The K-Absorption Edges and $K\beta_{2,5}$-Emission Lines of Two Zn-Ni Alloys*

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A double crystal spectrometer has been used to measure the shapes of the $K\beta_{2,5}$-emission lines and the K-absorption edges of zinc and nickel in two zinc-nickel alloys containing 17 percent zinc and 30 percent zinc by weight, respectively. These lines arise from transitions of valence and 3d electrons into the empty K shell. In the two alloys the zinc emission line and absorption edge are shifted about a volt toward lower energies and the line is narrowed. Nickel is changed only slightly. The results indicate that the higher energy valence electrons of zinc are shared with nickel and probably go into $3d$ states about the nickel atoms.

INTRODUCTION

THE metals of the first transition group have an unfilled $3d$ band which is responsible for their ferromagnetism, high electronic specific heats and low conductivities.[1] In nickel this band lacks completion by only 0.6 electron per atom and therefore is filled in an alloy of nickel with 60 atomic percent copper or 30 atomic percent zinc, assuming that the $4s$ electrons of copper and zinc are completely shared. There is much evidence, based on the magnetic properties of these alloys, that such a sharing of electrons actually takes place. A full discussion may be found in reference 1. Later work[2] has made it doubtful if the sharing is really complete, but there can be no doubt that it is considerable and also that the degree of filling of the $3d$ band is one of the most important factors in determining the magnetic, electrical, and thermal properties of these alloys.

We have made x-ray measurements on two zinc-nickel alloys containing 17 percent zinc and 30 percent zinc by weight, respectively. They are two of those used by Dr. Wheeler of Vassar College in her recent work[2] on the paramagnetic susceptibilities of a series of copper-nickel and zinc-nickel alloys. The reader is referred to her paper[2] for details of their preparation and heat treatment. The present paper seems to be the first report on the x-ray spectra of this alloy series. Both of the present alloys crystallize in the face-centered cubic system, as does pure nickel. The limit of solubility of zinc in the nickel lattice is about 39 percent zinc at room temperatures, and the solution is not accompanied by any great distension of the lattice. The lattice constant increases by less than 2 percent in going from pure nickel to the 30-percent zinc alloy.

Our experimental procedure was the same as that described in the preceding paper on the brasses[3] except that smaller pieces, about 0.03 cm thick and 0.6 cm in diameter, were soldered to the copper target for the measurement of emission lines. The same precautions as before[3] were observed in correcting for the W $L\beta_1$ line which is just on the high frequency side of Zn

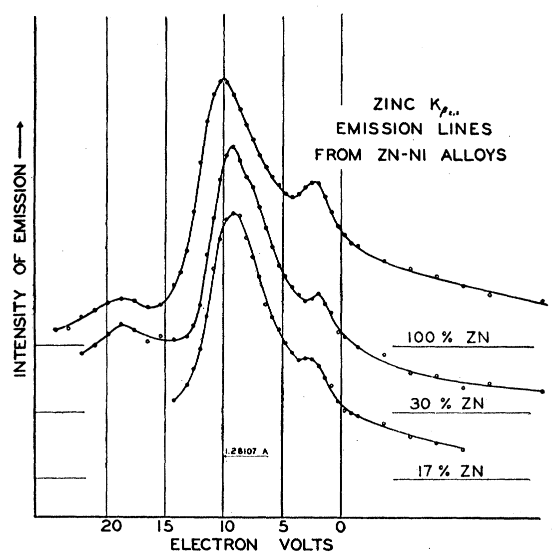

FIG. 1. Zinc $K\beta_{2,5}$-emission lines from zinc-nickel alloys.

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[1] N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford Press, 1936), p. 189.

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

[3] J. A. Bearden and H. Friedman, Phys. Rev., preceding paper.

$K\beta_2$. Another tungsten line, $L\alpha_2$, interferes with the measurements on Ni $K\beta_5$, but its intensity is too low to cause any error. However, the same procedure was followed of outgassing the filament while shielding the target with a molybdenum plate. None of the emission lines was run with more than 300 watts expended in the target. Absorption foils were rolled to a thickness of approximately 0.001 cm and absorption measurements were made as previously described.[3]

Experimental Results

The experimental results are shown in Figs. 1 to 3. The scale of intensity of each emission curve, Figs. 1 and 2, has been adjusted so that they have the same height. Successive curves are displaced vertically and the zeros of emission indicated by the two horizontal lines under each curve.

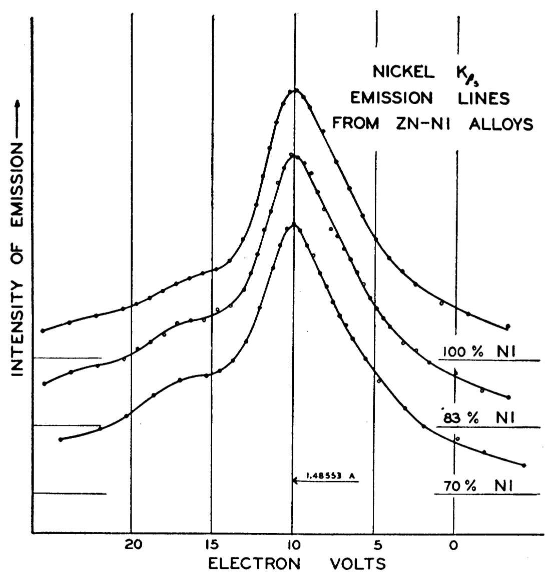

FIG. 2. Nickel $K\beta_5$-emission lines from zinc-nickel alloys.

No shifts of the peak of the nickel line were observed, but the main peak of the zinc line in the alloys was shifted about 0.9 ev toward lower energies with respect to that of pure zinc. The low frequency zinc peak due to $3d$ emission is not shifted by more than 0.3 ev. We have also measured the widths at half-maximum, and the asymmetries of these lines, and obtained the data shown in Table I. The asymmetry is defined as the part of the width at half-maximum

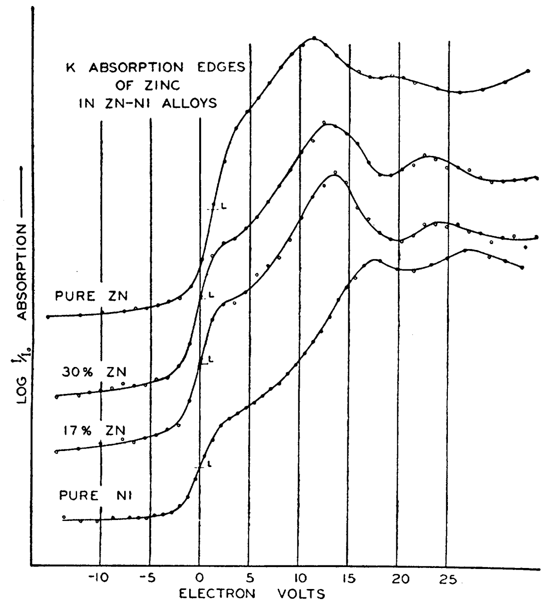

FIG. 3. The K-absorption edges of pure nickel and of zinc from zinc-nickel alloys.

on the low frequency side of the peak of the line divided by the part on the high frequency side. It is one for a symmetrical line.

In both nickel and zinc there is considerable satellite intensity, so half-widths have been measured to the projection of the straight part of the high frequency side of the line as described in reference 3. This involved only small corrections. The low frequency $3d$ peak of the zinc line also was subtracted before making half-width measurements. No corrections have been made in the tabulated half-widths for the crystal or the width of the K excited state.

Only four absorption edges are shown in Fig. 3, as the nickel edge in the alloys is indistinguishable from that of pure nickel. However, the zinc edge, just as with the emission line, shows marked changes from the pure metal to the alloy, notably a shift to lower energies of 1.3 ev of the point L marking the top of the Fermi distribution.[4] The absolute wave-lengths corresponding to the point L are, pure zinc 1.2807A, pure nickel, 1.4852A.

It is believed that the errors in the absolute energies of the peaks of the lines and the tops of the Fermi distributions are no greater than

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

± 0.3 ev, while the half-widths of the lines are probably correct to ± 0.2 ev.

Discussion

The narrowing of the zinc line and the shift to lower energies of its main peak are most easily explained as results of the loss of higher energy zinc electrons to the empty states in the narrow $3d$ band of nickel. However, this evidence is not conclusive, as the same effects would be produced if alloying merely cut down the intensity of emission on the high frequency side of the zinc line, perhaps by changing the transition probability, without actually ionizing the zinc atom. Farineau[5] has published some soft x-ray lines involving the valence electrons of nickel and aluminum in a series of nickel-aluminum alloys. His voltage resolving power is greater that that obtainable in the hard x-ray region, and he was able to show that the aluminum line from alloys of increasing nickel content does not shift or narrow if one measures along the bottom of the line but rather that the intensity of high energy emission is greatly reduced.

Better evidence for a lowering of the top of the Fermi distribution as nickel is alloyed with zinc is furnished by the shift of the zinc absorption edge. This amounts to 1.3 ev according to our measurements, and there can be no serious error due to the finite width of the K excited state and the crystals, as the method of determining[4] the point L takes into account these factors. It is quite conceivable that the change from the hexagonal close-packed structure of pure zinc to the face-centered cubic lattice of the alloys could cause such a shift, but this is not likely in view of the results of Bearden and Friedman,[3] who found no displacement of the zinc edge in the α-brasses, which have also a face-centered cubic lattice but no holes in the $3d$ band.

The results on nickel indicate that the electrons lost by zinc go into a band in which the density of states is high and the probability of transitions to or from the K shell low. These are both characteristics one would expect of the nickel $3d$ band. The first conclusion may be understood by the following reasoning. If the

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

Table I. *Widths at half-maximum and asymmetry of zinc line from alloys.*

Line	Width in ev	Asymmetry
100 Ni	7.1	1.7
83 Ni	7.4	1.5
70 Ni	7.6	1.4
100 Zn	9.4	2.8
30 Zn	7.2	1.8
17 Zn	7.2	1.7

energy densities of states at the highest filled levels were the same in zinc and nickel, the shifts of the absorption edges due to taking a certain number of electrons from zinc and placing them around nickel would be inversely proportional to the atomic concentrations of the elements and in opposite directions. This would predict a displacement of the nickel edge of about 0.6 ev toward higher energies in the 70 percent Ni alloy. No shift was observed, indicating that the nickel lattice can accommodate a considerable number of electrons without greatly increasing the energy of the highest filled level. On the other hand, the transition probability to these states must be low because in nickel they are empty and contributing to the intensity of the initial absorption, while in the alloys they are filled and make no contribution to the absorption. Experimentally no change in the appearance of the absorption edge is detectable. The fact that only minor changes occur in the nickel emission line is in agreement with the above conclusions. Most of the structure of both the emission line and absorption edge of nickel must be due to the $4s$ band which overlaps the $3d$. As long as there are empty states in the $3d$ band, however, very few electrons will go into the $4s$ band and the changes in the emission and absorption spectra with alloying will be slight.

It is not possible to say just what fraction of an electron per zinc atom is lost to the lattice in these alloys, but it must be greater than the 0.1 electron per atom which zinc[3] loses when completely surrounded by copper, since no shift of the zinc absorption edge is observed in any of the brasses. On the other hand, the ionization of the zinc in the present alloys is almost certainly not as great as the 1.4 electron per atom which it would lose if the $4s$ electrons were completely shared with the nickel. The simple free electron theory would predict in this case a lowering of the top of the Fermi distribution of about 3.4 ev, but no shift of the zinc absorption edge or narrowing of the line of this magnitude is observed. Wheeler[2] found that the paramagnetic suceptibilities of these alloys do not approach zero as the concentration of zinc approaches 30 atomic percent, which would seem to show that some 3d states remain unfilled even when the total number of electrons in the lattice is sufficient to fill them. One would expect this if the sharing is incomplete, i.e., if after a certain ionization of the zinc core is reached it is energetically more favorable for electrons to shield the zinc than to go into nickel 3d states. It is interesting to note that Wheeler always found a higher paramagnetic susceptibility for a zinc-nickel alloy containing X atomic percent zinc than for a copper-nickel alloy containing $2X$ atomic percent copper. If sharing were complete there would be the same number of electrons in the $3d$ band in each case; however, one would expect greater deviations from complete sharing with zinc because of its higher charge. There is x-ray data in agreement with the results of Wheeler, Farineau and Morand[5, 6] and Friedman and Beeman[7] have published some emission lines from nickel in nickel-aluminum and nickel-copper alloys which indicate that when nickel is present in concentrations of less than 50 percent, its 3d band narrows and the highest $3d$ levels are reduced to somewhat lower energies. This would tend to give a more complete filling of the band in the nickel-copper than in the nickel-zinc alloys.

Some conclusions of interest can be drawn from the remaining data, particularly the widths and asymmetries of the zinc lines. The observed narrowing of the zinc line in the alloys would be expected simply because of the partial ionization of the zinc atom, but a decrease in width of 2.2 ev is more than can be accounted for in this way. In addition, the fact that the asymmetry decreases rather than increases with alloying shows that the larger part of this narrowing is due to a loss of intensity on the low frequency side of the line. A glance at Fig. 1 makes this apparent. The 3d peak is seen to be much further down the low frequency side of the line in the alloys than in pure zinc, indicating that the $4s$ emission at the same wave-length as the 3d peak is less intense in the alloys relative to the main peak of the line. The reason for this is probably that the stronger field of zinc lowers its $4s$ band sufficiently with respect to that of nickel so that the least energetic zinc $4s$ electrons cannot escape from their parent atom at all when zinc is largely surrounded by nickel, as in the present alloys. Under these circumstances they would behave very much as atomic $4s$ electrons and have no chance of making a transition to the K shell.

It is to be noted that here, as with the brasses, the zinc $3d$ electrons appear to be tightly bound and but little affected by alloying. No sign of emission due to them is found in the nickel lines.

We wish to thank Dr. Mary A. Wheeler for kindly lending us the alloys used in this research, and the members of the Baltimore-Washington solid-state seminar for numerous discussions of the material involved. The financial assistance given by the American Philosophical Society is greatly appreciated.

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

[7] H. Friedman and W. W. Beeman, Phys. Rev., following paper.