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X-ray spectra, magnetic moments, and band theories of Cu-Ni alloys

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Significant differences between modern band theories proposed for Cu-Ni solid solutions leave uncertain the mechanism responsible for their observed ferromagnetism. X-ray spectroscopy, a sensitive probe of the relevant unfilled $3d$ states, appears to agree with ferromagnetic coherent-potential-approximation (CPA) calculations but not with paramagnetic CPA or average-T-matrix-approximation calculations. Repeated K-edge measurements and new L absorption edges of Cu and Ni are internally self-consistent and agree with published M spectra but not with the related appearance-potential spectra.

I. THEORETICAL INTRODUCTION

The first band model for solid-solution alloys, proposed by Mott and Jones[1] over forty years ago, was eminently successful in explaining the linear decline of the saturation magnetic moment of nickel upon alloying with "electron-donor" metals such as copper. In this model, it was assumed that the constituent atoms share a common valence-electron band so that the extra electrons of copper fill the lower-lying empty $3d$ states in nickel, progressively diminishing the number of such states in the alloy in proportion to its copper content. More recent experiments, however, have cast doubts on the validity of this rigid-band model. For example, photoemission experiments strongly suggest the existence of two separate Cu and Ni bands present in proportion to the alloy's composition.[2,3] The rigid-band approach has been replaced, therefore, in modern calculations by the average-T-matrix approximation[4] (ATA) and the coherent-potential approximation[5-7] (CPA). These calculations agree especially well with experimental probes of the occupied-state electronic structure provided, for example, by photoemission and x-ray emission spectroscopies.[3,7] They have not provided as unambiguous an explanation of the magnetic saturation moment dependence on composition, however, as did the early Mott and Jones model.

In recent calculations, the near disappearance of the nickel moments, when copper concentrations exceed 60 at. %, is attributed to a drop of the high-density portion of the nickel-based $3d$ band below the Fermi level at these compositions. The density at the Fermi level then becomes small and remains relatively independent of concentration for copper contents exceeding 60 at. %, as predicted by the CPA calculations of Stocks, Williams, and Faulkner.[5] The ATA calculations similarly support the conclusion that the nickel $3d$ band lies below the Fermi level for large copper concentrations.[4] On the other hand, the ferromagnetic CPA calculations of Inoue and Shimizu do not agree with this.[6] Their local density of states for nickel does not show a decrease in the number of $3d$ holes up to 55 at. % copper concentration. The progressive decrease in the nickel moments is accounted for completely by relative shifts of the majority-spin subband relative to the minority-spin subband until, at 55 at. % copper, the net moment of nickel is essentially zero even though the number of nickel-based $3d$ holes is undiminished. This is reminiscent of an earlier schematic model proposed by Beeby.[8]

It should be noted that single-site CPA and ATA band calculations of the magnetic-moment distribution in Ni-Cu alloys all involve single-site averages in which it is assumed that every Ni atom is surrounded by the same average effective medium. As has been shown by neutron scattering experiments,[9-11] however, the local moment on a Ni atom in any given Ni-Cu alloy can vary from zero to approximately 0.6 μ_B as a strongly nonlinear function of its local environment. Thus, in calculations of magnetization, single-site averaging may lead to errors at least as great as any differences between different CPA and ATA band calculations. This single-site averaging is known not to lead to large errors in local spectral weight functions (local densities of states for each chemical species in an alloy), however, so that x-ray spectra should be an excellent probe to test the relative validity of different CPA and ATA calculations for Ni-Cu alloys.

It should be emphasized at this point that the addition of copper to nickel decreases the total density of unfilled $3d$ states by simple dilution in addition to whatever effect it has on the number of holes at nickel atom sites. Fortunately, it is possible to separate the CPA calculated density of states into local copper and nickel components[6,7] so that the local nickel density of states can be used directly to deduce the magnetic moment of nickel. This also makes it possible, in an alloy, to compare the nickel (or copper) x-ray absorption edge to the local density of states.

Because x-ray absorption spectroscopy probes the normally unfilled states in an alloy, it is especially well suited to examining the possible changes in such states produced by alloying. When the number of empty states is much smaller than the number of filled ones (0.6 as compared to 9.4 electrons, respectively, per nickel atom), the superior sensitivity of this probe becomes even more important. Since the ferromagnetic moment of nickel is also tied to this small number of empty states, only probes of the density-of-states distributions at or above the Fermi level are considered here. Following a brief review of previous work, the way that the requisite alloy foils were prepared and examined is described below, followed by a discussion of how well the x-ray absorption spectra agree with predictions of the ferromagnetic CPA calculation.

II. REVIEW OF EXPERIMENTAL RESULTS

Using synchrotron radiation, Gudat and Kunz have measured the M absorption spectra of a series of Cu-Ni alloys.[12] In this experiment, the inner-level $3p$ electron is excited to unoccupied states above the Fermi level so that, consistent with dipole selection rules, the normally empty d-s states are probed, yielding a large broad peak. It was found that the alloy spectra can be matched with a superposition of the corresponding absorption edges for pure copper and nickel, suitably weighted to reflect their concentration, even for copper concentrations corresponding to a full suppression of the nickel magnetic moment. Contrarily, Azároff and Das previously reported a progressive decline in the initial area under the nickel K absorption curve[13] for copper concentrations up to 60 at.%. This result was interpreted in terms of the rigid-band model as a decrease in the density of p-admixed $3d$ holes and correlated with the declining nickel magnetic moment. It is possible to reinterpret this observation in terms of the modern calculations of Stocks *et al.*[5] but not those of Inoue and Shimizu.[6]

In a related experiment, Ertl and Wandelt have examined the Cu-Ni system by means of appearance-potential spectroscopy[14] (APS). Their measured density of states at the Fermi level also agrees with that obtained by Stocks *et al.* but not with the ferromagnetic CPA calculation. Resistivity data and NMR spectra of Cu-Ni alloys led Beal-Monod to conclude, however, that each nickel atom contains about 0.82 $3d$ holes,[15] supporting the Inoue and Shimizu calculations. Positron annihilation measurements appear to be inconclusive as to whether any nickel $3d$ holes remain in concentrated copper alloys.[16] The results suggest that copper has little effect on the electronic structure of nickel atoms and agree, within experimental error, with the ATA calculations of Bansil, Schwartz, and Ehrenreich.[4] Finally, the nickel L_{III} absorption edges were measured in several Cu-Ni alloys by Van den Berg who noted a significant narrowing of the edge in a 60-at.% Cu sample.[17] Since these measurements did not correct for the x-ray thickness effect,[18] which can introduce serious errors,[19] it is difficult to discern the true effects of alloying on the recorded spectra.

The nickel K absorption edges measured by Azároff and Das[13] also were not properly corrected for the thickness effect, whose full importance had not been appreciated at that time. K spectra also are limited by transitions to states having some p-type symmetry so that they do not probe the d states directly. In collecting their M absorption spectra, Gudat and Kunz used well-characterized alloy films and compared them to sandwiches of copper and nickel films having the same effective thicknesses as the alloys.[12] The x-ray thickness effect, therefore, was properly eliminated from this experiment. The M spectra are somewhat broadened by multiplet and other effects so that they cannot be compared directly to one-electron band calculations.[20] It was decided, therefore, to measure the K and L absorption spectra of Cu-Ni solid solutions making due allowance for the thickness effect. Szmulowicz and Pease have shown that, for K and L absorption spectra of nickel, there is good agreement between experiment and one-electron augmented-plane-wave calculations even when core-hole many-body effects are neglected.[21] (This conclusion, incidentally, does not apply to L emission or M absorption spectra of pure nickel.) Similarly, a recent study of equiatomic NiAl showed good agreement between the nickel L_{III} absorption edge and the calculated one-electron unoccupied state density.[22] The L_{III} edge of nickel, consisting of a sharp spike (so-called white line), appears to reflect accurately dipole-allowed transitions to local empty $3d$ states. This spike can be expected to decrease if the holes are progressively filled or to remain undiminished if the calculations of Inoue and Shimizu apply.

III. EXPERIMENTAL PROCEDURE

The measurement of nickel and copper K edges requires foils less than ten microns thick. Mechanically rolled foils previously described by

Azároff and Das[13] were used again in the present study. L-edge measurements, however, require alloy foils about 1000 Å thick. Starting with master ingots, induction melted and vacuum annealed as before,[13] the final foils were obtained by flash evaporation of the alloy ingots. The procedure employed[23] has produced uncontaminated homogeneous thin films having compositions very near to those of the master alloys. The compositions of the actual foils used in the present study were checked by using the powder method of x-ray diffraction to determine the solid solution's lattice constant and referring to a calibration curve that included literature values. The compositions reported below are accurate within ±5% for L-edge samples and within ±2% for K-edge foils.

Because of the expected relevance of this study to understanding their ferromagnetic behavior, a few flash-evaporated foils were checked by measuring their low-temperature saturation moments on a vibrating-sample magnetometer. As can be seen in Fig. 1, where the squares represent published values measured on bulk samples,[24] the saturation magnetic moments of the foils follow the expected decline with increasing copper content.

The alloy foils thus characterized were placed in an automatic multiposition holder that alternately interposes each of the foils in the incident x-ray beam at the same energy setting of the analyzing crystals. The computer-controlled, two-crystal vacuum spectrometer[25] employed silicon crystals with 0.8-eV resolution at the Ni K edge and rubidium-acid-pthalate crystals with 0.9-eV resolution at the Ni L_{III} edge. A tungsten anode was placed in the high-intensity x-ray tube for copper and nickel K edges and for Cu L-edge measurements while a copper anode was used for Ni L_{III} edges. The flow-proportional counter had a beryllium window for measuring K and a polypropylene window for L spectra.

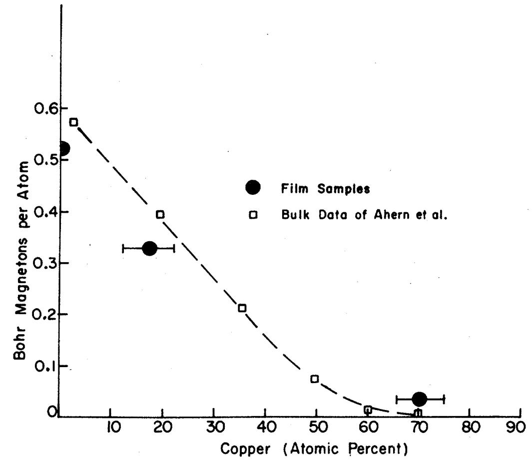

FIG. 1. Saturation magnetic moments of flash-evaporated Cu-Ni foils referred to the bulk values (squares) of Ahern, Martin, and Sucksmith (Ref. 24).

The x-ray thickness effect modifies the fine structure at an absorption edge and is particularly important in transition-metal L edges which feature a sharp maximum at the main edge. It has been demonstrated that the effects which alloying has on an absorption spectrum can be separated from thickness effects by calibration procedures using foils of several different thicknesses.[19,23] Such a procedure was used for both the K and L absorption spectra measured in the present experiment as described next.

IV. EXPERIMENTAL RESULTS

The measured nickel L_{III} and L_{II} edges are shown in Fig. 2 for several solid solutions and for pure nickel foils. The curves are arranged in ascending order of the effective thickness of nickel present in each absorber. It is clear in Fig. 2 that the principal effect of increasing the effective thickness of nickel is to diminish the contrast of the $3d$ maximum (labeled B). This thickness effect occurs because the instrumental

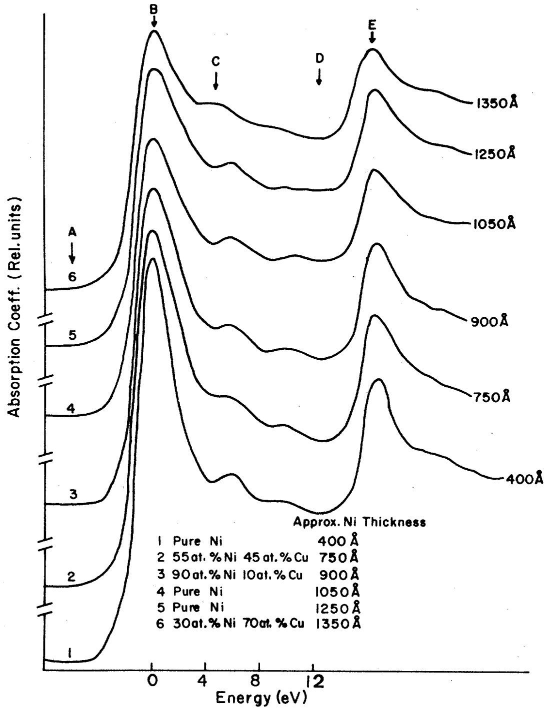

FIG. 2. Nickel $L_{II,III}$ absorption edges in several Cu-Ni alloys and pure metal foils arranged in order of increasing effective thickness, with data normalized to point D.

"window" admits photons having considerably lower energies than those ostensibly being measured[18] so that it is more pronounced for the L_{III} edges than for L_{II} edges. By plotting the ratios of $(\mu_B - \mu_A)$ vs $(\mu_D - \mu_A)$ on the left in Fig. 3 and $(\mu_E - \mu_D)$ vs $(\mu_D - \mu_A)$ on the right, it is possible to correct for the effective thickness of nickel. First note that pure nickel absorbs in proportion to its thickness (triangles in Fig. 3) so that, when the three alloys are similarly displayed, the fact that their ratios fall very nearly on the curve for pure nickel demonstrates that there is no change in the 3*d* peak at *B* (or *E*) that is not due to the thickness effect. In other words, alloying copper to nickel does not affect the L_{III} or L_{II} absorption spectra, strongly suggesting that the number of unfilled 3*d* states per nickel atom remains the same. In fact, the only changes noted in suitably corrected *L* absorption spectra were an apparent smoothing of the spectra to the left of *C* in Fig. 3 and a slight shift of *C* to lower energies with increasing copper content.

The nickel *K* edges were remeasured for a series of Cu-Ni solid solutions, and, after correction for thickness effects, no significant decline was observed in the threshold region as a function of copper concentration. In fact, the only changes noted in the Ni *K* spectra were progressive shifts of the high-energy fine-structure maxima to lower energies, probably reflecting the increasing lattice-constant values.

The copper *K* absorption edges were also measured for the same Cu-Ni alloy samples. As previously noted,[13] there is a slight change in the inflection occurring about 4 eV above the onset of absorption (Fermi energy) which, in the present study, could be shown to involve a shifting of the inflection point to higher energies with increasing nickel content. The fine-structure maxima also shift, from their energy values in pure copper, to higher energies in accordance with the decreasing lattice-constant values.

Finally, the Cu L_{III} absorption spectra were measured for several solid-solution alloys. These data, however, are "troubled" by experimental difficulties absent in the other spectral measurements. The Cu *L* edge is only 80 eV above the Ni *L* edge, which interferes, therefore, with the measurement of the copper edge. Moreover, even though a tungsten target was used for the measurements, copper impurities present in the anode introduced a fairly prominent Cu $L\beta$ peak. This causes instrumental distortions which are difficult to correct, and complicate the assessment of the thickness effect in the alloy spectra. As can be seen in the two spectra reproduced in Fig. 4, the valley marked *B* shifts to a higher energy within the alloy, confirming the more reliable *K*-edge data. This suggests that there is an increase in the energy separating localized copper states from the Fermi energy as the nickel concentration increases. A small but real change in the first absorption maximum (labeled *A*) can be noted that is not due to thickness effect. Since a corresponding change is not evident in the *K* edges, even though they are less sensitive, it is not further considered here because of the experimental uncertainties cited above.

V. DISCUSSION AND CONCLUSIONS

The most important result of the present study is that there is no diminution in the peak at the

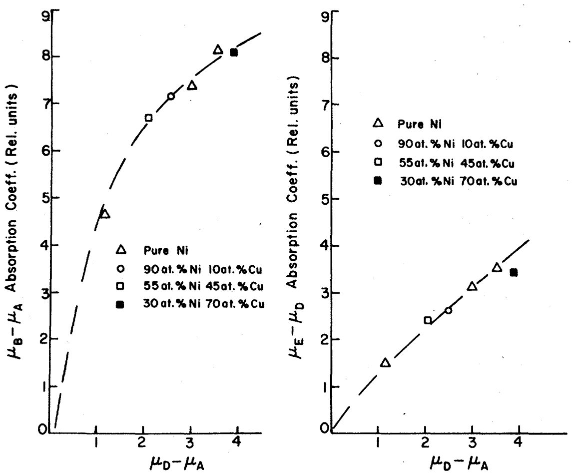

FIG. 3. Thickness-effect calibration curves for L_{III} on the left and L_{II} edges on the right.

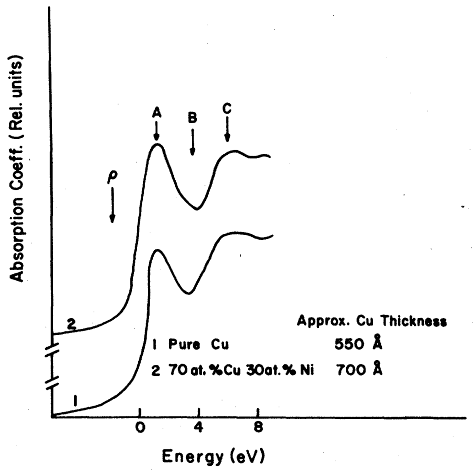

FIG. 4. Copper L_{III} absorption spectra in pure copper and a Cu-Ni solid solution.

Ni L_{III} edge in Cu-Ni alloys up to 70 at.% copper despite the progressive decline of the saturation magnetic moment in the same samples. The remeasured Ni K edges similarly show no diminution in the threshold region of the edge once the thickness effect is removed. These results are in full agreement with the M-edge data of Gudat and Kunz[12] so that now all x-ray absorption-edge results are consistent in indicating no decrease in the number of $3d$ holes in copper-rich solid solutions. Only the reported appearance potential spectra seem to disagree[14] even though, like L_{III} absorption spectra, they involve excitation of a nickel $2p$ electron to an unoccupied $3d$ state.

The x-ray absorption results are also in agreement with the band calculations of Inoue and Shimizu[6] but not with paramagnetic CPA calculations[5] nor with ATA calculations.[4] In an alloy, it is appropriate to compare the nickel x-ray absorption spectrum to the local density of states per nickel atom. Combining the up- and down-spin components calculated by Inoue and Shimizu[6] for unoccupied "localized nickel states per atom," the total local density of unoccupied nickel states per nickel atom is plotted in Fig. 5 for three solid solutions. No decline in the density of empty states can be seen up to 50 at.% copper. Inoue and Shimizu explain the decline in the saturation magnetic moment instead by a realignment of the spin-up and spin-down subbands as shown in Fig. 6 for two solid solutions. Note that the two subbands are very closely paired at the 50:50 composition.

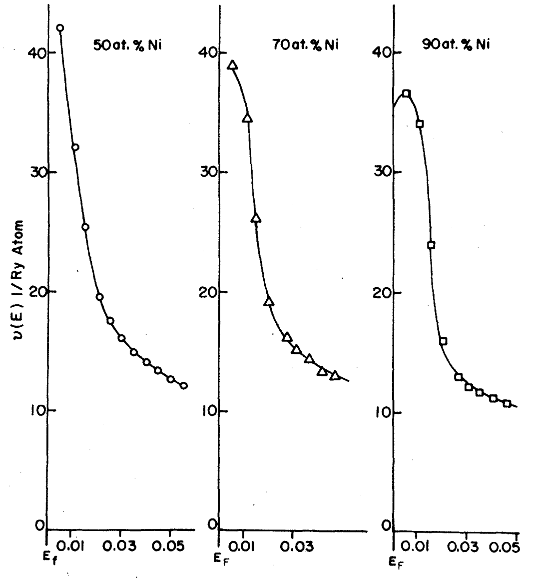

FIG. 5. Total localized density of unoccupied states per nickel atom for three Cu-Ni alloys computed from calculations of Inoue and Shimizu (Ref. 6).

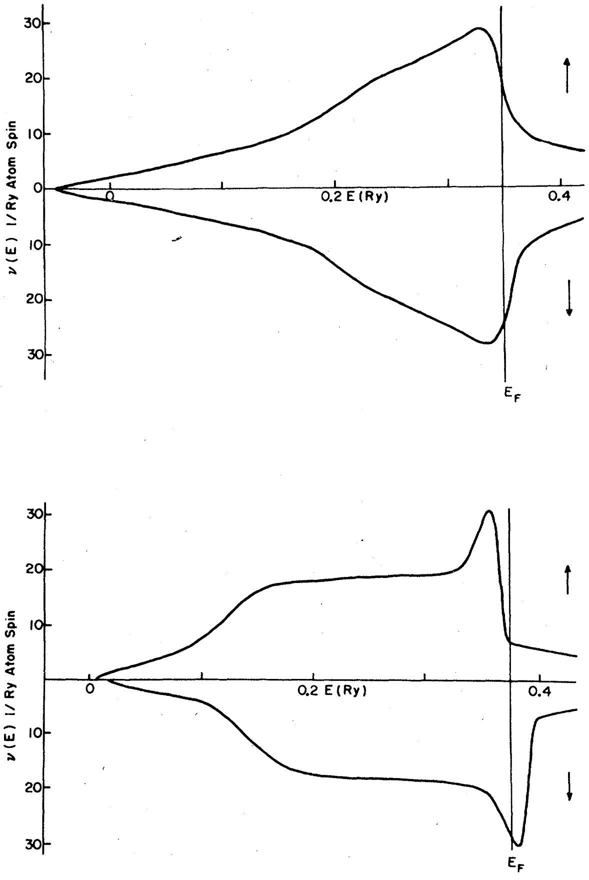

FIG. 6. Realignment along the energy axis of the spin-up and spin-down local nickel density of states in two Cu-Ni solid solutions. (After Inoue and Shimizu, Ref. 6.) Upper curve, 50 at.% nickel. Lower curve, 90 at.% nickel.

It is of interest to recall in this connection that, some years ago, Beeby proposed a model to explain the ferromagnetism in transition-metal alloys in which the average moments per atom are reduced by progressively equalizing the populations of spin-up and spin-down subbands.[8] Although devised for solid solutions of high-valency metals like Al and Si, it predicts a smoothing of the $3d$ band structure by hybridization with the valence-conduction electrons of the impurity atoms as well as a shifting of the $3d$ subbands. Such smoothing may explain the observed changes in the nickel L_{III} edge preceding C in Fig. 2.

It is conceivable that some of the apparent disagreement with paramagnetic CPA calculations arises because of the highly localized region of the Wigner-Seitz cell sampled by x-ray spectra. The *K*, *L*, and *M* absorption edges, after all, are sensitive to the electronic structure of nickel within the regions of the 1*s*, 2*p*, and 3*p* core orbitals, respectively. A direct calculation of the x-ray absorption spectra for Cu-Ni, along the lines already followed by Stocks *et al.* for Cu-Ni emission spectra,[7] might help clarify this point.

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