ELECTRONIC STRUCTURE OF AMORPHOUS Co-P AND Ni-P METALLIC ALLOYS: EVIDENCE FOR SHORT-RANGE ORDER

J. Rivory, B. Bouchet, Yves Bertrand

To cite this version:

J. Rivory, B. Bouchet, Yves Bertrand. ELECTRONIC STRUCTURE OF AMORPHOUS Co-P AND Ni-P METALLIC ALLOYS: EVIDENCE FOR SHORT-RANGE ORDER. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-430-C8-432. 10.1051/jphyscol:19808107. jpa-00220202

HAL Id: jpa-00220202
https://hal.archives-ouvertes.fr/jpa-00220202

Submitted on 1 Jan 1980

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.
ELECTRONIC STRUCTURE OF AMORPHOUS CO-P AND Ni-P METALLIC ALLOYS :
EVIDENCE FOR SHORT-RANGE ORDER

J. Rivory, B. Bouchet and Y. Bertrand

Laboratoire d'Optique des Solides*, Université Pierre et Marie Curie, 4 place Jussieu
75230 Paris Cédex 05, France.
Laboratoire de Spectroscopie II, U.S.T.L., place Eugène Bataillon, 34080 Montpellier, France.

Résumé. - Les propriétés optiques de couches semi-transparentes d'alliages amorphes Co-P et Ni-P préparées par évaporation rapide sous vide sont déterminées dans un grand domaine spectral. Elles sont comparées d'une part à celles de couches de Co et Ni purs, d'autre part à celles de composés cristallins Co$_2$P et Ni$_3$P. Lessimilarités observées entre les spectres optiques des alliages amorphes et des composés cristallins suggèrent la présence d'arrangements atomiques locaux de type Co$_2$P et Ni$_3$P dans l'état amorphe. Nos résultats mettent en cause la validité d'un modèle simple d'hybridation des états p du phosphore avec les états d du métal de transition dans ces alliages métalliques amorphes.

Abstract. - The optical properties of thin semi-transparent amorphous Co-P and Ni-P alloy films prepared by flash-evaporation under vacuum are determined over a large energy range. They are compared to those of pure Co and Ni films on the one hand, of crystalline Co$_2$P and Ni$_3$P films on the other hand. The similarities observed between the optical spectra of the amorphous alloys and of the crystalline compounds suggest the presence of local atomic arrangements of the Co$_2$P and Ni$_3$P type in the amorphous state. Our results tend to question the validity of a simple nearly-free electron model and is in favor of an hybridization of the P p-states with the transition metal d-states in these amorphous metallic alloys.

1. Introduction. - During the last few years, Co-P and Ni-P have been the most extensively studied amorphous metallic alloys; their structure (1) and their magnetic properties (2) and, in the Co-P case, their optical properties (3) have already been investigated. Until recently, a model proposed in order to describe the electronic structure of these materials, i.e., a simple rigid band model in which the metalloid atoms add their valence electrons to the transition metal conduction band without any interaction was widely accepted (4). It was applied to Au-Si alloys by Tauc et al. (5) and to Pd-Si alloys by Schlegel et al. (6) in order to interpret their optical properties.

In this paper, we intend to show that our optical results on both Co-P and Ni-P amorphous alloys are in contradiction with a rigid band model but favour a model based on p-d hybridization. They also suggest the existence in the amorphous alloys of a local atomic arrangement close to that of the crystalline compounds Co$_2$P and Ni$_3$P.

2. Experiment. - Thin films were deposited under classical vacuum onto amorphous silica substrates at room temperature by flash-evaporation, from alloys electrodeposited on tungsten wires. The film thickness ranged from 200 to 600 Å and was determined by an X-ray interference method (1% accuracy).

Reflectance and transmittance measurements were performed on these films in air between 0.5 and 6.7 eV; the reflectance of thicker opaque samples was moreover measured from 4 to 10 eV under vacuum.

The complex dielectric constant was deduced from the reflectance and transmittance data in the visible and near U.V. range; a Kramers-Kronig analysis of the reflectance data over the whole spectral range was also used, with the help of ellipsometric measurements for the fitting procedure.

The P concentration was determined by microprobe analysis with relatively high uncertainties; the room temperature value of the resistivity was then used to compare samples. The structure was controlled by electron microscopy and electron diffraction. The crystallization processes for both Co-P and Ni-P have already been described (3, 7).

3. Co-P alloys. - Figure 1 shows the optical absorption $\varepsilon_2/\lambda$ versus energy ($\varepsilon_2$ being the imaginary part of the dielectric constant) for an amorphous Co-P alloy with a resistivity $p = 120 \, \mu \Omega \cdot cm$ and for pure Co. Except at low energies, both spectra present a rough overall similarity. The
For the amorphous alloy, we find maxima at 2, 5.4, 7 eV and also a faint structure around 4.3 eV. In pure Co, a prominent structure is observed at 0.8 eV, two smaller ones at 2 and 5.4 eV. The optical absorption for the amorphous alloys does not vary with the P concentration. For a more concentrated sample (p = 134 μg/cm), the structures are only more pronounced, as seen on figure 2. The spectrum of the same sample after annealing at 490°C is also given on figure 2 for comparison; complete crystallization and phase separation have been achieved, leading to a mixture of Co and Co₂P.

Well-defined peaks at 3.4 and 7 eV are seen for amorphous Ni-P, while peaks at 1.4 and 4.5 eV are observed for pure Ni. Like for Co-P, the low-energy peak disappears, but two important new structures appear at 3.4 and 7 eV. The crystallization of the amorphous alloys brings further information. Figure 4 shows the optical absorption for a Ni-P alloy in the amorphous state (p = 122 μg/cm) and after annealing at 375°C, when it consists in a mixture of Ni and Ni₃P. The absorption peak at 1.4 eV characteristic of pure Ni reappears again, but the strong absorption at 3.4 eV is seen both in the amorphous and the crystalline state; it must be characteristic of Ni₃P.
5. Discussion. - The disappearance of the low-energy absorption peak observed for both pure Co and Ni when going to the amorphous alloys is indicative of a shift of the Fermi level, in agreement with the decrease of the magnetization as the P concentration increases (2). One can imagine a shift to higher energies if one assumes a filling of the d band due to the electrons transferred from P to the metal. A different model has however been proposed by Amamou and Krill (8), deduced from photoemission measurements on crystalline Co$_3$P$_4$B$_8$ and amorphous Co$_{78}$P$_{14}$B$_8$. An hybridization between the P and B p-states and the Co d-states is assumed leading to the presence of more available electronic states in the low part of the d-band, the upper part being similar to that of pure Co. The majority band is then less filled and this lowering of the Fermi level also reduces the magnetic moment. Our results tend to support the latter model. For pure Co, the absorption peak at 5.4 eV is related to transitions from the bottom of the d band to $E_F$. This peak is also observed for amorphous Co-P at about the same location. On the contrary, the peak at 7 eV (and possibly the one at 4.4 eV) which appears for the alloys is related to transitions involving the hybridized phosphorus p-states; such information was obtained by photoemission on Co$_{78}$P$_{14}$B$_8$ by (8). We may, in the same way, conclude that in Ni-P amorphous alloys, the phosphorus p states are hybridized with the Ni d states. The fact that the peak at 3.4 eV is also observed in the crystalline phase tends to prove the presence of a local atomic arrangement in the amorphous state very similar to that in Ni$_3$P. An early band structure calculation for Ni$_3$P (9) shows a peak in the density of states above $E_F$, which can be involved in transitions from the d band occurred at energies near $E_F$. Similar calculations for Co$_2$P (10) could account for the small peak at 4.4 eV in Co-P amorphous alloy.

Acknowledgement. - This work has been sponsored in part by the "Direction des Recherches, Etudes et Techniques" under contract n° 79/440.

References

(9) RAEKE, J. and SCHLESINGER, M., Solid State Commun. 11 (1972) 1597.