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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* 1, Université Pierre et Marie Curie, 4 place Jussieu 75252 Paris Cédex 05, France.

*Laboratoire de Spectroscopie II, U.S.T.L., place Eugène Bataillon, 34060 Montpellier, France.

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-P and Ni-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-P and Ni-P type in the amorphous state. Our results tend to question the validity of a simple nearly-free electron model and in favour 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, (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, moreover, that 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 transmission 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 $\rho = 120 \, \mu\Omega\cdot cm$ and for pure Co. Except at low energies, both spectra present a rough overall similarity. The
different structures are indicated by arrows. 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 (\( p = 134 \mu \text{g/cm}^2 \)) 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 Co\(_2\)P.

Between 0.6 and 2 eV, we notice a broad absorption band with essentially two peaks at 0.8-0.9 eV and 2 eV, like in pure Co.

4. Ni-P alloys. - The comparison between the optical absorption of an amorphous Ni-P alloy

\( (p = 110 \mu \text{g/cm}^2) \) and of pure Ni, shown in figure 3, reveals more important differences than between amorphous Co-P and pure Co.

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 bring further information. Figure 4 shows the optical absorption for a Ni-P alloy in

the amorphous state (\( p = 122 \mu \text{g/cm}^2 \)) and after annealing at 375°C, when it consists in a mixture of Ni and Ni\(_3\)P (7). The absorption peak at 1.4 eV characteristic of pure Ni appears again, but the strong absorption at 3.4 eV is seen both in the amorphous and the crystalline state; it must be characteristic of Ni\(_3\)P.
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$_78$P$_{14}$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.

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