Effect of Alloying on the Aluminum K and Nickel L X-Ray Emission Spectra in the Aluminum-Nickel Binary System

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The aluminum $K\alpha_4/K\alpha_3$ satellite-line intensity ratio and the aluminum K and nickel L emission bands from a series of aluminum-nickel binary alloys have been studied using 6-kV electrons and a flat-crystal x-ray vacuum spectrometer equipped with a flow counter. The $K\alpha_4/K\alpha_3$ intensity ratio varies in a linear manner with aluminum content, going from 0.48 in the pure metal to 0.84 in the 4 Al–96 Ni alloy. As the aluminum content is decreased, the Al K band shifts progressively to lower energy and becomes more symmetrical in shape. The K-band intensity maximum shifts in a linear manner with aluminum content although the Ni L_{III} band does not. It appears from the data, however, that the Ni L_{III} emission edge broadens considerably as the nickel content is decreased and that the overlapping high-energy satellite becomes progressively weaker.

I. INTRODUCTION

ALTHOUGH the investigation of soft–x-ray emission band spectra of metals and alloys has been the subject of several investigations, little is really known of the effect of alloying on the emission spectra of the light metals. Recent publications by Appleton[1] and Thompson and Kellen[2] provide a good review of the work done to date and the problems of interpreting the results. The reader, however, is left with the impression that large changes are not seen in the metal spectrum as a result of alloying. Apparently the alloy systems which have been investigated so far do not result in much of a change in the band spectra but we intend to show that there are alloy systems in which both the band and line spectra undergo rather large changes.

Previously we have shown that the aluminum K spectrum, especially the K band and the $K\alpha_3$ and $K\alpha_4$ satellite lines, change significantly between metal and oxide[3,4] and other aluminum compounds.[5,6] This led, in turn, to a study of some aluminum binary alloy systems and the results of the aluminum-nickel system are presented here.

II. EXPERIMENTAL TECHNIQUES

A. Instrumentation

The flat-crystal vacuum spectrometer used for this study has been described previously.[7] Characteristic soft x rays were produced by electron bombardment. The electron beam was operated at 6 kV and 1 to 5 mA for the aluminum spectra and 5 kV and 2 to 8 mA for the nickel spectra. An EDDT crystal (ethylene diamine

[1] A. Appleton, Contemp. Phys. 6, 50 (1964).
[2] B. J. Thompson and P. F. Kellen, *Developments in Applied Spectroscopy* (Plenum Press, Inc., New York, 1965), Vol. 4.
[3] D. W. Fischer and W. L. Baun, J. Appl. Phys. 36, 534 (1965).
[4] W. L. Baun and D. W. Fischer, Phys. Letters 13, 36 (1964).
[5] W. L. Baun and D. W. Fischer, Nature 204, 642 (1964).
[6] W. L. Baun and D. W. Fischer, Air Force Materials Laboratory Report No. AFML-TR-64-350, 1964 (unpublished).
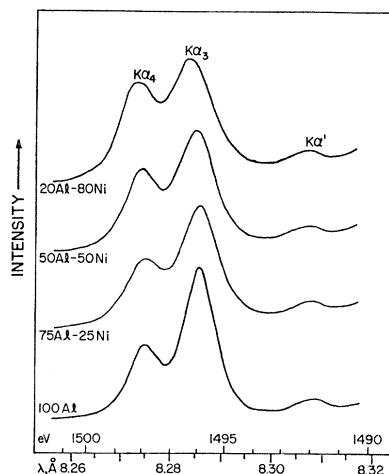[7] D. W. Fischer and W. L. Baun, Spectrochim. Acta 21, 443 (1965).

d-tartrate, $2d=8.8030$ Å) was used for Al K, gypsum ($2d=15.207$ Å) was used for Ni L. The detector was a thin window-flow proportional counter using an argon-methane (P-10) flow gas. A sample holder accommodating four specimens was used so that samples could be compared under exactly the same conditions. Usual operating vacuum was 10^{-5} Torr or better. All recording electronics including pulse-height analyzer were Picker equipment except for a low-noise preamplifier by Tennelec. The resultant rate meter scans and the curves shown in the figures have a mean deviation of $\pm 2\%$.

B. Sample Preparation

The Al–Ni samples were prepared primarily by arc melting in an argon atmosphere. Many alloys were also prepared by levitation melting. The x-ray diffraction patterns from products obtained by each technique were identical. At compositions where stoichiometric compounds were formed such as $NiAl_3$ and Ni_2Al_3, very fine powders were pressed into pellets and sintered. At these points where single-phase compounds were formed, both the x-ray diffraction patterns and x-ray emission spectra were recorded and found to agree well for samples prepared by sintering, arc melting, and levitation melting.

The samples were mounted on the anode in the form of solid pellets. The brittle alloys were also ground into fine powder and spread in a thin layer on the anode surface. No differences in either the aluminum K or nickel L spectra were observed between these two methods. Four samples were mounted at one time, one of them always being the pure aluminum metal which was used as a calibration standard. All of the Al $K\alpha_3/K\alpha_4$ ratios and Al K-band shifts and shape changes were measured in relation to the pure-metal spectrum.

III. EXPERIMENTAL RESULTS

A. Aluminum K Spectrum

It has previously been shown that the intensity ratio and wavelength position of the Al $K\alpha_3$ and $K\alpha_4$

FIG. 1. Aluminum $K\alpha'$, $K\alpha_3$, and $K\alpha_4$ from some Al–Ni alloys.

TABLE I. Comparison of Al $K\alpha_4/K\alpha_3$ intensity ratio in the Al–Ni system using macro- and micro-area excitation.

Sample	$K\alpha_4/K\alpha_3$ Macro-area excitation	$K\alpha_4/K\alpha_3$ Microprobe
Pure Al	0.48	0.48
85 Al–15 Ni (2 phase)	0.54	0.50 Al rich
		0.55 Ni rich
75 Al–25 Ni (Al$_3$Ni)	0.57	0.57
65 Al–35 Ni (2 phase)	0.61	0.60 Al rich
		0.63 Ni rich
50 Al–50 Ni (AlNi)	0.66	0.66

satellite lines are strongly dependent on the state of chemical combination of the aluminum.[3-6,8]

The largest change in the $K\alpha_4/K\alpha_3$ intensity ratio occurs when going from the pure metal to the oxide where the ratio jumps from 0.48 to 0.92. It was found that other aluminum compounds give $K\alpha_4/K\alpha_3$ intensity ratios which fall between these two extremes.[5] The aluminum intermetallic compounds give ratios between 0.48 and 0.85 while the semiconductor and insulator compounds give ratios between about 0.85 and 0.98. In a previous publication we listed these ratios for the metal and oxide as 0.50 and 0.94, respectively.[3] Owing to increased resolution we have altered these values to 0.48 and 0.92.

In most of the work done on binary alloy systems, an effort has been made to study only well characterized

single-phase compositions. We, however, were also interested in looking at two-phase alloys and so, for the aluminum-nickel system, examined a series of alloys which differed in aluminum content in steps of about 5 at. % from pure aluminum down to 4 Al–96 Ni.

Figure 1 shows the $K\alpha_4$ and $K\alpha_3$ lines obtained from a few of the alloys. As the aluminum content decreases, the intensity of $K\alpha_4$ increases with respect to $K\alpha_3$. If we make a plot of the Al $K\alpha_4/K\alpha_3$ intensity ratio versus atomic percent aluminum we obtain the linear relationship seen in Fig. 2. From this, one would expect that, in the two-phase alloys, we are seeing an average aluminum content, because of the large beam size ($\frac{3}{4}$ in. $\times \frac{1}{4}$ in.). This fact was confirmed by using a microprobe beam, the results of which are listed in Table I. A metallurgical mount was made of a few selected alloys. The single-phase alloys gave the same $K\alpha_4/K\alpha_3$ intensity ratio with both the macro-area and micro-area excitations. In a two-phase alloy, such as 85 Al–15 Ni, the microbeam probe could excite each phase selectivity. It was found that the Al-rich and
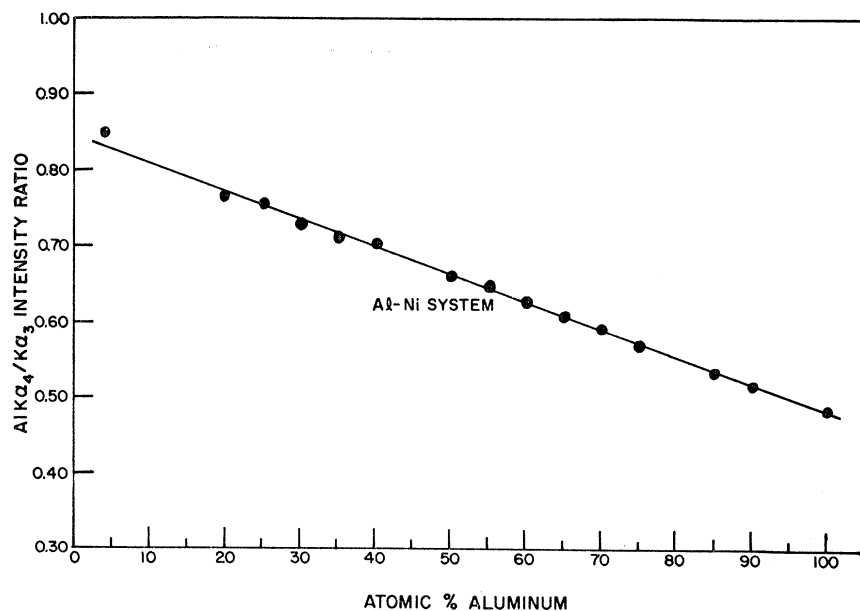

FIG. 2. Variation in Al $K\alpha_4/K\alpha_3$ intensity ratio with alloy composition in Al–Ni system.

[8] B. Nordfors, Arkiv Fysik **10**, 279 (1956).

TABLE II. Uncorrected aluminum K emission characteristics in Al–Ni system.

Target	Al $K\alpha_4/K\alpha_3$	Al $K\beta$ position (eV)	Al $K\beta$ half-width (eV)	Al $K\beta$ base width (eV)	Al $K\beta$; A_i	Al $K\beta$; A_c	Al $K\beta$ edge width (eV)
100 Al	0.48±0.01	1557.3±0.1	6.0±0.1	15.4±0.8	2.7±0.2	3.7±0.2	2.1±0.1
90 Al–10 Ni	0.52	1556.9	7.0	14.4	2.2	2.7	3.0
85 Al–15 Ni	0.54	1556.7	6.9	14.4	1.9	2.3	3.2
75 Al–25 Ni	0.57	1556.2	6.5	14.5	1.4	1.9	3.7
65 Al–35 Ni	0.61	1555.8	6.2	14.9	1.4	1.7	3.9
60 Al–40 Ni	0.63	1555.6	5.7	14.1	1.4	1.6	4.0
50 Al–50 Ni	0.66	1555.3	6.0	14.3	1.4	1.3	4.2
40 Al–60 Ni	0.70	1555.0	6.5	14.2	1.3	1.2	4.2
35 Al–65 Ni	0.72	1554.7	6.6	13.9	1.3	1.2	4.3
25 Al–75 Ni	0.76	1554.4	6.8	13.8	1.3	1.2	4.5
20 Al–80 Ni	0.77	1554.2	6.8	13.9	1.3	1.2	4.5
4 Al–96 Ni	0.84	...	...	...	...	...	...
Al_2O_3	0.92	1552.9	6.4	12.8	1.0	1.0	4.0

Ni-rich phases each gave different $K\alpha_4/K\alpha_3$ ratios and that the ratio seen by the macro-size beam gave an average of the two. This satellite line intensity ratio is reproducible to within ±1% and we have been able to use it as a quantitative tool for determining the aluminum content to within ±2% (atomic) in Al–Ni alloys. This technique may be compared to a measurement such as a lattice parameter determination in that once a curve such as that seen in Fig. 2 has been obtained, it is not necessary to run standards with each sample. The $K\alpha_4/K\alpha_3$ values obtained for a series of the alloys are shown in column 1 of Table II. They were obtained simply by dividing the peak intensity of $K\alpha_4$ by the peak intensity of $K\alpha_3$ after correcting for background. Several of these alloys were run ten or more times and the results indicate the intensity ratios listed in Table II have a deviation of no more than ±0.01.

$K\alpha_3$ and $K\alpha_4$ also shift slightly as the aluminum content is decreased. Between 100 Al and 4 Al–96 Ni the shift is about 0.4 eV to higher energy and appears to be fairly linear with composition for the entire system.

Al K Band

In terms of wavelength shift and band shape change the K band ($K\beta_1$) is more strongly affected by the state of chemical combination than any of the other aluminum emission lines.[3]

The Al K band has been studied in a few aluminum binary alloys[9–12] but as Appleton points out,[1] some of the results are subject to doubt. Recently, Nemnonov and Finkel'shtein have reported changes in the Al K band from a few single-phase aluminum-transition metal alloys.[13] For the Al–Ni system they show a change in

shape and shift in position of the Al K band compared to the pure Al metal.

We have studied the Al K band from a large number of Al–Ni alloys, both one- and two-phase structures. Figure 3 gives an indication of the changes which take place in the band as the aluminum content is varied. These curves are taken directly from ratemeter scans with no corrections applied to them. Although they probably do not represent the true shape of the valence-band structure it is assumed that the changes which occur are due to the effect of alloying.

It should be noted, however, that other parameters such as sample self-absorption and electron bombardment energies in excess of threshold potentials can profoundly affect the shape of emission bands.[14–17] All of our Al K bands were obtained at 6 kV so that the bombardment energy effect should be the same for all alloys but the changing self-absorption may be contributing in some way to the changes in band shape.

One obvious change is the shift of the intensity maximum to lower energies as the aluminum content is
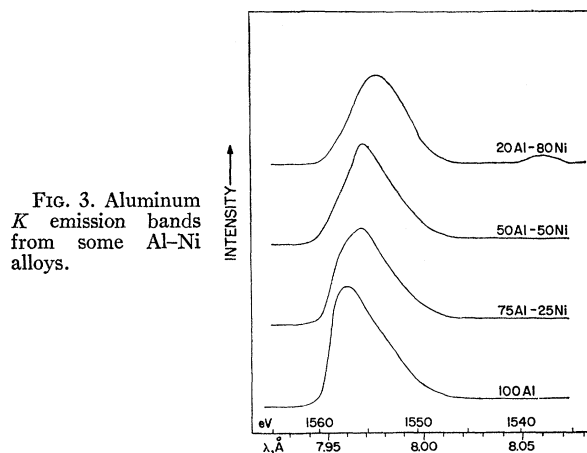

FIG. 3. Aluminum K emission bands from some Al–Ni alloys.

[9] J. Farineau, Ann. Phys. (Paris) 10, 20 (1938).
[10] J. Farineau, J. Phys. Radium 10, 327 (1939).
[11] H. W. B. Skinner and J. E. Johnson, Proc. Phys. Soc. (London) 34, 109 (1938).
[12] K. Das Gupta, California Institute of Technology Technical Report No. 6, 1963 (unpublished).
[13] S. A. Nemnonov and L. D. Finkel'shtein, Bull. Acad. Sci. USSR, Phys. Ser. 25, 1015 (1961).

[14] R. D. Deslattes, Phys. Rev. 133, A399 (1964).
[15] D. Chopra and R. Liefeld, Bull. Am. Phys. Soc. 9, 404 (1964).
[16] R. Liefeld and D. Chopra, Bull. Am. Phys. Soc. 9, 404 (1964).
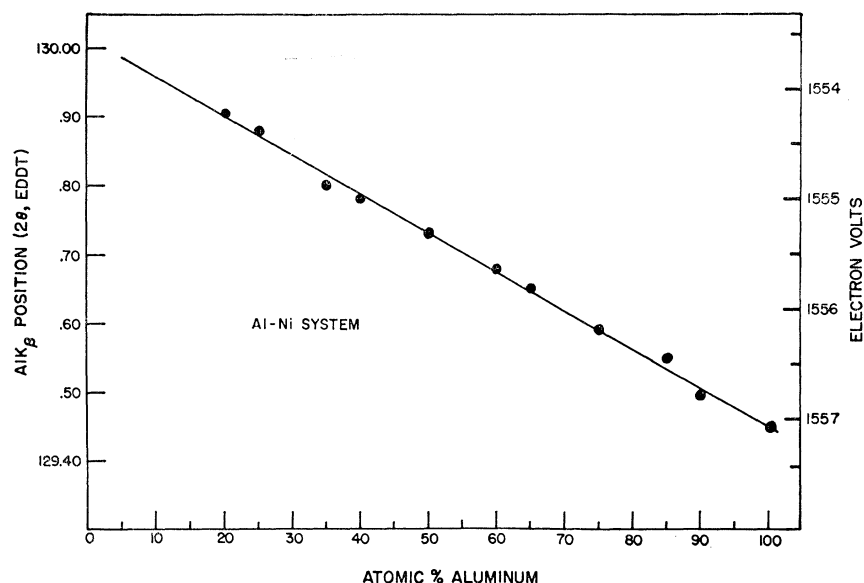[17] R. J. Liefeld, Bull. Am. Phys. Soc. 10, 549 (1965).

FIG. 4. Al K-band shift with alloy composition in Al–Ni system.

decreased. If one plots these energy positions versus the aluminum content for the whole Al–Ni system, a linear relationship such as seen in Fig. 4 is obtained. Using an EDDT crystal, these maxima can be determined to within ± 0.1 eV. The measured positions are listed in column 2 of Table II. Due to the weak intensity of the Al K band, there is in our particular experimental arrangement a lower limit of the aluminum content for which the band profile is strong enough to obtain accurate measurements of position and shape at 6 kV. For the Al–Ni system the limit is about 15 at. % Al and for this reason no K-band measurements are given for lower concentrations.

It is also quite apparent that the shape of the K band changes considerably as the aluminum content changes. The factor contributing most to this change is the broadening of the emission edge. The uncorrected edge width is listed in the last column of Table II and the variation is shown in Fig. 5. This increased broadening
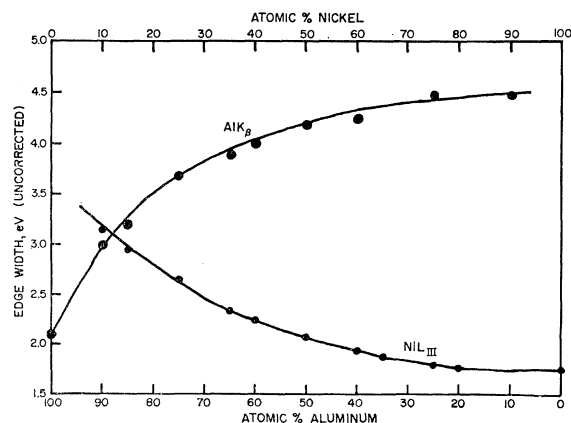
makes the K band become more and more symmetrical about the intensity maximum as the aluminum content is decreased.

As the alloy composition varies so does the K bandwidth. The uncorrected values obtained are listed in columns 3 and 4 of Table II. The bandwidth at half-maximum intensity (half-bandwidth) can be measured fairly accurately but the full bandwidth is subject to much more uncertainty because of the slow tailing off of the long-wavelength side of the band. It is apparent, however, that the band becomes progressively narrower as the aluminum content is decreased. The half-bandwidth varies much differently from the full bandwidth as is illustrated in Fig. 6. In going from Al metal to the 90 Al–10 Ni alloy, the width progressively decreases
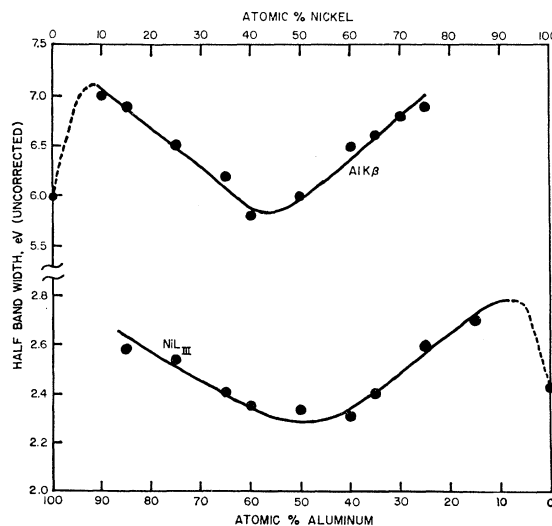

FIG. 5. Variation in uncorrected emission edge width for Al K and Ni L_{III} bands in Al–Ni system.

FIG. 6. Variation in uncorrected half-bandwidths for Al K and Ni L_{III} bands with alloy composition in Al–Ni system.
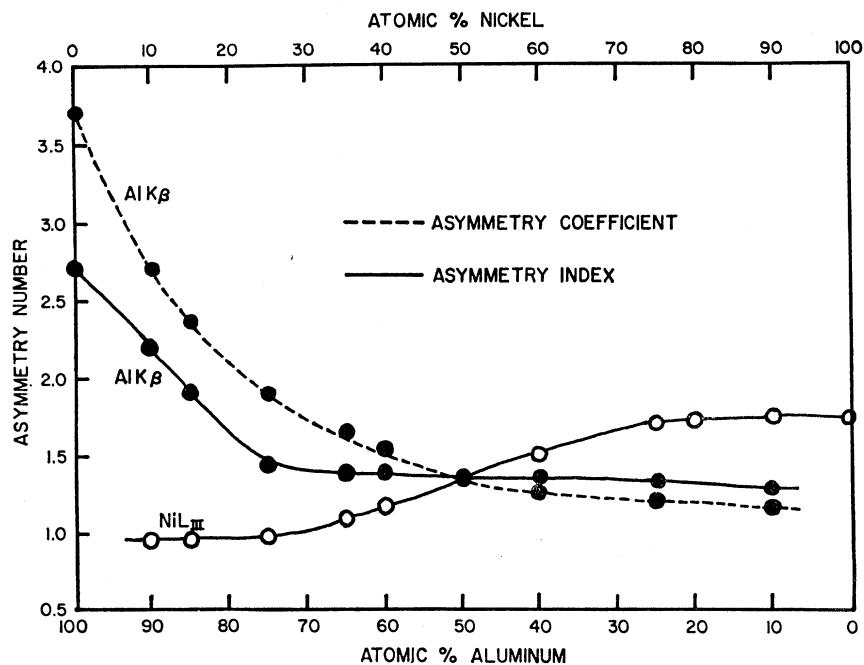
FIG. 7. Change in asymmetry of Al K and Ni L_{III} bands with alloy composition in Al–Ni system.

but as the Al content is further decreased the width starts increasing again. The same effect is seen in the Ni L_{III} band as will be explained later.

Since the Al K band undergoes such an obvious change in shape it is perhaps of interest to determine a numerical measure of the band asymmetry. Allison[18] introduced a term which he called the asymmetry index. This index is obtained by taking the ratio of the part of the full width at half-maximum lying to the long-wavelength side of the maximum ordinate to that part on the short-wavelength side. The values obtained for the Al–Ni alloys are listed in Table II under the symbol A_i. We are not convinced that this number has much meaning for Al K bands in alloys but Blokhin and Nikiforov[19] were able to correlate the asymmetry index to the average magnetic moments of corresponding crystals for the $K\alpha_{1,2}$ lines of iron-group elements. Due to the considerable tailing effect of the long-wavelength side of the K band we feel that another number, which we will call the asymmetry coefficient (A_c), gives a better indication of the total band asymmetry. This coefficient is determined by measuring the ratio of the low-energy band edge width at 5% and 95% of maximum intensity above background to the high-energy edge width at 5% and 95% maximum intensity above background. The results are given in Table II under the symbol A_c. A comparison of the manner in which both the asymmetry index and the asymmetry coefficient of the Al K band vary with alloy composition in the Al–Ni system is shown in Fig. 7.

[18] S. K. Allison, Phys. Rev. **44**, 63 (1933).
[19] M. A. Blokhin and I. Ya. Nikiforov, Bull. Acad. Sci. USSR, Phys. Ser. **28**, 689 (1964).

The asymmetry coefficient undergoes a smoother and larger variation than does the asymmetry index. In the pure metal the asymmetry coefficient is 3.7 which means that the low-energy side of the band is about four times as broad as the high-energy edge. This gives a little better indication of the band shape than the asymmetry index. In the oxide, the Al K band becomes quite symmetrical with both the asymmetry index and asymmetry coefficient being equal to 1.0.

As the alloy composition varies, therefore, the Al K band displays significant changes in energy position, half-bandwidth, full bandwidth, emission edge breadth, and over-all shape as characterized by the asymmetry index and asymmetry coefficient. For the two-phase alloys the band is an average of the shapes seen for each phase.

Nemnonov and Finkel'shtein[13] also noted that the K band from Ni–Al alloys occupies an intermediate position between pure Al and Al$_2$O$_3$ although their band shapes do not entirely agree with ours. The main difference is in the shape of the high-energy edge for NiAl$_3$ and NiAl. This may be due to slightly better resolution on their part although we obtain a narrower half-bandwidth than they do. The difference could also arise from different alloy compositions or different methods of sample excitation.

B. Nickel L Spectrum

There are two emission bands of interest in the nickel L spectrum, these being the L_{II} (or $L\beta_1$) and L_{III} (or $L\alpha$) bands at 14.280 and 14.571 Å, respectively, for the pure metal. The largest shift observed for the L_{III} band was less than 0.20 eV between Ni metal and

FIG. 8. Ni L_{III} emission bands from some Al-Ni alloys.

TABLE III. Uncorrected Ni L_{III} emission band characteristics in Al-Ni system.

Target	Half-bandwidth (eV)	Edge width (eV)	Asymmetry index
100 Ni	2.43±0.08	1.73±0.08	1.74±0.04
80 Ni–20 Al	2.66	1.76	1.72
75 Ni–25 Al	2.60	1.78	1.70
65 Ni–35 Al	2.40	1.86	1.60
60 Ni–40 Al	2.31	1.93	1.50
50 Ni–50 Al	2.34	2.09	1.30
40 Ni–60 Al	2.34	2.25	1.15
35 Ni–65 Al	2.41	2.34	1.08
25 Ni–75 Al	2.54	2.67	1.00
15 Ni–85 Al	2.59	2.94	0.98
10 Ni–90 Al	2.64	3.14	0.95

the 10 Ni–90 Al alloy. The L_{III} band is about 5 times as intense as the L_{II} band in the metal and consequently our study was confined mainly to L_{III} because L_{II} was difficult to obtain with enough intensity for low nickel content in the alloys. In general, however, most of the changes discussed for the L_{III} band also apply to L_{II}.

Some of the experimental band shapes observed for Ni L_{III} from Al–Ni alloys are shown in Fig. 8. Here again, the curves are taken directly from ratemeter scans with no corrections applied to them. Liefeld and Chopra[15–17] have shown that the shape of Ni L_{III} from bulk samples is dependent to some extent on the electron-beam potential and on sample self-absorption. We therefore obtained all the Ni bands at the same beam potential (5 kV) although the self-absorption effect, of course, changes as the alloy composition is varied. Accordingly, it must be realized that the changes observed in the L_{III} band may be due, in part, to this changing self-absorption.

For the Al–Ni system the most obvious change in Ni L_{III} occurs at the high-energy edge. As the nickel content is decreased the edge becomes broader and the intensity of the satellite band decreases considerably. The uncorrected edge width for a series of the alloys is listed in Table III. This variation is shown in Fig. 5 along with that observed for the Al K band edge. An interesting observation is that the two curves are practically mirror images of each other. As the nickel content is decreased the Ni L_{III} edge broadens rather

slowly down to about 60% nickel and then broadening increases more noticeably as the nickel is further decreased. On the other hand, the Al K band edge increases appreciably as soon as alloying occurs and starts to level off as the aluminum content is further decreased. The net effect is that the average of the two edge widths remains fairly constant.

The Ni L_{III} bandwidth also varies with alloy composition. It is rather difficult to measure the full bandwidth because of the overlap of the satellite band but the half bandwidth can be measured rather accurately and its variation with composition is shown in Fig. 6, again compared to that observed for the Al K band. Both bands display the same type of half-width variation. A rather interesting point is that the narrowest band measured for Ni L_{III} is from the alloy with 60 at. % nickel while the narrowest band measured for Al K is at 60 at. % aluminum.

As with the Al K band there is also a change in the asymmetry index of the Ni L_{III} band with alloy composition as can be seen in Fig. 7. The measured values are given in Table III. One difference in the two bands is that the Ni L_{III} band has an asymmetry index of less than one for low nickel concentrations. In other words, the high-energy half-width becomes larger than the low-energy half-width which we have never observed to happen for the Al K band. Because of the satellite interference, we were unable to obtain accurate asymmetry coefficients for the Ni L_{III} band but this value also appears to become less than one for nickel concentrations below about 15 at. %.

When going from metal to oxide, the Ni L_{II}/L_{III} intensity ratio changes from 0.20 to 0.28 at 6 kV. For the Al–Ni system, however, this ratio appears to remain constant at 0.20 for the whole range of compositions investigated.

ACKNOWLEDGMENT