

Soft-X-Ray Appearance Potential Spectra of Ni/Cu Alloys

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Appearance potential spectra from Ni/Cu alloys reveal that in no case do d holes enter the sites of Cu atoms, but on the other hand that d holes at Ni sites exist even at Cu contents of more than 55%. The derived densities of states at the Fermi level are in very good agreement with results of Stocks, Williams, and Faulkner, calculated on the basis of the coherent potential approximation.

The electronic structure of binary alloys is currently undergoing intensive investigation by experimental and theoretical methods using the Ni/Cu system as a test object. This system has previously been considered to be a good example for the validity of the rigid-band model,¹ but a series of experiments with photoemission,^{2,3} x-ray-emission,⁴ and specific-heat measurements⁵ are clearly in contradiction to this concept. Lang and Ehrenreich⁶ therefore proposed the so-called minimum-polarity model, whereafter in Ni/Cu alloys the constituents retain the electronic configurations of the pure phases. As a consequence each lattice site would remain electrically neutral, whereas with the rigid-band model the sites would have considerable ionic character. It can be assumed that the minimum-polarity model is also an oversimplification, since a partial charge transfer between Cu and Ni atoms is to be expected. A theoretical model for these charging effects had already been given in 1965 by Stern.⁷ More recently an extension of the minimum-polarity model in its simple form has been given by Kirkpatrick, Veličký, and Ehrenreich⁸ on the basis of the coherent potential approximation (CPA) of Soven⁹ and Veličký, Kirkpatrick, and Ehrenreich.¹⁰ Stocks, Williams, and Faulkner¹¹ have made detailed calculations of the densities of states in Ni/Cu alloys on the basis of this approximation.

In contrast to photoemission experiments, investigations by means of x-ray appearance potential spectroscopy (APS)¹² provide specific information about the electronic parameters associated with individual atoms under the influence of the alloy composition. The total x-ray emission of a sample which is bombarded by electrons with varying energy is measured. The excitation of core electrons to unfilled states above the Fermi level leads to the appearance of small characteristic peaks on a slowly varying background of bremsstrahlung, which are re-

solved by electronic differentiation.

The intensity of this additional emission is under certain conditions (assuming constant oscillator strength and a sufficiently high lifetime of the core hole¹³) proportional to the product of the number of atoms ν and the self-convolution

$$\int_{E_F}^E n(W)n(E-W)dW$$

of the density of states per atom, $n(E)$, above the Fermi level.¹⁴ The height of a (differentiated) APS peak is to a first approximation given by

$$\gamma \propto \nu n^2(E_F), \quad (1)$$

and depends therefore very sensitively on the density of states $n(E_F)$ at the Fermi level.

In particular, AP spectra of the $3d$ transition metals with their high densities of states at E_F have been measured, and binding energies and spin-orbit splittings have been derived.¹³ On the other hand, Cu cannot be detected in normal APS¹⁵ because of the filled d band and the relatively low density of sp states. After an improvement of the sensitivity, only a weak step could be observed.¹⁶

The aim of the present study was to investigate the existence of d holes at Cu and Ni sites in Ni/Cu alloys, and to determine the variation with alloy composition of the densities of states at the Fermi level.

The electrons used for excitation have energies below 1000 eV and penetrate only a few atomic layers into the solid, so that information is obtained only from the surface layers, as is the case with the photoemission experiments. It is therefore essential to use well-defined surfaces; this was achieved here by careful argon-ion bombardment and annealing in ultrahigh vacuum. The surface composition of an alloy may deviate considerably from that of the bulk. Therefore, the surface compositions were determined by means of a quantitative analysis of Auger electron spectra¹⁷; this method was also used to

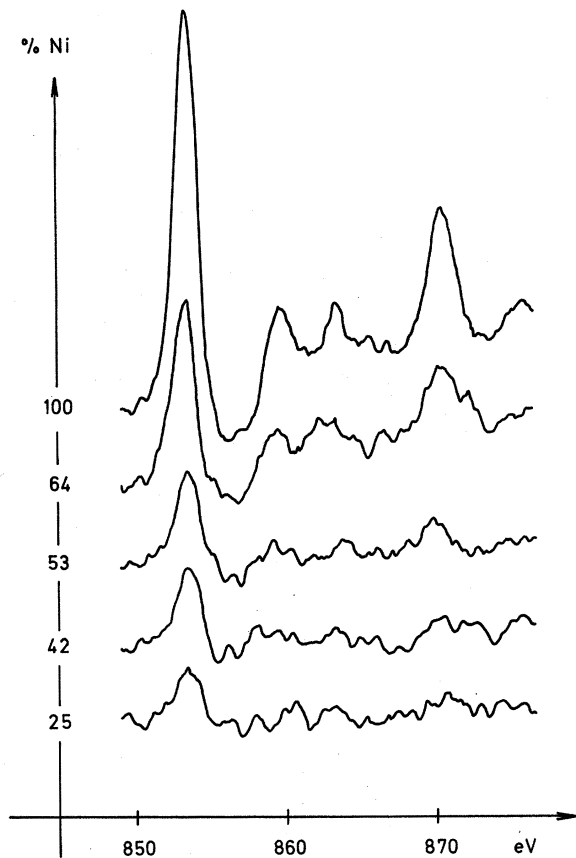


FIG. 1. Appearance potential spectra of Ni $2p$ electron excitation from pure Ni and Ni/Cu alloys containing 64, 53, 42, and 25% Ni.

monitor the surface cleanliness.

Appearance potential spectra obtained from pure Ni and from four alloys with different compositions are shown in Fig. 1. The peaks located between 870 and 875 V are caused by excitation of $2p$ electrons from L_2 levels of Ni; the larger peak between 850 and 855 V originates from excitation of L_3 states of Ni. The heights of the L_3 peaks were used for the determination of the densities of states.

It is remarkable that even alloys with more than 55% Cu show pronounced peaks which are caused by the existence of d holes at Ni sites. The rigid-band model demands a complete filling of d states at higher Cu concentrations. On the other hand, according to this model d holes should also exist at the sites of Cu atoms with alloys containing less than $\approx 55\%$ Cu. In this case an APS peak would be expected in the energy range of 920–930 V (due to excitation of $2p$ electrons from L_3 states of Cu), which, however, was not observed at any alloy composition.

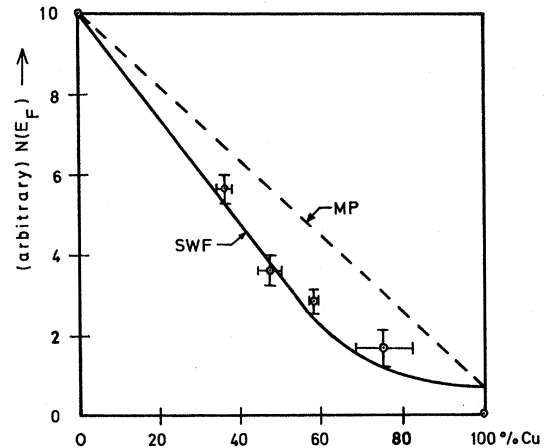


FIG. 2. Densities of states at the Fermi level. Circles, experimental values derived from APS. Solid line, theoretical curve calculated by Stocks, Williams, and Faulkner (Ref. 11) using CPA. Dashed line, limiting case of the minimum-polarity model in its simple form (Ref. 6).

These findings demonstrate clearly that the rigid-band model is not valid for this alloy system.

Using Eq. (1) the densities of states per volume unit at the Fermi energy $N(E_F) = \nu n(E_F)$ were determined from the heights of the Ni L_3 peaks. The results (in arbitrary units) are shown in Fig. 2 as a function of the alloy compositions. $N(E_F)$ decreases more strongly with increasing Cu content than according to the simple form of the minimum-polarity model,⁶ whereafter a linear variation should occur. This problem could not be solved unequivocally by Hüfner *et al.*,³ since the steep decrease of the density of states at E_F causes a high degree of uncertainty of the values derived from photoemission measurements. The analysis of APS data on the basis of Eq. (1) is certainly a rough approximation, but the values so obtained are in very good agreement with the theoretical curve calculated by Stocks, Williams, and Faulkner¹¹ on the basis of the improved CPA model. It is therefore concluded that this theory provides an adequate description of the electronic properties of Cu/Ni alloys and, furthermore, that the APS method may be used successfully to study such problems experimentally.

It should be mentioned that no information can be obtained directly from the width of the Ni L_3 peaks, since these are strongly influenced by the limited resolution of the instrument (≈ 1.5 V) and by lifetime broadening of the $2p$ core holes in Ni.^{13,18}

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Electron States and Disorder in Amorphous Ge Films Studied by Secondary-Electron Emission Spectroscopy

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Structure in the secondary-electron emission spectrum of amorphous Ge films is interpreted as due to features in the density of conduction states, the magnitude of which is shown to be sensitive to disorder effects determined by substrate deposition and annealing temperatures. Activation energies for the reordering processes are determined for deposition and annealing temperatures from 20 to 500°C. The results provide evidence for density-of-states features associated with a random-network, metastable phase.

Although a comprehensive theory of the electron states in amorphous elemental semiconductors has yet to be developed, there have been a variety of theoretical discussions of the problem.³ One approach has been to consider the density of states of small clusters of tetrahedrally bonded atoms,^{4,5} while the opposite approach has considered the effects of imposing various degrees of disorder on a periodic lattice so that the analytical techniques of "band structure" determination may be applied.⁶⁻⁸ Whatever their respective merits and limitations, however, all would appear to be qualitatively in accord in predicting a well-defined "pseudogap" in the density of states, corresponding closely to that separating the valence and conduction bands in the crystalline solids.³ It is now clear that the existence of such a gap can be explained as a consequence of short-range order, and that the electronic properties of both the crystalline and the amorphous phases are largely determined by this short-range order. The nature and extent of the long-range order is responsible mainly for the finer structure in the

density of states.^{2,4}

A point of departure between the various theoretical approaches is the question of what extent features in the crystalline density of states are retained in the amorphous solid. More specifically, which features in the crystalline density of states relate to short-range order, corresponding to those states along the covalent bond directions, and which features are averaged out because of long-range disorder in the amorphous solid so as to become unresolvable experimentally? The "disordered band structure" approach^{7,8} suggests that, if sufficient long-range order is retained, the valence band density of states is preserved almost completely and, although the conduction-band features are much more strongly relaxed, certain weak structure may persist depending on the extent of long-range order. The results of multiple-scattering theory, applied to clusters of tetrahedrally bonded atoms,^{4,5} also indicate that some fine structure might be preserved in the density of states of the amorphous solid. In contrast, the tight-binding approach of