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Copper and Nickel X-Ray $K\beta_2$- and $K\beta_5$-Emission Lines and K-Absorption Limits in Cu-Ni Alloys*

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The shapes of the Cu $K\beta_{2,5}$ lines and Ni $K\beta_5$ lines from Cu-Ni alloys vary smoothly with composition. The trend with increasing percentage of the emitting atoms is always toward a flattening out of the peaks of the lines. To explain the observed shapes it has been proposed that the major effect of alloying is a loss of 3*d* band dipole radiation with increasing dilution of the emitting atom. The absorption limits, in contrast to the emission lines, show no influence of alloying. The Cu K limit continues to look like that of pure Cu even when the emitting atom is almost completely surrounded by nickel nearest neighbors, and similarly no changes are observed in the nickel edges even down to 21 percent nickel.

THE $K\beta_5$ line of pure Ni and the $K\beta_{2,5}$ line of pure Cu, as well as their K-absorption limits have been previously measured.[1,2] The present paper reports an extension of these measurements to three alloys of Cu and Ni having the compositions by weight 30 percent Cu—70 percent Ni, 54 percent Cu—46 percent Ni, 79 percent Cu—21 percent Ni. Cu and Ni form a complete series of solid solutions with the face-centered cubic structure. Furthermore, the lattice constant decreases linearly, with increasing Ni content, by only 2 percent. Pure Cu has a constant of 3.59A and Ni, 3.52A. The effect of alloying on the $K\beta_2$ and $K\beta_5$ lines and on the K-absorption limits can therefore be studied independently of crystal structure changes over the entire range of composition.

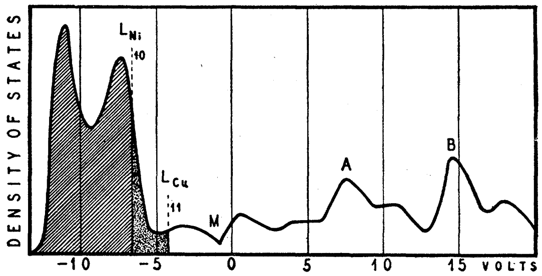

FIG. 1. Density of states as a function of energy in Cu. Lines labeled L_{Ni} and L_{Cu} give the energies to which the bands are filled in Ni (assuming same energy levels as for copper) and in Cu by 10 and 11 band electrons per atom, respectively.

An explanation of the shape of the pure Cu $K\beta_{2,5}$ emission has been given[2] based on the results of calculations by Krutter and Slater (Fig. 1) of the electronic 3*d* and 4*s* energy bands of Cu. The extra emission on the low frequency side was attributed to the 3*d* band. Slater,[3] in calculating the ferromagnetism and electronic specific heat of Ni, extrapolated the Cu band calculations to the case of Ni and obtained order of magnitude agreement with experiment. This extrapolation consisted of lowering the surface of the Fermi distribution down to where the Cu band system would be filled with ten electrons per atom. The effect of cutting off the portion of filled states in the 4*s* band extending beyond the limit of 3*d* would be to give a nickel $K\beta_5$ line

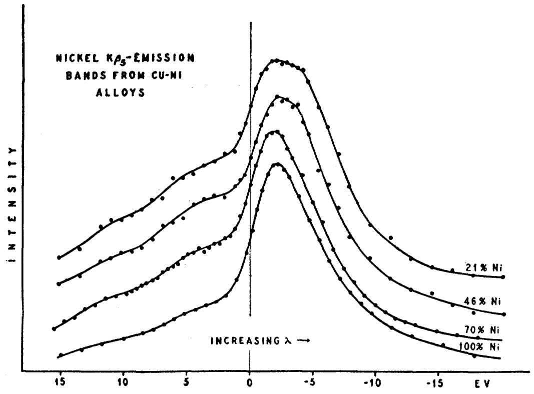

FIG. 2.

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

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

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

[3] J. C. Slater, Phys. Rev. **49**, 537 (1936).

with no hump like that found for Cu $K\beta_{2,5}$ on the high frequency side. If the experimentally observed Ni $K\beta_5$ is drawn in on the Cu $K\beta_{2,5}$ with the copper low frequency peak matching the nickel peak, the extra emission on the copper may be attributed to emission from the portion of the band system between L_{Ni} and L_{Cu} in Fig. 1. In alloying copper and nickel, one might therefore expect the addition of copper to nickel to produce simply a filling in on the high frequency side of Ni $K\beta_5$ corresponding to a raising of the surface of the Fermi distribution beyond the limit of the 3*d* band. The nickel *K*-absorption edges, correspondingly, would be expected to follow the surface of the Fermi distribution to higher energies with increasing copper content. The experimental results reported here, however, are considerably more complex, and evidently the direct extrapolation of the copper band system to nickel and the above simple picture of the effect of alloying are unjustified. In the following we shall give a description of the experimental data, a comparison with other related data, and lastly an attempt to explain this variety of experimental material.

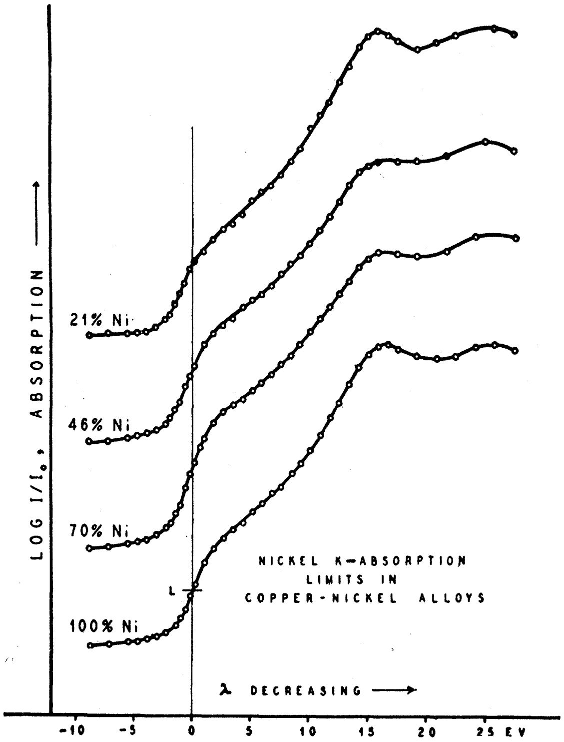

FIG. 4.

EXPERIMENTAL

The double crystal spectrometer and the technique of intensity recording is fully described in reference 3 of a preceding paper.[4] Specific precautions taken for nickel $K\beta_5$ measurements because of the W $L\alpha_2$ line on its high frequency side are described in the preceding

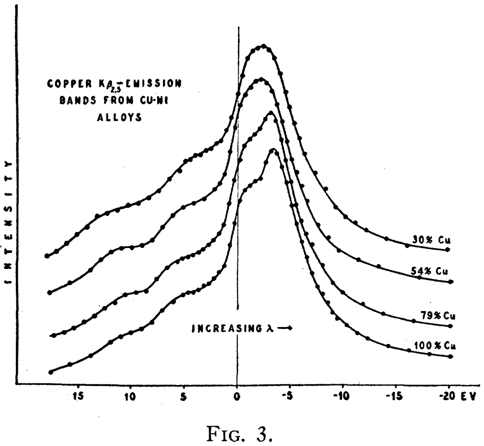

FIG. 3.

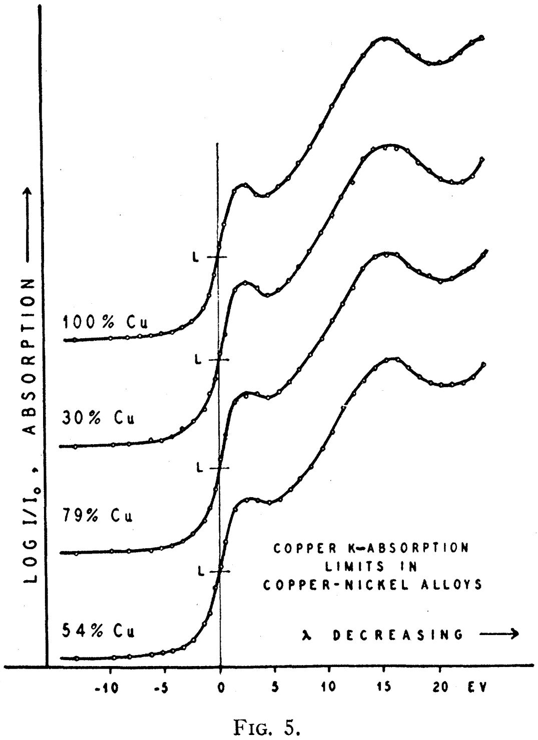

FIG. 5.

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[4] J. A. Bearden and H. Friedman, Phys. Rev. this issue.

paper by Bearden and Beeman[5] on nickel-zinc alloys. The measurements shown in Figs. 2, 3, 4, and 5 are the results on a set of alloys supplied us by the American Platinum Company. Target samples were about 1 mm thick, and foils for absorption measurements were rolled from the above samples to a thickness of about 0.001 cm. As a check on the alloys used, the measurements have been repeated with two duplicate sets of alloys, one loaned us by Dr. Mary Wheeler[6] of Vassar College, and the other by Dr. B. Kurrelmeyer[7] of Brooklyn College. Measurements on all three sets agree within the experimental error.

Figures 2, 3, 4, and 5 give, respectively, the nickel $K\beta_5$ emission for pure nickel and the three alloys, the copper $K\beta_{2,5}$ emission for pure copper and the alloys, and the corresponding nickel and copper K-absorption limits. The abscissae are labeled positively and negatively with respect to a zero corresponding to a transition of a K electron of the pure metal into the lowest empty levels of the valence electron band system. The zero is determined by matching the initial absorption rise to an arctangent curve as described in reference 1. Positive abscissae correspond to unfilled levels above the Fermi distribution, and negative abscissae to filled levels below the surface of the Fermi distribution. The scales of ordinates have been adjusted so that all curves have the same total height from top to bottom, and successive curves have been displaced equal distances vertically to facilitate comparison.

The experimental results indicate that the copper absorption begins at the same energy, within a probable error of 0.3 ev, in the pure metal and in the alloys. Three of the nickel curves of Fig. 4 fall together within the 0.3 ev limit, but the low nickel percentage nickel K edge appears to be displaced at the inflection point L by 0.8 ev from the pure nickel edge. This displacement is very uncertain because of the considerable difficulty experienced in obtaining sufficiently good data on such a low percentage nickel alloy to make possible an accurate determination of the inflection point L. Repeated measurements on this nickel K edge in 21 percent nickel have, however, indicated a mean value for the L abscissa much closer to that found for the alloys with higher percentages of nickel than is indicated in Fig. 4.

TABLE I. *Widths of* Ni $K\beta_5$ *and* Cu $K\beta_{2,5}$ *lines at half-maximum.*

PERCENT Ni	Cu WIDTH	Ni WIDTH
0.0	8.2 ev	
21	7.8	8.8 ev
46	8.0	7.9
70	8.0	7.5
100		7.2

The emission lines show marked changes in shape but hardly any shift of the line as a whole. If one defines the center of the line as its horizontal midpoint at the half-maximum intensity, then any shifts of the center are less than one-half ev for both copper and nickel. The widths of the lines measured in the manner described in reference 4 are given in Table I.

Only in nickel is any trend noticed. The copper widths are equal within the experimental error.

DISCUSSION

I. Emission lines

The work of Farineau on the $L\alpha$-emission lines of copper and nickel in alloys with each other and with aluminum[8, 9] shows quite definitely that the 3*d* bands of these elements tend to narrow up when the distance between like atoms is increased by alloying. The magnitude of this narrowing is not easy to estimate quantitatively, but appears from his microphotometer traces to be in the neighborhood of from 25 to 30 percent for the smallest concentrations. It generally is not very noticeable until the emitting atom is reduced to a concentration of less than 50 percent, and the nickel line actually appears to widen when the nickel is present in large amounts in a copper-nickel or aluminum-nickel alloy. Farineau has attributed this initial widening to the filling of the empty states in the nickel 3*d* band by the valence electrons of the other component of the alloy.

Comparing our results with the data of Farineau, it appears at first that a consistent

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[5] J. A. Bearden and W. W. Beeman, Phys. Rev., preceding paper.

[6] Mary A. Wheeler, Phys. Rev. **56**, 1137 (1939).

[7] W. H. Keesom and B. Kurrelmeyer, Phys. Rev. **57**, 1068A (1940).

[8] J. Farineau and M. Morand, J. de phys. et rad. **9**, 447 (1938).

[9] J. Farineau, J. de phys. et rad. **10**, 327 (1939).

interpretation of both sets of experimental evidence would not be easy to attain. In contrast to his data, our results for the alloys are mostly in the direction of a broadening or smearing out of the emission line structures present in the pure metals. The two sets of data can, however, be shown to agree if one ascribes the changes in appearance of the $K\beta_{2,5}$ lines in the alloys to a loss of 3*d* emission. This can be seen as follows. The narrow low frequency peak in copper has been ascribed to 3*d* emission. It is superposed on a broad band of 4*s* emission. This same sharp 3*d* emission is present in nickel, but since the nickel 3*d* band is partially empty, the high frequency limits of the 3*d* and 4*s* emission coincide. Emission from 3*d* and 4*s* therefore adds up to give a rather sharp peaked but structureless nickel line. Now, if this 3*d* emission disappears in the alloys, there will remain only the broad 4*s* emission band, which is what the experimental results show. The nickel line appears rather flatter and broader across the top at greatest dilution of nickel than does copper in the lowest percentage copper alloy, but this is not unexpected for two reasons. First, we have measured nickel in a 21 percent nickel alloy, while our lowest percentage copper alloy contains 30 percent copper. Secondly, the nickel 3*d* emission is probably broader than that of copper, due to the greater radius of the nickel 3*d* wave functions and its loss would leave a flatter 4*s* emission. It should also be noticed that the loss of 3*d* emission does not appear to be large until the percentage of the metal concerned falls to 50 or below. This is in general agreement with Farineau's findings on the narrowing of the 3*d* band.

In seeking to explain why the narrowing of the 3*d* band should cause a disappearance of the 3*d* emission in the $K\beta_{2,5}$ lines, one is forced to the conclusion that this emission is dipole radiation resulting from a mixture of "*p*" function at the top of the 3*d* band. This is rather plausible. Experimentally it is clear that we are getting radiation from only a part of the 3*d* band. If one considers the 3*d* radiation of pure nickel and copper apart from the broad underlying 4*s* band radiation, and corrects the former for the width of the crystals and the *K* excited state (about 2 ev) it is evident that the band levels giving rise to this radiation extend over a range of not more than one ev. But Farineau's work indicates that the complete 3*d* bands of copper and nickel are between three and five ev[10] in width. It is also clear from the position of the 3*d* emission close to the high frequency side of the $K\beta_{2,5}$ line in both copper and nickel, that the states giving rise to the radiation are at the top of the 3*d* band. On theoretical grounds one would expect any admixture of "*p*" function in the 3*d* band to be greatest near its upper limit because there the energy of the states is more nearly that of the atomic 4*p* levels. Krutter's calculations of the band structure of copper also showed a much greater admixture of "*p*" function near the top than near the bottom of the 3*d* band.[11] If this interpretation of the radiation is accepted, then it is understandable enough that when like atoms are separated in a dilute alloy, the decreased interaction of similar atomic states which leads to a narrowing of the band will also lead to a reduction in the admixture of "*p*" function in the band.

The above hypothesis is in fairly good agreement with the experimental data on the other alloys, the greatest difficulty arising in the interpretation of the zinc 3*d* emission. The $K\beta_5$-emission line of zinc from the pure metal and its alloys indicates a 3*d* band not more than one-half volt wide, and about eight ev below the top of the Fermi distribution.[12] In the previous work the zinc 3*d* radiation has been interpreted as quadrupole because the band seems too narrow to contain any appreciable admixture of other wave functions, and also because the same line persists in the spectra of elements of higher atomic number where the 3*d* orbits must be definitely atomic in character. The zinc 3*d* radiation is affected hardly at all by alloying, another indication of the atomic character of the electrons. The question then arises why quadrupole radiation does not give definite indication of the entire extent of the copper and nickel 3*d* bands, and the answer seems to be that if the band is three to five ev wide instead of one-half ev, the emission is

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[10] In arriving at these figures a correction of 1.0 ev for the width of the L_{III} excited state has been subtracted from the photographed band width.

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

[12] J. A. Bearden and H. Friedman, Phys. Rev. this issue.

spread over too great an interval to be noticeable compared to the more intense *3d* dipole radiation. The quadrupole transition is prominent in zinc and elements of higher atomic number only because the band is narrow and therefore the density of states high. There is also the evidence of the $L\alpha$ line[13] on the width of the zinc *3d* band. It would seem to indicate a band somewhat wider than one-half ev, perhaps as wide as 2.0 ev. Theoretically one would expect a very rapid narrowing of the *3d* band with atomic number as soon as the *3d* wave functions become so small that those of nearest neighbors overlap only in the region of exponential decay of the wave functions. This probably occurs near the end of the first transition group. In addition, the distance between nearest neighbors is greater in zinc than in any of the immediately preceding metals. Both factors will tend to narrow the zinc *3d* band.

It would also be expected that the *3d* radiation of copper and nickel, if it is dipole, would disappear in alloys of these elements with zinc. Unfortunately the zinc-nickel measurements[5] have not been carried out on alloys of sufficiently high zinc content to furnish a test. The results on the brasses,[4] while somewhat complicated, do, however, indicate a loss of *3d* band dipole emission upon lowering the copper content of the alloys.

The emission line widths given in Table I are what one would expect from a loss of the narrow 3d emission. Because of this loss, half-width measurements are made lower on the *4s* emission band in the alloys than in the pure metals. This probably explains the considerable widening of the nickel line. The copper line keeps about the same width throughout the series, but in copper the loss of *4s* electrons to nickel tends to narrow the line, compensating for the other effect.

II. Absorption edges

In a previous paper[2] the K-absorption edges of pure copper and nickel were discussed. The experimental results on copper were found to be in good agreement with the band calculations of Krutter and Slater (Fig. 1) and the differences between copper and nickel, mainly the absence in nickel of the absorption minimum about 4 ev beyond L in the copper edge, seemed understandable because of the greater overlap of the nickel wave functions.

However, the curves of Figs. 4 and 5 show that no appreciable difference from the pure Cu K-absorption limits appears in the Cu absorption limit for any of the alloys and similarly, all the nickel curves are closely alike. These results are supported by the data of T. Hayasi[14] on the pure metals and a 50–50 Cu-Ni alloy. The above data indicate that it is not entirely correct to compare the structure of the absorption edge with the calculated bands. The failure to find any effect of alloying cannot be taken as evidence for the identity of the two band systems, since the two absorption edges are quite different, particularly the structures close to the initial absorption. It would appear, rather, that the lower energy states into which the K electron can be excited are determined mainly by the field of the absorbing atom itself and not by the periodic lattic field. It has been suggested by several authors[15, 16] that the ionization of the K shell of the absorbing atom leaves its outer electrons moving in a field similar to that of the atom of next higher atomic number. As a consequence, the states which should be used in any attempted explanation of the observed absorption of pure copper are not those calculated by Krutter and Slater for the normal copper lattice, but rather the allowed states for an electron about an atom of zinc occupying one of the sites in a copper lattice. These are sometimes called reduced states. Since electrons tend to cluster around an ionized atom and shield its extra positive charge, it seems quite likely that the wave function of the ejected K electron does not extend any great distance from the absorbing atom and therefore that the energy distribution of the final states will not be very sensitive to whether the surrounding atoms happen to be copper or nickel. These considerations probably do not apply to absorption structure except within a very few volts of the edge, since an electron ejected with any considerable velocity

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[13] J. Farineau, Ann. de physique **10**, 20 (1938).

[14] T. Hayasi, Tohoku Univ. Sci. Reports **25**, 598, 606, 661 (1936).

[15] H. W. B. Skinner, Proc. Roy. Soc. **140**, 277 (1933).

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

cannot be thought of as remaining in the vicinity of the parent atom.[17] Even close to the edge the structure must be somewhat similar to what one would calculate for the normal lattice, since all the general features of the absorption data of reference 1 can be understood without introducing the idea of reduced states. We might expect then that absorption structure close to the edge should be less sensitive to alloying than are the emission lines, since in the final state of the emission process the *K* shell is filled and the structure of the line will be determined by which state of the normal lattice band is left empty. However, the failure of the copper and nickel edges to show any change at all in the copper-nickel alloys may be partly due to peculiarities of this alloy series. The two metals have about the same number of 4*s* electrons in the pure state, nickel 0.6 4*s* electron per atom and copper 1.0, necessitating very little shift of the top of the Fermi distribution on alloying. Also, the field of a copper and of a nickel atom at a neighboring lattice point should be rather similar, since the differences in the outer shells of the two atoms consist mostly of the extra 3*d* electrons added to copper. Their wave functions have small radii compared to the 4*s* so that the shielding of the extra nuclear charge of copper is good at a distance comparable to the lattice distance.

It is not surprising that in the brasses there are changes of the absorption edge with alloying[12] since the peculiarities of the copper-nickel series are absent. The brasses exist in several phases, there are considerable changes in the population of the 4*s* band from one end of the series to the other, and differences in the atomic fields of Cu and Zn must extend some distance from the atom because of the large radius of the 4*s* wave function.

The nickel absorption edges in the nickel-zinc alloys show no changes, but this is at least partly due to the absence of measurements on alloys containing a large percentage of zinc.

The failure to find a shift of the initial absorption in the copper-nickel series is in agreement with some measurements of Bor, Hobson and Wood[18] on the optical constants of the same alloys. Pure Cu has an absorption maximum beginning at about 5900A and extending to shorter wave-lengths. Mott[19] believes this absorption is due to transitions of 3*d* electrons to the first empty states of the 4*s* band. If 4*s* electrons are shared with Ni, this absorption should shift to larger wave-lengths in the Cu-Ni alloys. Experimentally only a very slight shift is noticed, much less than that predicted by the theory.

III. Conclusion

There now exist x-ray measurements of the band structures of the alloy systems Cu-Ni, Zn-Ni, Cu-Zn, Al-Cu, and Al-Ni, as well as a few other isolated alloys. References to the latter can be found in Skinner's review article on soft x-ray spectroscopy in the 1938 "Reports on Progress in Physics." The results indicate that in nearly all binary alloy systems the band electrons distribute themselves quite differently around the two constituents of the same alloy. Farineau[13] has reported identical emission lines from Al and Mg in Al_2Mg_3 and in Al_3Mg_2, but these appear to be the only such cases. As a rule there are great differences not only in the general appearance of the emission lines and absorption edges of the same alloy, but also in the energy breadth of the filled levels which one deduces for the two components from the widths of their emission lines. This latter is particularly well illustrated by the Al-Cu and Al-Ni series.[9] Pure Al has an emission band 11 or 12 ev wide, Cu about 8 or 9, and Ni 5 or 6 (these widths are not corrected for the lifetime of the excited state), and the bands maintain these same widths throughout the whole alloy series. The only evidence for a sharing of the higher energy electrons of Al with Cu or Ni is the reduction in the alloys of the intensity of the high frequency part of the Al line and a slight broadening of the Cu and Ni lines. There is, however, no shift of the high energy limit of the Al emission and there-

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[17] However, comparing the zinc absorption edge in an α-brass or in the zinc-nickel alloys with the edges of Cu or Ni, one sees differences in the shape of the curves as much as 15 or 20 ev from the initial absorption.

[18] J. Bor, A. Hobson and C. Wood, Phys. Soc. Proc. **51**, 942 (1939).

[19] N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford Press, 1935).

fore no evidence for a lowering of the absolute energy of the top of the Fermi distribution with alloying. This is the same kind of behavior as that exhibited by the zinc line in the brasses[12] which was there discussed from the viewpoint of the shielding of the zinc ion by the lattice electrons, leading to a much smaller residual positive charge about the zinc than would be the case with complete sharing and therefore a smaller than anticipated reduction in the intensity of the high frequency side of the line. The data seem to show that when metals of high and low valence are alloyed the charge density around the atoms of higher valency is decreased somewhat compared to what it would be in the pure metal, but that the energy of the highest filled states is decreased hardly at all. These facts may be summarized by stating that the differences in the average internal potentials of two metals are at least as important as are differences in the kinetic energies at the top of the Fermi distribution in determining how their filled levels will adjust themselves when the two are alloyed. Ordinarily only the latter difference is considered, but the experimental results indicate that the smaller average potential of the higher valence metal of a binary alloy lowers the energy of the whole band about as fast as its extra valence electrons raise the kinetic energy of the highest filled levels. The total energy of the highest filled levels therefore does not change with alloying. Such an assumption explains not only the failure to find any shifts of absorption edges or emission lines, but also the existence of emission lines with quite different widths from the two components of the same alloy. The electrons about the atom of higher valence have a wider distribution in energy because of the lower potential. The above discussion properly applies only to conduction electrons. Empty states in the *3d* band in nickel may be favorable enough energetically to permit a considerable ionization of an element of higher valency. An actual lowering of the Fermi distribution was found in the Ni-Zn series although Farineau does not find it in the Ni-Al alloys.

A second conclusion which is well substantiated by all the data is that the atomic *3d* states of copper and nickel are broadened mainly by interaction with the *3d* states of identical neighboring atoms and only slightly by interaction with the states of unlike atoms. Both Farineau's work and our own indicates that mere separation of like atoms produces an appreciable narrowing of the *3d* band. The narrowing seems to be independent of what alloy of copper or nickel is used.

We are greatly indebted to Professor J. A. Bearden, under whose direction this work was carried out. It is a pleasure to acknowledge the assistance given by members of the Baltimore-Washington solid state seminar through discussion of these problems, and the financial assistance granted to Professor Bearden by the American Philosophical Society which has made the experimental measurements possible. We also wish to thank Dr. Mary Wheeler and Dr. B. Kurrelmeyer for the loan of their alloys.