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*Department of Solid State Physics, Lomonosov State University, Moscow¹⁾ (a),
Laboratory of Surface and Interface Physics, Eötvös University, Budapest²⁾ (b), and
Department of Solid State Physics, Voronezh State University³⁾ (c).*

On the Electronic Structure of Small Ni-P Clusters

By

V. S. STEPANYUK (a), A. SZÁSZ (b), A. A. KATSNELSON (a), B. L. GRIGORENKO (a),
and O. V. FARBEROVICH (c)

A self-consistent electronic-structure calculation for small Ni-P clusters is performed. There is no charge transfer from P to Ni. It is shown that the cluster effects are important in the mesoscopic ranges.

Die Elektronenstruktur von kleinen Ni-P-Clustern wird selbstkonsistent berechnet. Dabei tritt kein Ladungstransfer von P zu Ni auf. Es wird gezeigt, daß die Clustereffekte in den mesoskopischen Bereichen wesentlich sind.

1. Introduction

Recently the structures and electronic states of small clusters attract much attention [1]. A lot of questions, however, related to the effects of short and medium range order in various metal-metalloid systems are not cleared up yet [2].

Due to some interesting properties of the Ni-P amorphous systems [3], which may serve as a basis for extensive applications of the technique [4], the time-consuming study of the electronic structure of this compound is justified. Several previous theoretical works dealing with this system are based on a rigid-band model [5]. It was concluded that the increasing phosphorus concentration results in a charge transfer from P to Ni; finally, the d-band of nickel will be saturated. A non-self-consistent calculation was carried out [6] by means of the KKR-CPA method for the Ni₇₄P₂₆ model system, in a disordered (glassy) state. It was found that practically there is no charge transfer from the metalloid to the metal state. A similar result was also obtained by the LCAO method [7] for crystalline Ni₃P and amorphous Ni₇₅P₂₅ systems. The calculation for the Ni₃P system was carried out by the LMTO method [8]. The calculation showed that there is a significant charge transfer from phosphorus to the saturated d-band of nickel. Experimental investigations showed only a slight change in the charge and presence of holes in the Ni d-band [9]. The same result was also obtained by the discrete variation method (DVM) [10]. According to this, phosphorus could not be considered as real donor of charge, but, at the same time, it has an important role in developing the electronic structure while interacting with Ni. This is the reason why the study of the electronic structure in the Ni-P systems is very inconsistent.

¹⁾ Leninskie Gory, SU-117234 Moscow, USSR.

²⁾ Muzeum krt. 6-8, H-1088 Budapest, Hungary.

³⁾ SU-394693 Voronezh, USSR.

As we previously stated [11], a change of the nearest phosphorus environment in the Ni-P system does not invoke changes in the density of electronic states of P. The question to be answered in this paper is how the number of metalloid atoms affects the electronic density of cluster states in a binary system.

The influence of various Ni-P clusters on local constructions of electronic structures have been examined. Calculations were performed by means of the X_s-SW (scattered-waves) cluster method, which is fully self-consistent. The clusters considered here are denoted by the central atom (C), the atoms in their first (A) and second (B) coordination shells. The subscript refers to the numbers of these atoms. For example f.c.c. is C₁A₁₂B₆, and in the case of pure Ni we get Ni₁Ni₁₂Ni₆.

2. Results of Calculations and Their Evaluation

2.1. Ni₁Ni₁₂Ni₆ and P₁Ni₁₂Ni₆

In the present work an attempt was made to determine the dynamics of changes in the electronic structure of Ni-P systems as a function of increasing phosphorus concentration. In the first stage of investigations calculations were made for the electronic structure of the Ni₁Ni₁₂Ni₆ cluster, modelling it by an ideal f.c.c. Ni crystal. The density of the obtained electronic states (Fig. 1) and results of band-structure calculations agreed well (see e.g. [12]), what justifies the applicability of the given cluster method for solving the above problems. This cluster model calculation with an ideal Ni crystal offers an easy way to formulate the questions concerning the changes of the electronic structure when we introduce a phosphorus atom into the cluster.

The analysis of the partial density of electronic states (DOS) of Ni₁Ni₁₂Ni₆ shows that a determining role in developing of valence states is played by the d-electrons of Ni at the Fermi energy. The cluster density of electronic states for P₁Ni₁₂Ni₆ (Fig. 2) suggests that in this cluster the upper valence states are formed primarily by d-states of Ni, with some contribution from p-states of P. At $E > E_F$ the relative influence of p-states of phosphorus will increase. The bottom of the conduction band is formed by p-states of phosphorus. The DOS of Ni in the Ni-P system is not changed considerably as compared to that in pure Ni, (Ni₁Ni₁₂Ni₆ cluster).

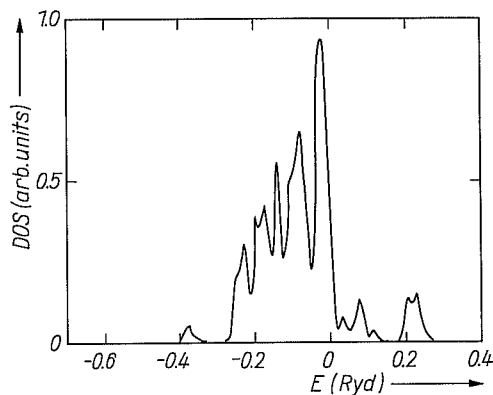


Fig. 1. Density of electronic states (DOS) of pure Ni, calculated by the proposed cluster method

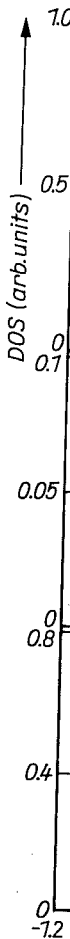


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2.2. The f.c.c. clusters $P_1Ni_{12}Ni_6$ and $P_1Ni_{12}P_6$

Considering that the short-range order (SRO) is similar both in the crystalline and the amorphous systems [13], we calculated what kind of changes will take place in the electronic structure due to the difference in the structure of the outer coordination shells from that of the inner one.

It was proved by the method of molecular dynamics (MMD) [14] that there is no P-P pair at first-neighbour distances in the Ni-P amorphous system; that is, the P atom is always surrounded by Ni atoms in its first coordination shell [15]. Thus, a realistic cluster has a central P atom in the shell of nearest-neighbouring Ni atoms, and the second coordination sphere may contain P atoms, too. In order to compare the processes which take place due to eventual changes in SRO of P atoms, a series of calculations was made

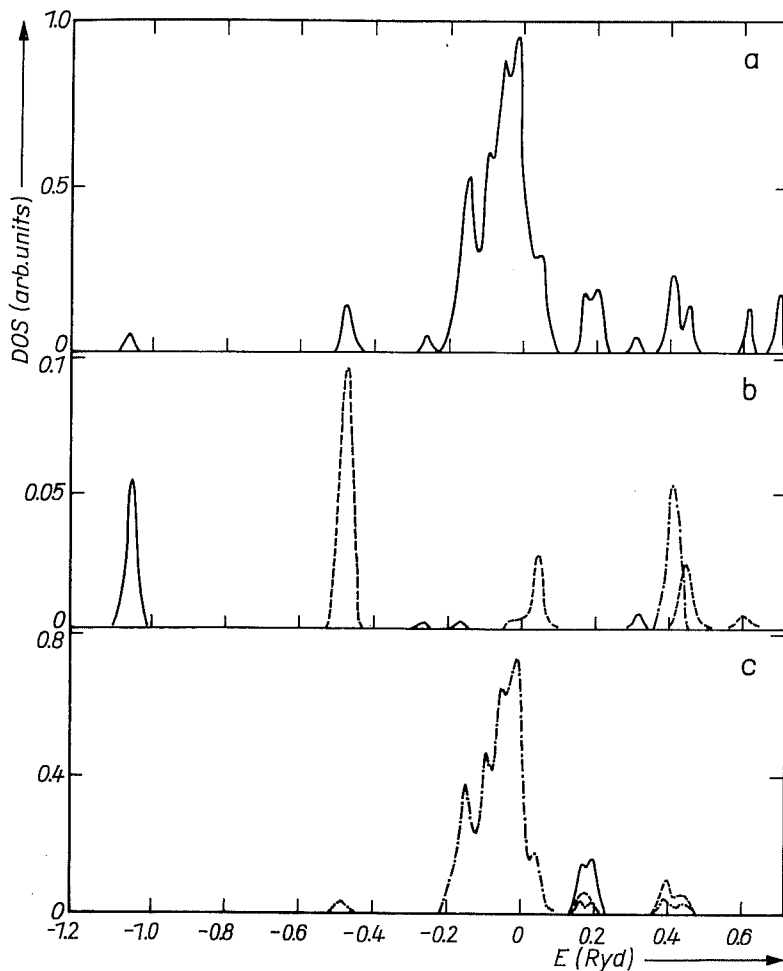


Fig. 2. The DOS of the $P_1Ni_{12}Ni_6$ f.c.c. cluster. a) Total DOS, b) partial DOS for P, and c) partial DOS for Ni (— s, - - - p, · · · · · d)

for the DOS of $P_1Ni_{12}Ni_6$, $P_1Ni_{12}Ni_6$ (f.c.c.), and $P_1Ni_8P_6$ (b.c.c.) clusters, supposing a symmetric configuration.

A comparison of the results of calculations for the $P_1Ni_{12}Ni_6$ cluster with experimental data [9] reveals a satisfactory agreement (Fig. 3).

A comparison of the DOS of clusters having the same symmetry but different composition in the second coordination sphere (see Fig. 2 and 3) showed fundamental differences:

(i) with increasing phosphorus concentration the contribution of P p-state increases significantly in the valence band, that is, valence states develop by hybridisation of P p-states and Ni d-states,

(ii) there is no charge transfer from phosphorus to nickel atom and vice versa.

Concerning the charge transfer, it is also worth noting that the density of Ni states at the Fermi energy (E_F) in the $P_1Ni_{12}Ni_6$ (f.c.c.) cluster becomes very small compared with that of the $P_1Ni_{12}Ni_6$ cluster.

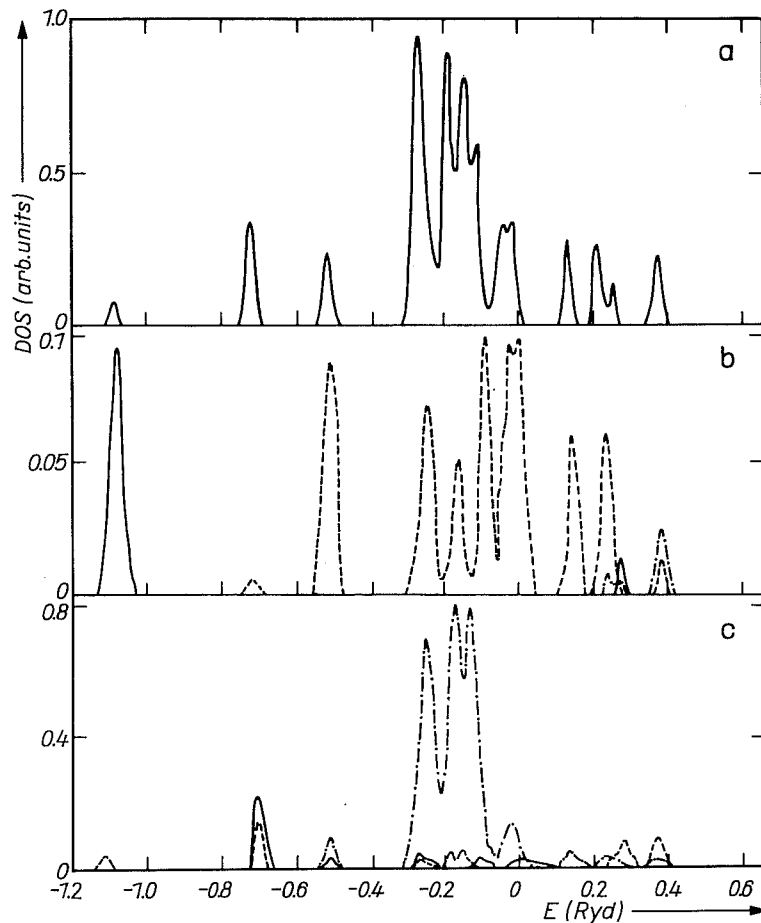


Fig. 3. The DOS of the $P_1Ni_{12}P_6$ (f.c.c.) cluster. a) Total DOS, b) partial DOS for P, and c) partial for Ni (— s, - - - p, · - · - · d)

From the experiments on amorphous Ni-P [9], weak changes were found in the DOS of Ni states compared with pure Ni. Our calculation shows that either no P atoms appear in the second sphere or the increase of the cluster dimensions results in an increase of the density of Ni states at E_F . In other words, the effect of the medium range order (MRO) can be of great importance, as it was also observed in [2].

2.3. $P_1Ni_{12}Ni_6$ (f.c.c.) and $P_1Ni_8P_6$ (b.c.c.) clusters

Comparing the DOS for $P_1Ni_{12}Ni_6$ (f.c.c.) (Fig. 3) and $P_1Ni_8P_6$ (b.c.c.) (Fig. 4) it can be seen that when passing from $P_1Ni_{12}P_6$ to $P_1Ni_8P_6$ the influence of p-states of phosphorus increases. In the $P_1Ni_8P_6$ cluster the DOS peak at 0.25 Ryd is less than the DOS at E_F . This has its origin in p-electrons of P, but a contribution of Ni d-electrons in the $P_1Ni_{12}P_6$ cluster also appears. No charge transfer from P to Ni in the $P_1Ni_8P_6$ cluster is to be observed, either.

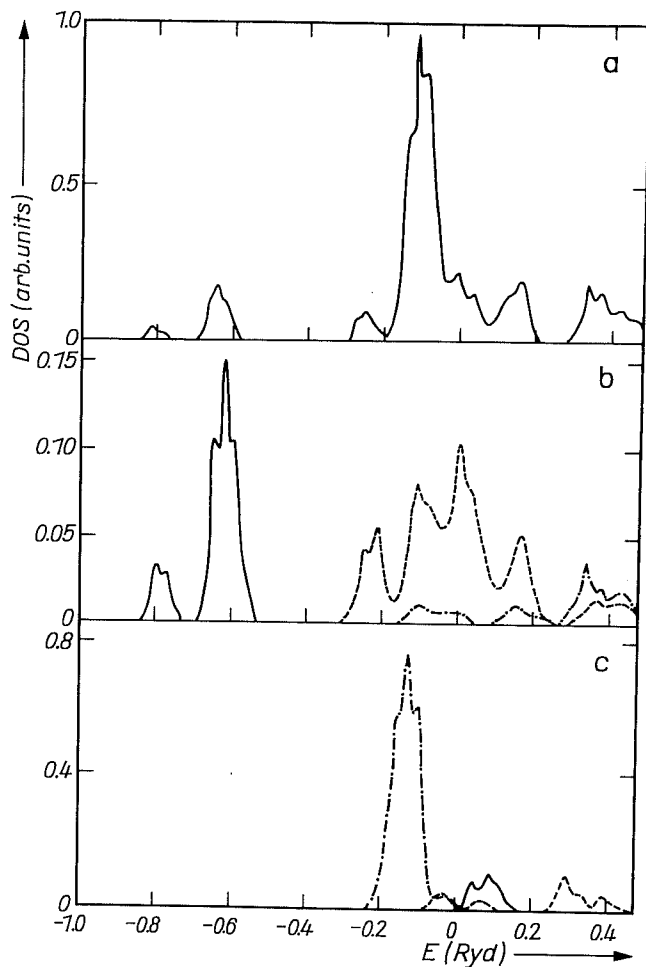


Fig. 4. The DOS of the $P_1Ni_8P_6$ (b.c.c.) cluster. a) Total DOS, b) partial DOS for P, and c) partial DOS for Ni (— s, - - - p, - · - · - d)

The change in symmetry results in a detectable change in the DOS of the whole cluster.

The Ni spectra obtained from SXES experiments [9] on the Ni-P amorphous system practically do not differ from the spectra derived from our calculations for $P_1Ni_{12}P_6$ and $P_1Ni_8P_6$ clusters. We observed a local minimum of the DOS at E_F which is indicative of stability [16]. Presumably there is one Ni atom in the second coordination sphere, moreover, the MRO is more effective than anticipated.

3. Conclusions

Our calculations may be summarized as follows:

1. phosphorus must not be considered as electron donor but it plays an important role in developing the electron structure of the Ni-P system;
2. the top of the valence band is formed by the d-state of nickel and p-state of phosphorus;
3. the changes taking place in the outer coordination spheres seem to exert an essential influence on the top of the Ni-P valence band. This shows that medium range order plays an important role in the building up a real Ni-P amorphous system.

References

- [1] C. CHAPON, M. F. GILLET, and C. R. HENRY (Ed.), Proc. 4th Internat. Conf. Small Particles and Inorganic Clusters, Aix-en-Provence, July 5 to 9, 1988, J. Phys. D **12** (1989).
- [2] E. BELIN, A. TRAVERSE, A. SZÁSZ, and F. MACHIZAUD; J. Phys. F. **17**, 1913 (1987).
- [3] A. SZÁSZ, J. KOJNOK, and E. BELIN, Solid State Commun. **64**, 775 (1987).
- [4] Proc. SUR/FIN Conf. Electroless Nickel, American Electroplaters and Surface Finishers Society, Orlando (USA) 1989.
- [5] S. W. MCKNIGHT and A. K. IBRAHIM, Phys. Rev. B **29**, 6570 (1984).
- [6] S. N. KHANNA, A. K. IBRAHIM, S. W. MCKNIGHT, and A. BASIL, Solid State Commun. **55**, 223 (1987).
- [7] K. H. JOHNSON, Adv. Quantum Chem. **7**, 143 (1973).
- [8] S. S. JASWAL, Phys. Rev. B **34**, 8937 (1986).
- [9] E. BELIN, C. BONELLE, S. ZUCKERMAN, and F. MACHIZAUD, J. Phys. F **14**, 625 (1984).
- [10] M. R. PRESS, S. N. KHANNA, and P. JENA, Phys. Rev. B **36**, 5446 (1987).
- [11] V. S. STEPANYUK, A. A. KATSNELSON, A. V. KOZLOV, O. V. FARBEROVICH, A. SZÁSZ, and J. KOJNOK, to be published in J. Phys. C.
- [12] V. S. STEPANYUK, A. V. KOZLOV, O. V. FARBEROVICH, and A. A. KATSNELSON, Fiz. tverd. Tela **32**, 75 (1990).
- [13] T. FUJIWARA and Y. ISHII, J. Phys. F **10**, 1901 (1990).
- [14] V. S. STEPANYUK, A. A. KATSNELSON, and A. SZÁSZ, to be published.
- [15] G. S. CARGILL III., in: Proc. 4th Internat. Conf. Rapidly Quenched Metals, Ed. T. MASUMATO and K. SUZUKI, J. Inst. Metals **1**, 389 (1982).
- [16] S. R. NAGEL and J. TAUC, Phys. Rev. Letters **35**, 380 (1975).

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