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Electronic structure of ferromagnetic Ni-Al solid solutions

Douglas M. Pease, Leonid V. Azároff, Canio K. Vaccaro, and W. A. Hines
Institute of Materials Science and Physics Department,
University of Connecticut, Storrs, Connecticut 06268
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The K and $L_{\rm III}$ x-ray absorption edges of Ni-Al alloys have been measured in the fcc solid-solution region. The absorption spectra recorded did not show any changes, due to the addition of aluminum, in the region of the spectra corresponding to unoccupied nickel $3d$ states. This result is in agreement with other measurements of nickel-rich solid solutions, and indicates that the addition of aluminum to nickel decreases the nickel magnetic moment, not by a filling of empty $3d$ states, but by a rearrangement of the spin-up and spin-down populations of the $3d$ subbands in apparent violation of Hund's rule.

I. INTRODUCTION

In describing the electronic structure of ferromagnetic nickel and nickel-based alloys, it is customary to assign five valence electrons per atom to one $3d$ subband of nickel and the balance to the other. Since the electrons in each subband have parallel spins, this satisfies the Pauli exclusion principle and extends Hund's rule to the case of metals and alloys. Such a maximal parallel spin alignment underlies general discussions of alloy magnetism,[1,2] in which the average magnetic moment per nickel atom equals the number of unoccupied states remaining in the minority-spin subband. The addition of aluminum to nickel is then expected to decrease the average nickel moment by the addition of aluminum $3s$-p electrons to the alloy's valence band, raising the Fermi level and thereby, progressively filling the minority-spin $3d$ holes.[3] This is not the only model that has been proposed, however, although it is the more popular one. Over a decade ago, Beeby presented a model for ferromagnetism in transition-metal alloys in which the average moments are reduced by progressively equalizing the populations of spin-up and spin-down subbands, as a result of alloying additions.[4] Beeby specifically applied this model to the case of binary alloys of aluminum and silicon with iron, cobalt, and nickel.

These two models lead to significantly different predictions regarding the density of unoccupied $3d$ states remaining above the Fermi level of the alloy. In the band-filling or electron-transfer model, by the time 8–10-at.% aluminum are added to nickel, its moment is reduced by a factor of 2 as a result of halving the density of unoccupied states.[3,5] In Beeby's model, conversely, the decrease in minority-spin unoccupied $3d$ states is compensated by a corresponding increase in majority-spin unoccupied states (from zero, initially) leaving the total density of empty $3d$ states effectively unchanged.

A fairly powerful method for studying the electronic structure of solids, soft x-ray spectroscopy has only seen limited application to nickel-aluminum alloys. Emission spectra have been recorded at several characteristic energies[6–10] but little or no attention has been paid to nickel-rich solid-solution alloys except by Cuthill *et al.*[7] Thus, Wenger *et al.*[10] correlated normalized intensities of L emission lines to calculated charge transfers but they did not examine alloys containing less than 25-at.% Al, thereby omitting the entire ferromagnetic solid-solution region. Their extrapolated value of charge transfer at, say, 10-at.% Al, is insufficient to account for the decreased moment on nickel atoms in that alloy. Emission spectroscopy based on electronic transitions from nearly filled bands, moreover, is not very sensitive to occupation changes caused by alloying because such changes are relatively small.

A more dramatic change can be expected to take place in x-ray absorption spectra in which transitions to empty states lying above the Fermi level are dominant. The only systematic examination of Ni-Al solid-solution alloys was carried out by Das and Azároff[11] who observed changes in the nickel K absorption spectra that could be interpreted in terms of progressive filling of the unoccupied $3d$ states up to about 6-at.% aluminum but required another mechanism (electron pairing was suggested) above this concentration. These measurements suffered from several limitations, however, including disregard of the thickness effect discussed below.

Still another form of x-ray spectroscopic analysis was applied to Ni-Al alloys by Suoninen and Valkonen who measured the asymmetry and widths of Ni $K\alpha$ lines in a series of solid solutions.[12] Although the mechanism by which the shapes of emission lines become altered is not firmly established, empirical correlations have been observed between the magnitude and widths of asymmetries of inner-shell emission lines, and the existence of unfilled $3d$ holes.[13,14] Surprisingly, Suoninen and Valkonen found no change in either the asymmetry or breadth of the Ni $K\alpha$ lines throughout the fcc solid-solution region, though both quantities are significantly smaller in the ordered NiAl phase.[12]

It was decided, therefore, to re-examine the Ni-Al solid-solution region using x-ray absorption spectroscopy as a probe, and using alloys carefully characterized as to composition and magnetic moment. Before proceeding with a description of this study and its results, we comment about how well x-ray spectra agree with one-electron band calculations for an unperturbed solid and the possible need to include many-body and other effects. In a recent careful APW calculation of K and L_{III} absorption and emission spectra of nickel,[15] the calculated spectra were smoothed by convolution with a Lorentzian whose width equalled the best estimate of the lifetime width of the core level. These were compared to experimental spectra corrected for instrumental broadening (window function). Although the results cannot be safely generalized, for the case of nickel the overall agreement regarding positions and strengths of spectral features for absorption (but not emission) spectra is good despite complete neglect of core-hole many-body effects. Thus, there is increased confidence that K and L absorption edges of transition metals do reflect the unperturbed one-electron band structure.

II. EXPERIMENTAL PROCEDURE

An experimental feature of great importance in any x-ray absorption-edge measurement is the existence of a strong thickness effect that modifies the recorded fine structure.[16,17] This thickness effect has been known for some time but is frequently neglected. It is particularly important in the case of transition-metal L absorption spectra which feature a sharp maximum close to the main edge (white line), but it is also important in K absorption spectra, particularly when the incident x-ray spectrum contains a characteristic emission line whose tails enter the instrumental "window".

It has been demonstrated that the effects which alloying has on an absorption spectrum can be separated from K edge thickness effects by calibration procedures using foils of several different thicknesses.[17] Such a procedure was used for both the K and L absorption spectra measured in the present experiment.

Probably the most important aspect of any experimental investigation such as the present one is the specimen preparation method. The specimens used for K edge measurements were prepared by vacuum melting the preweighed alloys in alumina crucibles followed by a homogenization anneal in an inert-gas atmosphere for 96 h at 1000 °C. Foils were reduced to the order of ten microns in thickness by successive rolling and stress-relief annealing. All samples were analyzed chemically and by x-ray diffraction in a back-reflection camera to determine their lattice constants. The alloy foils yielded diffraction diagrams characteristic of a single-phase fcc solid solution with a lattice constant that agreed with published data for the chemically determined compositions.

The specimens prepared for L absorption measurements were between 700 and 1600 Å thick and were formed by flash evaporation. Flash evaporation had been used previously by Duzevic *et al.* who demonstrated that their Ni-Al foils had the same composition as the bulk; they found it important, however, to use sintered and filed Ni-Al briquettes rather than coevaporating mixtures of Ni and Al powders.[18] We prepared master alloys by arc melting, followed by 120-h homogenization anneal at 1090 °C. They were analyzed chemically and by x-ray diffraction as above and then were filed with a tungsten carbide file. The powder thus formed was flash evaporated onto a glass slide covered by a carbon coating of $200\text{-}\mu\text{g/cm}^2$ thickness and the carbon substrate was floated off to yield the final sample. Blank slides placed next to the carbon-coated ones were used for subsequent specimen characterizations. Fresh tungsten boats were used for each evaporation, and the boat and chamber were given a prolonged bake out followed by cooling and liquid-nitrogen trapping before starting the evaporation, during which the pressure recorded by an ion gauge was about 3×10^{-6} Torr.

The evaporated alloy films yielded x-ray diffraction diagrams typical of single-phase fcc solid solutions but with slightly broadened lines. Thin-film lattice constants measured by back reflection agreed with those of the corresponding bulk ingots to within 1.2 at.% for all eight solid solutions examined. A representative specimen was also analyzed in a microprobe and no evidence of tungsten contamination was found.

To further characterize the samples, low-temperature saturation magnetic moments were measured for three alloy samples, and for flash evaporated pure nickel. Films of approximately 1000 Å thickness were flash evaporated onto glass slides. The evaporated material was scraped off the slides to form a powder whose saturation magnetic moment was measured in a vibrating sample magnetometer. Bulk nickel has a moment of 0.606 Bohr magnetons per atom; the moment decreases with alloying at a rate that extrapolates linearly to zero moment at 21.5-at.% aluminum.[4,5] A broken line indicating Crangle and Martin's experimental moments is shown in Fig. 1, along with our results for evaporated foils. Within the estimated uncertainties in film composition, the moments of the alloy samples agree with bulk values, although the pure nickel film has a saturation moment which is 13% lower than that of bulk nickel, (Fig. 1). Discrepancies between the moments measured on bulk and foil samples may be due to surface oxides or strains in the foils.[19,20] Since x-ray spectra reflect the average bulk properties throughout the foil, they are deemed to be relatively insensitive to trace impurities or strains. To test this assumption, pure nickel was flash evaporated onto thin foils (2 μm) of aluminum. The resulting foils were sandwiched so as to make up an effective thickness of flash-evaporated nickel sufficient to measure the *K* absorption edge, yet thin enough so that thickness effects were negligible. The *K* absorption edges of flash-evaporated and bulk nickel foils were measured from the main edge well into the extended-fine-structure region, and are compared in Fig. 2. Their obvious agreement supports our belief that the averaged electronic structure of the evaporation foils as measured by x-ray absorption spectroscopy is characteristic of comparable bulk samples.

Absorption measurements were carried out on an automatic two-crystal vacuum spectrometer built in our laboratory.[21] This spectrometer has been equipped with a computer-controlled multiposition sample holder which can be programmed to insert each of its samples in the incident x-ray beam in a fully reproducible manner. Thus, it is possible to measure the intensity transmitted through different foils (or the incident beam intensity) at each energy setting of the analyzing crystals, automatically, and under directly comparable conditions. For *K* edges, silicon crystals were used having a resolution of 0.8 eV at the nickel *K* edge. For *L* edges, rubidium acid pthalate (RAP) crystals were used with a resolution of 0.9 eV at the nickel $L_{\rm III}$ edge. The flow-proportional counter used to detect the transmitted x rays had a beryllium window for *K* and a carbon-coated polypropelene film for *L* edges. The high-intensity demountable tube had a tungsten anode for *K*, and copper anode for *L* edge measurements.

III. EXPERIMENTAL RESULTS

The *K* absorption spectra of three solid solutions containing 11.9-, 8.4-, and 5.5-at.% aluminum, respectively, and several thicknesses of pure nickel, were obtained in a single run of the spectrometer. The low-energy baseline was subtracted from each spectrum and the spectra were normalized by equating the heights of peak *E* and, separately equating the heights of valley *F*, so labeled in Fig. 2. The spectrum of the alloy foil containing 11.9-at.% aluminum, normalized to peak *E*, is displayed next to that for pure nickel curves transmitted through 12- and 16-μm foils similarly treated in Fig. 3. There is no detectable shift in the position of the Fermi level (inflection point in the initial rise at the main edge) but the high-energy fine structure (peaks labeled *C* and *E* in Fig. 2) is markedly broadened in the alloy. The area under shoulder *B* is enhanced relative to that in the 12-μm foil, and depressed relative to that in the 16-μm foils of pure nickel. This is an example of the thickness effect in the alloy sample whose effective nickel thickness lay between these values.

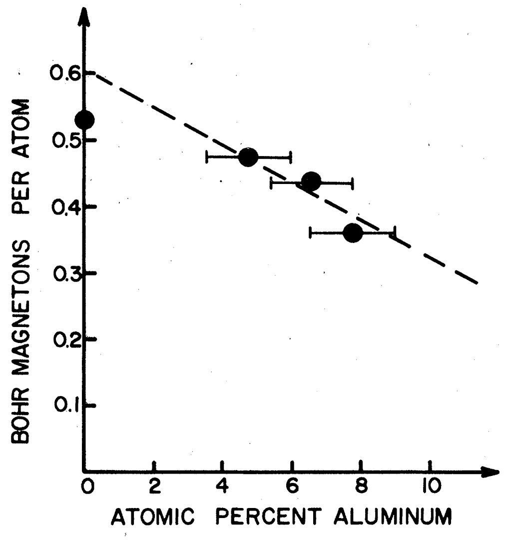

FIG. 1. Saturation magnetic moment of Ni-Al solid-solution films. (Broken curve shows bulk values. See Ref. 5).

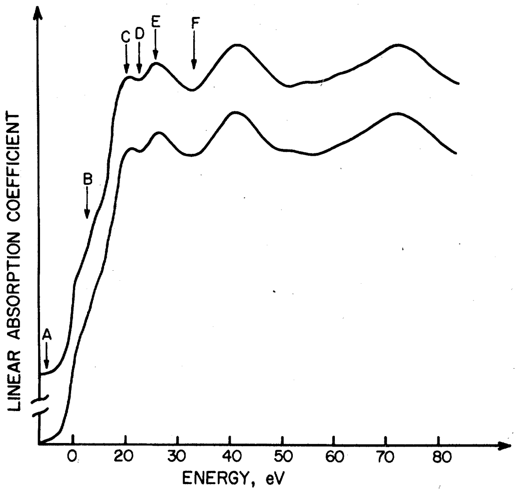

FIG. 2. Nickel *K* absorption spectrum of a flash-evaporated film (upper curve) and a nickel foil produced from bulk nickel (lower curve). The zero of the energy scale denotes the position of the Fermi energy.

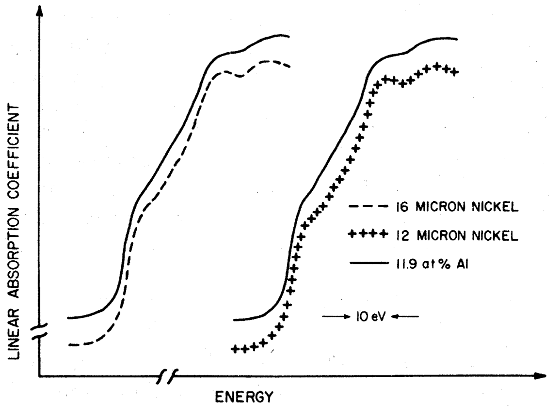

FIG. 3. Normalized nickel K absorption edges of an alloy containing 11.9-at.% Al (solid curves) compared to that of two thickness of pure nickel (broken curves).

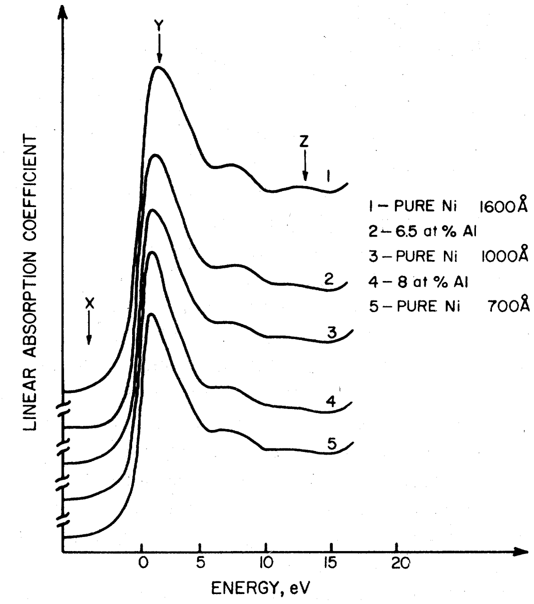

FIG. 4. Nickel L_{III} absorption edges of pure nickel films of varying thicknesses compared to that of two nickel-rich alloy films.

As previously reported,[17] when the integrated area under this shoulder as first defined by Azároff,[22] is plotted against the difference between the absorption coefficient values at points labeled E and A in Fig. 2 for Ni-Al solid solutions, no effect of alloying is observed. We repeated this process for spectra normalized to the valley labeled F and, again, saw no changes with alloying. Therefore, as far as the K absorption spectra of Ni-Al solid solutions are concerned, there is no detectable effect of alloying on the energy position of the inflection point (Fermi level) or the threshold region (transitions to unfilled $3d$ states having admixed p-type symmetry). The only effect of alloying is a broadening of the structure in the vicinity of peak C in Fig. 2. (transitions to empty np states) as a result of adding aluminum to the nickel matrix.

The L_{III} absorption spectra of two solid solutions containing 6.5- and 8.0-at.% aluminum, respectively, and several thicknesses of pure nickel, were recorded in a single run of the spectrometer. The curves obtained are shown displaced along the vertical axis in Fig. 4. after subtracting the low-energy background, but without normalization. The thickness effect is manifested in these spectra in a depression of the relative height of the pronounced peak labeled Y (white line) with increasing foil thickness. The differences between the absorption coefficient values at points Z and X, $\mu_Z - \mu_X$, are a measure of the relative effective thickness of nickel, so that it is possible to correct the thickness effect by comparison with the calibration foils of pure nickel. This is demonstrated in Fig. 5 where the difference $\mu_Y - \mu_X$, is plotted against $\mu_Z - \mu_X$ for the five foils whose spectra are shown in Fig. 4. As can be seen, all points lie on a single curve demonstrating that the only changes produced are due to the thickness effect[17] and not caused by alloying.

This result contradicts the expectation that the height of peak Y (due to dipole transitions to unfilled $3d$ states) would be suppressed by the addition of aluminum. In fact, the only effect of alloying that is evident in Fig. 4 is a slight broadening of peak Z,

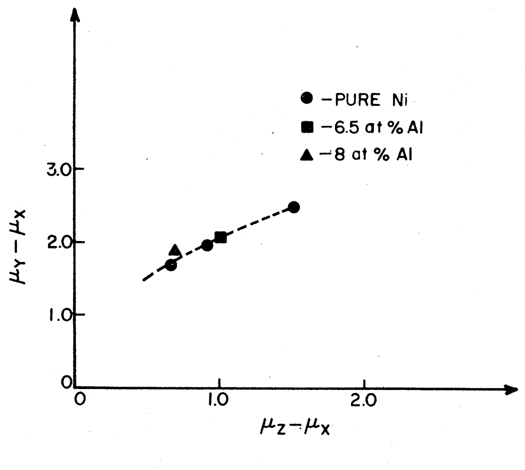

FIG. 5. Thickness-effect calibration for Ni-Al L_{III} absorption edges.

which is due to transitions of the photoejected L electron to unfilled higher-energy states. Although this broadening is barely within the confidence limits of the experiment, it confirms the similar broadening observed in the K absorption spectra. Similarly, as evident in Fig. 4, there is no shift of the Fermi level (initial rise) between the alloy spectra and those of pure nickel.

IV. DISCUSSION AND CONCLUSIONS

The inescapable conclusion to be drawn from the lack of change in either the K or L_{III} absorption spectra throughout the nickel-rich solid-solution region, is that the total density of unoccupied $3d$ states of nickel sites is not altered by the addition of aluminum. Similar conclusions can be drawn from the electronic specific-heat measurements of a series of nickel-based alloys. Gupta *et al.* found that the linear temperature dependence of the specific heat showed little variation within the solid-solution range of Ni-Al alloys.[23] According to all band calculations for nickel, including the most recent ones,[15,24] the Fermi level lies within a peaked $3d$ band and close to a high-energy edge. Thus, a progressive occupation of the unfilled $3d$ states in nickel should cause a small but systematic shift of the Fermi energy E_F but, even more importantly, it should cause a large change in the density of states at the Fermi level, $N(E_F)$. Since the electronic specific heat is closely related to $N(E_F)$, a decline in this density, due to band filling (charge transfer), would produce a significant change. Model calculations of $N(E_F)$ for such alloys, carried out by Waber,[25] show that the density drops to a low value in Ni-Cu solid solutions at about 60-at.% Cu but, for Ni-Al, $N(E_F)$ decreases only about 12% when 10-at.% Al is added, even though the magnetic moment of nickel is decreased by a factor of 2 at that concentration. This lack of change in the $3d$ density of states at nickel atoms is also observed in a recently completed average-t-matrix calculation carried out for fcc ternary Ni-Fe-Al solid solutions,[26] which exhibit a decreasing magnetic moment at nickel atoms much like that in binary Ni-Al solid solutions.[27] The density of states shows no shift of the Fermi level relative to the nickel (or iron) $3d$ peak upon aluminum addition, but instead, shows broadening of the bottom of the occupied $3d$ band.

The x-ray spectroscopic evidence now is unanimous that there is no significant change in the density of unoccupied states as a result of dissolving aluminum in nickel. The Ni K absorption edges properly corrected for thickness, and the asymmetries of the $K\alpha$ emission peaks do not change with alloying. The newly measured L_{III} absorption spectra which are particularly sensitive to the density of unfilled $3d$ states, similarly do not change throughout the solid-solution region tested. Even the oft quoted valence-band emission work of Wenger *et al.* shows an inadequate amount of charge transfer in the solid-solution region[10] to account for the much larger decline in the saturation magnetic moment. By comparison, K absorption spectra,[11] $K\alpha$ asymmetries,[14] and L emission spectra,[10] all show significant changes in the intermetallic ordered phases of the Ni-Al system.

If there is no band filling (charge transfer) in the nickel-rich solid solutions, how can one account for the declining nickel moment? In their original study, Das and Azároff speculated that this may be the result of electron pairing between adjacent Ni and Al atoms.[11] A more plausible model was subsequently suggested by Beeby who proposed that the aluminum $3s$ and nickel $3d$ states admix in the alloys causing a relative shifting of the nickel spin-up and spin-down subbands.[4] Such shifts, relative to a constant Fermi level, change the average number of unpaired electrons (in violation of Hund's rule) but not the average number of holes at each nickel-atom site. Beeby's model also predicts a smoothing of the $3d$ band structure by the proposed $s-d$ interaction but this is probably not measurable by x-ray absorption spectroscopy. Szmulowicz's spectral calculations[15] showed that the amplitude of the white line at the Ni L_{III} absorption edge is determined by the density of unfilled $3d$ states, but its width is primarily controlled by the natural width of the $2p$ core level and the instrumental-window function.

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