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HAL Id: jpa-00227309
https://hal.archives-ouvertes.fr/jpa-00227309
Submitted on 1 Jan 1987

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EXPERIMENTAL AND THEORETICAL SOFT X-RAY EMISSION SPECTRA OF Cu-Pd SUBSTITUTIONAL ALLOYS

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Resume.- La densité des états électroniques aux sites Cu et Pd dans les alliages de substitution Cu-Pd a été étudiée par spectroscopie d'émission de rayons X mous et par des calculs de type SCF-KKRCPA. Les résultats indiquent que le Cu-Pd peut être décrit comme un alliage à bande commune sans état lié virtuel Pd. On discute d'explications possibles du fait que la largeur de bande théorique du Pd est plus grande que la largeur expérimentale.

Abstract.- The electronic density of states on Cu and Pd sites in Cu-Pd substitutional alloys has been investigated by soft x-ray emission spectroscopy and SCF-KKRCPA calculations. The results indicate that Cu-Pd can be described as a common band alloy with no Pd virtual bound state. Possible origins for the larger theoretical Pd bandwidth with respect to the experimental one are discussed.

In a recent paper Winter et al. [1] reported self consistent field calculations of the electronic structure of substitutionally disordered Cu-Pd alloys using the KKR coherent potential approximation (SCF-KKRCPA). They found that off-diagonal disorder (i.e. randomness in the site-to-site hopping) dominates diagonal disorder (i.e. randomness in the d-orbital energies on each site). An important consequence of this is that Cu-Pd is, in the language of Winter et al., a common band alloy: there is one set of d states which occurs on both sites with different local projections. This is to be distinguished from rigid band alloys (in which the local densities of states are the same, or very similar, on both sites, e.g. Nb-Mo [21]), and from split band systems (in which there are two non-degenerate sets of d bands, each associated with one of the atomic components, e.g. Cu-Ni [3]). In particular, no Pd virtual bound state (VBS) lying above the Cu d bands was found in the Cu-rich alloys. This Pd VBS tends to occur in model tight-binding CPA calculations (which neglect off-diagonal disorder), and, indeed, much of the experimental x-ray photoemission (XPS) data [4] on Cu-Pd has been interpreted as showing a Pd VBS. However, Winter et al. also made first principles calculations of the XPS spectra and obtained excellent agreement with experiment. They concluded that XPS data do not support the VBS hypothesis.

In previous work [5] we showed how soft x-ray emission (SXE) spectra can be used to disentangle the local densities of states (LDOS) in binary alloys. A specifically useful aspect of such studies is that VBS systems show a characteristic increase in the emission band width with the concentration of the associated atomic species. If a Pd VBS is formed in Cu-Pd alloys, therefore, the width of the Pd L3 emission spectrum should increase with Pd content, similarly to the Ni L3 spectrum in Cu-Ni alloys. In Figure 1(a) we show the experimental Cu and Pd L3 emission spectra for several alloys, obtained as described previously [5]. Also shown in Figure 1(b) are theoretical spectra calculated from the SCF-KKRCPA results of Winter et al. [1] using the theory given by Durham et al. (including core hole lifetime broadening) [5]. Note first that the...
width of the Pd spectra shows no significant increase in as the Pd content rises - in fact it slightly decreases. This is the opposite of VBS behaviour. Moreover, all the spectra shift towards the Fermi energy with increasing Pd concentration. This is simply because electrons are being removed from the system and the Fermi energy falls in roughly rigid band-like fashion, again behaviour which does not occur in VBS systems. Both of these trends are apparent in the theoretical spectra, and we therefore confirm that no Pd VBS occurs in Cu-Pd alloys.

Agreement as to the shapes of the emission spectra is less satisfactory, at least for the Pd sites where there seems to be too much weight towards the bottom of the theoretical emission bands. A similar tendency has been reported in Auger [6] and angle-integrated ultraviolet photoemission spectra [7]. There has been a good deal of speculation about the reasons for this, most recently from Stefanou et al. [8], who calculated the LDOS on a Pd impurity in Cu. While earlier impurity calculations [9] gave results similar to the SCF-KKRCPA calculations for Cu-rich alloys, Stefanou et al. claim that the lower peak in the Pd LDOS is very sensitive to charge transfer, lattice relaxation (the Cu and Pd atoms have quite different sizes), and relativistic effects; when these factors are taken into account the lower Pd peak becomes much smaller. We have tested this suggestion by comparing the SCF-KKRCPA calculations on disordered Cu$_{0.75}$Pd$_{0.25}$ with ASA-LMTO self consistent band structure calculations on ordered Cu-Pd in the L1$_2$ structure. Figure 2 shows the Pd LDOS for both systems. Despite the fact that the two calculations are quite different and separate, the similarities are very striking - indeed the disordered LDOS looks simply like a smeared out version of the ordered one. We also show the effect on the ordered LDOS of including spin-orbit coupling in the otherwise semi-relativistic calculations, and of varying the sphere sizes of the two atoms; the effects are small. Since the LMTO calculation should handle charge transfer at least as well as the impurity calculations, we suggest that the factors put forward by Stefanou et al. [8] are not important influences on the shape of the Pd LDOS in ordered, and therefore disordered, Cu$_3$Pd alloys. (As an aside, our results indicate that the same is true of short range order in the disordered phase).
Fig. 2: theoretical Pd DOS in Cu$_{0.75}$Pd$_{0.25}$
(a) SCF-KKRCPA DOS in disordered phase.
(b,c,d) SCF-LMTOASA DOS in ordered Ll$_2$ phase
(b) no spin-orbit coupling and Pd space occupation 32%;
(c) no spin-orbit coupling and Pd space occupation 25%;
(d) with spin-orbit coupling and Pd space occupation 25%.

Fig. 3: calculated XPS (Mg Ka) and SXE spectra for ordered and disordered Cu$_3$Pd.
Figure 3 shows the calculated XPS and SXE spectra for the two phases. Again the results are very similar, and the discrepancies with experimental data will therefore remain in ordered Cu$_3$Pd. Indeed, as Figure 1 indicates, the agreement as regards SXE is no better even for pure Pd. We advance no explanation for this problem at present. However, we conclude that it has little to do with the disordered phase as such, and that the SCF-KKROPA description of random substitutional Cu–Pd alloys as common band systems with no Pd VBS is substantially correct. We note that this picture also gives an excellent account of short range order in the disordered phase [10], and will present a discussion of the energetics and structure of the ordered alloys in a separate paper.

References