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Electronic structure of Ni-Cu alloys: The *d*-electron charge distribution

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This work investigates charge redistribution in a series of Ni-Cu alloys using x-ray photoemission spectroscopy (XPS) and Ni/Cu $L_{3,2}$- and K-edge x-ray-absorption near-edge structure (XANES). XPS results show that the constituent d bands are well separated and shifted to a slightly higher binding energy upon dilution into the other host, indicating that the atomic sites in the alloy are not as well screened relative to the pure metal. However, no significant d-band narrowing is observed, suggesting that there is modest d-d interaction in the alloys. In contrast to the XPS observation, XANES results show a reduction in white-line intensity at both edges relative to the pure metal suggesting that both Ni and Cu sites gain d charge. The unoccupied Ni d band is far from fully occupied even at infinite dilution. The discrepancy between the implications of the XPS and XANES results is dealt with using a charge redistribution model in which s-p-d rehybridization takes place at both sites within the framework of electroneutrality and electronegativity considerations. It appears that both Ni and Cu gain a small but measurable amount of d charge in alloy formation through rehybridization (loss of non-d conduction charge). Possible connection between these results and the disappearance of ferromagnetism in $\mathrm{Ni}_{1-x}\mathrm{Cu}_x$ alloys at $x>0.6$ is discussed. [S0163-1829(98)04024-7]

I. INTRODUCTION

The electronic structure of binary nd-transition-metal ($n=3$, 4, 5) solid-solution alloys has traditionally received extensive attention.[1] More recently, particular emphasis has been placed on the evaluation of the nature of the alloy d band and d-charge redistribution at the constituent sites.[2–8] The energy distribution of the $3d$ electrons in Ni-Cu alloys is a classical example of alloying and has been described by the so-called rigid-band (RB) model.[9] In this model, the conventional wisdom has been that Ni and Cu form a fcc alloy in which the Ni d band becomes progressively filled with increasing Cu concentration. Ni and Cu are both fcc metals with atomic electronic configurations of $4s^1 3d^9$ and $4s^1 3d^{10}$, respectively, in the solid state and are traditionally described as d^9 and d^{10} metals. In Cu the d band is nominally full. The RB model assumes that the one-electron density of state wave function is the same for Ni, Cu, and Ni-Cu alloys; that is, that the constituents donate their valence electrons to a common band structure. This model predicts that the Ni d band is completely filled at a Cu composition of 60%. This finding correlates with the experimental observation of the disappearance of ferromagnetism at this composition.[10] However, investigations of a series of Ni-Cu alloys at the Ni and Cu $L_{3,2}$ edge using x-ray-absorption near-edge structure (XANES) by Cordts, Pease, and Azároff[11] and Meitzner, Fischer, and Sinfelt[12] show that the RB model fails in predicting the d-charge counts. Their results indicate that there is no significant decrease in the number of d holes as Cu concentration in these alloys increases. On the other hand, photoemission spectroscopy[13,14] and theoretical calculations[15,16] showed that while the binding energy of the Cu d band remains unchanged, the densities of states of the Ni $3d$ band are modified significantly in both width and line shape due to rehybridization. Unfortunately, owing to the limitations in the energy resolution in these earlier measurements, results of Cordts, Pease, and Azároff and Meitzner, Fischer, and Sinfelt were not conclusive. Furthermore, a resonant photoemission study[17] showed that electron transfer occurs from Ni $3d$ states to Cu $4s$ states in contrast to the direction proposed by the RB model. It should be noted that in metals the charge count at the atomic site (Wigner-Seitz volume) tends to remain neutral. Thus only a small fraction of net charge transfer will occur upon alloying. The cohesion is accomplished by d-d and itinerant sp type conduction electron interaction modified by the electronegativity difference of the constituent metals. Granted that electroneutrality is the rule, charge redistribution can still occur via hybridization without any significant net charge flow on and off a site. For example, in Au-transition and metalloid binary alloys,[2] Au loses d charge and overcompensates its loss by gaining non-d (sp) charge so that Au, the most electronegative element, gains a small net charge (typically, $\sim 0.1e$), in accord with electroneutrality considerations.

In this paper we report results from two sets of experiments for a series of Ni-Cu alloys with the following objectives in mind: (a) To reexamine the validity of the RB model with high-resolution results and (b) to investigate the systematic of d-d interaction and charge redistribution in binary transition-metal alloys in Cu and Ni with nominally full and nearly full d bands, respectively. We have carried out high-resolution x-ray photoemission spectroscopy (XPS) measurements of the Ni and Cu d valence band and XANES measurement at the Ni and Cu K and $L_{3,2}$ edges. The XPS measurements of the valence band probe the occupied densities of states just below the Fermi level. The XANES measurements of Ni and Cu $L_{3,2}$ edge probe directly the unoccupied Ni and Cu $3d$ states just above the Fermi level, while K-edge measurements probe the unoccupied states of p character. Results obtained from these measurements will provide information on the role of Ni and Cu d electrons and their redistribution in Ni-Cu alloying. This information is also relevant to the study of the electronic structure of bimetallic systems in general.

II. EXPERIMENT

The Ni-Cu samples were prepared by repeatedly quenching from the melt a stoichiometric amount in inert atmosphere of the pure constituents as described for similar compounds previously.[2] The single phase and concentration of the samples were confirmed using x-ray diffraction and energy-dispersed x-ray fluorescence analysis. High-resolution XPS measurements were made at the low-energy spherical grating monochromator (LSGM) beamline, and XANES measurements for Ni and Cu $L_{3,2}$ edge were also taken at the high-energy spherical grating monochromator (HSGM) beamline, respectively, at the synchrotron radiation research center (SRRC) in Hsinchu, Taiwan. The SRRC operated at 1.5 GeV with a stored current of 200 mA at injection. The LSGM beamline for the XPS measurements was equipped with an UHV chamber (base pressure $\sim 5 \times 10^{-10}$ torr during the measurements), which has an EAC-125 hemispherical electron energy analyzer. The samples were cleaned by repeated cycles of argon-ion bombardment and annealed to 550–600 °C for about 15 min. Some preliminary core level and exchange interaction to Ni $3s$ multiplet splitting measurements were carried out with an in-house XPS spectrometer using monochromatic Al $K\alpha$ x rays. The Ni and Cu $L_{3,2}$-edge XANES spectra of the Ni-Cu alloys were measured in an UHV vacuum chamber (base pressure of better than 5×10^{-9} torr) using total electron yield (sample current). The specimen's surface was cleaned by scraping *in situ* with a diamond file. Photon energies for all Ni and Cu $L_{3,2}$-edge XANES spectra had an energy resolution of ~ 0.4 eV, and were calibrated against the published spectra of pure Ni (Ref. 18) and Cu (Ref. 8) metal. The Ni and Cu K-edge XANES measurements were also carried out in a total electron mode both at the wiggle beamline of the SRRC and at X11A of NSLS (National Synchrotron Light Source) at Brookhaven National Laboratory. A Si(111) double crystal monochromator was used to record the spectra.

III. RESULTS AND DISCUSSION

Figure 1(a) and inset present the XPS spectra of Ni and Cu $3d$ valence bands in the $\mathrm{Ni}_{1-x}\mathrm{Cu}_x$ alloys at an *off*-resonance (below the Ni $3p_{3/2,1/2}$ threshold) photon energy of 60 eV. The Ni and Cu d components in the $\mathrm{Ni}_{1-x}\mathrm{Cu}_x$ d band are well separated. The peak height of the valence band at maximum intensity is normalized to unity for comparison. As expected, at low Cu concentrations the valence band is dominated by the Ni $3d$ band component at the Fermi level. The intensity of the Cu $3d$ band relative to that of Ni increases as Cu concentration increases. The shape of the Ni $3d$ band only narrows slightly even at low Ni concentration while no narrowing is noticeable for the Cu d band. It is generally recognized that the development of the alloy Ni $3d$ component which crosses the Fermi level in the pure metal may profoundly influence the onset of ferromagnetism near critical composition in the Ni-Cu alloys.[19] Close examination of the energy position of maximum intensity of the Cu and Ni $3d$ bands reveals that the Cu $3d$ band moves slightly toward the low-binding-energy side from ~ 2.7 eV below the Fermi level at $x = 0.1$ to ~ 2.3 eV at $x = 0.9$ as Cu concentration increases while the accompanying Ni $3d$ band moves toward the Cu d band. The binding energies of the Cu and Ni $3d$ band maximum as a function of Cu concentration are shown in Fig. 1(b). Extrapolation of Fig. 1(b) to $x = 0$ and 1 yields the position of maximum intensity of the d band at infinite dilution of ~ 2.1 and 0.1 eV for Cu and Ni, respectively. They are only shifted slightly relative to the metal.[17] The near invariance of the d-band width with composition also indicates that there is significant conduction (sp)-d electron scattering contribution to the width even for an isolated site in a dilute alloy (no nearest neighbors of like atoms). Similar binding-energy results for the Cu (Ni) d band shifts toward the low-binding- (high-binding-) energy side with increasing Cu content in $\mathrm{Ni}_{1-x}\mathrm{Cu}_x$ were also observed

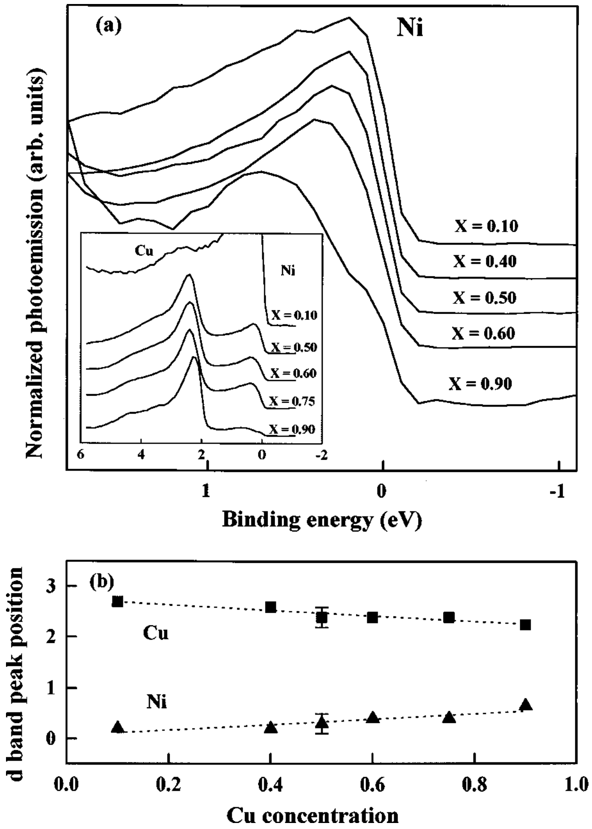

FIG. 1. (a) Representative Ni $3d$ valence-band spectra of Ni-Cu alloys. The inset presents the Cu $3d$ valence-band spectra. The intensities have been normalized to the maximum height of the bands. (b) A plot of Ni and Cu $3d$ binding-energy position vs Cu concentration x in alloys.

in a separate *on*-resonant photoemission study at the photon energy of 67 eV (Ni $3p_{3/2,1/2}$ threshold).[20] The positions of Cu and Ni $3d$ bands in our XPS spectra are in contrast to some earlier photoemission measurements[13,14] and theoretical calculations.[15,16] These earlier results showed that the energy separation between the Cu d band and the Fermi level is essentially unchanged. Nevertheless, in our high-resolution experiment, the Cu d band in the Ni-Cu alloys clearly moves to lower binding energy as the concentration of Cu increases, as observed in still other earlier reports.[17,21] Thus from the perspective of the individual components, the d band of both Ni and Cu moves slightly but noticeably towards the Fermi level as they change from infinite dilution to a dominant constituent in the alloy. We attribute this behavior to the result of charge redistribution at the Ni and Cu atomic sites.[2,17] Another approach in describing alloying is the repulsion model in which the constituent d band retains essentially its atomic character. According to the d-d repulsion model,[22] we would expect the Cu $3d$ band shifts to higher binding energies in Ni-Cu alloys with decreasing Cu concentration, accompanied by d-band narrowing. Based on electroneutrality arguments, the positive shift in binding energy of the Cu d band in the alloy relative to pure Cu is expected to be accompanied by the shifting of the Ni $3d$ levels in an opposite direction. However, experimentally the corresponding Ni d band appears to shift towards the Cu d band with increasing Cu concentration without noticeable d-d repulsion. At first glance, this finding indicates that both Ni and Cu are losing charge upon dilution into the other host. However, the Ni $2p$ XPS shows that the Ni $2p$ core levels in alloys shift slightly to lower binding energy, in opposite direction to the movement of the d band. The effect of the charge redistribution at both Ni and Cu atomic sites is further investigated using Ni and Cu $L_{3,2}$-edge and K-edge XANES spectra of which the white line probes directly the local unoccupied partial densities of states of d and p characters, respectively, above the Fermi level.

Figures 2 and 3 display the normalized Ni and Cu $L_{3,2}$-edge XANES spectra for a series of $Ni_{1-x}Cu_x$ alloys as well as Ni and Cu metals. According to dipole-selection rules, the dominant transition is from Ni (Cu) $2p_{3/2}$ and $2p_{1/2}$ to the unoccupied Ni (Cu) $3d$ electron states. The area under the white line in the Ni (Cu) $L_{3,2}$-edge XANES is predominately a convolution of the square of the transition matrix element and the unoccupied densities of states of d character (p to s transitions is relatively small). From Fig. 2, it is apparent that the shapes of the Ni $L_{3,2}$-edge XANES for the $Ni_{1-x}Cu_x$ alloys are nearly the same throughout the range of x values and closely resemble that of the pure Ni metal. In addition, the high-energy satellite structure which occurs at ~6.3 eV above the Ni L_3-edge main features in the XANES spectra is presumably caused by the excitation of Ni $2p_{3/2}$ photoelectrons to $4s$ states above the Fermi level[23] or due to a multielectron effect since Ni has a well-known 6-eV satellite associated with a poorly screened d^9 state in its photoemission spectra of both core and valence shells. The spectral line shapes at the Cu $L_{3,2}$-edge XANES spectra of Ni-Cu alloys (Fig. 3) closely resemble that of the pure Cu metal which exhibits a characteristic three-peak feature above the Cu L_3 edge. Similar three-peak features at Cu L_3-edge XANES spectra have been seen in fcc Cu-Au alloys. These features were attributed to the transition of electrons from the Cu $2p$ to the unoccupied d states above the Fermi level.[8] It should be noted that although the Cu d band is nominally full, s-p-d rehybridization results in unoccupied densities of states of d character above the Fermi level. This assignment is also supported by theoretical band model[24] and multiple-scattering calculations.[25] It should be noted that of the three-peak feature, noticeable variation is found mainly for the second and third peaks (first peak basically remains constant) in the Cu L_3-edge XANES spectra. They shift progressively to higher photon energy relative to the pure Cu metal as Cu

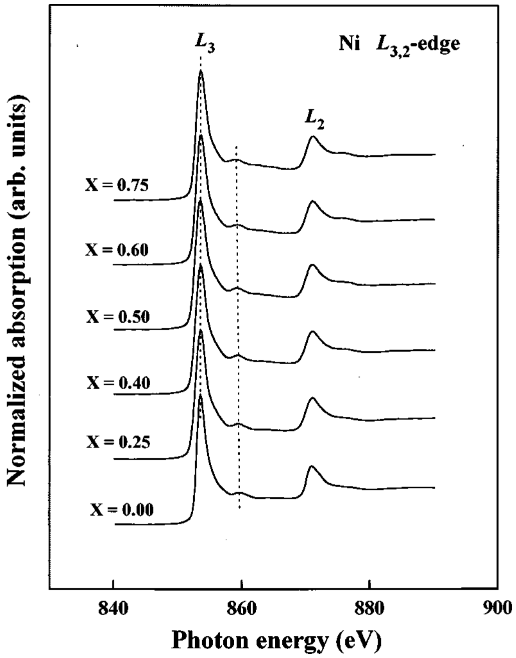

FIG. 2. Normalized Ni $L_{3,2}$-edge x-ray-absorption spectra of Ni-Cu alloys and pure Ni metal at room temperature.

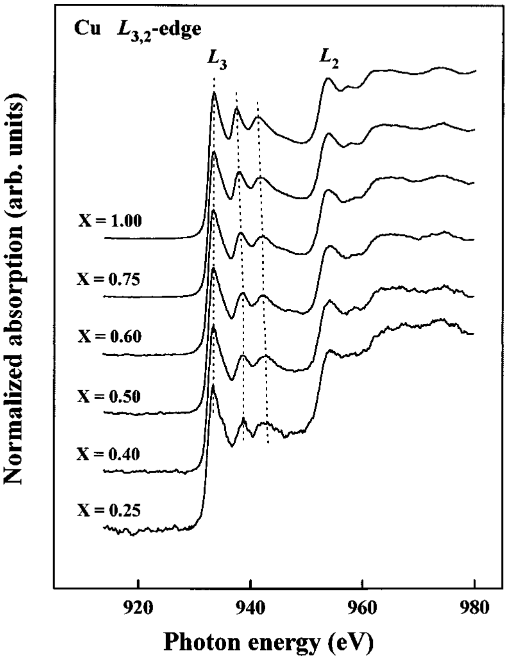

FIG. 3. Normalized Cu $L_{3,2}$-edge x-ray-absorption spectra of Ni-Cu alloys and pure Cu metal at room temperature.

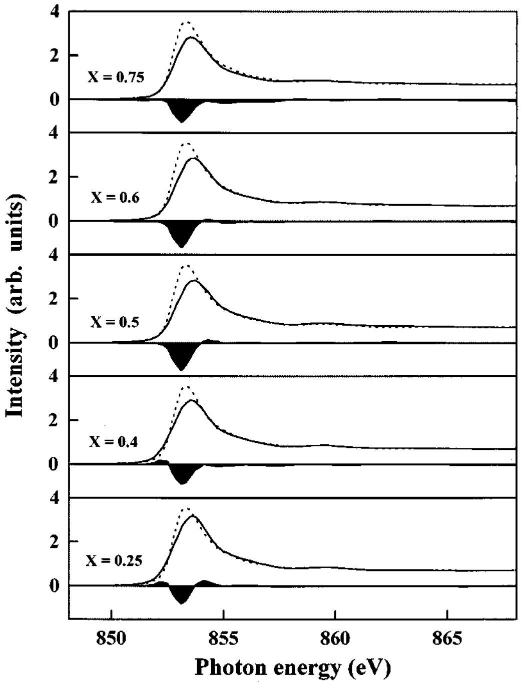

FIG. 4. Ni L_3-edge difference curve between alloy (solid line) and Ni (dotted line); the area under the difference curve in the region of interest is darkened.

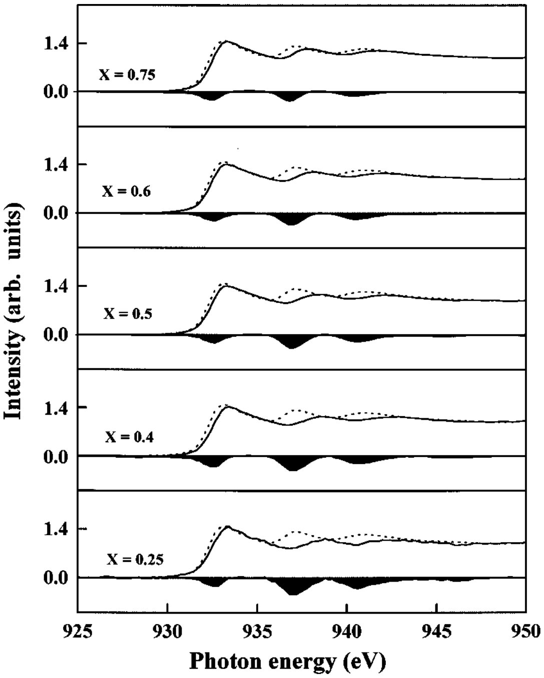

FIG. 5. Cu L_3-edge difference curve between alloy (solid line) and Cu (dotted line); the area under the difference curve in the region of interest is darkened.

concentration becomes more dilute in the Ni-Cu alloys. This observation is in line with the general trend found in the XPS study of the Ni-Cu alloys discussed earlier, which shows that the Cu $3d$ band shifts to higher binding energy. Presumably Ni-Cu d-d interaction drops the occupied states and pushes up the unoccupied states relative to the Fermi level. The shift of the Cu $3d$ three-peak pattern in the L_3-edge XANES is related to charge redistribution at the Cu and Ni atomic sites in alloys. However, in contrast to the three-peak features (mainly for second and third peaks) at the Cu L_3-edge XANES spectra, there is only a single white line and no observable shifts of the absorption features at the Ni L_3 edge for all the $\mathrm{Ni}_{1-x}\mathrm{Cu}_x$ alloys, except for the satellite structure above the Ni L_3 edge, which shifts slightly to lower photon energy with increasing Cu concentration. It should be noted that although it is common to observe similar XANES patterns for metals of the same crystal structure, especially in the extended x-ray absorption fine structures (EXAFS), the XANES for Ni and Cu (both are fcc) are quite different in that Cu has this interesting three-peak pattern. Pd and Ag, Pt and Au, for example, have quite similar XANES except for the presence and absence of white lines.[7,26] We tentatively attribute this observed distinct difference between Cu and Ni to either high resolution (instrument and long core hole lifetime) or a unique feature for $3d$ metals with filled or nearly filled d bands.

To qualitatively determine the direction of charge redistribution with Cu concentration in Ni-Cu alloys, we compared in Figs. 4 and 5 the difference in the area under the white line of the Ni and Cu L_3-edge XANES between the Ni-Cu alloys and Ni and Cu metals, respectively. All spectra have been normalized to an edge jump of unity. The threshold E_0 of the alloy spectra is aligned with that of the corresponding pure metals. The normalization procedure was carried out by matching the absorption coefficients from the preedge region at L_3 edge to several eV above L_2 edge for Ni edge, and from the preedge region at L_3 edge to several eV below L_2 edge for Cu edge. A different normalization procedure is used because the main feature in the Cu L_2-edge region is seriously inhibited by its large background absorption (Ni) as Cu becomes more dilute in the alloys. Assuming that the dipole transition matrix element remains a constant between the alloys and pure metals, the area under the difference curve (henceforth denoted as ΔA), i.e., the filled area, is proportional to the variation of unoccupied d holes at Ni and Cu between the alloys and metals, respectively. We have integrated the intensity of ΔA between 850.9 and 857.7 eV for Ni L_3 edge (excluding satellite structure) and between 931.0 and 947.0 eV for Cu L_3 edge, respectively. The results for the variation of the integrated intensity of ΔA at the Ni and Cu L_3 main features as a function of x are plotted in Fig. 6. The integrated intensities of ΔA for both metals decrease upon dilution into each other, indicating that the overall number of Ni (Cu) $3d$ holes decreases (increases) linearly with x in $\mathrm{Ni}_{1-x}\mathrm{Cu}_x$. The above result is in qualitative agreement with the previous findings[12] that the Ni $3d$ holes are only slightly filled with increasing x in the Ni-Cu alloys. In addition, we find that within the concentration ranges we studied, the slope in intensity of $\Delta A(\mathrm{Cu})$ at Cu L_3 edge ($|\mathrm{slope}|=2.3$) is quite close to that of $\Delta A(\mathrm{Ni})$ at Ni L_3 edge ($|\mathrm{slope}|=2.1$). This suggests that both Ni and Cu d orbitals are gaining a similar amount of d charge, a surprising result. Since charge must conserve and metallic systems tend to maintain charge neutrality locally, both Ni and Cu must then lose sp conduction charge count via rehybridization. Bearing in mind that both Ni and Cu have comparable electronegativity and the charge redistribution on and off sites is small in net charge counts, it is entirely possible both Ni and Cu gain

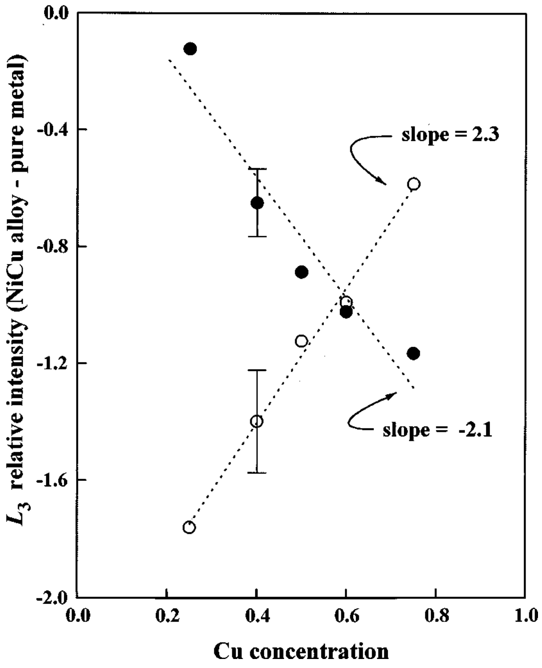

FIG. 6. Plot of difference curve intensity (ΔA) vs Cu concentration x in alloys. The solid circle and open circle represent the ΔA (Ni) and ΔA (Cu), respectively. The dashed lines serve only as a visual guide for the ΔA data.

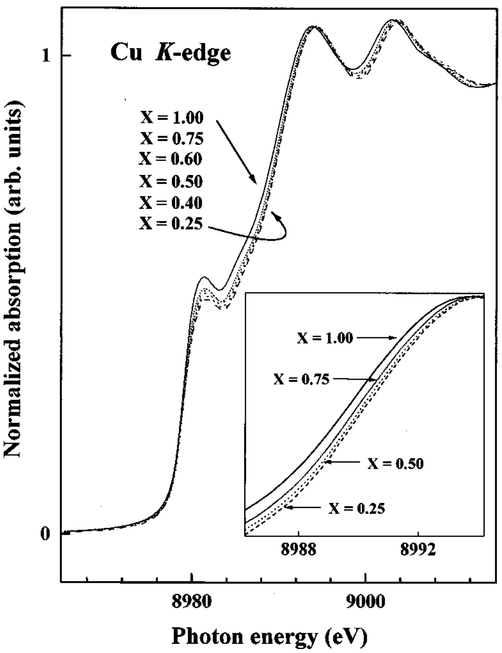

FIG. 8. Normalized Cu *K*-edge x-ray-absorption spectra of Ni-Cu alloys and pure Cu metal at room temperature. The region of threshold edge is inset on a magnified scale.

d charge and lose non-*d* charge. Although more recent theoretical calculation addressing charge transfer in Ni-Cu alloys is still lacking, earlier investigations have demonstrated that this kind of synergetic charge redistribution is a general behavior of transition-metal alloys.[2–8]

From Fig. 6, the ΔA trend at Ni and Cu L_3 edge demonstrates that both Ni and Cu gain *d* charge. Thus we can conclude that the charge flow is essentially a rehybridization of the *s*-*p*-*d* orbitals at both metal sites in Ni-Cu alloys. The *d* bands become more localized, gaining a small *d* count at the expense of losing some non-*d* conduction electrons (*sp*) so that there is negligible net charge transfer between the sites. The involvement of conduction electrons of *p* character in rehybridization can be revealed from the *K*-edge XANES which probes the unoccupied *p* states above the Fermi level. Figures 7 and 8 show the Ni and Cu edge *K*-edge XANES of

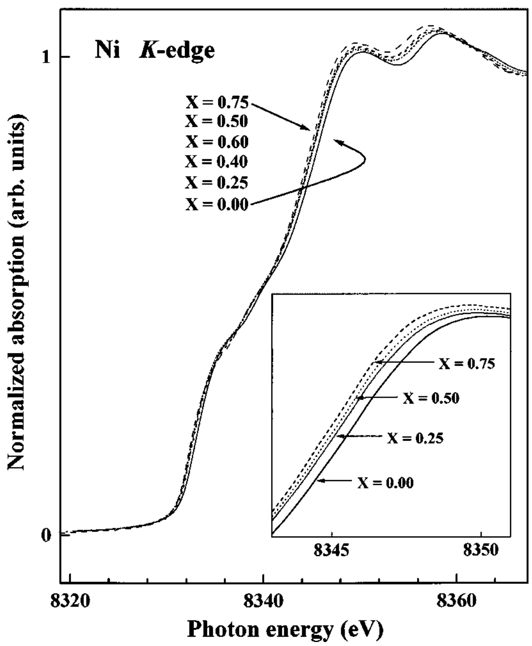

FIG. 7. Normalized Ni *K*-edge x-ray-absorption spectra of Ni-Cu alloys and pure Ni metal at room temperature. The region of threshold edge is inset on a magnified scale.

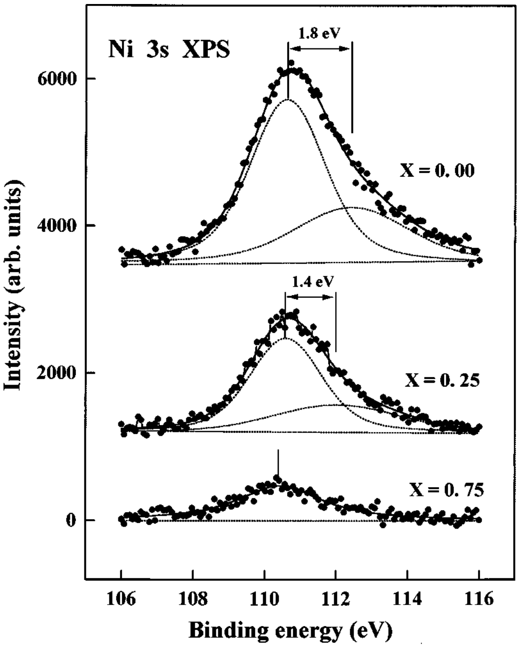

FIG. 9. The Ni 3*s* XPS spectra for some representative alloys. The final curves (solid line) were calculated by a summation of two individual peak curves shown by the dashed line. The experimental data were shown by the solid-circle line.

several representative compositions with Cu concentration above and below $x=0.6$. It can be seen that the absorption intensity just above the edge for the alloys increases at both K edges as x increases (Ni dilute in Cu). A similar trend for the same series of $Ni_{1-x}Cu_x$ alloys was obtained reproducibly at NSLS. This suggests that Ni loses p charge which compensates for the d charge gain seen in the Ni L_3 edge. The Cu results suggest that Cu gains p charge instead. Thus Cu must lose s charge to maintain electroneutrality locally. As mentioned earlier, ferromagnetism disappears when the Cu concentration is higher than $x=0.6$ in a series of $Ni_{1-x}Cu_x$ alloys. Interestingly, the experimental results of ΔA in Figs. 4 and 6 show that at $x>0.6$, the Ni white line is still very intense and the difference in intensities of the Ni L_3-edge white line is still quite small even at infinite dilution (extrapolation to $x=1$). It is apparent that the decrease in net magnetic moment in these alloys is not just related to diminishing Ni $3d$ holes. We tentatively propose that it is dilution and spd rehybridization that quenches the interatomic and s-d exchange interaction of the Ni atoms in the alloy. We have also measured the Ni $3s$ multiplet splitting.[27] Figure 9 shows the Ni $3s$ XPS spectra for some representative alloys. The multiplet splitting arises from the final state exchange splitting between the $3s$ core electron and the unpaired electron in the d band.[28] Its magnitude is related to the number of unpaired electrons (magnetic moment). For Ni metal the splitting is ~1.8 eV and it decreases as Cu is added and disappears at high Cu concentration. Finally, from Fig. 6, we notice that both Ni and Cu are showing a linear reduction in white-line magnitude. The value of $\Delta A(\mathrm{Ni})$ and $\Delta A(\mathrm{Cu})$ is more or less the same when $x=0.6$, beyond which the value of $\Delta A(\mathrm{Cu})$ is larger than that of $\Delta A(\mathrm{Ni})$ with increasing Cu concentration. The near-equal ΔA for Ni and Cu at $x=0.6$ is perhaps fortuitous and the relevance of this observation to magnetism awaits further investigation.

In summary, this work investigates the charge redistribution in a series of Ni-Cu alloys by using XPS and Ni/Cu L_3- and K-edge XANES spectra. The L_3-edge white-line difference curve of alloys relative to pure metals at Ni and Cu L_3 edge indicate unambiguously that both Ni and Cu gain d charge upon alloying while the K-edge results show Ni losing p charge and Cu gaining p charge. In addition, the analysis of ΔA values reveals that the correlation of ΔA between Ni and Cu L_3 edge may be related to the disappearance of ferromagnetism at a critical composition in Ni-Cu alloys. The XPS reveals the systematic movement of the constituent d bands in the valence-band spectra. All observations have been interpreted in terms of a rehybridization model.

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