PHYSICAL REVIEW B VOLUME 17, NUMBER 2 15 JANUARY 1978

High-resolution photoemission study of the surface and bulk electronic structure of copper-nickel alloys

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(Received 30 June 1977)

Energy-distribution curves (EDC's) of photoelectrons emitted normal to the surface of single crystals of $Cu_{0.03}Ni_{0.97}$, $Cu_{0.16}Ni_{0.84}$, and $Cu_{0.24}Ni_{0.76}$ have been measured at high energy and angle resolution. Incident photon energies of 11.83, 16.85, and 21.22 eV were used. The annealed alloy samples show a surface segregation of Cu, which is essentially restricted to the outermost atomic layer. By bombarding the samples with low-energy (600-eV) Ar ions, the Cu-enriched surface layer can be removed and the Cu surface concentration is then not much different from that of the bulk. By measuring the EDC's of the annealed samples, properties of the surface electronic structure of the Cu-rich surface layer are obtained, which in the Cu *d*-electron region is dependent on the single-crystal face and the Cu concentration. The EDC's of the bombarded surfaces are believed to represent mainly the bulk electronic properties of the alloys. In this case the Ni-derived states have similarities to those of pure Ni, whereas the Cu-derived levels show distinct differences in shape and position compared to the results of pure Cu. Both effects are qualitatively understood in the light of recent calculations of the complex band structure of Cu-Ni alloys.

I. INTRODUCTION

It has recently been demonstrated that by measuring directional photoemission normal to clean single crystals of tungsten, very direct information on the electronic structure along the corresponding symmetry lines in the Brillouin zone can be obtained.[1] When applying this technique to the noble[2,3] and ferromagnetic transition metals[4,5] we also found a strong correlation between the energy-distribution curves (EDC's) of the photoemitted electrons and the electronic properties of the relevant symmetry directions in $\vec{k}$ space. Following these ideas it seemed promising to also study directional photoemission at high energy and angle resolution for random alloy single crystals.

For the present work we have chosen a series of copper-nickel alloys in the Ni-rich region (Cu concentration ≤ 24 at.%). Cu-Ni is often regarded as a typical representative of a binary substitutional alloy; at high temperatures it forms a metallurgical simple system with fcc lattice throughout the entire composition range. Because of this simplicity and some other interesting properties Cu-Ni alloys are used as model substances in calculations of the electronic structure of random binary alloys. A number of density-of-states calculations by means of the coherent-potential approximation are now available[6-8] as well as calculations of the complex alloy band structure along main symmetry directions of the Brillouin zone based on the coherent-potential[9,10] and the average-t-matrix approximation.[11] We expected that, in particular, properties of the complex band structure may be derived from the measurements of directional photoemission from Cu-Ni single crystals.

A knowledge of the bulk electronic structure of Cu-Ni alloys is especially desirable for an explanation of the magnetic properties. Ni-rich alloys are ferromagnetic above a critical Ni concentration. Our alloy samples all belong to the ferromagnetic region. One of our aims was, therefore, to study whether the influences of magnetic interactions can be seen in the experimental results. In the light of the itinerant-electron theory of ferromagnetism[12] the exchange splitting between the majority and minority-spin Ni-derived subbands should be reduced in the alloys. Since our previous photoemission study[4] of single-crystals of Ni has shown that consequences of the band structure calculated within the concept of the itinerant-electron theory of ferromagnetism can be confirmed, it may be expected that systematic trends with increasing Cu concentration of possible magnetic origin are derivable and thus support our interpretation of the results from pure Ni.

Besides the bulk properties of Cu-Ni alloys, the surface electronic structure of the system deserves detailed experimental investigation. As a matter of fact, the photoemission technique is very suitable for such studies because of its high surface sensitivity. From a theoretical point of view the modification of the electronic states by the presence of the surface has been investigated by Morán-López *et al.*[13] and Berk.[14] Both authors find a narrowing of the local density of states at the surface of transition-metal alloys when compared with the bulk. A narrowing of the energy bands in the surface region might therefore be visible in the experimental EDC's.

Other interesting features of the surface of Cu-Ni alloys are the dependence of the surface concentration of the alloy constituents on various surface treatments and the electronic structure of the altered surface layer. That such effects occur was first deduced from studies of the catalytic activity of Cu-Ni alloys,[15,16] which can be changed in a drastic way by annealing, ion bombardment, and oxidation-reduction treatment. By using low-energy-Auger-electron,[17,18] ultraviolet-photoelectron-spectroscopy[19] (UPS) and ion-scattering experiments,[20] it has recently been established that the surface becomes enriched in Cu by annealing the samples. This is also expected on the basis of theoretical arguments.[21-23] On the other hand, sputtering is known to remove preferentially Cu from the surface.[24]

Previous UPS[19,25,26] and x-ray-photoelectron-spectroscopy[27] (XPS) studies have shown that the Cu-Ni system possesses a clear split-band pattern but have not revealed much fine-structure details within the Cu- and Ni-derived *d*-electron region. Apart from changes of the intensity ratio of the Cu- and Ni-related structures and of their energy position and width upon alloying, the main characteristics of the EDC's remain rather insensitive to sample preparation, surface treatment, orientation, and concentration of the alloy constituents. Soft-x-ray emission[28] and absorption[29] measurements have brought up similar information to the UPS and XPS experiments.

We show in the present work that by measuring directional photoemission of single-crystal faces more detailed information on the electronic structure of the Cu-Ni system is obtained than could be derived previously from angle-intergrating measurements.[19,25-27] Our EDC's are, in fact, quite sensitive to the Cu content and show a high degree of specificity in photoemission from different directions of the Brillouin zone. A comparable investigation of a paramagnetic (Cu-rich) Cu-Ni single crystal was reported quite recently by Gyorffy *et al.*,[10] who measured directional photoemission at different angles with respect to the surface normal and interpreted their results in terms of the complex bulk band structure calculated within the framework of the coherent-potential approximation. In our work we only consider photoelectrons emitted normal to the single-crystal faces. In addition to a discussion of the bulk properties we pay special attention to an investigation of the Cu-enriched surface layers, where the electronic structure shows a strong influence on various experimental parameters.

II. EXPERIMENT

We studied the following single-crystal faces of the Cu-Ni system: $Cu_{0.03}Ni_{0.97}(110)$, $Cu_{0.16}Ni_{0.84}(111)$, $Cu_{0.24}Ni_{0.76}(110)$, and $Cu_{0.24}Ni_{0.76}(111)$, where the subscripts refer to the mean bulk concentration determined by x-ray fluorescence technique to within an accuracy of 0.5 at.%. The crystals were grown by the Bridgman method.[30] An x-ray microanalysis of the alloy surfaces could not detect inhomogeneities to within 0.5 at.% on the scale of 2 μm, but precipitation of smaller clusters following the heat treatments may be possible[31] and eventually influence the measured spectra. Such effects will be discussed later.

The samples were prepared by spark cutting the bulk crystals. The desired orientations were obtained within an accuracy of 1.5° as deduced from Laue diffraction patterns, which showed the sharp spots of the corresponding fcc planes. After mechanical and electrolytical polishing, the samples were treated *in situ* by repeated anneal-sputter cycles. Annealing was performed at 750–800 K for 1–8 h in a base vacuum of 7×10^{-8} Pa in the preparation chamber of the photoelectron spectrometer.[32] An annealing time of 2 h was found sufficient to provide a Cu-rich surface of a high-temperature equilibrium phase, since no essential changes in the spectra could be observed when the samples were annealed for longer periods of, for example, 8 h. Because of the slow diffusion of Cu and Ni atoms at room temperature,[33] the surface composition remained stable during the measurements.

Sputtering was accomplished by bombarding the surface with Ar ions of 600-eV energy for 0.5–60 min. The flux of ions was $(1.2 \pm 0.2) \times 10^{13}$ ions /cm^2 sec as determined by means of an arrangement of small collectors instead of the sample and a picoamperemeter.

For comparison and in order to estimate the thickness of the Cu-rich surface layer we have also studied thin Cu films in the monolayer region, evaporated onto a Ni(111) single-crystal substrate. The average thickness of the films was monitored by a quartz oscillator with an accuracy of 0.3–0.5 monolayer.

The spectra were obtained by using the rare-gas resonance lines of He (21.22 eV), Ne (16.85 eV), and Ar (11.83 eV). Electron emission was measured normal to the surface of the samples within an acceptance cone of 10° full width. This means that, in general, the reduced wave-vector component $\vec{k}_{\parallel}$ of the photoelectrons inside the sample is approximately zero provided that periodicity of the lattice is preserved. Only a few and relatively weak elements of structure are explained by scattering from other directions of the Brillouin zone, where $\vec{k}_{\parallel}$ is not negligible. The EDC's were measured at room temperature. The base pressure in the analyzer chamber amounted to 10^{-8} Pa. The instrumental resolution was better than 0.06 eV for all measurements. A constant background was subtracted from the spectra and the raw data were corrected for the instrumental transmission function of the analyzer and for the doublet character of the Ne and Ar radiation. More details of the experimental apparatus have been published elsewhere.[32]

III. RESULTS AND DISCUSSION

A. Cu enrichment at the surface of annealed $Cu_{0.24}Ni_{0.76}(110)$

Evidence for Cu enrichment in the surface region of Cu-Ni alloys by means of an UPS study was already manifested in recent works of Yu *et al.*[19] This fact is also seen in the EDC's of our annealed samples by the high intensity of the Cu d-electron-related features, which are located at −4 to −2 eV with respect to the Fermi level E_F (Fig. 1). They are separated from the main Ni d-electron region of approximately −1.5 eV to E_F and overlap only with a weak feature observed at −2.6 eV for pure Ni.[4] To study the surface segregation in some more detail we attempted to remove the Cu-enriched surface layers by means of controlled Ar-ion bombardment following the annealing process and measuring the EDC's after each anneal-sputter cycle.

The results of this experiment are shown in Fig. 1, where a series of EDC's from $Cu_{0.24}Ni_{0.76}(110)$ obtained after different sputtering times at a photon energy of 21.22 eV are displayed. The uppermost curve corresponds to the spectrum of the annealed sample. The electronic structure of the Cu-derived d-electron region, represented by the features A, B, and C, is extremely sensitive to the surface treatment, while the Ni-derived states, mainly indicated by a peak a, remain unaffected. A short sputtering of the annealed sample decreases the intensity of the Cu peaks in a drastic way and, at the same time, moves peak B. This behavior is associated with the presence of a Cu-rich surface layer formed during the annealing process and which is continuously removed by the ion bombardment.

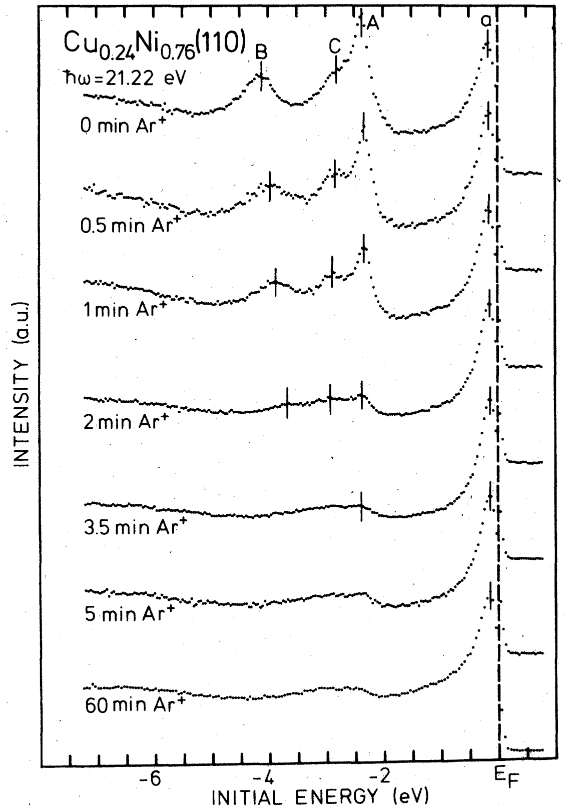

FIG. 1. Energy-distribution curves of photoelectrons emitted normal to the (110) face of $Cu_{0.24}Ni_{0.76}$ after different sputtering times following the annealing process.

We have examined whether a kind of depth composition profile of the annealed surface can be deduced from our measurements. Mainly two difficulties arise with respect to this problem. (i) The sputtering process itself causes a disturbance of the concentration profile within a certain damaged layer, which was estimated by Ho *et al.* to have a thickness of approximately 10 Å for Ar ions of 600-eV energy.[24] (ii) The peak heights in the EDC's are certainly related to the content of the alloy constituents, but no simple conversion between these values is possible. In addition, the intensity of the Ni-related peak a of the annealed and shortly bombarded surfaces is reduced by absorption in the Cu-enriched surface layer.

Keeping in mind these limitations we have assumed that from the intensity ratio of peak A to peak a one may obtain at least an estimate of the thickness and the composition profile of the Cu-rich surface region. By comparing the time variation of the experimental intensity ratio during the ion bombardment (see Fig. 1) with a model of preferred sputtering of a binary-alloy system,[24] we found reasonable agreement for sputtering times larger than 2 min. However, in the first

1–2 min of sputtering, when the Cu-rich surface layer is removed, the measured intensity ratio cannot be described by the kinetic model of Ref. 24, where a homogeneous bulk concentration is assumed at the beginning of the sputtering. Our main conclusion from this observation is that immediately after the removal of the Cu-rich surface layer essentially the bulk alloy composition is achieved in the surface region, which does not change too much with continued ion bombardment.

An estimate for the thickness of the Cu-rich surface layer can be obtained by calculating the time, which is necessary for the removal of one monolayer. Using the known sputter yields[24,34] and ion flux the results are 80 and 140 sec for clean Cu and Ni surfaces, respectively. For the alloy surfaces the equivalent time is assumed to lie within these limits. Since after a time of about 100 sec of sputtering the intensity ratio is already close to the calculated value according to the theory of Ref. 24, the Cu enrichment is essentially restricted to the outermost atomic layer. This conclusion is supported by the fact that the intensity ratio of the annealed sample is approximately equal to that of one monolayer of Cu on a Ni(111) face[35] (see Fig. 5).

The large Cu surface concentration is also expected on the basis of theoretical studies,[21,23] where a Cu concentration of 70% (Ref. 23) or of even more than 90% (Ref. 21) was derived for the first atomic layer of a Cu-Ni sample with a bulk concentration used in our measurements. Another experimental value for the Cu surface content was given by Watanabe *et al.*, who found Cu enrichment in the first layer to be about 75%.[18]

B. Photoemission from the alloys

Figures 2–5 show EDC's obtained at three different photon energies for the alloys, which were first annealed for 2 h (solid lines) and then sputtered for 3–3.5 min (dashed lines). We have chosen the length of the sputtering time in order to remove the Cu-enriched surface layer most completely but not to damage the bulk layers too seriously. The Cu content in the surface of the sputtered samples is somewhat different from the quoted value of the bulk. For $Cu_{0.24}Ni_{0.76}$ the surface region contains 21-at.% Cu as calculated from Eq. (5) of Ref. 24, and for sputtered $Cu_{0.16}Ni_{0.84}$ and $Cu_{0.03}Ni_{0.97}$ one obtains 14- and 2.6-at. % Cu, respectively. Because the difference in composition between the bulk and the sputtered surface is not too large, we may regard the EDC's of the sputtered samples as representative for the bulk, at least as concentration of the alloy constituents is concerned. Whether the damages introduced by the sputtering process have influences on the measured EDC's is not known precisely. From our studies of clean metals[2–5] we have seen, however, that only a few elements of structures of the EDC's are especially sensitive to ion bombardment. In most cases only a broadening of the observed structures is obtained for longer periods of sputtering (e.g., 10 min and more).

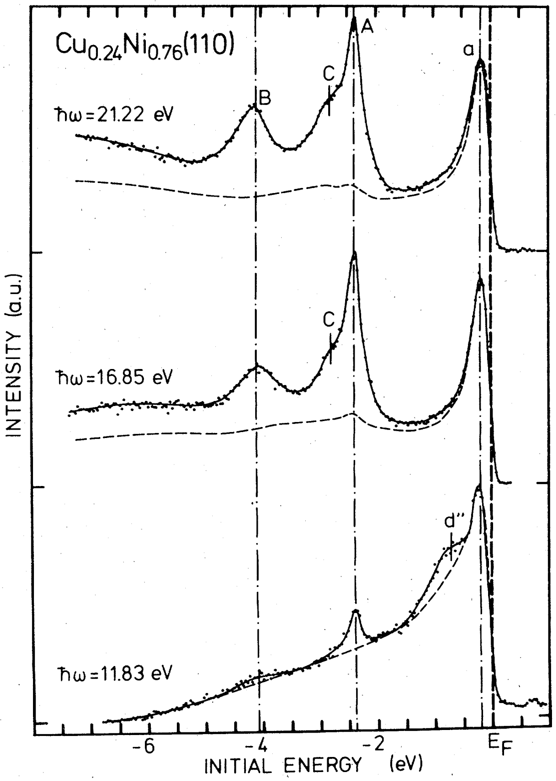

FIG. 2. Energy-distribution curves of photoelectrons emitted normal to the (110) face of annealed (full lines) and sputtered (dashed lines) $Cu_{0.24}Ni_{0.76}$.

The spectra of the annealed alloys correspond to a superposition of two or more component spectra, one characterizing the bulk and the others the Cu-rich layers. However, the bulk contribution to the total intensity of the peaks in the Cu *d*-electron region does not exceed 10% in any case, and therefore the Cu peaks can be attributed essentially to the electronic states of the Cu-enriched surfaces.

In addition to the EDC's of the annealed and sputtered surfaces, we show in Fig. 5 three EDC's (dashed-dotted lines) for a system, where Cu with an average thickness of about 2 Å has been evaporated onto a Ni(111) single-crystal face.

C. Surface electronic structure of the annealed alloys

Several theoretical models[21–23] have been applied to the problem of surface segregation of binary alloy systems. One of the most recent attempts was reported by Kerker *et al.*[23] who derived a mi-

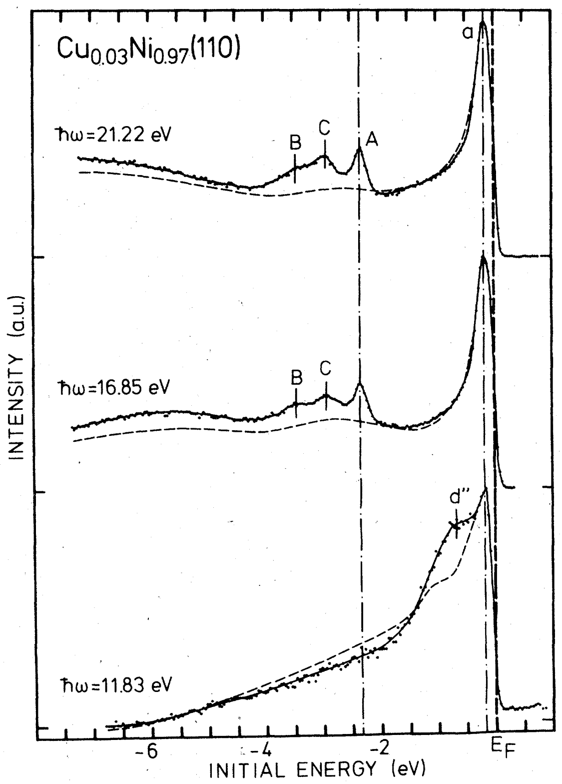

FIG. 3. Energy-distribution curves of photoelectrons emitted normal to the (110) face of annealed (full lines) and sputtered (dashed lines) $Cu_{0.03}Ni_{0.97}$.

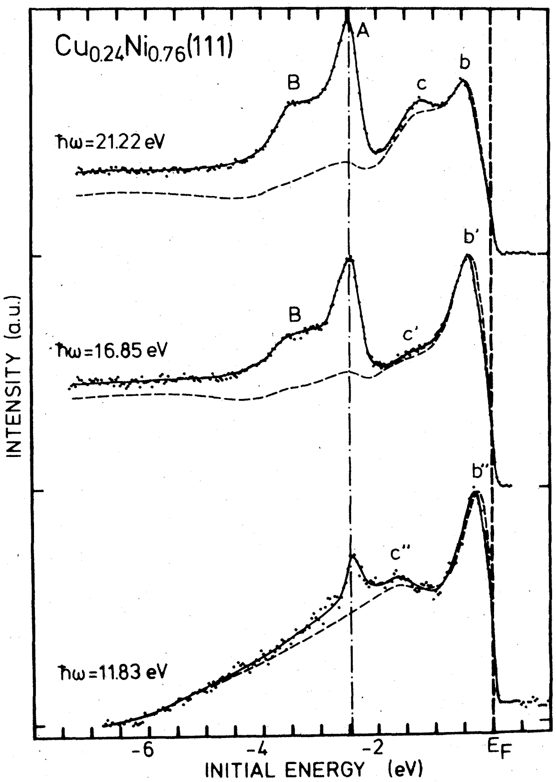

FIG. 4. Energy-distribution curves of photoelectrons emitted normal to the (111) face of annealed (full lines) and sputtered (dashed lines) $Cu_{0.24}Ni_{0.76}$.

croscopic theory for the electronic forces responsible for surface segregation. In this theory properties of the electronic structure play an important role and we therefore discuss our photoemission results from the annealed samples in some more detail. It has to be noted that the effect of the annealing temperature on the composition profile will not be considered in the present work. In this sense the annealing process is only regarded to be responsible for an acceleration of segregation, which would develop too slowly at room temperature for observation in an UPS experiment.

In Figs. 2 and 3 our results from $Cu_{0.24}Ni_{0.76}(110)$ and $Cu_{0.03}Ni_{0.97}(110)$ are shown. One of the most striking features of the EDC's of the annealed alloys (full lines) is the fact that the main peaks (*A*, *B*, *C*, and *a*) for either sample are stationary in the initial energy position when different photon energies are used. The intensity of the Cu-related peaks (*A*, *B*, *C*) compared to the Ni emission (*a*) is about the same for $\hbar\omega = 21.22$ and 16.85 eV. For $\hbar\omega = 11.83$ eV the Cu peaks of $Cu_{0.24}Ni_{0.76}$ are reduced because of an increased exit depth of the photoelectrons and they cannot be observed for $Cu_{0.03}Ni_{0.97}$. Invariance of structures indicates their relation to the density of initial states. In UPS studies of the (110) faces of the noble metals[2] the same effect has been found and was tentatively explained by surface photoemission, where the $\vec{k}$-conserving selection rule for the perpendicular component of the wave vector is relaxed and the EDC's, therefore, resemble the one-dimensional density of states of the corresponding symmetry direction in the Brillouin zone. As a matter of fact, the electronic structure of the annealed surfaces cannot be described by energy bands of a three-dimensional Brillouin zone but still we may assume that the Cu-related peaks at 16.85- and 21.22-eV photon energy reflect the density of states at the center of the surface Brillouin zone.

The electronic structure of the Cu-derived spectral region of the (110) faces of the alloys shows appreciable influences of the actual Cu concentration. This fact can be seen if one compares the EDC's from $Cu_{0.24}Ni_{0.76}$ measured after different sputtering times (Fig. 1) and those of $Cu_{0.24}Ni_{0.76}$ (Fig. 2) with the results of $Cu_{0.03}Ni_{0.97}$ (Fig. 3). Note that by bombarding the annealed $Cu_{0.24}Ni_{0.76}$ (110) surface for a time of 1 min a similar EDC is found as from annealed $Cu_{0.03}Ni_{0.97}(110)$. The energy position of *A* at -2.35 eV is practically independent from the Cu surface concentration,

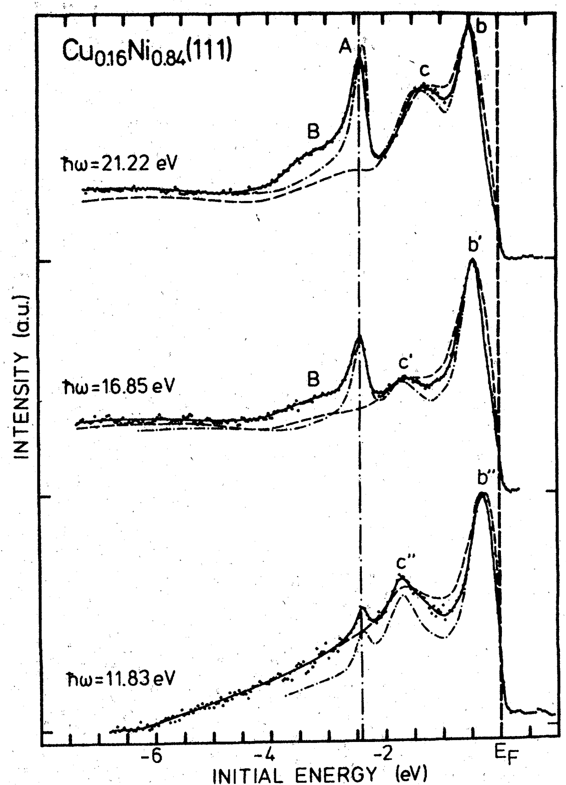

FIG. 5. Energy-distribution curves of photoelectrons emitted normal to the (111) face of annealed (full lines) and sputtered (dashed lines) $Cu_{0.16}Ni_{0.84}$. Emission from a 2-Å-thick Cu overlayer on Ni(111) is also shown (dashed-dotted lines).

whereas the low-energy states represented by peak *B* located at −4.1 eV for $Cu_{0.24}Ni_{0.76}$ shift towards higher energy with decreasing Cu content, and finally merge with the states corresponding to shoulder *C*.

It has to be emphasized that such effects were not observed by Yu *et al.*[19] who always obtained a structureless energy distribution in the Cu region independent from Cu surface concentration. Here we demonstrate that the Cu *d* electrons of the Cu surface layer mainly occupy two discrete energy levels whose energy position is influenced by the Cu concentration. The shape of the Cu-derived structures has no clear relationship to the emission of the (110) face of pure Cu.[2] It is true that peak *A* coincides with a main peak of Cu(110) but the rest of the structure has no counterparts in the EDC's of pure Cu.

Peak *a* of the alloy samples (Figs. 2 and 3) originates from Ni *d* electrons, which leave the sample through the Cu-rich surface layer. Comparing the Ni-related structures of the alloys with those obtained from pure Ni,[4] we do not find definite differences except for structure *d''* which will be discussed below. In Ref. 4 the pronounced peak of Ni(110) was related either with nondirect emission from the high density of majority spin states at the *X* point of the Brillouin zone or with emission from surface states. We now favor our first interpretation, which is also supported by the fact that structure *a* of the alloy sample does not show differences whether the Cu-rich surface layer is present or not (full line and dashed line). An interesting point is that the Cu surface layer obviously does not influence the emission mechanism of the Ni *d* electrons in the alloys compared to Ni. Since in Ref. 2 this mechanism was explained by the participation of unoccupied surface states, we may assume that these surface states persist in the annealed alloy samples. More experiments are needed to clarify the above interpretation.

The EDC's of the annealed (110) faces of the alloys obtained at a photon energy of 11.83 eV exhibit an additional shoulder labeled *d''*, which is absent in the spectra, where the Cu-rich surface layer is removed (dashed lines in Figs. 2 and 3). The occurrence of such structure is especially surprising for the Ni-rich sample $Cu_{0.03}Ni_{0.97}$, where the Cu-derived states cannot be identified directly due to the small Cu content and the large mean free path of the photoelectrons at a photon energy of 11.83 eV. In this case, the removal of the Cu-rich surface layer can only be deduced from the weakening of shoulder *d''*. As explanation for this effect we suggest that elastic scattering of photoelectrons at the Cu surface layer might contribute to the energy distributions of the normally emitted photoelectrons. A similar effect has been observed by Anderson and Lapeyre[36] for W(100), where a small H_2 coverage caused umklapp scattering via reciprocal vectors of the surface superstructure. In our case diffuse scattering might also be possible. Further studies at different take-off angles have to be performed to support the above explanation.

In Figs. 4 and 5 our results from the (111) faces of $Cu_{0.24}Ni_{0.76}$ and $Cu_{0.16}Ni_{0.84}$ are displayed. In addition, emission from an evaporated Cu overlayer of 2-Å mean thickness onto a Ni(111) substrate is shown (dashed-dotted lines in Fig. 5). Again the Cu-related structures *A* and *B* show large differences when measured from the annealed and the bombarded surfaces, whereas the Ni region remains fairly unaffected by the surface treatment. As in the case of the (110) faces we therefore believe that the Ni-derived structures can essentially be associated with the bulk properties of the alloys, which will be discussed in Sec. III D.

The energy position of *A* and *B* is independent from photon energy, which means that as for the annealed (110) faces they may be interpreted as representative for density of initial states. The Cu d electrons mainly occupy levels, which give rise to the pronounced maximum A at a similar energy position as the maximum of the (110) faces. Occupied states at this energy are also observed for the thin Cu overlayer on the Ni(111) face (Fig. 5). It shall be mentioned here that for Cu overlayers with increasing thickness the emission of bulk Cu(111) gradually develops.[35] For the annealed samples a shoulder B appears about 1 eV below peak A. In this energy region clear differences are observed between the results from the (110) and (111) faces of the alloys. As for the (110) faces no relationship of the Cu-related structures is present compared to those of bulk Cu (111).[3]

Whether a narrowing of energy bands in the alloys occurs in the presence of the surface[13,14] cannot be deduced from our EDC's with certainty. From our measurements of Cu,[2,3] and Ni,[4] no manifestations of such effects could be found for the pure metals. Since the Ni-derived states in the alloys have similar widths as in pure Ni, a narrowing of these states near the surface is not indicated. The Cu subbands of the bombarded surfaces show a reduced width when compared with the EDC's of the pure metal but this may also be caused by alloying effects (see Sec. III D).

D. Bulk electronic structure of the alloys

According to our discussion in Sec. III A, the surface concentration of the shortly bombarded alloy samples is not much different from the concentration of the bulk. We assume that the measured EDC's of such surfaces (dashed lines in Figs. 2–5) reflect properties of the bulk electronic structure insofar as the ECD's of pure Cu (Ref. 2) and Ni (Ref. 4) surfaces may be related to the bulk band structure. This does not exclude the possibility that surface processes still are important at the applied photon energies. It has been suggested,[2] for example, that an explanation of EDC's of Cu (110) is possible by a surface photoemission process, where transitions from bulk energy bands occur to unoccupied surface states. Our concept is therefore somewhat different from that of Ref. 19, where it is assumed that for photon energies in the range near 20 eV mainly surface properties are probed because of a small escape depth of the photoelectrons.

If one compares the EDC's of the bombarded alloy surfaces with those of pure Cu,[2,3] and Ni,[4] the most striking observations are as follows. (i) The Ni-derived peaks of $\mathrm{Cu}_{0.03}\mathrm{Ni}_{0.97}$ (110) and $\mathrm{Cu}_{0.24}\mathrm{Ni}_{0.76}$(110) closely resemble the emission of pure Ni. (ii) The Ni-derived structures of the (111) faces of $\mathrm{Cu}_{0.16}\mathrm{Ni}_{0.84}$ and $\mathrm{Cu}_{0.24}\mathrm{Ni}_{0.76}$ also show certain similarities to those of Ni, but some characteristic differences are also observed. (iii) The Cu-derived features for every alloy sample have a rather low intensity, which is less than might be expected from the Cu content. Only for the samples containing 16% and 24% Cu structures may be identified, which correspond to Cu d electrons. These structures, contrary to the Ni-related peaks, do not reveal similarities to emission of the faces of Cu. The small hump appearing at −2.7 eV in the EDC's of $\mathrm{Cu}_{0.03}\mathrm{Ni}_{0.97}$(110) is probably due to transitions of Ni d electrons, since a similar structure is measured for pure Ni.

The effect of alloying for these Ni-rich samples is apparently more pronounced for the Cu electronic states than for the Ni d electrons. This fact is consistent with the theoretical works of Refs. 7, 8, and 11, where the Ni states of Cu-Ni alloys for small Cu content retain much of their characteristics of pure Ni, while for the Cu states an appreciable broadening is expected. In the theoretical results reported by Kirkpatrick *et al.*[6] a continuously increasing broadening of the main maximum of the Ni density of states also is obtained, if Cu is diluted in Ni more and more. This effect can hardly be seen in our measurements: the Ni peak a of $\mathrm{Cu}_{0.24}\mathrm{Ni}_{0.76}$(110) (Fig 2) has approximately the same width as for pure Ni.[4]

At this point it has to be remembered that we do not measure angle-integrated properties and a comparison with computed bulk density of states has to be carried out with special care. Only the general behavior of angle-integrated properties may possibly be extracted from our experimental data and a comparison with calculations of the alloy complex band structure[9–11] would be more appropriate. Before we do so some more general facts in our experimental data will be discussed.

The Ni peaks of the (111) faces of the alloys (Figs. 4 and 5) clearly show a shift with photon energy (b-b'-b'' and c-c'-c''). Such shifts are usually explained by the occurrence of direct transitions, which might therefore be present in our Ni-rich alloy samples. However, a possible chemical clustering of Ni atoms cannot be ruled out completely,[31,37] and may also lead to observable direct transitions from Ni clusters. We do not believe that such effects are dominant in our case, since the differences in the Ni region of the EDC's from the annealed and bombarded surfaces are fairly small. We would expect more pronounced clustering after sputtering, which was performed at room temperature and could accelerate the formation of clusters by transfer of activation energy through the bombarding Ar ions.

The Cu transitions in the alloy samples are found in the energy region between –4 and –2 eV. A dependence from photon energy is not observed and the emission may therefore be related to the density of states by nondirect transitions. Some fine structure details are seen for $Cu_{0.24}Ni_{0.76}$ (Figs. 2 and 4). For $Cu_{0.16}Ni_{0.84}(111)$ (Fig. 5) only a weak hump may be recognized in the Cu subband region and eventually assigned to the Cu impurity level. Because of the weakness of all these features a definite interpretation is somewhat uncertain, however.

Properties of the complex band structure of Cu-Ni alloys as calculated by Bansil *et al.*[11] by means of the average-t-matrix approximation, should be directly observable in our experimental results. Following this theory for Ni-rich alloys the Ni subbands are expected to persist with some additional broadening compared to pure Ni and would explain our observation of direct transitions in the EDC's of the (111) faces for the Ni d-electron region. A certain increase of the widths of the direct Ni transitions is also observed with increasing Cu concentration in the experimental EDC's. This fact may be deduced by comparing the measurements of Figs. 4 and 5, where the Ni-derived features appear less resolved for $Cu_{0.24}Ni_{0.76}$. Such behavior is understood on the basis of the results in Ref. 11.

According to the theory the broadening of the Cu subbands should be enhanced when compared with the Ni bands and could account for our conclusion that for the Cu d-electron region density of initial states are seen. The main difference between our measurements and the calculation is the energy position of the Cu subbands, which appear much closer to the Fermi level than was predicted theoretically.

Finally, possible influences of the ferromagnetic properties of our alloy samples are discussed. According to the itinerant-electron theory of ferromagnetism,[12] a reduction of the exchange splitting in the Ni-rich Cu-Ni alloys with increasing Cu content is expected. It has to be mentioned that the 11.83-eV EDC of the annealed Ni(111) face shows a doublet structure near the Fermi level, which was tentatively explained by transitions from bands of opposite spin.[4] This doublet should disappear in the alloy spectra because of the reduced exchange splitting, which is actually observed in our EDC's (Figs. 4 and 5). However, the doublet of the annealed Ni(111) face could also be removed by evaporating ultra-thin films of Cu onto Ni (see Fig. 5) and even by sputtering of Ni(111) for a few minutes. The surface sensitivity of one component of the doublet structure may probably be expected, since it was interpreted in Ref. 4 as due to a surface photoemission process[38] from a high-density-of-states region of majority spin electrons, and the second component as due to direct transitions from a minority spin band. But it is obvious that lack of such doublet structure in the alloy EDC's does not necessarily confirm consequences of the itinerant-electron theory of ferromagnetism for the Cu-Ni system. We therefore conclude that no direct answer can be obtained regarding the problem of ferromagnetism in Ni and the Cu-Ni alloys by our room temperature measurements of Cu-Ni samples.

IV. CONCLUSION

By measuring angle-resolved photoemission spectra normal to single-crystal faces of Cu-Ni alloys in the Ni-rich region and employing a photoelectron spectrometer with high energy and angle resolution we have shown above that results are obtained, which could previously not be found in angle-integrating measurements of single crystals or polycrystals of Cu-Ni. The advantages of this technique are especially valuable for the study of the surface electronic structure of the annealed alloys, where Cu segregation in the outermost atomic layer is observed. The EDC's of such surfaces reveal pronounced differences in the Cu-derived energy region on sample orientation of the single crystals and on Cu concentration, and they may be related to the density of initial states of Cu d electrons with $\vec{k}_{\parallel}$ approximately zero. The Ni emission is practically independent from the Cu surface layer.

After shortly bombarding the annealed samples the Cu-enriched surface layer can be removed and the surface concentration is not much different from that of the bulk. In this case the EDC's are considered to represent bulk properties and a relation to the complex alloy band structure is obtained. Compared to the pure metals the Cu-derived states are then shifted to the Fermi level and have no similarities to emission of Cu, while the Ni-derived states show only minor differences to those of pure Ni. Both effects are understood on the basis of recent theoretical investigations of the Cu-Ni system. A clustering of Ni atoms cannot be ruled out completely in the alloys but is not believed to be very important in our measurements. A surprising fact, therefore, is the occurrence of direct transitions in the Ni regime for the (111) faces of the alloys. A narrowing of energy bands in the surface region cannot be deduced from our experimental results with certainty. Regarding magnetic interactions in the alloys no conclusive evidence is found either to support or to contradict requirements of the itinerant-electron theory of ferromagnetism in these Ni-rich samples.

Future studies of single-crystal faces of Cu-Ni alloys should include angle-resolved measurements at different take-off angles of the photoelectrons for the annealed and shortly bombarded surfaces. In the first case information can be provided, whether a two-dimensional energy band structure exists for the Cu-enriched surface layer, and in the second case more properties of the complex alloy band structure may be deduced. An extension of such measurements to alloys in the Cu-rich region seems also promising and could support the recent angle-resolved photoemission results on $Cu_{0.77}Ni_{0.23}(100)$ as reported by Gyorffy *et al.*[10]

ACKNOWLEDGMENTS

The authors wish to thank Dr. E. Biller and Dr. F. Spörel for providing us with the Cu-Ni single-crystals and for many helpful discussions. We are indebted to Professor J. Peisl for making possible the use of the facilities of the Institute. This work has been supported financially by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 128, by the Alexander von Humboldt Stiftung (Germany) and by the National Research Council of Technical Sciences (Finland).

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[38] However, we cannot explain the discrepancy, why surface photoemission is still observed for the Ni-related features of the annealed (110) faces of the alloys, where also a Cu surface layer is present, and not for the (111) faces.