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# Photoemission evidence of surface segregation at liquid-nitrogen temperature in Zn-Pd system

A. Fasana, I. Abbati, and L. Braicovich
*Instituto di Fisica del Politecnico, Milano, Italy and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Milano, Italy*

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We present photoemission results on the Zn-Pd system (~ 88 at.% Zn) which show a pronounced modification of the *d*-band density of states after cooling to ~ 85 K. The Zn 3*d* peak increases, clearly showing a segration of Zn at the surface upon cooling; a modification of Pd 4*d* density of states takes place in the mean time with a sharpening of the 4*d* peak. The interpretation of this last result is still open to controversy. Results for 0.1 monolayer of Pd on Zn(0001) are also given.

Photoemission investigations of the electron state of multicomponent systems (e.g., binary metallic alloys) at different temperatures is still at the beginning; this is surprising since the temperature is obviously one of the most important parameters and photoemission is a very powerful technique. Further work is needed in this field and, in particular, on the behavior at low temperatures. In this case, interesting effects might happen since the entropic contribution to the free energy becomes less important, so that the equilibrium of the system is not necessarily dominated by the maximum of the entropy; this could originate inhomogeneities which should be reflected in the electron states. Sometimes this happens also above room temperature. An important contribution in this field is the photoemission evidence of the spatial modulation of the composition in Cu-Ni alloys pointed out by Lin *et al.*[1] Effects on the electron states with rearrangements in the surface region have also been seen with photoemission after cooling at liquid-nitrogen temperature (LNT) for Si-Pd and Si-Pt systems.[2]

We present here a noteworthy and, in a sense, puzzling effect seen in the surface region for the Zn-Pd system (~ 88 at.% Zn) in the course of a research on the interaction between a *d* metal and an (*sp*) metal. The approach is strictly experimental and this Communication intends to present open problems in order to stimulate a discussion instead of presenting interpretations which are at present premature; this could also stimulate structural investigations with methods not available in our laboratory.

We have measured angle-integrated photoelectron energy distribution curves (EDC's) excited with He I ($h\nu = 21.2$ eV) resonance light from a lamp differentially coupled to the measurement chamber (base pressure $1 \times 10^{-10}$ Torr).[3] The sample could be transferred from the preparation chamber (base pressure $1 \times 10^{-10}$ Torr) to the measurement chamber and could be cooled to ~ 85 K (conventionally called LNT) by circulating liquid nitrogen in the crystal holder. In the preparation chamber the Zn(0001) face of a crystal cleaved in air was cleaned by argon sputtering and annealed to 120 °C. Pd was evaporated by an *e* gun and the evaporation was monitored by a quartz oscillator. No contaminant on the sample has been seen by Auger spectroscopy *in situ*. The Zn-Pd sample has been prepared *in situ* by diffusion of Pd in Zn after the deposition of Pd onto the Zn(0001) face.

Due to the diffusion at room temperature (RT), Pd is diluted in Zn; this is clearly seen through the modification of the EDC's in Fig. 1 where the 4*d* structure of Pd becomes weaker, and the peak is seen at higher binding energies. This process is analogous to that seen in Zn-Cu with the same method.[4] The shift of the *d* peak towards higher binding energies is typical of all situations where *d* atoms are diluted in (*sp*) metals so that *d* levels are renormalized towards a more atomic value in the sense explained in Refs. 5 and 6. The time evolution of the spectra gives information on the diffusion mechanism which is of no interest for the present discussion and will be presented elsewhere. Here we want to note that the spectrum labeled with $t_\infty$ is stationary at least over several days within the sensitivity of the measurements and that it does not depend on the initial coverage (we have tried coverages from 12 to 25 monolayers thick). The $t_\infty$ spectrum corresponds to a Pd concentration around 11–13 at.% so that in a random system each Pd atom is mostly surrounded by Zn atoms as nearest neighbors. The temperature effect reported here refers to this $t_\infty$ situation and is pointed out clearly in Fig. 2. The main experimental results are the following: (i) The Zn 3*d* peak increases while the Pd 4*d* total intensity decreases upon cooling; (ii) the shape of the EDC in the 4*d* region is changed considerably. The main peak at − 3.9 is definitely more pronounced and the *d* contribution (extending up to $E_F$) is definitely less intense after cooling; (iii) the times required to transform the system from one state to the other are very different. During cooling

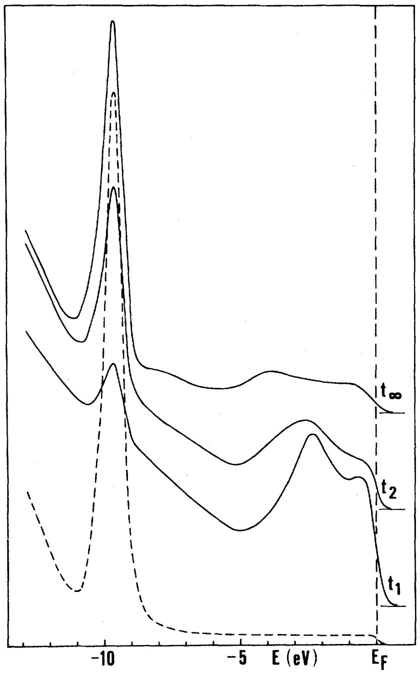

FIG. 1. Angle-integrated photoelectron spectra $h\nu = 21.2$ eV) from clean Zn(0001) (dotted line), after deposition of 15 Pd monolayers, and at increasing times in seconds: $t_1 = 500$, $t_2 = 10^5$. The $t_\infty$ spectrum is stationary within the sensitivity of the measurements.

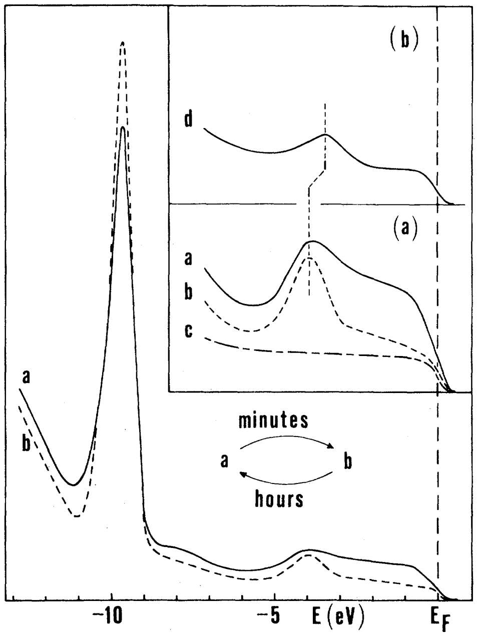

FIG. 2. Temperature effect on Zn-Pd system (Zn $\simeq$ 88 at.%). Spectrum ($h\nu = 21.2$ eV) at room temperature (curve a) and after cooling at $\simeq$85 K (curve b). The same spectra are expanded three times in insert (a) where the spectrum of clean Zn(0001) is also shown by curve c. The spectrum of 0.1 monolayer of Pd on Zn(0001) is given in insert (b).

the change takes place within the time of the experiment, so that it is faster than minutes. In order to recover the RT situation it is necessary to wait for 12–14 h at RT or for several hours at 80 °C. As far as the transformation temperature upon cooling is concerned, we cannot give any information due to technical limitations of the apparatus. It is to be noted that the effect is not instrumental; we have done accurate Auger analysis on the sample at LNT and have not seen contaminants on the surface.

The first result is particularly important and its interpretation is free of ambiguities. The increase of the Zn emission with the decrease of the total 4*d* emission of Pd is the clear evidence of a Zn enrichment of the sample surface region. By relying upon the available values of the escape depths,[7,8] it is possible to estimate that one monolayer of Zn is segregated at the surface. Thus the sample becomes inhomogeneous at low temperature as it might be expected from the reduced importance of the entropic contribution to the free energy. This is the first time that a segregation at LNT is seen for a metallic alloy. The fact that the segregation takes place at such a low temperature within minutes can be understood on the basis of the following considerations: The process does not require displacements of atoms over long distances and the atomic mobility of Zn atoms near the surface is very high.[9] Since long times at RT are required to go back to the original situation, one must conclude that the system, after gaining energy with Zn segregation, has to overcome an activation barrier to recover the RT situation.

The discussion of the second result concerning the modification of Pd 4*d* density of states upon cooling is much more controversial. The mere inspection of the photoemission spectra at RT and at LNT [see insert (a) of Fig. 2] might suggest that the spectrum at LNT corresponds to a situation of higher Pd dilution; the narrower (at half height) *d* band could indicate a reduction of (*d*-*d*) interaction between Pd atoms, and this could be consistent with the line shape at LNT which is similar to a resonance of a localized *d* state in a free-electron system. (Note: We neglect in this argument spin-orbit splitting which is smaller than the resonance width as is seen from the EDC's of isolated Pd atom in Zn; see below.) Nevertheless, this simple picture can hardly be accepted because it is in conflict with other arguments. First of all, there is no simple connection with the spectra of isolated Pd atoms in Zn. This has been measured by depositing a little amount of Pd (0.1 monolayers) onto Zn(0001) and by monitoring the peak position during the diffusion of Pd into Zn. In a systematic series of experiments of this kind, which will be reported elsewhere,[10] we have obtained a diffusion coefficient $D = (4.6 \pm 0.5) \times 10^{-19}$ cm$^2$/sec at room temperature and an activation energy basically equal to the energy of formation of a vacancy into Zn. This last fact, the value of the diffusion coefficient and the use of a single crystal as a substrate, rule out the possibility of a grain boundary diffusion; thus the peak position of the resonance of Fig. 2(b) (which is basically constant during the decay) refers to Pd diluted in Zn, i.e., totally surrounded by Zn, and not partially, as would be the case in grain boundary diffusion. The position of this Pd resonance [Fig. 2(b)] is relevant in the present discussion. It is known, and also confirmed by Fig. 1, that the reduction of $d$-$d$ interaction due to the increase of dilution originates an increase of the average binding energy; thus the fact that, in the sample with 12 at.% Pd, the 4$d$ peak is at higher binding energy than for diluted Pd atoms and shows that an explanation of the measured cooling effect cannot be based only on a dilution effect. The increase of the binding energy remains to be explained and could come from the balance of direct Pd-Pd interaction and of the interaction via the Zn-free electrons.

A mere dilution effect at LNT is hard to accept also for consistency with the previous result on Zn segregation which shows clearly that the system at LNT tends to become inhomogeneous, as it might be reasonable from a thermodynamic point of view.

The above arguments against a dilution explanation do not demonstrate that the opposite process (typically a spinodal decomposition with the formation of regions having different Pd concentrations) takes place. In effect, only model calculations can assess if the modification of the density of 4$d$ states upon cooling can be consistent with a spinodal rearrangement of the system in alternate regions with different Pd concentrations. In the absence of these calculations there is no obvious way to reconcile without ambiguities the measured photoemission spectra with a decomposition process or with a dilution effect. This is the problem which is left open for further investigations which could be stimulated by the present paper.

In conclusion, we have presented clear evidence of the segregation of Zn at the surface in a Zn-Pd sample upon cooling to liquid-nitrogen temperature; this result is consistent with the thermodynamic possibility of inhomogeneities at low temperatures. The interpretation of the modification of the Pd 4$d$ density of states which takes place at the same time is not yet possible.

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