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Ultraviolet photoelectron spectroscopy of zinc-copper systems during atomic diffusion

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We have measured the energy-distribution curves (EDC's) ($h\nu = 21.2$ eV) during atomic diffusion in the following Zn-Cu samples: an evaporated Zn substrate with 120-Å Cu overlayer, an evaporated Zn substrate with 55-Å Cu overlayer, and a Zn(0001) face with 55-Å overlayer. Owing to diffusion, the intensity of the Cu-3d structure decreases with time and that of the Zn-3d structure increases. In the case of an evaporated substrate, a fast decay of the Cu signal is seen owing to Cu diffusion along Zn grain boundaries; a lower extreme for this diffusion coefficient $D'_{\mathrm{Cu,Zn}}$ is between 8×10^{-15} and 8×10^{-14} cm^2/sec. Diffusion of Zn along Cu grain boundaries also takes place with $(3 \lesssim D'_{\mathrm{Zn,Cu}} \lesssim 20) \times 10^{-17}$ cm^2/sec. In all the samples a slower bulk diffusion of Cu in Zn is seen; in this case the decay of the Cu signal can be fitted with a simple theoretical model giving $(3 \leq D_{\mathrm{Cu}} \leq 5) \times 10^{-19}$ cm^2/sec. This diffusion takes place in conditions of chemical-concentration gradient as shown by the EDC's, where a marked modification of Cu-3d structure is seen during diffusion; the most evident spectroscopic result is a shift (up to 1.6 eV) of the Cu-3d peak towards higher binding energies. The chemical-concentration conditions originate a diffusion coefficient which is about two orders of magnitude greater than that of Cu in Zn in the limit of low concentration. We discuss qualitatively the importance of the energy associated with electron states in determining this increase of D_{Cu}, and we show, on a spectroscopic basis, that about an order of magnitude can be accounted for in this way.

I. INTRODUCTION

The electron states of the Zn-Cu system have been studied by photoemission both in the case of bulk alloys[1,2] and of Cu deposed onto Zn surfaces[3,4]; the electron states have been calculated for β-brass,[5] α-brass,[6] and for a hexagonal overlayer of Cu onto a Zn (0001) face.[4] Photoemission results for related systems such as Cd-Ag are also available.[7] Thus the relevant spectroscopic results for various systems containing Zn and Cu in equilibrium are rather well understood; it seemed sensible and timely to apply the UPS (ultraviolet photoemission spectroscopy) method to the study of the Zn-Cu system in conditions far from equilibrium in which atomic diffusion is a consequence of concentration gradients.[8] This is the subject of the present paper in which we give a spectroscopic discussion of bulk Cu diffusion in Zn in conditions of chemical gradient, i.e., in conditions in which the variation of the chemical potential for reasons other than entropy of mixing cannot be neglected.[9] In this connection we discuss the importance of the electron-state energy in increasing the diffusion coefficient with respect to the condition of extreme dilution of Cu in Zn; this discussion would be hardly possible without the present *spectroscopic* basis. We also obtain a measurement of the Cu diffusion coefficient in Zn.

Moreover, we evaluate the Zn diffusion coefficient along Cu grain boundaries and we obtain a lower extreme for the Cu diffusion coefficient along Zn grain boundaries.

The present work has also some methodological value which is beyond the specific interest of the results on the Zn-Cu system.

II. EXPERIMENTAL METHOD

The experiments were carried out by deposing a thin Cu overlayer onto a Zn substrate and by measuring the UPS spectra of the system at increasing times. Owing to the diffusion, the intensity of the Cu-3d peak decreases while that of the Zn-3d peak increases. From this time-evolution information on the diffusion near the surface are obtained; in the meantime information on the nature of the bonds of Cu diffusing in Zn are given by the modification of the shape and of the position of the Cu-3d peak. These effects are well seen with good sensitivity and resolution with UPS.[10]

In the standard diffusion experiments with electron spectroscopy the concentration profile $n(x,t)$ versus depth x after diffusion time t is obtained by means of sputtering. The present experiment differs from the standard ones in several respects:

(i) Since sputtering is not used, the environment of the diffusing atoms is not perturbed and meaningful spectroscopic results on the electron states during diffusion are obtained.

(ii) The diffusion coefficient D is not obtained from the fitting of the profile[11] but in a more indirect way by fitting the time evolution of the intensity of the Cu-3d peak. If $I_{\mathrm{Cu}}(t)$ is the area of the Cu-3d structure at diffusion time t, the ratio $R_{\mathrm{Cu}} = I_{\mathrm{Cu}}(t)/I_{\mathrm{Cu}}(0+)$ giving the Cu intensity normalized to that immediately after Cu deposition may be easily expressed in the three-step model of photoemission[12] as

$$R_{\mathrm{Cu}}(t,D)=\int_0^\infty n_{\mathrm{Cu}}(x,t,D)e^{-x/L}\,dx. \qquad (1)$$

The optical-absorption distance is not present in (1) since it is much higher than the electron escape depth L; the value of L is also constant over the $3d$ linewidth.[13] Formula (1) is particularly simple because we have assumed that the matrix element for optical excitation is independent of the concentration. In the present angle-integrated experiment at $h\nu = 21.2$ eV, this approximation is reasonable since (i) Janak *et al.*[14] demonstrated that the final states in the calculation of the energy-distribution curve (EDC) from Cu can be adequately described by nearly-free-electron functions; this description is obviously even more satisfactory when the Zn concentration increases, i.e., the matrix elements do not depend strongly on the Cu concentration through final states; (ii) for pure Cu Janak *et al.*[14] showed that photoemission from d-bands is marginally influenced by initial-state effects on the matrix elements owing to their little dispersion. This argument should work also in our case at decreasing Cu concentration since the shift of the $3d$-Cu peak seen in the present experiment is basically due to a charge-decompression mechanism, as discussed below, rather than to dispersion effects. The function $n_{\mathrm{Cu}}(x,t,D)$ is the Cu concentration profile normalized so that $R_{\mathrm{Cu}}(0,D)=1$ and is taken as the solution of the diffusion equation with appropriate boundary conditions. We will assume D as a constant parameter so that the fitting between calculated and measured $R_{\mathrm{Cu}}(t)$ functions gives an average D value. Less accurate although satisfactory D values are obtained than in the sputtering-profile experiments since an integral property of $n_{\mathrm{Cu}}(x,t)$ is measured; this is the price to pay in order to obtain spectroscopic information on the electron states during diffusion.

(iii) A sputtering-profile experiment on a thick diffusion couple[11, 15] gives the value of the interdiffusion coefficient $\tilde{D}$; in the present case the overlayer is very thin and is rapidly consumed by the diffusion so that one obtains, to a good approximation, the diffusion coefficient of Cu atoms in the Zn substrate. This coefficient is the one under chemical gradient[9] as will be shown later.

For all these reasons the experiments similar to the present ones are in a sense complementary to those based on sputtering profiles; it seems particularly challenging to extend the application of the method to other systems having d-electron peaks which are particularly well detected in the photoelectron spectra.

III. APPARATUS AND THE EXPERIMENTAL PROCEDURE

The apparatus had two connected UHV chambers: one for sample preparation and the other for the electron-spectroscopy measurements. In both chambers the pressure was $\sim 1\times 10^{-10}$ Torr. All the UPS measurements were carried out with He I (21.2 eV) light and the EDC's integrated over the angles were measured with a spherical-grid retarding-potential analyzer (solid angle $\simeq 0.5\times 2\pi$ Sr). The light was incident normally onto the sample; the windowless He lamp was differentially pumped and the He pressure in the chamber during the measurements was in the 10^{-9} Torr range. A LEED-Auger apparatus was also available. The sample preparation chamber was equipped with a Zn evaporator, a Cu evaporator, a quartz thickness monitor, and an argon-ion gun.

The following sets of measurements were taken.

(i) A Zn substrate (~5000 Å) (deposition rate $\simeq$10 Å/sec) was evaporated onto the manipulator head and a mass of Cu equivalent to 120 Å of bulk Cu was deposed onto it successively (deposition rate $\simeq$0.2 Å/sec). The EDC's were measured before Cu deposition (time 0^-) and at increasing times after deposition over a period of about 3 d.

(ii) We prepared a Zn evaporated substrate adjacent to a (0001) face of a single crystal cleaned by sputtering and annealed at 130 °C. The crystal face gave a high-quality LEED pattern. Then we covered both substrates with the same Cu evaporation equivalent to ~55 Å [evaporation rates as in (i)]. The EDC's from both the samples were measured alternately at increasing times in order to obtain an accurate comparison between the diffusion in the single crystal and in the Zn evaporated film.

In all measurements the samples were at room temperature (295 °K); the temperature of the sample did not change during evaporation.

In all cases no impurity was detected with UPS. The purity of the evaporated films was also tested in a separate set of measurements with Auger spectroscopy. The overall stability of the apparatus was carefully tested. The long term drifts were lower than 2% with negligible influence on the results.

At the end of the measurements a portion of the evaporated substrate (shielded from Cu deposition) was explored with a scanning electron microscope[16] although no systematic analysis was carried out.

IV. RESULTS

The EDC's measured at increasing times are collected in Figs. 1 and 2. Figures 1 and 2(a) refer to the case of a polycrystalline substrate with 120- and 55-Å Cu, respectively, while Fig. 2(b) refers to

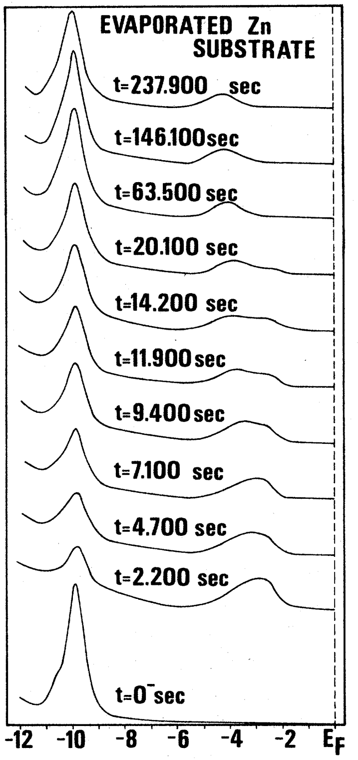

FIG. 1. Photoelectron energy-distribution curves from a sample constituted by an evaporated Zn substrate with 120-Å Cu deposition at time $t=0$ sec. The curves measured at increasing times are labeled by the time at which the Cu-3d peak is measured. The curve at $t=0^-$ sec is that of pure Zn. The curves are measured with HeI light ($h\nu=21.2$ eV) and are plotted vs the initial energy measured in eV from the Fermi level E_F.

the case of a Zn (0001) face with 55-Å Cu.

The d-state peaks are the fingerprints of Zn and Cu in the EDC's. The prominent peak ~10 eV below the Fermi level E_F is due to 3d-Zn electrons, while the structure around ~3 eV below E_F is due to Cu 3d electrons.

The evidence of diffusion is dramatic: at increasing times a marked increase of the Zn structure and a marked decrease of the Cu structure are evident, while the shape and the position of the Cu-3d structure change significantly when Cu concentration decreases.

V. EVALUATION OF THE DIFFUSION COEFFICIENTS

The time dependence of the EDC's is clearly exploited by plotting the area of the Zn and Cu-3d structures versus time. We have collected in Figs. 3 and 4 the values of $R_{\mathrm{Cu}}=I_{\mathrm{Cu}}(t)/I_{\mathrm{Cu}}(0^+)$ and of $R_{\mathrm{Zn}}=I_{\mathrm{Zn}}(t)/I_{\mathrm{Zn}}(0^-)$ for all the measurements. The solid lines interpolate the values pertaining to the crystalline substrate and the dashed lines the values pertaining to the evaporated substrates; the black

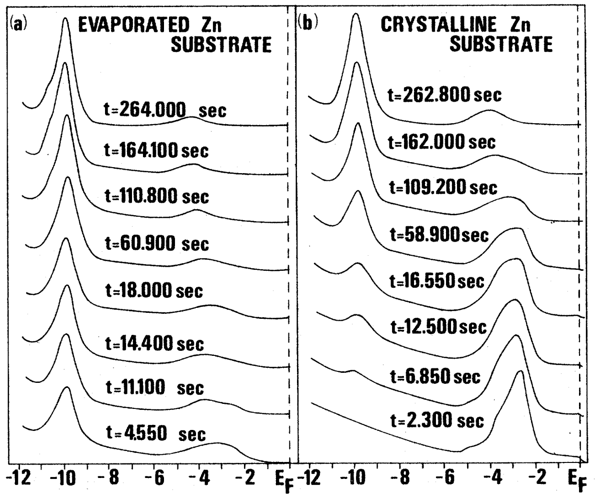

FIG. 2. Photoelectron energy-distribution curves from a sample constituted by an evaporated Zn substrate with 55-Å Cu deposition (a) and from a sample constituted by a (0001) Zn face with the same 55-Å deposition (b). The curves measured at increasing times are labeled by the time at which the Cu-3d peak is measured. The curves are measured with He I light ($h\nu=21.2$ eV) and are plotted vs the initial energy measured in eV from Fermi level E_F.

points refer to the 55-Å deposition and the open points to the 120-Å deposition. The value $I_{\mathrm{Zn}}(0^-)$ is the result from the EDC taken before Cu evaporation while $I_{\mathrm{Cu}}(0^+)$ is taken from the first EDC measured after the Cu deposition onto the Zn single crystal; in this case no Zn signal is seen and the EDC is that of bulk Copper.

A. Grain-boundary diffusion

The curves of Fig. 3 shows clearly that the diffusion of the Cu is very fast at short times in the

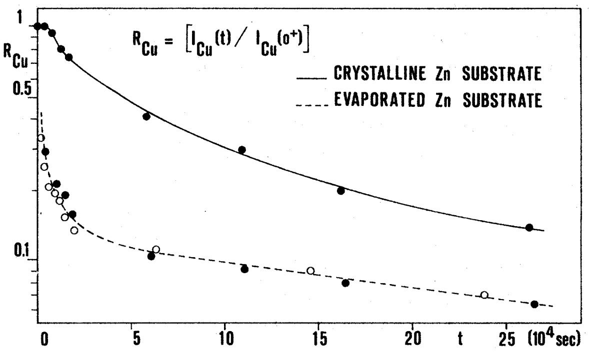

FIG. 3. Ratio$_{\mathrm{Cu}}=I_{\mathrm{Cu}}(t)/I_{\mathrm{Cu}}(0^+)$ between the area of the Cu-3d structure at time t and the area immediately after the Cu deposition. The open points refer to the measurements of Fig. 1 and the black points to the measurements of Fig. 2. The dashed line interpolates the results for evaporated Zn substrates and the solid line interpolates the results for the (0001) Zn substrate.

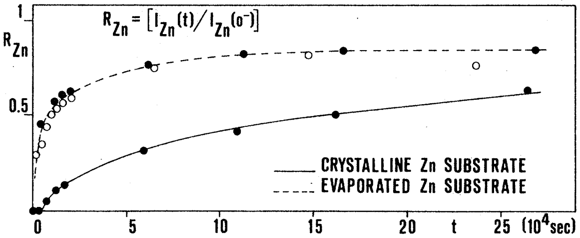

FIG. 4. $\text{Ratio}_{Zn} = I_{Zn}(t)/I_{Zn}(0^-)$ between the area of the Zn-3*d* structure at time *t* and the area before the Cu deposition. The open points refer to the measurements of Fig. 1 and the black points to the measurements of Fig. 2. The dashed line interpolates the results for evaporated Zn substrates and the solid line interpolates the results for the (0001) Zn substrate.

case of evaporated substrate, while a slower process operates at longer times. The initial fast process is absent or is extremely reduced in the case of the single-crystal substrate.

As the consequence of the fast diffusion a great fraction of the Cu deposited onto the Zn film goes beyond the region explored with photoemission and the overlayer is already semitransparent to Zn photoelectrons in the first EDC's. The R_{Cu} values from the two sets of measurements with the evaporated substrate are very similar in spite of the difference in the initial Cu quantity. Thus the initial process is so fast that the memory of the quantity of deposed Cu is lost on the time scale of the experiment.

We attribute the fast process which is peculiar of the evaporated substrate to the diffusion of Cu along Zn grain boundaries. It is well known that grain boundaries are preferential paths which act as short circuits for the diffusing atoms; evidence of this process for many other film systems is given in the review paper by Baluffi and Blakely[17] and the present results give the spectroscopic evidence of this process for the Zn-Cu system.

Approximately ~65% of the Cu-3*d* signal is lost in less than $\Delta t \simeq 2000$ sec; on the basis of the escape depths of Ref. 13 we can say that the Cu thickness is reduced from $d_0 = 120$ Å to $d < 10$ Å. This gives a lower extreme for the diffusion coefficient $D'_{\text{Cu, Zn}}$ of Cu along Zn grain boundaries

$$D'_{\text{Cu, Zn}} \gtrsim \frac{(d_0 - d)^2}{4\Delta t}\frac{1}{\alpha} \simeq \frac{d_0^2}{4\Delta t}\frac{1}{\alpha}$$

$$\simeq 4\times 10^{-16}\frac{1}{\alpha}\ \text{cm}^2/\text{sec}, \qquad (2)$$

where α is a dilution factor equal to the transverse area of the grain boundaries divided by the area of the sample.[18] The value $\alpha D'_{\text{Cu, Zn}}$ is the effective diffusion coefficient in the experiment; in order to obtain $D'_{\text{Cu, Zn}}$ and independent evaluation of α is needed. The order of magnitude of α is fixed in the following way.

(i) We have seen with the electron microscope that the film is made of islands having transverse dimensions ~2000 Å. This result together with the typical grain boundary sizes quoted in Ref. 18 fixes $1/\alpha \lesssim 200$.

(ii) Zn films prepared in identical conditions in another experiment[19] showed in the He I EDC and oxygen uptake 4–5 times greater than a single crystal. Thus the crystallites are hardly smaller than several hundreds of angstroms otherwise a too large surface will be available for chemisorbtion. This limits $1/\alpha \gtrsim 20$.

The lower extreme of $D'_{\text{Cu, Zn}}$ is thus between 8×10^{-15} and 8×10^{-14} cm²/sec.

The grain-boundary diffusion coefficient $D'_{\text{Zn, Cu}}$ of Zn along Cu grain boundaries can be estimated from the curve $R_{Zn}(t)$ of Fig. 4 pertaining to the crystalline substrate (solid line). In this case the initial fast rise of the Zn signal is basically due to short-circuit diffusion of Zn in the Cu overlayer. The flux J_{Zn} of Zn atoms arriving at the sample surface can be estimated from the increase of $R_{Zn}(t)$ and one obtains in analogy with Ref. 20

$$D'_{\text{Zn, Cu}} \simeq J_{Zn}\frac{d}{c}\frac{1}{\alpha} \simeq 10^{-18}\frac{1}{\alpha}\ \text{cm}^2/\text{sec}, \qquad (3)$$

where *d* is the overlayer thickness, *c* is the Zn concentration at the interface and α is dilution factor. Another approximate expression for $D'_{\text{Zn, Cu}}$ may be obtained according to Hall and Morabito[18] from the time of first appearance of the Zn signal. This relation combined with (3) gives

$$(3 \lesssim D'_{\text{Zn, Cu}} \lesssim 20)\times 10^{-17}\ \text{cm}^2/\text{sec}$$

and

$$30 \lesssim 1/\alpha \lesssim 200.$$

The fact that $D'_{\text{Zn, Cu}}$ is considerably lower than $D'_{\text{Cu, Zn}}$ is consistent with the fact that grain-boundary diffusion is faster when the grain material has a low melting point as discussed by Baluffi and Blakely.[17]

B. Bulk diffusion

In order to evaluate the diffusion coefficient of Cu in bulk Zn it is convenient to consider, in a first step, the results in the case of evaporated substrate. In this case the initial fast diffusion is so rapid that the overlayer is consumed in a short time and a reasonable boundary condition for the diffusion equation is $n(x,0) = \delta(x)$ giving the well-known Gaussian solution. By inserting it in (1) one obtains a theoretical function $R_{Cu} = F(L,D,t)$. Once the escape length *L* is given (10 Å in the present case) the best fit of measured $R_{\mathrm{Cu}}(t)$ with the theoretical curve gives the value of D. In order to do a meaningful fitting it is necessary to eliminate the effect of the initial fast diffusion. A simple and reasonable way is that of fitting the measured $R_{\mathrm{Cu}}(t)$ function only beyond a short time t_0 chosen in such a way that the effect of grain-boundary diffusion is exhausted before t_0 and by assuming $R_{\mathrm{Cu}}(t_0) = 1$, i.e., by assuming t_0 as the initial time of slow diffusion. Within the spatial resolution of the measurements, the $\delta(x)$ boundary condition for slow diffusion is still valid since the average diffusion length due to this process is smaller than the electron escape depth; strictly speaking this is a proof *a posteriori* based on the internal consistency of the treatment. The fitting is presented in Fig. 5 with $t_0 = 4000$ sec; the agreement between theory and measurements is very good and $D = 3\times10^{-19}$ cm^2/sec is obtained. We have ascertained that the choice of t_0 is not critical and has little influence on the D value. The fact that the fast diffusion can be separated out with this procedure is confirmed by a calculation of $R_{\mathrm{Cu}}(t)$ by assuming $D \simeq (1/\alpha)D'_{\mathrm{Cu,Zn}}$. In this case the theoretical curve decays to negligible values before t_0.

This estimation of D is confirmed by the consideration of the results pertaining to the crystalline substrate. In this case the calculation of the $n(x,t)$ function to be inserted in expression (1) is much more difficult; we have interdiffusion with an overlayer which is consumed along the time scale of the experiment. Luckily enough, such a detailed theory is not necessary to confirm the previous value of D; it is sufficient to fit the long-time behavior of the experiment. This can be done by decomposing the overlayer in a number of sheets and by considering their diffusion with increasing initial times with a δ-like boundary condition for each of them. This rough way to account for interdiffusion is obviously much more satisfactory at longer times. Within this scheme the fact that $R_{\mathrm{Cu}}(t)$ decays more rapidly in the crystal than in the film at long times may be qualitatively understood. In fact, even at long times $R_{\mathrm{Cu}}(t)$ contains a contribution coming from the copper which began the diffusion a relatively short time earlier; this fact increases the slope of the calculated $R_{\mathrm{Cu}}(t)$ since the slope of $R_{\mathrm{Cu}}(t)$ with δ initial condition is higher at short times (see Fig. 5). By dividing the Cu overlayer in 15 sheets we did a fit of the measurements for $t \gtrsim 10^5$ sec which is presented in Fig. 6; the fitting is satisfactory and the value $D_{\mathrm{Cu}} = 5\times10^{-19}$ cm^2/sec is obtained in reasonable agreement with the estimation given above.

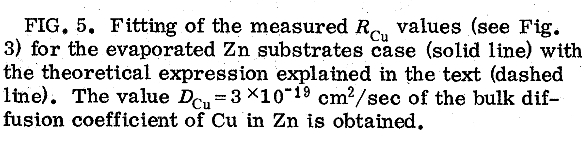

FIG. 5. Fitting of the measured R_{Cu} values (see Fig. 3) for the evaporated Zn substrates case (solid line) with the theoretical expression explained in the text (dashed line). The value $D_{\mathrm{Cu}} = 3\times10^{-19}$ cm^2/sec of the bulk diffusion coefficient of Cu in Zn is obtained.

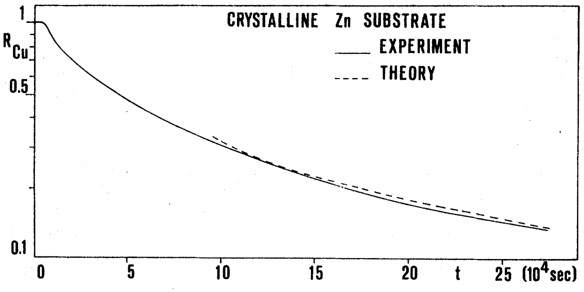

FIG. 6. Fitting (for $t \gtrsim 10^5$sec) of the measured R_{Cu} values (see Fig. 3) for the (0001) Zn substrate case (solid line) with the theoretical expression explained in the text (dashed line). The value $D_{\mathrm{Cu}} = 5\times10^{-19}$cm^2/sec of the bulk diffusion coefficient of Cu in Zn is obtained.

Thus the bulk diffusion coefficient of Cu in Zn is $(3 \leq D \leq 5)\times10^{-19}$ cm^2/sec at room temperature[21]; this is the average value along the history of the sample in the present experiment.

VI. ELECTRON STATES AND DIFFUSION MECHANISM

As far as the Cu $3d$ states are concerned the most relevant results shown by Figs. 1 and 2 are the narrowing of the structure and its shift towards higher binding energies when Cu concentration decreases. This effect has its counterpart in the spectroscopy of Zn-Cu alloys: by assuming the maximum of the $3d$ structure in bulk Cu as a reference point, a shift of $\simeq 1$ eV has been seen in β-brass[1] and a shift of $\simeq 1.3$ eV has been seen in 20% Cu alloy.[2] The extrapolation to zero Cu concentration of all the data of Ref. 2 gives a shift of $\simeq 1.6$ eV. This shift indicates that Cu is more "atomic" when diluted in Zn; in the language of Ref. 22 this is basically due to the fact that the *sp* charge is decompressed with respect to bulk copper and this fact renormalizes the *d* states to higher binding energies, i.e., towards the situation of the isolated atom where the maximum decompression occurs. This charge decompression takes place also in the present case in the layer explored by UPS. At short times some evidence of Cu not diluted is given in the EDC's (shoulder around 2.5 eV) while at long times all the Cu atoms are diluted in the sense that the (Cu-Cu) interaction has little effect on the electron states and only a shifted *d* line is seen in the EDC's. One can state that the correlation between the concentration decrease and the *d*-state shift in the present experiment is similar to that in bulk alloys. In consideration of this fact it is interesting to compare the diffusion coefficient of the present experiment with those quoted in the literature for Cu-Zn alloys. The relevant features are (i) in the Zn reach systems such as ϵ-(Cu-Zn) and γ-(Cu-Zn) alloys the *D* values are much higher than the *D* value of the present experiment (3–4 orders of magnitude difference on the basis of the results of Refs. 23–25 extrapolated to room temperatures). (ii) In β-brass[26] the extrapolation of the Cu diffusion data to room temperature is difficult but it is possible to state that the Cu diffusion coefficient is much smaller than in the present experiment (probably three orders of magnitude).

These facts point out the well-known importance of structural properties in determining the *D* values; the *D* values for equilibrated alloys help very little in predicting the behavior near surfaces and interfaces and *ad hoc* experiments are needed.

The phases formed near the surface have very different behavior from that of the alloys having similar composition in spite of the analogies in the electron density of states. Probably the behavior of vacancies is important in determing these differences, since the diffusion in these systems is basically due to a vacancy mechanism.[27]

The above situation must not be thought of as the proof that the contribution of electron-state energy to the diffusion process is not important; we have only shown that this effect is not the only one to be considered. The importance of electron-state energy is pointed out if one compares the diffusion coefficient of Cu at low concentration in Zn (Ref. 28) with the present value which is a mean value in a situation where chemical gradient effect due to high Cu concentration are present. In the present case our *D* is about two orders of magnitude higher than in the case of Cu diluted in Zn. The electron energy contribution to this reinforcement factor is not negligible as is shown by the present rough speculations which are possible since *spectroscopic* results on diffusion are available.

According to the Darken theory[9,29] the reinforcement factor in conditions of no vacancy flow is given by

$$1+\frac{d\ln\gamma}{d\ln N}, \tag{4}$$

where *N* is the fractional percentage of Cu and γ is the chemical activity. If μ' indicates all contributions to the chemical potential with the exception of the entropy of mixing, the Darken factor can be written

$$1+\frac{N}{kT}\frac{d\mu'}{dN}\approx 1+\frac{N}{kT}\frac{\Delta\mu'}{\Delta N}. \tag{5}$$

A contribution to μ' comes from the electron-state energy of Cu atoms which gain binding energy along diffusion as shown by Figs. 1 and 2. This contribution can be evaluated provided that the measured shift of the 3*d* peak can be correlated to the total electron energy variation of the system. This can be done only approximately on the basis of a very crude model which, nevertheless, is in our opinion rather pictorial. The argument largely relies upon the discussion of cohesive energy of Refs. 30 and 31. The authors demonstrated that the renormalization of total atomic Hartree-Fock energy gives a relevant contribution (~30%) to the cohesive energy of Cu, the rest being due to hybridization energy which increases with bandwidth. The relevance of renormalization energy is typical of noble metals as shown in Ref. 31, while this contribution is negligible for transition metals. In our experiment, when Cu concentration decreases, the narrowing of the *d* band of diffused Cu proceeds at slower rate than the shift due to renormalization; thus a rough assumption is that during diffusion the electron-state-energy variation is dominated by the renormalization effect. We have assumed that the variation of Hartree-Fock energy calculated in Ref. 30 is linear in the 3*d* shift and we have calculated the variation of energy in Eq. 5 by considering the shifts corresponding to the cases $N=\frac{1}{2}$ (see also Ref. 1) and $N\ll\frac{1}{2}$ (at the end of the experiment). On this basis one finds that the reinforcement factor in Eq. 5 can reach at most an order of magnitude. The argument is not quantitative and must not be overestimated in consideration of the numerous approximations involved and of the difficulties in total energy calculations. Nevertheless it shows, on a phenomenological basis, the relevance of electronic contribution to the diffusion.

VII. CONCLUSION

We have presented photoelectron-spectroscopy results taken on the Cu-Zn system during atomic diffusion and we have pointed out significant modifications of the shape of the EDC's as a consequence of the diffusion. The discussion of these results has been carried out at two distinct levels: one kinetic and the other spectroscopic.

The consideration of the kinetics (i.e., the time dependence of the Cu- and Zn-3*d* peak intensities) allow diffusion coefficients to be determined. We have measured the bulk diffusion of Cu in Zn in conditions of chemical concentration gradient, we have evaluated the Zn diffusion coefficient along Cu grain boundaries and we have obtained a lower extreme for the Cu diffusion coefficient along Zn grain boundaries.

The most relevant spectroscopic result is the shift of the Cu-3*d* structure towards higher binding energies during the diffusion process; this is the consequence of the reduction of the Cu-Cu interaction with a decompression of the Cu atoms which gain binding energy during diffusion. On this phenomenological basis we have shown that it is possible to discuss qualitatively the contribution of electron-state energy to the diffusion process. Although this contribution is not the most important one in determining the increase of D_{Cu} with respect to the case of low Cu concentration, it is by no means negligible since it increases the diffusion coefficient for approximately an order of magnitude.

We have incidentally shown the usefulness of the present experimental method and interpretation scheme which can greatly help also in the study of the diffusion of other systems having *d* peaks in their density of states.

ACKNOWLEDGMENTS

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