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Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

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Cu-Ni alloy films have been investigated in the vicinity of the onset of 3p electron absorption in the photonenergy range 50 to 90 eV. The spectra obtained can be described as a stoichiometric superposition of the individual Cu and Ni metal spectra. Any rearrangement of the states due to an alloy interaction is of no great influence. This result is in general agreement with results on soft x-ray emission, UV and x-ray photoelectric emission. It is in contradiction to the rigid band model and supports more recent alloy theories such as the coherent-potential approximation. This result, moreover, supports the interpretation of the wide structures in the transition metal spectra as a predominantly atomic effect.

Dünne Schichten einer Cu-Ni Legierung wurden in der Umgebung der Absorption der 3p Elektronen im Photonenenergiebereich 50 bis 90 eV untersucht. Die Spektren können als stöchiometrische Superposition der Spektren von Cu und Ni beschrieben werden. Veränderungen der Zustände durch die Legierungsbildung sind ohne merklichen Einfluß. Dieses Ergebnis zeigt die gleiche Tendenz wie Röntgenemissionsmessungen im weichen Röntgengebiet und Photoelektronenuntersuchungen im UV- und Röntgengebiet. Es steht im Widerspruch zum "rigid-band-model" und unterstützt neuere Theorien wie die "coherent-potential approximation". Darüber hinaus spricht dieses Ergebnis für eine atomare Deutung der breiten Maxima in den Spektren der Übergangsmetalle.

There is still a tendency among experimentalists and theoreticians to interpret the structure at the onset of deep shell transitions in terms of a solid state density of states of the empty part of the conduction band, whereas there is now sufficient evidence that the situation is far more complicated. Even from a solid state point of view the creation of a well localized, positively charged hole along with the transition of the electron adds additional complication to the one-electron interpretation, as was shown for the relatively simple spectra of the light metals. An edge anomaly occurs which was explained by a theory of Mahan (1) and Nozières et al. (2). Fano and co-workers (3) could demonstrate that an atomic picture is a good starting point for the interpretation of the 4d transitions in the rare earth metals and they argue that it should be of equivalent relevance for the 3p transitions in the transition metals Ti to Ni. The large structure observed at the onset of these transitions (4, 5) (Fig. 1) definitely originates from transitions into the empty part of the d band (shell). The amplitude of the structure decreases in accordance with the filling-up of d states. The extreme width of the structure, however, (e.g. 25 eV for Cr in Fig. 1) has nothing to do with the width of the unfilled d band which is known not to exceed 5 eV. The most plausible recent interpretation (3) of this width is the following:

Because of the exchange interaction the final state configuration $3p^5 3d^{N+1}$ is split into a series of lines spread out over the range of the observed structure. Due to autoionization interaction between these lines and the underlying continuum of 3d electron transitions and due to a shift of some of the lines to energies above the ionization limit the lines are broadened and smeared. This theory has yielded excellent agreement with the experiment for the 4f transitions in some rare earth metals (3). Because of the lack of a numerical calculation for the transition metals it is not quite clear, at

the present moment, why this line structure almost completely disappears (while it is observed in the rare earth metal spectra) and whether or not additional solid state interactions need to be included in order to explain the spectra.

The one feature which is unaffected by all these complications is the correlation between the magnitude of the edge structure and the supposed number of empty states in the d shell. The magnetic properties of Cu-Ni alloys have long been interpreted in terms of the filling of a rigid d band (6) by the extra electron of Cu, with the filling completed at about Cu-Ni 1:1. A drastic reduction of the Ni 3p edge as compared to a stoichiometric superposition of the absorption spectra of the two constituents could be expected from this model. Although, no experiment seems to have given relevant information on the empty part of the d band there is much experimental evidence that the rigid-band model (6) is inadequate to describe the density of states of the filled states. Measurements of soft x-ray emission by Clift et al. (7), uv-photoemission by Seib and Spicer (8,9) and x-ray photoemission by Hüfner et al. (10) are well described by a stoichiometric superposition of individual Cu and Ni contributions.

A theoretical approach completely different from the rigid-band model is the virtual-bound-state model (11,12) which is adequate for dilute alloys (Ni as the impurity). Its predictions are in good agreement with the results for dilute alloys and hold even for higher Ni concentrations than those which could be tolerated on the basis of the assumptions underlying the model. Another approach by Ehrenreich and co-workers (13) and Stockset al. (14) based on Soven's coherent-potential approximation (15) (CPA) gives good agreement with the experimental observations over the whole range of concentrations.

Experimental Method

A. Measuring procedure

The spectra were obtained by measuring the transmittance of thin films making use of the synchrotron radiation continuum of the 7.5 GeV electron accelerator DESY. The measurements were performed with a special plane grating monochromator (16) developed at DESY, which gives monochromatized light at a fixed exit slit in the energy range 35 - 300 eV. The spectrum is almost free from higher order radiation. A rotating beam splitter (to be described elsewhere (17)) together with two open Cu-Be multipliers (Johnston) allows for a comparison of two samples in equivalent light beams. The electronics measure a signal proportional to the ratio of the transmittances of the two samples. There is only a small correction of $\sim 3\%$ to be applied in the energy range of interest (50 - 90 eV) because of a small asymmetry of the two channels. This system enabled us to eliminate structure in the primary spectrum of the monochromator and could compensate for the effects of thin carbon layers covering the samples by putting identical carbon films into the reference beam. The spectra (Fig. 2) did not need any further computer processing.

B. Film preparation

Cu-Ni alloys were obtained by simultaneous evaporation from two sources: Cu from a resistance heated Mo boat, Ni from a 2 kW e-gun (Varian) in a vacuum of $\sim 10^{-5}$ torr with a rate of $\sim 1 \text{ \AA}/\text{sec}$. The evaporation was controlled by a oscillating quartz crystal monitor with a rate meter (Balzers) which was calibrated against a Tolansky interferometer. The Cu source was first heated until its evaporation rate was stable to within $\pm 10\%$ over the necessary time. The e-gun was then hand regulated to give a described rate, thus adding it to the Cu rate. A shutter was opened to control the total film thickness.

In addition sandwich samples were prepared with the same amount of Cu and Ni as in the alloy but separated by an 80 Å thick C film to prevent diffusion. The films were evaporated onto a collodion covered Cu mesh. The collodion was dissolved in a methanole/acetone mixture. One sandwich film, which was prepared without a carbon layer between Cu and Ni, was annealed for 1 h at 300° C in the vacuum. The two constituents had apparently diffused into each other forming an alloy. The spectrum of this film was identical to those of the other alloy samples.

Results

The spectra of a typical pair of Cu-Ni 1:1 alloy and sandwich films are shown in Fig. 2. Both sandwich and alloy contained an equivalent of 150 Å Cu and 150 Å Ni. Figure 2 also includes the spectra of a 150 Å Cu sample and a 150 Å Ni sample. From a qualitative comparison with the absorption coefficients in Fig. 1 the onsets of 3d transitions in Ni at 65 eV and the Cu 3d transitions at 74 eV (there has been a small error in the location of this edge in a previous publication (18)) can be recognized.

Both alloy and sandwich spectra roughly agree with each other. One has to bear in mind that the two samples can differ both in composition by $\pm 10\%$ and relative thickness by $\pm 5\%$. A possible background of $\sim 5\%$ straylight under these experimental conditions would affect both spectra in the same way. The statistical fluctuation was in the order of $\pm 0.5\%$.[†] Five different Cu-Ni 1:1 pairs were investigated. At a less elaborate stage of the experiment we have also measured samples with concentration ratios 5:2 and 1:3. All these spectra gave essentially the same result: Cu-Ni alloys have an absorption which is virtually obtained by a stoichiometric superposition of the individual metal spectra.

Discussion

The result obtained is clearly equivalent to that obtained for the occupied d states. The rigid band model does not give a correct description for either the filled d states or the empty d states. Each Ni atom carries approximately one unfilled d state along with it, irrespective of its environment.

There is much support for this behaviour from the experimental facts on dilute alloys (Ni as the impurity) which are well described by the virtual bound state model. In this model individual Ni atoms are embedded into a Cu matrix. The Ni d states are positioned halfway between the Cu d band and the Fermi level. Due to the hybridization with the Cu s electrons the d states are broadened and become virtual-bound-states. The simplest theory gives a Lorentzian line shape for these states with a tail extending to energies above the Fermi level. The total number of electron states contained in this tail is again one electron (1.5 according to Myers et al. (19)). The virtual bound state in Cu-Ni has been investigated in photoemission by Seib and Spicer (8,9) in a sample with 13 % Ni actually beyond the concentration region for which individual Ni atoms could be expected to be embedded in Cu. Beaglehole et al. [20] have investigated Cu-Ni alloys down to concentrations of 1 % Ni by optical means with a differential reflectometer. Their results show that the virtual-bound-state model predictions are fairly insensitive to concentration and seem to extend beyond the limit of very low concentration.

The full range of concentrations can be treated by the coherent-potential approximation (CPA) which is essentially a multiple scattering description of the electronic states. It was shown for the occupied d states in Cu-Ni by

Stocks et al. (14) that the predictions of the CPA are consistent with the virtual-bound-state model in the low concentration limit. Since it appears to be unreasonable to assume that the predictions of the CPA change drastically at the Fermi level a CPA calculation for the density of the empty part of the conduction band ought to agree with our experimental results.

The other aspect of our result is a certain justification of the relevance of atomic calculations for the interpretation of the transition metal spectra. The transitions from the 3p shells to the fairly localized 3d states are obviously insensitive to the atomic environment. We could even speculate that, apart from a few weak lines at the onset of the 3p transitions similar to those observed in the 4d transitions of the rare earth metals, no major difference would be observed in the spectra of transition metal vapours. The presence of these lines in the rare earth metal spectra even in the solid phase, could be understood as a consequence of the better shielding of the 4f states as compared to the 3d states in the transition metals.

Moreover, the principle of superposition appears not to be restricted to Cu-Ni because at an early stage of these experiments we have obtained less accurate spectra of Fe-Mn and Cr-Mn with essentially the same result.

References and Footnotes

† If one tried to find an explanation for the fact that the Ni edge is a little larger and the Cu edge a little smaller in the alloy one could account for this by assuming that there is somewhat less Ni and somewhat more Cu in the alloy. This would also explain the differences in the low and high energy regions of our measurements. Another small feature at the limit of detectability appears to occur with the small structure at 66.5 eV which was interpreted by Brown et al. (5) as being due to the spin orbit splitting of the Ni edge. This seems to be less pronounced in the alloy spectrum. A comparatively small structure occurring in the sandwich and the Cu spectrum at 78 eV appears to be reduced in the alloy spectrum.

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Figure Captions

Fig. 1 Absorption coefficients of Cr, Ni and Cu. The data for Cr and Cu have been taken from Ref. 4, whereas the data for Ni are a composition of the results of Ref. 4 and 5. In addition the average of the absorption coefficients of Cu and Ni is given.

Fig. 2 Transmittance of a Cu-Ni (1:1) alloy film and a Cu-Ni sandwich film. In addition the transmittances for pure Cu and Ni films are given.

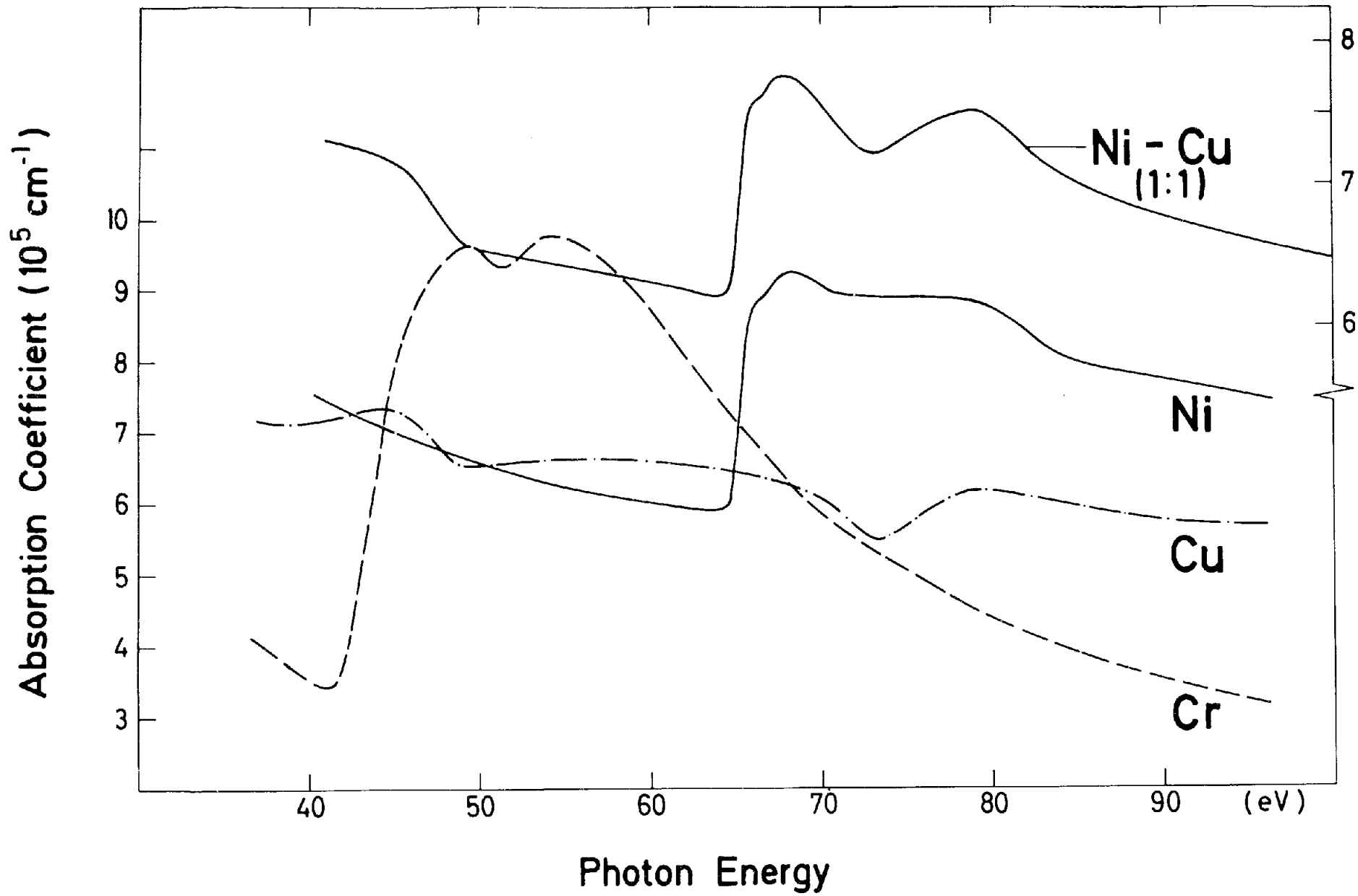


FIG. 1

