



NICKEL AND COBALT ELECTRON DISTRIBUTION IN AMORPHOUS METALLIC Ni-P AND Co-P

E. Belin, D. Fargues, C. Bonnelle, J. Flechon, F. Machizaud, J. Rivory

► To cite this version:

E. Belin, D. Fargues, C. Bonnelle, J. Flechon, F. Machizaud, et al.. NICKEL AND COBALT ELECTRON DISTRIBUTION IN AMORPHOUS METALLIC Ni-P AND Co-P. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-427-C8-429. 10.1051/jphyscol:19808106 . jpa-00220201

HAL Id: jpa-00220201

<https://hal.science/jpa-00220201>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

NICKEL AND COBALT ELECTRON DISTRIBUTION IN AMORPHOUS METALLIC Ni-P AND Co-P

E. Belin, D. Fargues, C. Bonnelle, J. Flechon*, F. Machizaud* and J. Rivory**

*Laboratoire de Chimie Physique, L.A. 176, Université Pierre et Marie Curie, 75231 Paris Cédex 05, France***Laboratoire de Physique des Dépôts Métalliques, Université de Nancy I, Case Officielle 140, 54037 Nancy Cédex, France****Laboratoire d'Optique des Solides, Université Pierre et Marie Curie, 4, place Jussieu 75230 Paris Cédex 05, France.*

Résumé.— Les spectres d'émission et d'absorption 2p 3/2-3d du nickel et du cobalt dans les amorphes métalliques Ni-P et Co-P ont été étudiés. Il n'a pas été observé de modification du spectre d'émission relativement au métal pur cristallisé. Par suite, les distributions Ni 3d occupées dans ces deux matériaux doivent être semblables. Néanmoins des différences apparaissent dans le spectre d'absorption. Il a été possible d'identifier la partie de la distribution électronique du nickel qui en est responsable d'après un calcul APW de la densité d'états. A l'aide des résultats des spectroscopies X et XPS, nous avons conclu qu'il n'y a pas de déplacement du niveau de Fermi lorsque le nickel est rendu amorphe par la présence d'environ 15 % d'atomes de phosphore. Nos expériences sur l'amorphe métallique Co-P conduisent à des conclusions semblables.

Abstract.— 2p 3/2-3d emission and absorption spectra of nickel and cobalt in amorphous metallic Ni-P and Co-P have been studied. No modification of the emission spectrum with respect to the pure crystallised metal is observed. As a consequence, it may be deduced that the 3d filled distribution of both materials is similar. But, differences appear in the absorption spectrum; by comparison with an APW calculation of density of states, we can identify the part of the Ni distribution which is involved in this modification. By combining X-ray and ESCA measurements, we may conclude that there is no shift observed in the position of the Fermi level, when the nickel is amorphised by the presence of about 15 % phosphorus atoms. From our experiments, similar results seem to be observed for the amorphous metallic Co-P.

In this paper, we present a study by X-ray spectroscopy of two amorphous alloys of a transition metal with a metalloid.

X-ray spectroscopy allows the investigation of both filled and empty states with a given angular momentum for each element present in any material. We have applied it to a study of the density of 3d states of Ni and Co in amorphous Ni-P and Co-P, comparatively to those of pure Ni and Co. For that purpose, we have undertaken the analysis of both emission and absorption 3d-2p^{3/2} spectra. In the emission, because of the transition probabilities, the 2p^{3/2} hole is preferentially filled by an electron originating from a 3d level, and in absorption, a 2p^{3/2} electron is promoted up to an empty 3d or 4s level.

The experiments have been carried out by means of a 500 mm radius bent crystal vacuum high resolution spectrometer. The crystals, used in first order reflection are a beryl (10 $\bar{1}$ 0) for nickel and mica (002) for cobalt; they show no anomaly of the reflected intensity in the spectral

range explored. The emission spectra are obtained by electron bombardment of solid target with a 45° take off angle and analysed in a direction perpendicular to that of the incident electrons; for the absorption the bremsstrahlung of a W target goes through the very thin absorbing sample, then it is analysed. The spectra are recorded by means of a thin window A-CH₄ gas flow proportional counter placed behind an adjustable slit. The spectra are scanned by successive steps along the Rowland circle. The instrumental resolution is about 0,13 eV for nickel and 0,17 eV for cobalt.

The Ni-P samples have been chemically deposited by means of an oxydo reduction in the liquid phase (1). The Co-P ones have been prepared by flash evaporation from a wire onto which an electrolytic deposition of Co-P has been made as described in ref.2. The depositions were made onto a copper plate for the emissions or a 0,5 μ m thick aluminum screen for the absorption. In both cases, their thickness was between 50 and 100 nm. The concentra-

tion of P in Ni-P and Co-P are near the eutectic; that is about 15 and 19 atomic percent respectively. In Ni-P most of the P atoms are the centre of icosahedral Ni clusters and only a few percent of the atoms are randomly distributed.

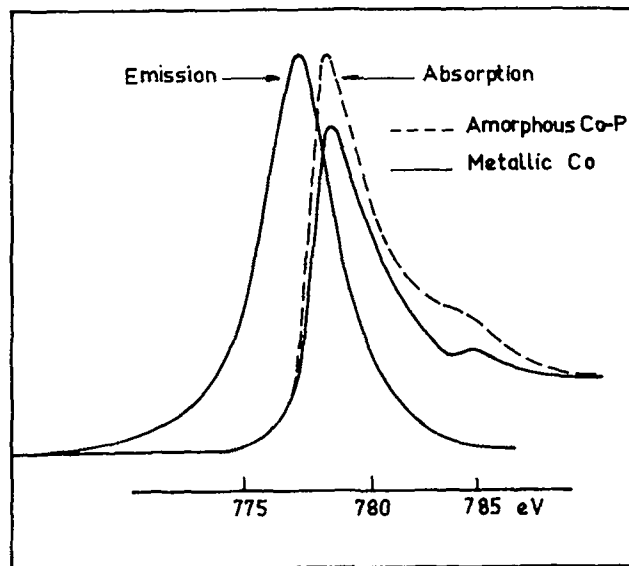
In Co-P, the structure seems to be constituted by clusters of 9 atoms of Co surrounding one P, 3 or 4 atoms being closer to the P atom (3). In pure cobalt samples prepared by evaporation, two allotropic forms are present: mainly with hcp and a few percent of fcc structures.

XPS experiments have been performed on the same samples in order to determine the binding energy of the inner $2p^{3/2}$ level. The apparatus we used is an AEI 200 B instrument whose resolution was about 1.2 eV in our experiments.

The results we have obtained by X-ray spectroscopy for Ni-P have been partly described elsewhere (4). Let us notice that we have observed no shape modification and no shift of the emission curve between the nickel in amorphous NiP and the pure metal. On the contrary, some changes appear in the absorption spectrum. The Ni absorption curve consists principally of a line A and an absorption jump followed by a feature B at about 6 eV towards higher energies relative to A. From an APW calculation performed for fcc paramagnetic Ni $2p^{3/2}$ absorption taking into account the broadening due to the inner level (5), it is possible to attribute A and B respectively to transitions towards pure 3d and d-s bands. For Ni-P, the principal line A is shifted towards higher energies and the feature B is considerably smoothed out. Moreover, we have measured by XPS the energy of the Ni $2p^{3/2}$ level in both metallic and amorphous Ni; within the precision of the experiment (± 0.2 eV) no shift was observed. So we assume that in Ni-P the shift of the principal maximum of A is attributable to a shift of nickel pure 3d unoccupied states at the threshold, and the modification in B, to a modification of d and also s states at about 6 eV above the threshold.

The $3d-2p^{3/2}$ emission and

absorption spectra of pure crystallised Co and amorphous Co in Co-P are plotted in the figure. As the effective thickness of Co in



Co-P absorbing screen is not well known, the absorption curves are normalized with respect to the absorption jump. For the emission, the energy of the incident electrons is about 1200 eV: this energy has been chosen in order to minimize the reabsorption effects (7). We observe neither a shift of the emission band maximum nor a change in its full width at half maximum which is 3.60 ± 0.2 eV, nor modifications of the satellite emission situated towards the higher energies of the band. Then, the two emission curves are identical. The $3d-2p^{3/2}$ absorption spectrum of pure cobalt is very similar to that of pure Ni: a very intense peak A an absorption jump and a structure B at about 6 eV from A towards the higher energies. In Co-P, we observe no shift of the peak A within the experimental accuracy but the structure B is very strongly attenuated as for Ni-P. Let us note that the height of the line A is very sensitive to the thickness of the absorbing screen (6) (7). Then the variation of A height is not significant because the number of absorbing Co atoms is not quite adjusted between pure Co and Co-P screens. XPS measurements are in progress in order to determine the binding energy of Co $2p^{3/2}$ in both the pure metal and the amorphous Co-P.

Calculations of the density of occupied states have been made for hcp ferromagnetic (8) or paramagnetic (9) cobalt, and ferromagnetic amorphous Co (10), but unlike nickel, there is no calculation in a large energy range concerning the empty states above Fermi level. So, at present, considering the similarity of the properties of Ni and Co and our X-ray spectroscopy results, we assume that the discussion about Ni may also be applied to Co. It must be emphasized that our results may not be interpreted by partial or total filling of the incomplete 3d band of Co or Ni in the amorphous alloys by the phosphorous electrons. Recent XPS experiments (11) lead to a discussion in the same way. Indeed if the 3d band was being filled, the 3d configuration would tend towards that of Cu, and the spectra to those of Cu. Consequently, for nickel, the emission would be expected considerably broaden and for Ni and Co, the absorption line would decrease appreciably because such a line does not exist in the $2p\ 3/2 - 3d$ absorption spectrum of Cu. In fact, in our spectra, within the experimental precision, the width of the emission bands are unchanged when the metal is amorphised by the presence of P. As for the absorption, we observe a variation in the intensity of A, in the amorphous with respect to the pure metal but this varies in an opposite way for Ni and Co. The, if p electrons fill the 3d bands, this filling must be small enough not to introduce observable changes in the spectra. For this condition to be satisfied, the charge transfer must be less than about 0.1 or 0.2 electron for Ni or Co respectively.

In the same way, because no shift in the $2p\ 3/2$ levels and the emission bands is seen, it is possible to assume that the position of the Fermi level does not change in the limits of the experimental accuracy.

In conclusion, from our results, we propose that the observed modifications involve principally an order effect; this influences essentially the s extended states and only partially the more localised d states.

BIBLIOGRAPHY

- (1) J. FLECHON, Thèse Nancy, 1960.
- (2) B. BOUCHET, Thèse 3ème cycle, Paris 1979.
J. RIVORY, B. BOUCHET, J. Phys. F. Metal Phys., 9, (1979) 327
- (3) J.F. SADO, Thèse de Doctorat d'Etat, Orsay, 1976.
- (4) E. BELIN, C. BONNELLE, J. FLECHON, F. MACHIZAUD (to be published)
- (5) F. SZMULOWICZ, D.M. PEASE, Phys. Rev. B17, (1978) 3341
- (6) L.G. PARRATT, C.F. HEMPSTEAD, E.L. JOSSE, Phys. Rev., 105, (1957) 1228
- (7) C. BONNELLE, Thèse de Doctorat d'Etat, Paris, 1964.
- (8) F. BATAILLAN, I. ROSENMAN, Phys. Rev. B11, (1975) 545.
- (9) S. WAKOH, J. YAMASHITA, J. Phys. Soc. Japan, 28, (1970) 1151.
- (10) S.N. KHANNA, F. CYROT-LACKMANN, M.C. DESJONQUERES, J. Phys. F Metal Phys., 9, (1979) 79.
- (11) A. AMAMOU, G. KRILL, Solid State Com., 31, (1979) 971.