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To cite this version:

A. Amamou, D. Aliaga-Guerra, P. Panissod, G. Krill, R. Kuentzler. ELECTRONIC STRUCTURE IN AMORPHOUS AND CRYSTALLINE NICKEL PHOSPHOBORIDES THROUGH PHOTOEMISSION, NMR AND SPECIFIC HEAT. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-396-C8-399. <10.1051/jphyscol:1980897>.

HAL Id: jpa-00220552
https://hal.archives-ouvertes.fr/jpa-00220552
Submitted on 1 Jan 1980

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ELECTRONIC STRUCTURE IN AMORPHOUS AND CRYSTALLINE NICKEL PHOSPHOBORIDES THROUGH PHOTOEMISSION, NMR AND SPECIFIC HEAT

A. Amamou, D. Aliaga-Guerra, P. Panissod, G. Krill and R. Kuentzler

L.A.M.S.E.S. (No 306), Université Louis Pasteur - Institut Le Bel,
4, rue Blaise Pascal 67070 Strasbourg Cedex, France.

Résumé.- Nous présentons une étude des propriétés de photoémis- sion, RMN, chaleur spécifique et aimantation du système NiPB dans l'état amorphe et cristallin. Nous proposons un modèle simple de structure électronique interprétant ces propriétés. Les résultats de photoémis- sion sont aussi comparés à ceux obtenus pour les systèmes FePB et CoPB.

Abstract.- We present a study of photoemission, NMR, specific heat and magnetization properties on the NiPB system in the amorphous and crystalline states. The electronic structure can be interpreted in a simple model which explains coherently the various properties. The photoemission results are also compared to those obtained for FePB and CoPB systems.

Introduction :

Several studies have been carried out on the amorphous NiPB system. The magnetization properties for concentrations of \(\sim 80\) at \% Ni have been interpreted by the presence of magnetic clouds in a paramagnetic matrix /1/; NMR studies /2,3/ aimed in particular to the comparison of the quadrupolar parameters on boron with those obtained in crystalline Ni$_3$B, give conclusive evidence that the boron atoms in the amorphous structure retain to a significant extent the local symmetry of the crystalline counterpart. Specific heat investigations /4/ show that the electronic specific heat increases noticeably with the nickel concentration. At our knowledge, little work has been carried out on crystalline Ni$_3$P and Ni$_3$B; these compounds are characterized by short metal-metalloid interatomic distances which favor covalent bonding.

On another hand, recent photoemission studies on amorphous and crystalline CoPB /5/ and FePB /6/ systems show that the electronic structure can be interpreted in a covalent bonding model. The present work is aimed to implement the previous study on NiPB systems; the evolution of valence band in transition metal-metalloid systems (Fe, Co, Ni)PB is also considered.

Experimental procedure :

An amorphous sample Ni$_3$P$_{12}$B$_8$ has been prepared by the rapid quenching technique. Ni$_3$P has been prepared by sintering the appropriate constituents during 3 days at 900°C; then the ingot was melted in an induction furnace and finally annealed during 3 days at 900°C. Ni$_3$B has been prepared by sintering the appropriate constituents during one week at 900°C. The samples have been controlled by the X-rays analysis.

The magnetization properties have been performed for field up to 52 kOe and temperatures between 4.2 and 300 K; the investigated temperature range for specific heat measurements was 1.5 to 6 K. The NMR measurements have been carried out by the spin echo technique between 4.2 K and room temperature. The photoemission properties (XPS and UPS) have been studied by an ESCA (VG Mark III); the XPS azimuthal investigation did not show the presence of surface effects. Full details on experimental procedures can be found elsewhere, respectively ref. 7, 8, 9, 5.
Experimental results:

For Ni$_3$B and Ni$_3$P the magnetization can be separated into 3 terms (/1,10/): a weak ferromagnetic one which is attributed to nickel precipitate; a very small Curie-Weiss type contribution due to magnetic impurities and a temperature independent term related to the matrix susceptibility $\chi'$. The experimental $\chi'$ values are $0.95 \times 10^{-6}$ emu/g for Ni$_3$B and $0.40 \times 10^{-6}$ emu/g for Ni$_3$P; these values suggest the presence of a non negligible density of states due to nickel d electrons. A previous study on NiPB amorphous system shows that $\chi'$ varies with the alloy composition; it has been interpreted as the sum of the matrix contribution and of non magnetic impurities contribution.

![Graph](image)

**Fig. 1**: Specific heat of crystalline Ni$_3$B and Ni$_3$P for Ni$_{78}$P$_4$B$_8$ see ref. 4.

The experimental data of the specific heat on Ni$_3$B and Ni$_3$P can be described in a classical way: $C = \gamma T + B T^2$ (Fig. 1). $C$ includes the terms of electronic specific heat and of the phonons; the units for $C$ are given in mJ/mole K where a mole is 0.75 Ni + 0.25 B or P. The obtained $\gamma$ values are higher for Ni$_3$B (2.80 mJ/mole K) than for Ni$_3$P (1.44 mJ/mole K) but they are appreciably lower than that for pure nickel (7.04 mJ/mole K).

However, these values confirm the presence of a noticeable d density of states at the Fermi level. For Ni$_{78}$P$_{14}$B$_8$ the $\gamma$ coefficient /4/ is close to that of Ni$_3$P likely due to the high relative concentration of phosphorus in the amorphous alloy. The Pauli susceptibilities can be tentatively determined from the $\gamma$ coefficients; this point as well as the Debye temperatures will be discussed in a further paper.

For NMR, the Knight shift and the relaxation rate $(T_1 T)^{-1}$ for $^{11}$B and $^{31}$P in Ni$_3$B and Ni$_3$P respectively have been determined. The obtained results can be analyzed in the same way as previously /2/ for Ni$_{78}$P$_{14}$B$_8$; the relaxation rate on the metalloid can be separated in a Korringa term and a Giovannini-Heeger term. If we neglect the enhancement effects, the Korringa relaxation can be interpreted in terms of local susceptibilities on the boron and phosphorus sites. The experimental data suggest that the contribution of s electrons can be neglected since the Korringa ratio is much larger than 1. The roughly evaluated Pauli susceptibility $\chi_p^L$ of the metalloid p electrons are rather low compared to the total susceptibility; it is of $0.12 \times 10^{-6}$ emu/g for Ni$_3$B and $0.18 \times 10^{-6}$ emu/g for Ni$_3$P; the error can reach $0.05 \times 10^{-6}$ emu/g. For Ni$_{78}$P$_{14}$B$_8$ the $\chi_p^L$ is of $0.12 \times 10^{-6}$ emu/g on phosphorus and $0.06 \times 10^{-6}$ emu/g on boron /2/. These values suggest the presence of a low contribution of the metalloid p electrons to the total density of states at the Fermi level.

About photoemission, let us first remind that for the valence band of pure nickel an abundant literature has been devoted to the relationship between the calculated d density of states and the experimental band structure determined by photoemission /11,12,13/. Our experimental results for pure nickel are in good agreement with those.
Fig. 2: Valence band spectra obtained with the Al Kα radiation in crystalline and amorphous nickel phosphoborides.

obtained elsewhere /14/. For XPS the electron distribution curve (EDC) shows a full width at half maximum of 2.7 eV; the total width of the d band is estimated to 4.5 eV and the total width of the valence band is about 11 eV; the maximum A of the EDC referred to the Fermi level is at 0.9 eV, a slight shoulder B can be noticed at about 2.2 eV. These values have been determined in the same way as previously /5,6/.

For the metal-metalloid compounds, the high density regions of the EDC's obtained in XPS are expected to reflect mainly the structure of the d band /5,6/. The EDC's obtained by XPS on crystalline Ni₃B, Ni₃P and amorphous Ni₇₈P₁₄B₈ are similar to that of pure nickel (Fig. 2). The maximum A is slightly closer to E_F (0.7 eV); the shoulder B is at about 1.6 eV for Ni₃P and Ni₇₈P₁₄B₈, meanwhile it is at the same energy as for pure nickel for Ni₃B. All the EDC's are the same as for pure Ni within the experimental accuracy; the total of the valence band is of about 13 eV for Ni₃B and 16 eV for Ni₃P and Ni₇₈P₁₄B₈. These large values can be attributed to the presence of s-p states due to the metalloid; the UPS results will be presented in detail in a further paper. The lack of well defined photoemitted contribution attributable specifically to the metalloid s-p states suggests that such states are spread out over the valence band.

Discussion:

The present study on magnetic specific heat, NMR and photoemission properties of amorphous Ni₇₈P₁₄B₈ and crystalline Ni₃B and Ni₃P can be briefly summarized as follows. The properties of the amorphous alloy are very similar to the crystalline counterparts; in particular, the values of the electronic specific heat, the relaxation rates and the characteristics of the valence band are closer to those of Ni₃P than to those of Ni₃B; this is likely attributable to the higher relative concentration of phosphorus in the investigated alloy. The investigated alloys are paramagnetic and an appreciable d density of states is present at the Fermi level; the evaluated local susceptibilities on phosphorus and boron suggest the existence of a low contribution of the metalloid p electrons to the total density of states at the Fermi level. The photoemission results indicate that the d band structure is quite similar to that of pure nickel. Therefore the various properties can be interpreted in a model of covalent bonding band structure, the upper part being mainly related to d electrons. In such a model the metal-metalloid bonding induces a vanishing of the exchange splitting and a strong change in the density of states at the Fermi level.

On another hand, studies /5,6/ on amorphous and crystalline FePB and CoPB systems have shown
that a similar model can be applied in order to interpret the various properties. For the FePB system, the d band, when compared to that of pure iron, is strongly modified. For the CoPB system, the modification is less sensitive; and the present study shows that in the NiPB system such a modification is negligible. Therefore it seems that the filling of the d band of the transition elements involves an increase of the correlation between electrons which involves an increasing stability of the d band.

Acknowledgements:

The authors wish to express their appreciation to Dr M.A. Khan for valuable discussions; thanks are also due to Mrs Ravet for her help concerning the samples preparation and X-ray studies.

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