

## Extended X-ray absorption fine structure analysis of Ni-P and Fe-P amorphous alloys at the phosphorus K-edge

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Amorphous alloys have unusual physical properties, such as excellent corrosion resistance, owing to their short-range order and lack of grain boundaries. The presence of metalloids, such as P, B, C, Si etc., lead to the formation of amorphous or glassy structure. In a previous study, Lalvani *et al.* [1] have studied the structure of the alloys by X-ray absorption near edge structure (XANES) spectroscopic analysis. The energy levels used in the study of the structures were quite low (less than 2200 eV) which enabled the investigation of P K-edge. Their research indicated both a metalloid P character in amorphous Ni-P and the transfer of charge from Ni to P-p orbitals in the material. The also show that the scratching of the sample leads to a  $p^{5+}$ -oxidized feature. The Fe-P sample appeared to indicate a stronger (relative to the Ni-P sample) transition to metal-P hybridization.

Lalvani *et al.* [2] also conducted extended X-ray absorption fine structure (EXAFS) investigations at the Ni K-edge and Fe K-edge of Ni-P and Fe-P samples. Their investigations showed the existence of short range order in both samples with major peaks of the Fourier

transformed spectrum at about 2 Å. The estimated bond lengths were about 2–3 Å. The following is an EXAFS investigation of Ni-P and Fe-P at the P K-edge.

Fe P and Ni-P samples were produced by electrodeposition. Electrodeposition of Fe-P was carried out using a bath consisting of 200 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 7 g/L sodium hypophosphite, 8 g/L glycine and 0.5 g/L of oxalic acid. A plating solution consisting of 150 g/L  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 45 g/L  $\text{NiCl} \cdot 6\text{H}_2\text{O}$ , 40 g/L phosphoric acid and 40 g/L phosphorus acid was used for Ni-P electrodeposition. The pH of the solutions for Fe-P and Ni-P electrodeposition were kept at 1.0 and 1.4, respectively. The substrate used was a 25  $\mu\text{m}$  thick copper foil. Significant agitation was provided during electrodeposition with a magnetic stirrer. The anode and cathode were placed parallel to each other at a distance of 4 cm. The current densities and temperature conditions were: 0.05–0.23  $\text{A}/\text{cm}^2$  and 50–65 °C for Ni-P and 0.02–0.1  $\text{A}/\text{cm}^2$  and 40–50 °C for Fe-P deposition. The elemental composition of the deposits was found by atomic absorption spectroscopy. Additional experimental conditions are also provided elsewhere [3, 4].

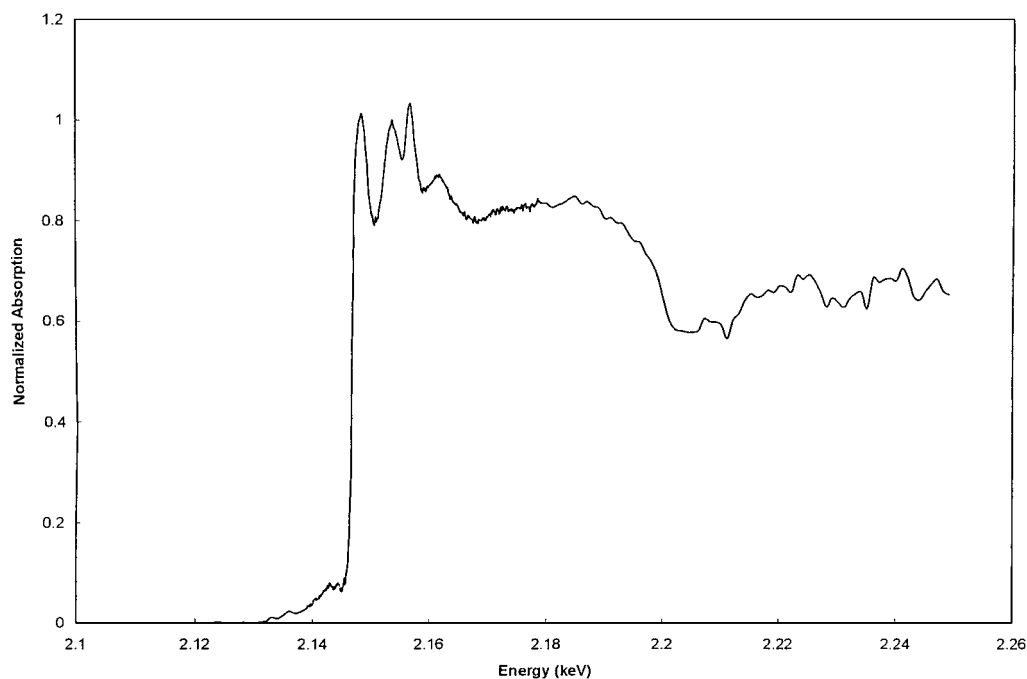


Figure 1 EXAFS spectrum for Fe-P sample at the P K-edge.

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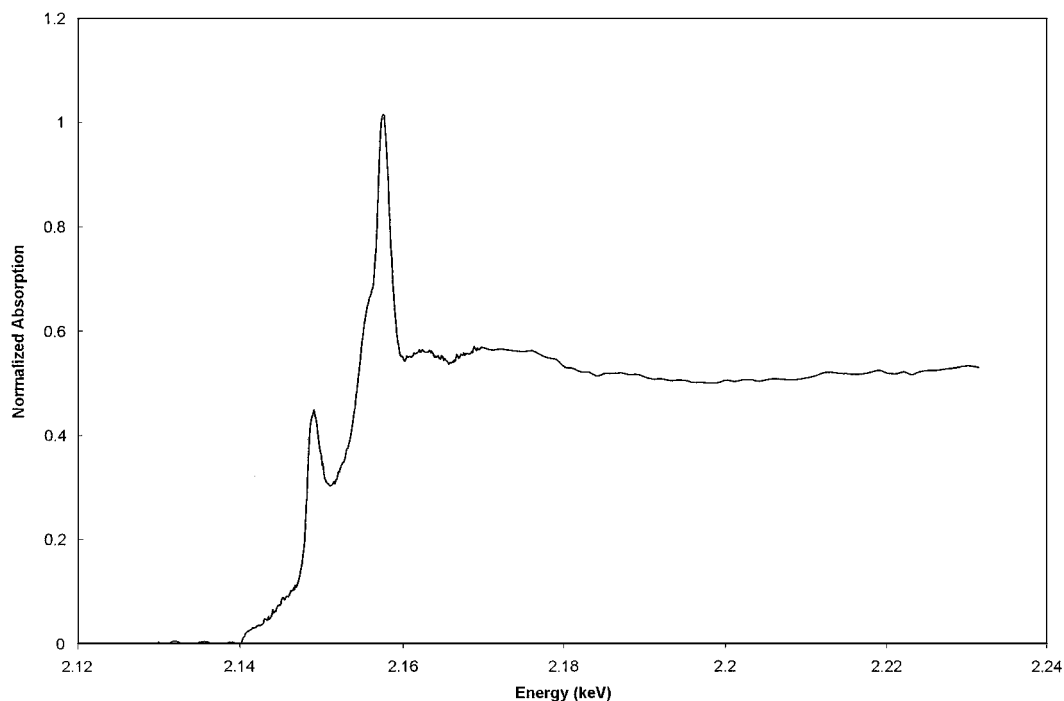


Figure 2 EXAFS spectrum for Ni-P sample at the P K-edge.

Normalized EXAFS functions  $\chi(k)$  were obtained using the standard procedure [5]. Absorption above the edge was fitted using the two-cubic spline. The EXAFS spectra (absorption coefficient vs. energy) are plotted for both, Fe-P and Ni-P samples in Figs. 1 and 2. Peaks were observed at 2.149, 2.154, 2.157 and 2.162 keV in the EXAFS spectrum for the Fe-P sample (Fig. 1). For the Ni-P sample (Fig. 2), a minor peak at the energy level of about 2.149 keV and a major peak at 2.157 keV followed by two minor peaks at 2.162 keV and 2.169 keV are observed. The Fourier transform of  $\chi(k)$  performed with a  $k^2$  weight and a Hanning window

function is presented in Figs. 3 and 4. In order to remove the noise from the experimental data, a back-Fourier transform was performed on the main peak, the range of which is shown in Figs. 3 and 4. The resulting filtered Fourier transformations of  $k^2\chi(k)$  were then compared to the calculations from the computer code FEFF 7 [6]. P-metal pairs were only considered due to the fact that no metalloid—metalloid nearest neighbors have been reported in similar alloys [7]. Using single shell data analysis, the bond length of the P-Fe sample was estimated to be about  $2.56 \pm 0.00891 \text{ \AA}$  and that of P-Ni to be  $2.69 \pm 0.00254 \text{ \AA}$ . The coordination number was

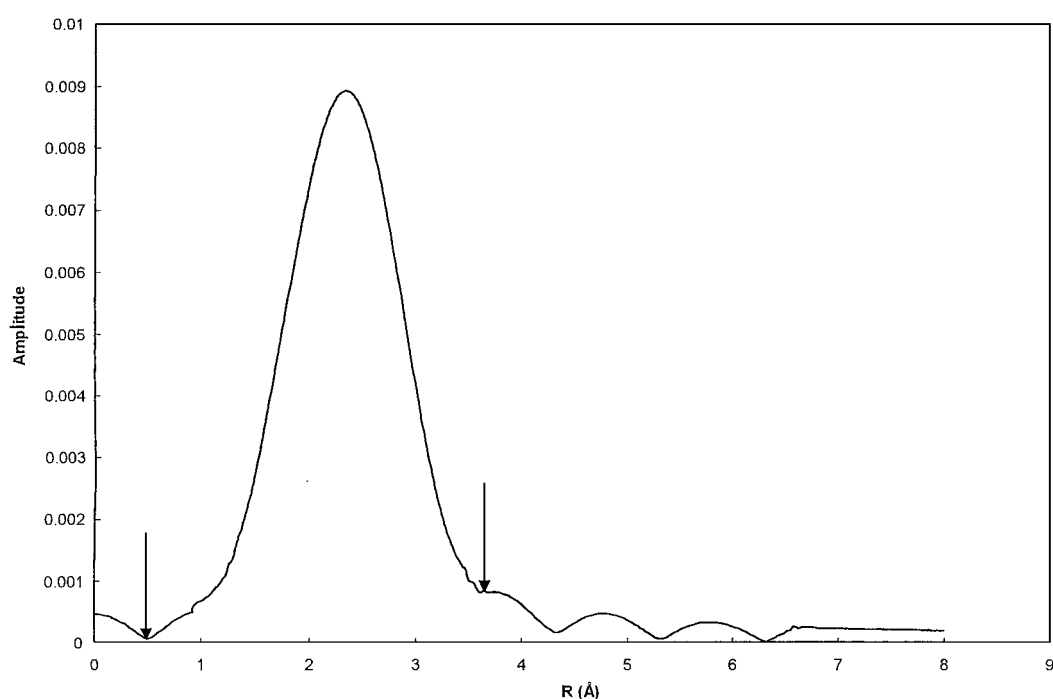


Figure 3 Fourier transform of EXAFS spectrum of Fe-P at the P K-edge.

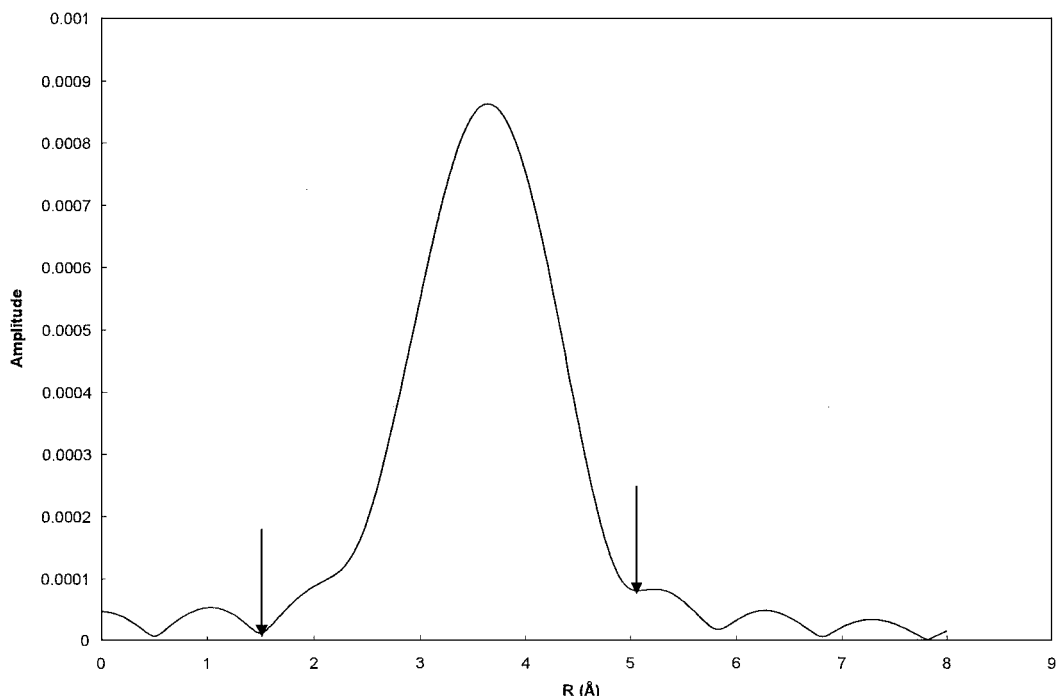


Figure 4 Fourier transform of EXAFS spectrum of Ni-P at the P K-edge.

estimated to be about 3.53 for the Fe-P sample and 6.202 for the Ni-P sample while the disorder parameter values were  $0.009 \pm 7.84 \times 10^{-6}$  and  $0.07 \pm 7.39 \times 10^{-5}$  for Fe-P and Ni-P, respectively. Due to the extremely restricted  $k$  range the coordination number has a large error associated with it. The Fourier transformations of the EXAFS spectrum for the Fe-P (Fig. 3) shows a major peak at 2.3 Å while that of the EXAFS spectrum for the Ni-P sample (Fig. 4) shows a major peak at approximately 3.5 Å. This observation is significant in that it shows no long range order.

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