ quadrupole emission falling somewhat centrally with respect to the $4s$ band emission could produce such an effect. The main objection to this interpretation thus far is that no account has been taken of the $3d$ dipole radiation to be expected from "p" function mixed in the $3d$ band. The calculations of Krutter indicate enough mixing of "p" function near the top of the $3d$ band to give an appreciably intense $3d$ dipole intensity of small breadth, rather than a broad weak emission, and the experimental separation of the double structure is in agreement with a separation of about 1.5 to 2.5 ev predicted both by the atomic spectra data and the band calculations. The effect of diluting copper in the alloy lattice should be a narrowing of the Cu $3d$ band and with decreasing width, the amount of "p" function going into the description of the $3d$ band becomes less and less. It might be expected that the low frequency hump on copper, if due to $3d$ band dipole emission, would disappear with increasing dilution of copper. Experimentally it has been found that within the limits of the precision with which we could compare absolute intensities on different curves, about ten percent, there was no change in the low frequency intensity of Cu or Zn per atom in the alloy series. In the pure copper, the extra low frequency emission is only about ten or fifteen percent of the total peak intensity and even a complete disappearance of this extra intensity might be missed in our measurements. Actually, the curves do seem to indicate a loss of intensity on the low energy side of Cu, as can best be seen by comparison of curves B to F in Figs. 1 and 2. If the high energy structures of the curves are matched, it is evident that the left sides of the copper curves drop in intensity relative to their corresponding zinc curves. In curve F, the copper emission at the low energy side has fallen definitely below the high energy peak, while in zinc, both sides are just about equal in intensity. Since we have good reason to believe that zinc low energy $4s$ emission remains constant, the above results indicate a loss of low energy emission in copper that can best be

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[10] H. Friedman and W. W. Beeman, Phys. Rev. this issue.

attributed to decreasing $3d$ dipole emission. We might therefore conclude that the close similarity between Cu $K\beta_{2,5}$ and Zn $K\beta_2$ in all the alloys is to a great extent accidental. The low frequency structure of Zn $K\beta_2$ must be all $4s$ band emission, but that of copper $K\beta_{2,5}$ must contain appreciable $3d$ emission. Only the high kinetic energy $4s$ band electrons are completely shared and almost all the observed changes with alloying are consequently confined to the high energy portions of the emission bands.

C. Extent of sharing of high kinetic energy electrons

When Zn atoms and Cu atoms are combined to form a brass alloy, each Cu atom contributes one electron and each Zn atom contributes two electrons to the total number of conduction electrons. If these electrons are considered to form a uniform charge density distributed through the lattice, it is impossible to explain many properties of the alloys, such as conductivities, energies of superlattice formation, melting points, lattice expansions, etc.

For small amounts of Zn in solid solution in Cu, the resistance increases considerably. Part of the resistance of a dilute solid solution is due to the thermal vibrations giving rise to a definite scattering probability dependent on the temperature. In addition the periodicity of the lattice field is further disturbed by the abnormal electron distribution about each foreign atom. If upon addition of Zn to Cu, the extra $4s$ electron is considered as belonging to the lattice rather than the atom, then the increased resistance should be proportional to the scattering power of the extra field due to the Zn atoms. In calculating the resistance introduced by this extra field, Mott[11] has found that a finite resistance can be obtained only if the greater charge of the Zn atoms is shielded by part of their extra valence electrons. In other words, the Zn atoms tend to retain much of their extra charge rather than give it up to the lattice. Mott has calculated the magnitude of this screening effect and applied the results to the calculation of the charge distributions in β-brass.[12] His calculations have yielded the result that the polyhedral cell about each Cu^+ ion contains a total negative charge $-0.075\,e$ and the cell about each Zn^{++} ion is positively charged with a total $+0.075\,e$, where e is the electronic charge. That the order of magnitude of this calculation is correct was borne out by the good agreement obtained between the Madelung energy for the superlattice calculated with such charges, and the observed energy of formation of the superlattice.

In the superlattice, each Zn atom is completely surrounded with Cu as nearest neighbors, and the charge on a zinc polyhedron in this case, $0.075\,e$, is the maximum possible for a Zn-Cu alloy. The disordered alloys will give an equivalent charge on a Zn polyhedron only when the Zn is present to a small atomic percent, so that the probability of being completely surrounded by Cu is high.

Manning[13] has pointed out that a negative charge around the Cu atoms in a Cu-Zn alloy accounts for the expansion of the lattice and for the lowering of the freezing point, with addition of Zn to Cu. He has also indicated that the positive charge on Zn atomic polyhedra makes it possible to explain some apparent discrepancies between the coefficients of diffusion in Cu of the elements following Cu in the periodic table and of Cu itself diffusing in Cu.

The data presented in Figs. 1 and 2 are in agreement with the above theories that Zn loses electronic charge to Cu in a brass alloy, and offer some quantitative support for Mott's calculation of the magnitude of the charge on an atomic polyhedron. The electrons that leave Zn for Cu in the alloys must be the high kinetic energy electrons, near the top of the conduction band. If then the intensity of the low frequency portion of the Cu emission and of the Zn $K\beta_2$ emission is assumed to be constant throughout the alloy series, the peak intensity per atom of Cu on the high frequency side increases by about 30 percent of its mean value in going from 100 percent Cu to 0 percent Cu, and for Zn the intensity on the high frequency side decreases by about the same amount in going from 100 percent Zn to 0 percent Zn. The fact that the β-brass does not show the maximum sharing of electrons may be taken as indication that even

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[11] N. F. Mott, Proc. Camb. Phil. Soc. **32**, 282 (1936).

[12] N. F. Mott, Proc. Phys. Soc. **49**, 258 (1937).

[13] M. F. Manning, Phys. Rev. **55**, 682A (1939).

with the x-ray tube operating at low power, the surface of the target is heated sufficiently to destroy the ordered structure.[14] According to the above-mentioned calculation by Mott, the maximum charge lost by a Zn atom in a Cu-Zn alloy should be about 0.1 *e*. If the experimental data is to be compared with this result, one should consider not the change in peak intensity but the change in integrated intensity due to $4s$ emission. This latter change is of the order of 5 percent if one compares the pure metal emission of Cu atoms with emission from Cu atoms when they occur in greatest dilution in Zn. Since the total integrated intensity under the $K\beta_2$ curve is given by two conduction electrons per atom in pure zinc, a loss of 5 percent in integrated intensity indicates a loss of 0.1 electronic charge.

The result that the peak of $K\beta_5$ in Zn does not appreciably change its position relative to the high frequency side of $K\beta_2$ in the entire alloy series might be taken as further indirect evidence for the small sharing of conduction electrons between Cu and Zn in an alloy. Reference to Bacher and Goudsmit's atomic spectra terms[15] gives the following energy relations:

Zn II $3d^9 4s^2$ lies 7.6–8.1 volts above $3d^{10}4s$

Zn III $3d^9 4s$ lies 9.9 volts above $3d^{10}$.

Zn II has the same nuclear field as Zn III but one external $4s$ electron has been added on and the shielding effect of this electron is sufficient to raise the $3d$ levels of Zn II two ev relative to those of Zn III. If this atomic data may be applied to the alloys, one should expect the separation of $3d$, given by Zn $K\beta_5$, and $4s$ given by $K\beta_2$, to change by about 2 ev between pure Zn and Zn in dilute solution in Cu, assuming Zn to lose all of its extra electron to Cu. If, however, as predicted by Mott's calculation, the maximum loss of charge is only about 10 percent of an electron, the greatest shift expected would be of the order of 0.2 ev, which agrees with the observations of Fig. 2.

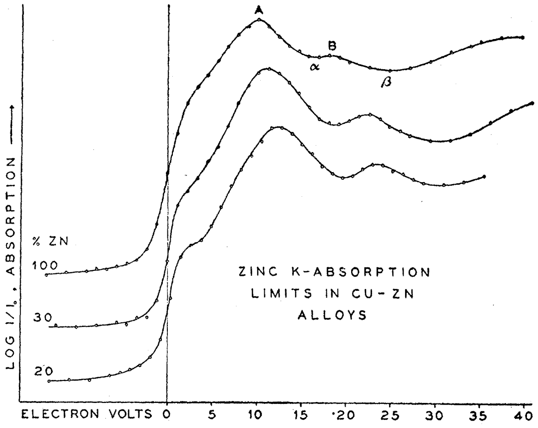

FIG. 3. Ordinates of all curves are expanded so as to have the same height from top to bottom. Curves are not corrected for second-order radiation. Zero abscissa corresponds to the wave-length of the pure metal absorption edge.

D. Absorption limits

Figure 3 shows the results obtained for the Cu *K*-absorption limits in pure Cu and in 90 percent Cu, 80 percent Cu, and 70 percent Cu α-brasses. Figure 4 shows the corresponding data for the Zn *K*-absorption limits in pure Zn, 30 percent Zn and 20 percent Zn. Copper and zinc in the same alloys show very similar absorption near the edge.

The ordinate of the inflection point (marked *L* on the 100 percent Cu curve in Fig. 3) of the initial absorption jump contour, is a measure of the density of states into which the initial absorption takes place. It has been assumed[1] that the initial absorption in Cu takes place into empty "*p*" states in a part of the $4s$ band where "*p*" function is decreasing slowly with increasing energy. The addition of Zn to Cu in the α-brasses should push the absorption at first to lower densities of "*p*" function. Experimentally, with increasing zinc content, the initial Cu absorption (measured by the ordinate *L* in Fig. 3) decreases more and more slowly in the ratio 5.2 : 4.8 : 4.5 : 4.4 from 100 percent Cu to 70 percent Cu. The initial Zn absorption

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[14] With the x-ray tube powers employed, and the known width of the focal spot, we have calculated a surface temperature for the β-brass alloy target of about 400 to 500°C. The measurements could be carried out with thinner alloy samples and lower powers so as not to raise the surface temperature above 50°C. However, with the technique employed in these measurements, we have not been able to heat treat the β-brass to restore a completely ordered structure after soldering the alloy sample in place on the target. The solder diffuses through a thin sample rather quickly. We plan to alter the experimental procedure now used in such a manner as to assure complete ordering of the β-brass during measurements, and the results then obtained would offer a direct check on our above interpretation.

[15] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932).

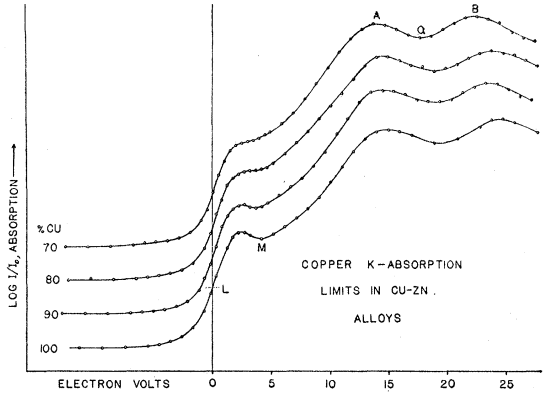

FIG. 4. Ordinates of all curves are expanded so as to have the same height from top to bottom. Curves are not corrected for second-order radiation. Zero abscissa corresponds to the wave-length of the pure metal absorption edge.

increases in the three curves of Fig. 4 in the ratio 7.0 : 7.1 : 10.2. An increasing density of "*p*" function near the top of the 4*s* band could be expected only if the 4*p* band overlapped the 4*s* band, since the top of the 4*s* band is pure "*s*" function. The above-mentioned experimental data indicate that for the 30 percent Zn alloy the surface of the Fermi distribution is situated in a region of electronic states where the 4*s* band is overlapped by 4*p*. In pure Cu, the dip marked *M* in Fig. 3 has been attributed to a gap or very slight overlap between 4*s* and 4*p* bands. With increasing Zn content this minimum in absorption washes out. At 10 percent Zn there is still a slight dip in the Cu absorption, but at 20 percent and 30 percent Zn in both the Cu and Zn absorption edges, the dip is no longer present. If the interpretation of the dip for pure Cu is correct, the data show that addition of Zn to Cu has the effect of causing a greater overlap of 4*s* and 4*p* bands.

The secondary absorption structures for Cu *K* absorptions all look like those of pure Cu, as would be expected on a free electron picture, since there is no change in lattice structure. But the corresponding Zn secondary structures bear closer resemblance to that of pure Zn in its hexagonal lattice, than to pure Cu. Evidently the atomic field and not the lattice type is the more important factor in determining secondary absorption structure even out to 30 volts. No shift of the edges greater than the experimental error of 0.3 volt has been detected, in agreement with the data on emission.

Work on the optical constants of brasses[16] shows absorption limits in the neighborhood of 5500 angstroms. These absorptions have been interpreted as due to transitions from filled 3*d* levels of Cu to the empty states above the Fermi surface. In the range of α-brasses up to 25 atomic percent Zn no shift of this absorption greater than 0.4 ev has been observed.

CONCLUSION

All the data on emission and absorption indicate no shift of the Fermi surface on alloying comparable to the shift expected on a simple free electron theory. Addition of Zn to Cu, however, does produce, in emission band structures, evidence of an increased number of high kinetic energy electrons about Cu and a corresponding decrease about Zn. This charge transfer is not nearly as large as expected for a complete sharing of valence electrons between Cu and Zn, but is in agreement with an alloy picture in which each component maintains a very large percentage of its valence charge.

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[16] Lowery, Wilkinson and Smare, Proc. Phys. Soc. **49**, 345 (1937).