

KFKI-1980-09

K. VAJSZ
CS. HARGITAI
G. HERMS
H. STEIL

HIGH-ANGLE X-RAY DIFFRACTION STUDIES ON
AMORPHOUS Ni-P ALLOYS OF LOW P CONTENT

Hungarian Academy of Sciences

**CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS**

BUDAPEST

2017

HIGH-ANGLE X-RAY DIFFRACTION STUDIES ON
AMORPHOUS Ni-P ALLOYS OF LOW P CONTENT

K. Vajsz, Cs. Hargitai, G. Herms*, H. Stell*
Central Research Institute for Physics
H-1525 Budapest 114, P.O.B. 49, Hungary

*Wilhelm-Pieck University, Physics Department,
25 Rostock, Universitätsplatz 3. GDR

ABSTRACT

The structure of the amorphous low P content (11.3 and 15.8 at.% P) NiP alloy was examined by high-angle X-ray diffraction method. Partially crystalline NiP samples were also studied in the same way. The structural informations, the total interference, total pair-correlation and radial distribution functions and their characteristic parameters are presented in this paper. A comparison with earlier results of Cargill and Ichikawa is also made. It suggests the possibility of a continuous extrapolation of the pure Ni amorphous structure to the NiP amorphous alloy having 25 at.% P content.

АННОТАЦИЯ

Изучалась структура аморфного сплава NiP содержащего P в количестве 11.3 и 15.8 ат% методом рентгеновской диффракции. Образцы частично кристаллического NiP также изучены этим же методом. Структурные информации, полная интерференция, полная парная корреляция и радиальная функция распределения и их характеристические параметры даются в статье. Данные сравниваются результатами Каргила и Ичикава, на основе которого непрерывная экстраполяция аморфной структуры чистого Ni к структуре сплава NiP содержащий 25 ат% P, кажется возможной.

KIVONAT

Kis foszfor tartalmu (11,3 és 15,8 at.% P) NiP amorf ötvözet szerkezetét vizsgáltuk nagyszögű röntgendiffrakciós módszerrel. Ezzel a módszerrel tanulmányoztunk részben kristályos NiP mintákat is. A dolgozatban közöljük a szerkezeti információkat, a teljes interferencia, teljes pátkorrelációs és radiális eloszlás függvényeket és ezek jellemző paramétereit. Eredményeinket összehasonlítottuk Cargill és Ichikawa korábbi eredményeivel. Ez a tiszta amorf Ni és a 25 at.% P tartalmu amorf NiP szerkezete közti folytonos extrapoláció lehetőségét sugallja.

I. INTRODUCTION

The structure of the amorphous NiP alloy system obtained by several methods has been studied by X-ray diffraction. The main purpose of this paper is to present the structural informations, the total interference functions, total pair-correlation and radial distribution functions of NiP samples in the low P content range, prepared by chemical deposition. The X-ray analysis of this composition range has not been carried out yet.

A brief comment is made on the atomic distributions in NiP based on the comparison of our results with those of Cargill [1] and Ichikawa [2].

An investigation on partially crystalline NiP samples has also been done.

II. EXPERIMENTAL METHODS

The foils prepared by chemical deposition were about $30 \times 25 \text{ mm}^2$ in size and about $30 \text{ }\mu\text{m}$ in thickness. The experimental intensity curves were obtained by symmetrical transmission diffraction geometry technique. The graphite monochromator was located in the primary beam as shown in *Fig. 1*. $N = 40000$ constant counts were measured step by step 10 times. Since the counting statistics is uniform under this condition, the statistical error of the experimental intensity is 0.5 per cent.

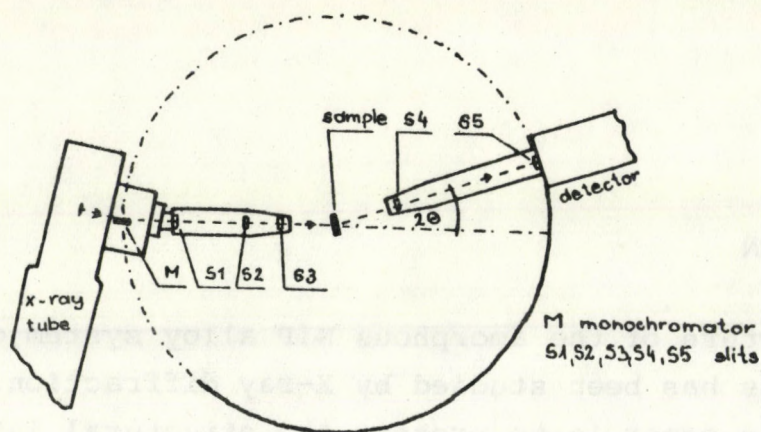


Fig. 1

The symmetrical transmission geometry

Using $\text{Mo}_{K\alpha}$ radiation the measured angle range was $\theta = 1^\circ - 60^\circ$ by $\Delta\theta = 0.2^\circ$ steps.

III. ANALYSIS OF THE INTENSITY PATTERNS

Since the amorphous structure has a continuous distribution of atoms, the X-ray intensity, $I_{\text{coh}}(K)$, coherently scattered from more than one species of atoms can be written as,

$$I_{\text{coh}}(K) = \langle f^2 \rangle + \langle f \rangle^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin Kr}{Kr} dr \quad (1)$$

where $K = \frac{4\pi \sin\theta}{\lambda}$, $\langle f^2 \rangle = \sum_i c_i f_i^2$, $\langle f \rangle = \sum_i c_i f_i$, and 2θ , c_i , f_i are the scattering angle, the atomic concentration and the atomic scattering factor of the i -th kind of the atoms, $\rho(r)$ the radial density function, and ρ_0 the average number density of atoms.

As the total interference function $I(K)$ is defined by

$$I(K) = [I_{\text{coh}}(K) - \langle f^2 \rangle - \langle f \rangle^2] / \langle f \rangle^2 \quad (2)$$

the total pair-correlation function $g(r)$ can be evaluated as the Fourier transform of $I(K)$ by the following relation

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^{\infty} K[I(K)-1] \sin Kr \, dK. \quad (3)$$

The radial distribution function

$$\text{RDF}(r) = 4\pi r^2 \rho_0 g(r) \quad (4)$$

is also frequently used to discuss the amorphous structure. The area below the first peak of the RDF(r) gives the coordination number N of the nearest neighbour atoms.

IV. DATA ANALYSIS

The observed intensity data (I_{obs} in arbitrary units) must be corrected for background, absorption and polarization.

The background intensity such as the air-scattering and the sampleholder scattering was measured without sample and then subtracted from the observed intensity.

The absorption correction in symmetrical transmission arrangement is rather simple [3]:

$$A(K) = \frac{1}{\sqrt{1 - \left(\frac{\lambda}{4\pi}\right)^2 K^2}} \exp \left[\mu t \left(1 - \frac{1}{\sqrt{1 - \left(\frac{\lambda}{4\pi}\right)^2 K^2}} \right) \right]$$

The polarization correction factor given by Whittaker [4] is the following

$$P(K) = 1 - \frac{m}{1+m} \left(\frac{\lambda}{2\pi}\right)^2 K^2 + \frac{m}{1+m} \frac{1}{4} \left(\frac{\lambda}{2\pi}\right)^4 K^4$$

where $m = \cos^2 2\alpha$, 2α is the Bragg angle of the monochromator.

The sum of the coherent and incoherent intensity is obtained in arbitrary units.

$$I_{\text{coh}}(K) + I_{\text{incoh}}(K) = [I_{\text{obs}}(K) - I_{\text{backg}}(K)] P^{-1}(K) A^{-1}(K) \quad (5)$$

The corrected intensity was converted to absolute units by the Krogh-Moe-Norman [5] and the high-angle [6] methods. The

comparison of the results of these procedures makes the control of the scaling possible.

a) Krogh-Moe-Norman method

$$\alpha = \frac{\int_0^{\infty} K^2 [\langle f^2 \rangle + I_{\text{incoh}}^{\text{eu}}(K)] dK - 2\pi^2 \rho_0 z^2}{\int_0^{\infty} K^2 [I_{\text{obs}}(K) - I_{\text{backg}}(K)] P^{-1}(K) A^{-1}(K) dK}$$

b) High-angle method

$$\beta = \frac{\int_{K_{\text{min}}}^{K_{\text{max}}} [\langle f^2 \rangle + I_{\text{incoh}}^{\text{eu}}(K)] dK}{\int_{K_{\text{min}}}^{K_{\text{max}}} [I_{\text{obs}}(K) - I_{\text{backg}}(K)] P^{-1}(K) A^{-1}(K) dK}$$

The difference between α and β was only 1 per cent in our cases.

As the monochromator was located in the primary beam the incoherent intensity could be calculated using the fitting parameters reported by Hajdu [7].

The evaluation of the measurements was carried out by an R-40 computer. For this purpose we used the computer program for liquids by Hajdu and Radnai [8], modified for amorphous materials.

V. RESULTS AND DISCUSSION

In the first step the corrected coherent intensity was determined in absolute units. These functions can be seen in *Fig. 2*.

Two samples $\text{Ni}_{86.4}\text{P}_{13.6}$ and $\text{Ni}_{82.8}\text{P}_{17.2}$ proved to be partially crystalline. Obviously they contain much more amorphous phase than crystalline one. Heating was not applied, they began to crystallize during the deposition. The identification of the sharp crystalline peaks showed segregations of fcc Ni ($a=3.52 \text{ \AA}$) and tetragonal Ni_3P ($a=8.931 \text{ \AA}$, $c=4.388 \text{ \AA}$) crystallites. In *Table 1* the diffraction lines are identified.

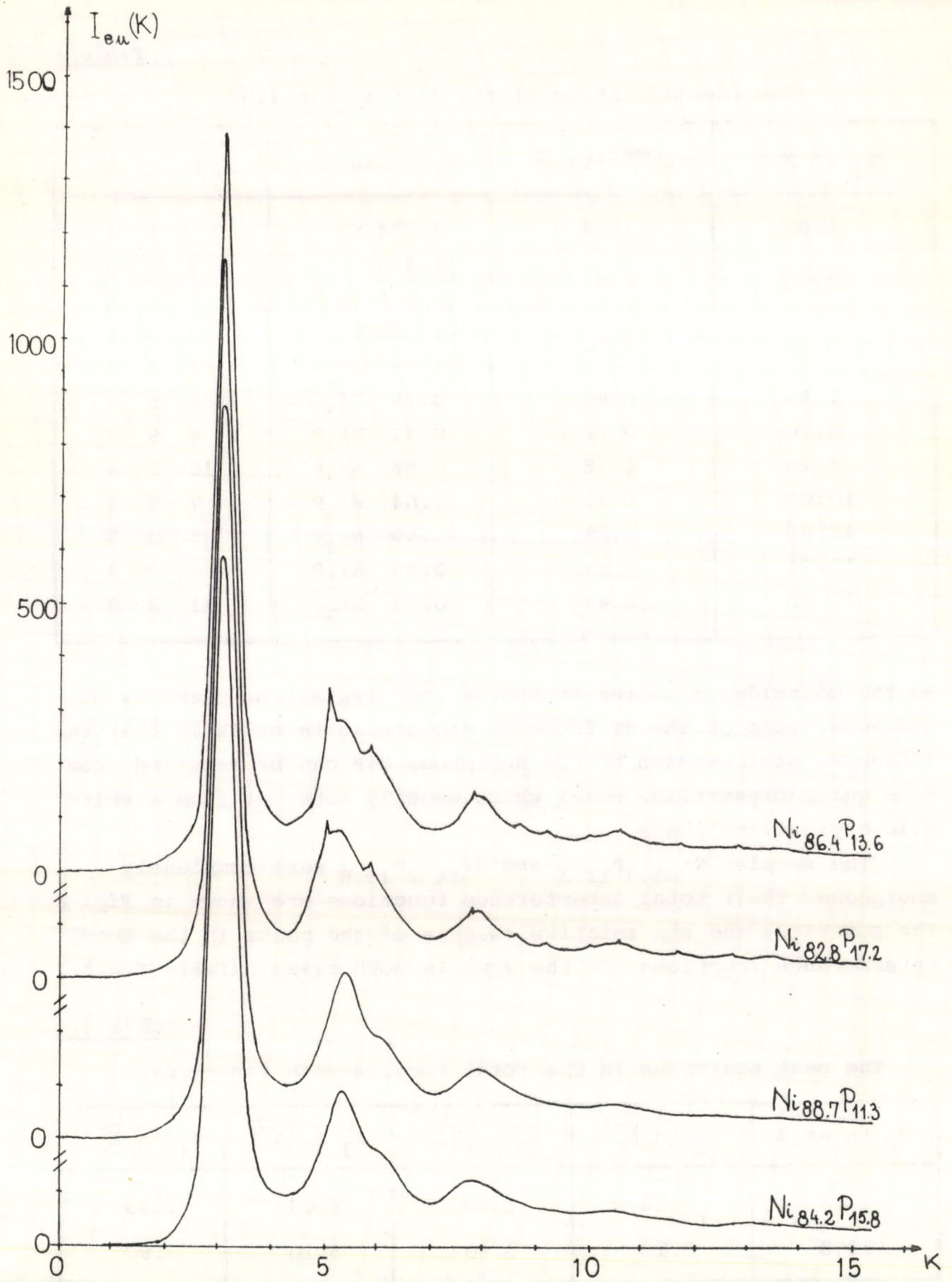


Fig. 2

Coherently scattered intensity curves of NiP samples

Table 1

The identification of the diffraction lines

K_i in \AA^{-1}	d_i^{meas} in \AA	d_i^{calc} in \AA	h k l
3.08	2.04	2.034 Ni	1 1 1
5.03	1.25	1.246 Ni	2 2 0
		1.259 Ni ₃ P	3 2 3
5.90	1.06	1.062 Ni	3 1 1
		1.065 Ni ₃ P	2 0 4
7.88	0.80	0.79 Ni ₃ P	8 5 3
8.70	0.72	0.72 Ni ₃ P	6 9 3
9.25	0.68	0.68 Ni ₃ P	10 2 4
10.02	0.63	0.64 Ni ₃ P	7 9 4
10.60	0.59	0.59 Ni ₃ P	5 10 5
11.71	0.54	0.55 Ni ₃ P	9 11 4
12.80	0.49	0.49 Ni ₃ P	11 2 7

As the coincidence of the amorphous and crystalline peaks is not characteristic of the diffraction picture it is unlikely that the intensity distribution of the amorphous NiP can be received from some quasi-crystalline model which usually sets out from a suitable crystalline phase.

The samples Ni_{88.7}P_{11.3} and Ni_{84.2}P_{15.8} were completely amorphous. Their total interference functions are shown in Fig. 3. The positions and the relative heights of the peaks in the total interference functions are the same in both cases. (Table 2.a,b.)

Table 2.a

The peak positions in the total interference functions

c_P in at. %	K_1 in \AA^{-1}	K_2 in \AA^{-1}	K_3 in \AA^{-1}	K_4 in \AA^{-1}
11.3	3.12	5.40	6.05	7.95
15.8	3.13	5.40	6.10	7.90

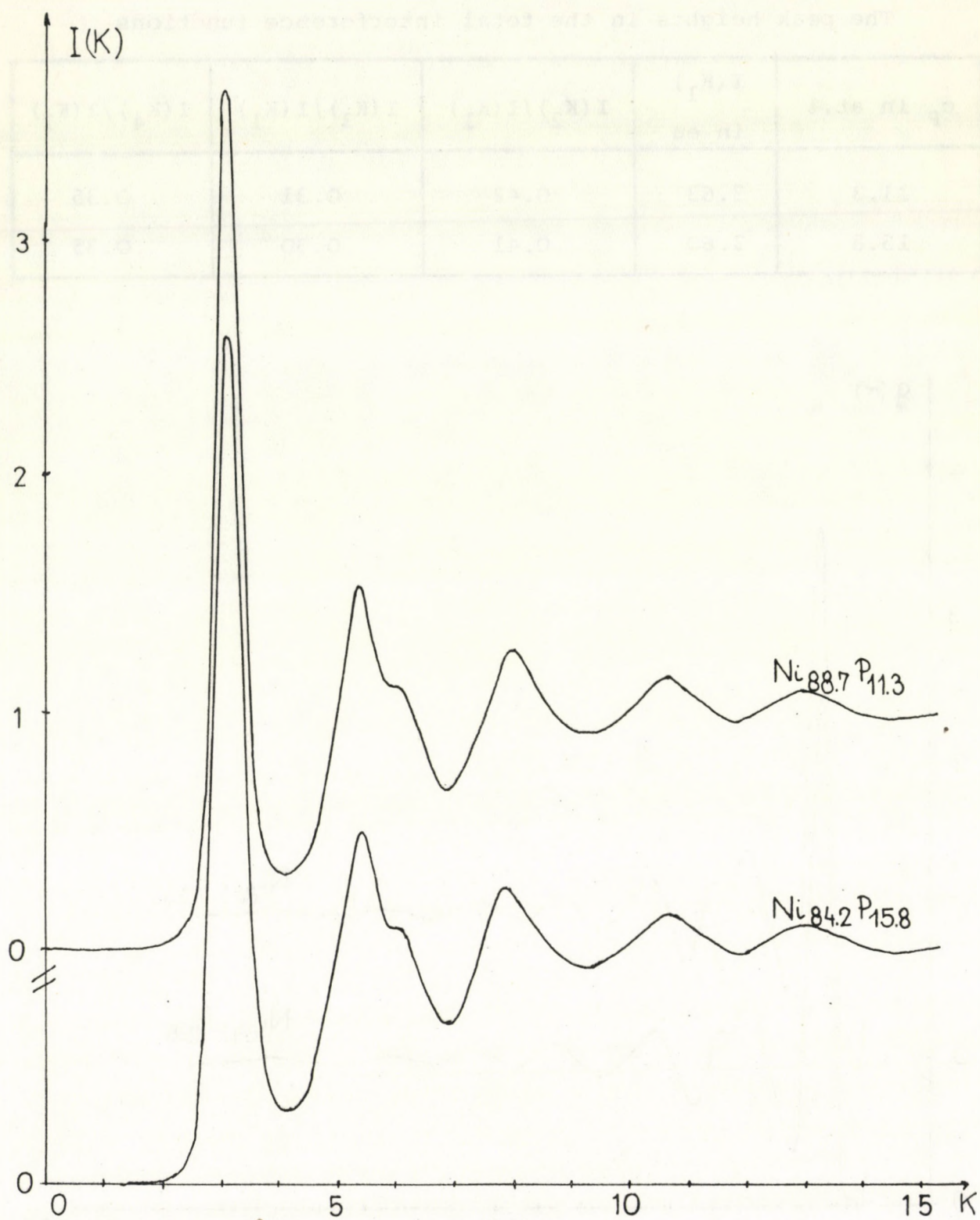


Fig. 3
The total interference functions of NiP at low P content

Table 2.b

The peak heights in the total interference functions

c_P in at.%	$I(K_1)$ in eu	$I(K_2)/I(K_1)$	$I(K_3)/I(K_1)$	$I(K_4)/I(K_1)$
11.3	3.63	0.42	0.31	0.35
15.8	3.60	0.41	0.30	0.35

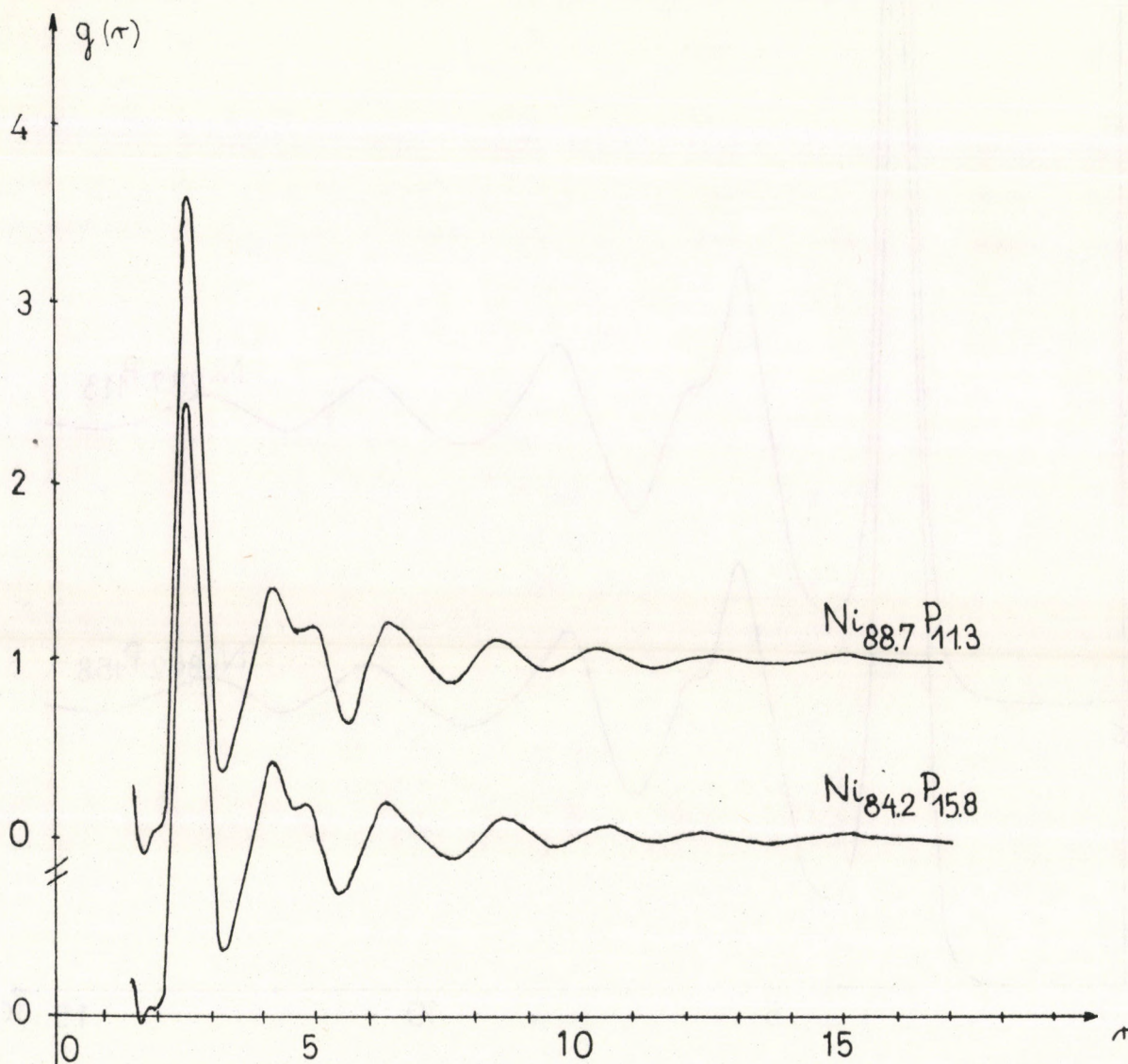


Fig. 4

The total pair-correlation functions

At 11.3 at.% P content the absolute height of the peaks is 1 per cent greater than at 15.8 at.% P. The increase is caused by more Ni atoms scattering the X-rays more strongly than P.

After Fourier transformation of the reduced total interference functions the total pair-correlation functions $g(r)$ and RDF(r) are obtained according to (3) and (4).

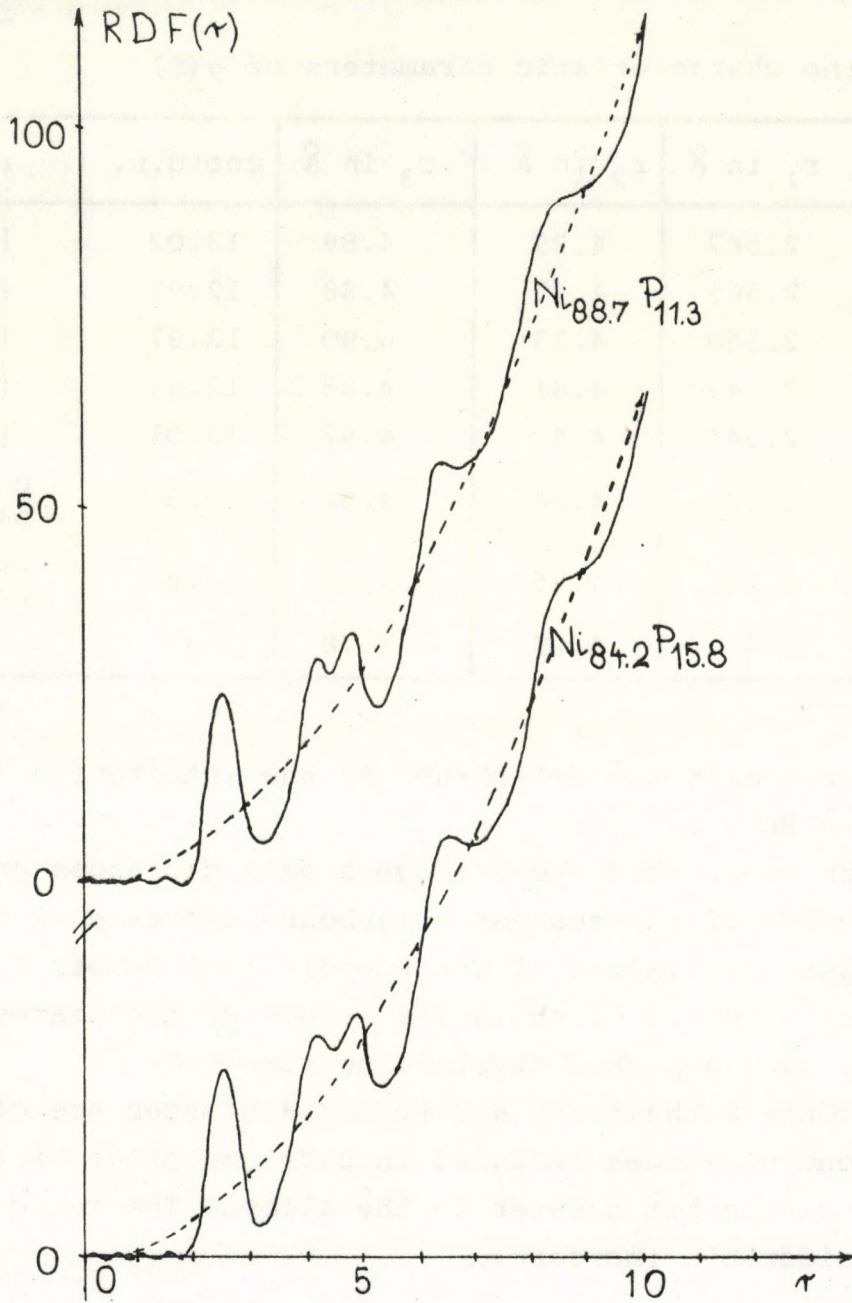


Fig. 5
The radial distribution functions

In order to compare our results with those of Cargill [1] and Ichikawa [2] the characteristic parameters of $g(r)$ are summed up in *Table 3*. This table contains the peak positions r_1 , r_2 , r_3 and the coordination numbers.

In *Table 4*, the weight of metal-metal, metal-metalloid and metalloid-metalloid pairs in the correlation functions are given.

Table 3

The characteristic parameters of $g(r)$

c_P in at.%	r_1 in Å	r_2 in Å	r_3 in Å	coord.n.	ref.
26.2	2.567	4.29	4.89	13.02	[1]
24.0	2.565	4.45	4.88	12.97	[1]
22.8	2.560	4.33	4.90	12.97	[1]
21.1	2.547	4.41	4.88	12.98	[1]
18.6	2.544	4.43	4.92	13.01	[1]
15.8	2.50	4.26	4.86	12.5	pres. paper
11.3	2.49	4.25	4.87	12.3	pres. paper
am.Ni	2.48	4.25	4.78	-	[2]

The coordination number was determined by the integration to the first minimum in RDF(r).

It has been found that the average atomic distances and the coordination number of the nearest neighbours decrease as the P content decreases. The values of the coordination number differ only a little bit from 12 which is the number of the nearest neighbours in a closed packed crystalline structure.

At low P content the first and second distances are close to the corresponding values measured in pure amorphous Ni [2], but they are a little bit greater in the alloys. The value of r_3 shows more considerable increase.

Table 4

The weight of the atom pairs in the scattering

c_P in at.%	$W_{Ni-Ni}^{(0)}$	$2W_{Ni-P}^{(0)}$	$W_{P-P}^{(0)}$
26.2	0.71	0.26	0.02
24.0	0.73	0.25	0.02
22.8	0.74	0.24	0.02
21.1	0.77	0.22	0.01
18.6	0.79	0.20	0.01
15.8	0.826	0.166	0.008
11.3	0.876	0.120	0.004

On the basis of these results it can be concluded that the atoms in the amorphous NiP alloys are arranged in a close packed structure. (The density of the samples is only about 6 per cent less than in the crystalline state.) The diffraction pattern is determined mainly by the metal-metal and metal-metalloid pair distribution because of the weaker X-ray scattering ability and low concentration of metalloid atoms. Due to their more than 70 per cent weight the metal-metal distances dominate. Therefore in the X-ray diffraction measurements this alloy is characterized by the metal skeleton. The effect of the metalloid atoms shows up in each coordination spheres.

Finally it should be emphasized that at low P content the characteristic distances in the total pair-correlation functions of the amorphous NiP alloy smoothly interpolates between the corresponding values of the pure amorphous Ni and those of the higher P content (20-25 at.%) NiP alloy, which suggests the possibility of a continuous extrapolation of the pure Ni amorphous structure to the amorphous Ni₃P alloy having 25 at.% P content.

The experiments were carried out at the Physics Department of the Wilhelm Pieck University in Rostock. We are greatly indebted to Prof. H. Ulbricht, Prof. G. Becherer and Dr. I. Kósa Somogyi for their support. We wish to thank Mrs. I. Bagi for preparing the samples and dr. L. Takács for the stimulating discussions.

REFERENCES

- [1] G.S. Cargill III.: J. Appl. Phys. 41, 12, 1970
- [2] T. Ichikawa: Phys. Stat. Sol. A19, 707, 1973
- [3] L.E. Alexander: X-Ray Diffraction Methods in Polymer Science Wiley, New York, 1969
- [4] E.J. W. Whittaker: Acta Cryst. 6, 222, 1953
- [5] J. Krogh-Moe: Acta Cryst. 9, 951, 1956, N. Norman: Acta Cryst. 10, 370, 1957
- [6] N.S. Gingrich: Rev. Mod. Phys. 15, 90, 1943
- [7] F. Hajdu: Acta Cryst. A28, 250, 1972
- [8] F. Hajdu, T. Radnai: J. Appl. Cryst. 8, 488, 1975





Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Krén Emil
Szakmai lektor: Kisdi Dávidné
Nyelvi lektor: Kósa Somogyi István
Példányszám: 305 Törzsszám: 80-105
Készült a KFKI sokszorosító üzemében
Budapest, 1980. február hó