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# EXELFS OF METALLIC GLASSES

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## ABSTRACT

The feasibility of using extended energy-loss fine structure (EXELFS) obtained from ~1 nm regions of metallic glasses to study their short-range order has been examined. Ionization edges of the metallic glasses in the electron energy-loss spectrum (EELS) have been obtained from PdNiP bulk metallic glass and Ni<sub>2</sub>P polycrystalline powder in a transmission electron microscope. The complexity of EXELFS analysis of L- and M-ionization edges of heavy elements (Z>22, i.e. Ni and Pd) is addressed by theoretical calculations using an *ab initio* computer code, and its results are compared with the experimental data.

## INTRODUCTION

Analysis of extended energy-loss fine structure (EXELFS) in an electron energy-loss spectrum (EELS) is an ideal technique for determining the structure of amorphous materials with a high spatial resolution. It has been advanced enough in recent years such that, in some cases, the quality of the results is compatible to its X-ray analog, extended X-ray absorption fine structure (EXAFS) [1]. However, most of EXELFS analysis has been restricted to the K-ionization edge of lighter elements. For heavier elements, more complex ionization edges such as L- and M-edges have to be dealt with. The aim of our study is to obtain information on the short-range structure of bulk metallic glasses. The X-ray based techniques have a poor spatial resolution, which, therefore, cannot directly reveal, for example, the early stages of nucleation and phase separation. In principle, our electron energy-loss spectrometer is capable of acquiring the K-edge data for the light elements (Z ≤ 22). In practice, it is limited to about Z ≤ 17 due to the poor signal-to-noise ratio in the higher energy-loss range, beam damage, contamination and instrumental stability. Therefore, the structure around heavy elements can be determined only from their ionization edges in a lower energy-loss range. In this paper, the complexity involved with the EXELFS analysis of L- and M-edges of the heavy elements viz. Ni and Pd is addressed by comparing theoretical  $\chi(k)$  functions (oscillatory component of the EXELFS) with various initial states of transition in an atomic shell. The theoretical  $\chi(k)$  functions were generated by an *ab initio* EXAFS computer code called FEFF 7 [2]. Then, the combined effect of the various  $\chi(k)$  functions was compared with the experimental data. Further discussion of the experimental data is presented elsewhere in these proceedings [3].

## BACKGROUND

EXELFS (or EXAFS) is a quantum interference phenomenon. Due to interaction with an incoming high-energy electron (X-ray), a core electron is ejected from an atom in the specimen and is represented by an outgoing spherical wave. Weak oscillations arise from interference between the outgoing spherical wave and the elastically backscattered wave from neighboring atoms. Approximating the ejected-electron wavefunction at the scattering atom by a plane wave and assuming that multiple scattering can be neglected, the theory gives the oscillatory component as [4]

$$\chi(k) = \sum_j \frac{N_j}{r_j^2} \frac{f_j(k)}{k} \exp(-2r_j/\lambda_i) \exp(-2\sigma_j^2 k^2) \sin[2kr_j + \phi_j(k)], \quad (1)$$

where  $r_j$  is the radius of a particular shell of neighboring atoms,  $N_j$  is the number of atoms in shell  $j$  and  $N_j/r_j^2$  (as a function of  $r$ ) is partial radial distribution function (RDF). Therefore,  $\bar{\chi}(k) = |RDF|$  can be obtained as the modulus of the Fourier transform of (1).

The FEFF 7 code was used for theoretical calculations of the  $\chi(k)$  functions for Pd M<sub>1</sub>-, M<sub>2</sub>-, M<sub>3</sub>-, M<sub>4</sub>-, and M<sub>5</sub>-edges of a Pd crystal (fcc) and Ni L<sub>1</sub>-, L<sub>2</sub>-, L<sub>3</sub>-edges of a Ni<sub>3</sub>P crystal (tetragonal).

## EXPERIMENTAL

Five specimens were investigated in this study: two Pd<sub>80-x</sub>Ni<sub>x</sub>P<sub>20</sub> (x=20 and 40) bulk metallic glasses, a polycrystalline Pd metal foil (99.95%, Goodfellow metals) and Ni<sub>2</sub>P polycrystalline powder. These specimens were thinned first by mechanical polishing and then to electron transparent thickness by an ion-beam using a Precision Ion Polishing System (PIPS, Gatan Inc.). The thickness of the analyzed area was in the range of 30 - 40 nm.

A Philips EM400 120 keV transmission electron microscope (TEM) with a LaB<sub>6</sub> thermionic emission gun, and a VG HB501 dedicated scanning transmission electron microscope (STEM) with a cold field-emission gun were used in this investigation. Both microscopes were equipped with Gatan 666 Parallel Electron Energy-Loss Spectrometers (PEELS). The former microscope acquired EXELFS with a spatial resolution of ~50 nm and its effective collection semi-angle for EELS was 8 mrad. The latter microscope acquired EXELFS with a spatial resolution of ~1 nm and its effective collection semi-angle for EELS was 18 - 20 mrad.

## DATA ANALYSIS

The iterative gain averaging method [5] was used to minimise the gain variations in the photodiode array of the PEELS system. After the removal of the dark-current noise from a raw spectrum, the pre-edge background was subtracted by using a pre-edge curve fit to a power-law model. The contribution of plural scattering was removed by applying the Fourier-ratio deconvolution [4] (a software routine in Gatan, EL/P 3.0).

The WinXAS package [6] was used for data processing. The program performs the following steps:

1. Conversion of the scale of  $\chi(E)$  from energy to k-space,  $\chi(k)$ .

The magnitude,  $k$ , of the wavevector of the ejected electron is given by

$$k = 2\pi/\lambda \cong [2m_0E_{kin}]^{1/2} / \hbar = 5.123(E - E^0)^{1/2}, \quad (2)$$

where  $E_{kin}$  is the kinetic energy of the ejected inner-shell electron and  $E^0$  is the energy corresponding to  $E_{kin} = 0$ . Here, the maximum of the ionization edge was taken as  $E^0$ .

2. Isolation of the oscillatory component of the EXELFS ( $\chi(E)$  function) by using n-spline fitting over the k range of interest.

3. Correction for k-dependence of backscattering by multiplying with  $k^n$  where n=1, 2 or 3.

4. Truncation of  $\chi(k)*k^n$  by multiplying with a window function.

5. Fourier transform of  $\chi(k)*k^n$  to give a raw RDF (phase shift uncorrected),

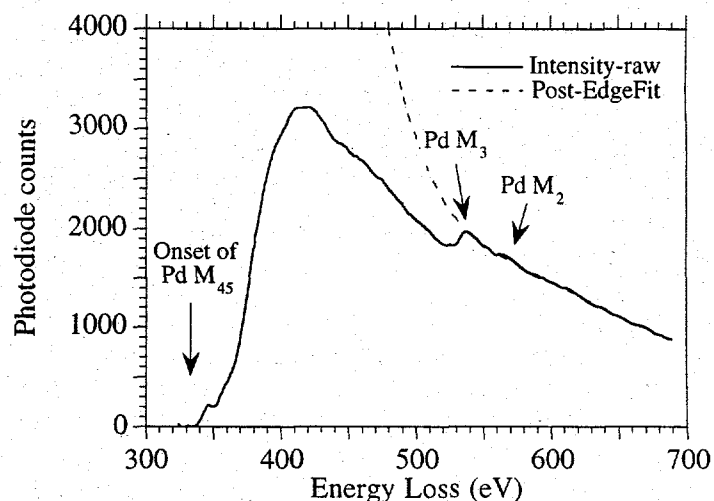
$$|FT(\chi(k)*k^n)| = |RDF|.$$

6. Correction for phase shifts to convert  $|RDF|$  peak positions into interatomic distances.

## RESULTS AND DISCUSSION

### Pd M-edges

Fig. 1 shows a typical EEL spectrum of a Pd M-edge of Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> bulk metallic glass. M<sub>1</sub>-, M<sub>2</sub>-, M<sub>3</sub>-, M<sub>4</sub>-, and M<sub>5</sub>-edges are located at ~670, 559, 531, 340 and 335 eV, respectively. The maximum of the intensity is located at ~70 eV after the threshold of the M<sub>4</sub>-, and M<sub>5</sub>-



**Fig. 1** Typical EEL spectrum of a Pd M-edge of Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> bulk metallic glass.

edges. The EXELFS oscillations are clearly visible beyond the intensity maximum and extend beyond the M<sub>2</sub>- and M<sub>3</sub>-edges. Since the M<sub>1</sub>-edge step was not recognizable and, beyond the M<sub>1</sub>-edge, all the transitions, i.e. M<sub>1</sub>-, M<sub>2</sub>-, M<sub>3</sub>-, M<sub>4</sub>- and M<sub>5</sub>-edges contribute to the EXELFS, the experimental analysis was carried out on the EXELFS beyond the M<sub>2</sub>- and M<sub>3</sub>-edges.

To examine the combined effect of M<sub>1</sub>-, M<sub>2</sub>-, M<sub>3</sub>-, M<sub>4</sub>-, and M<sub>5</sub>-edges on the Fourier transform (FT) of the  $(\chi(k)*k)$ -function, the M-edges of Pd (fcc) metal were theoretically examined, using the FEFF 7 code. Although the accuracy of the results of M-edges may be less than that of K-edge, useful results are still expected. Fig. 2 shows calculated  $\chi(E)$  functions for each single ionization edge, i.e. M<sub>1</sub>-, M<sub>2</sub>-, M<sub>3</sub>-, M<sub>4</sub>-, and M<sub>5</sub>-edges, multiplied by appropriate weighting factors [7]. The dominant contribution from the M<sub>4</sub>-, and M<sub>5</sub> transitions is clearly shown. Therefore, the total contribution of all the  $\chi(E)$  functions is very similar to those of M<sub>4</sub>-, and M<sub>5</sub>-edges but with some minor deviations due to the small contributions from the M<sub>1</sub>-, M<sub>2</sub>-, M<sub>3</sub>-edges as demonstrated in Fig. 3. In general all the curves show 1st, 2nd and 3rd nearest neighbor (nn) peaks at almost the same radial distances. Differences between  $FT(\chi(k)*k)$  of the M<sub>5</sub>-edge and the sum of all the edges are a slight shift of the 1st nn peak and the appearance of a shoulder peak at  $\sim 3$  Å in the FT of the latter. The  $FT(\chi(k)*k)$  of M<sub>5</sub>-edge is almost identical to that obtained from the K-edge (not shown). Thus, the result obtained from the M<sub>5</sub>-edge can be used for structural analysis and may be regarded as the true RDF. It should be also noted that, unlike the Ni L-edge (discussed later), the FT of the Pd M-edge is rather insensitive to the choice of the range of k, which adds an extra reliability to the calculation.

The above results may be compared with experimental results from polycrystalline Pd and Pd<sub>60</sub>Ni<sub>20</sub>P<sub>20</sub> bulk metallic glasses in Fig. 4. Generally the theoretical prediction and the experimental results agree well with each other. Also, good agreement with the literature [7] was obtained despite the fact that, ideally, the FT range should be to higher k values to reduce distortion caused by the combined effect of the M<sub>23</sub> and M<sub>1</sub> EXELFS oscillations. The 2nd nn peak is split, which is a characteristic of random close packing of hard spheres in a metallic structure. Further details of these observations are discussed in another paper [3].

### Ni L-edges

As an example, a typical EEL spectrum of an Ni L-edge from Ni<sub>2</sub>P polycrystalline powder is shown in Fig. 5. L<sub>1</sub>-, L<sub>2</sub>- and L<sub>3</sub>-edges are located at  $\sim 1007$ , 871 and 853 eV, respectively.

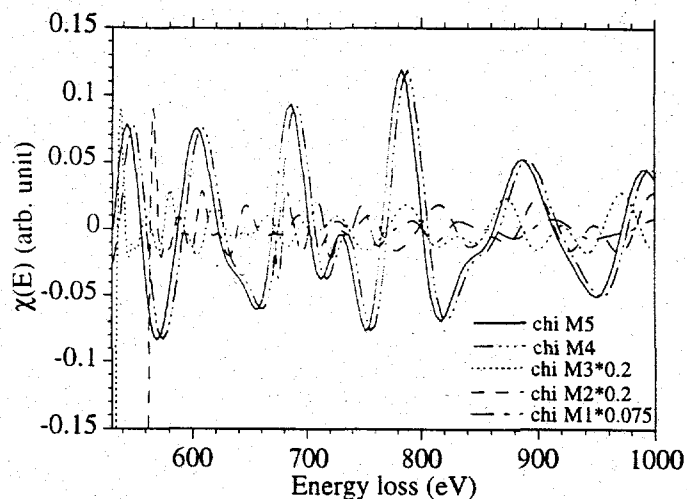


Fig. 2 Calculated  $\chi(E)$  functions for  $M_1$ -,  $M_2$ -,  $M_3$ -,  $M_4$ -, and  $M_5$ -edges of Pd (fcc).

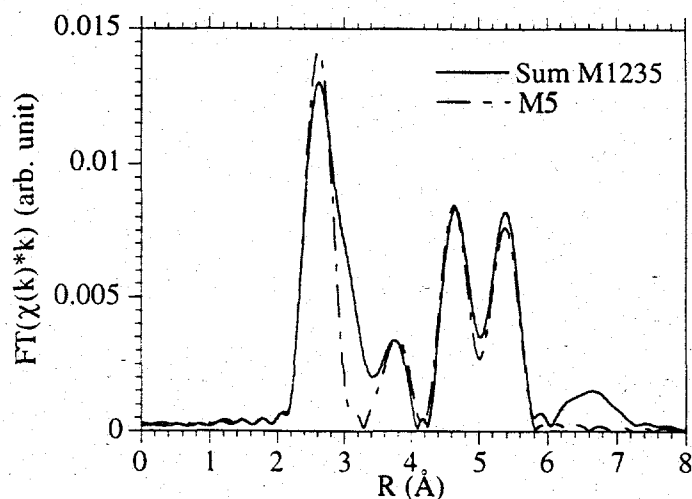
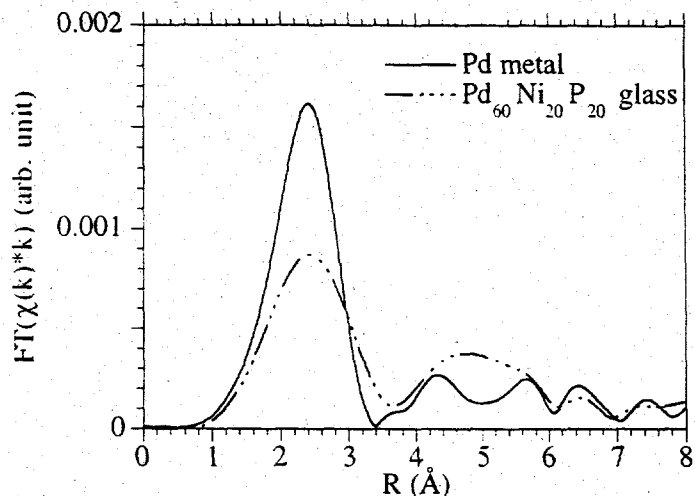


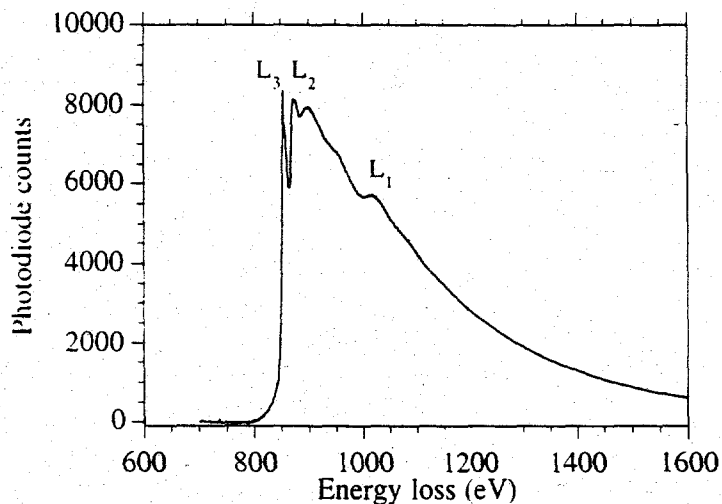
Fig. 3 Fourier transform of  $(\chi(k)*k)$  of  $M_5$ - and the sum of the  $M_1$ -,  $M_2$ -,  $M_3$ - and  $M_5$ -edges of Pd (fcc).

Unlike the Pd M-edge EEL spectrum, the Ni  $L_2$ - and  $L_3$ -edge peaks are distinctively sharp. They are equivalent to white lines, well known in X-ray absorption spectroscopy. The  $L_2$ -edge appears 18 eV above the  $L_3$  peak, due to spin-orbit splitting.

The same theoretical analysis as for the Pd M-edges was applied to the Ni L-edges of  $Ni_{180}P_{20}$ , which was chosen because of its similarity to the  $Ni_{80}P_{20}$  glass regarding short-range order [8]. Fig. 6 shows that the analysis of the Ni L-edge EXELFS is sensitive to the choice of the range of  $k$  for the FT performed. It is complicated by the interference between  $L_2$ - and  $L_3$ -EXELFS. The former effect is observed as the extinction of the first major peak in the  $L_3$  (2, 20) from the other two FTs. The latter effect is responsible for the reduction of the first peak in  $L_3$  (6.4, 17.4). Thus, for Ni L-edges, direct FT of the sum of L-edges above the  $L_1$ -edge provides a severely distorted RDF.



**Fig.4** Fourier transform of  $(\chi(k)*k)$  obtained experimentally from Pd metal and Pd<sub>60</sub>Ni<sub>20</sub>P<sub>20</sub> bulk metallic glasses (without phase shift correction).

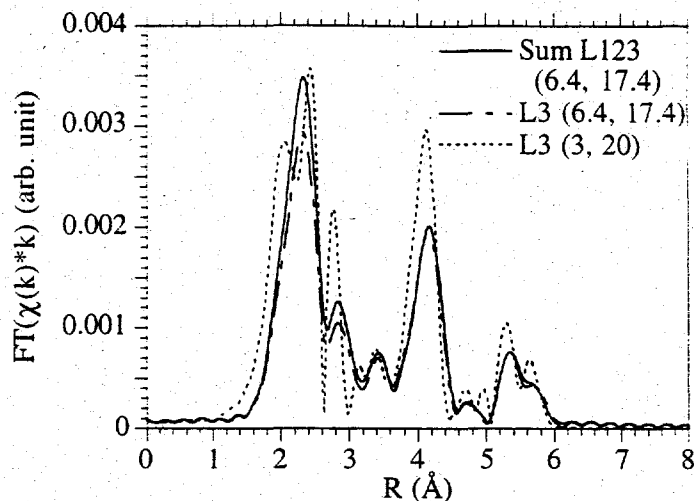


**Fig. 5** Ni L-edges of Ni<sub>2</sub>P polycrystalline powder

## SUMMARY AND FUTURE WORK

The theoretical study shows that, for the Pd M-edge, the FT of the sum of all M-edges is in good agreement with the true partial RDF. For Pd metal, the FT of the experimental M-edge EXELFS agrees with the theoretical EXELFS. However, the analysis of the Ni L-edges is very sensitive to the selection of the range of the FT and affected by the interaction between L<sub>2</sub> and L<sub>3</sub> EXELFS. The FTs of experimental EXELFS agree better with the FT of the  $(\chi(k)*k)_{sum}$  than those of a single ionization edge. To improve the analysis of these edges, a more accurate structural model for the theoretical calculations, optimizing parameters for both theoretical and experimental analysis, deconvolution of overlapped edges [9], comparison with near-edge structures and systematic compositional changes will be examined in future.





**Fig. 6** Theoretical Fourier transform of  $(\chi(k)*k)$  of Ni L-edges of  $\text{Ni}_2\text{P}$ . The brackets show the range of  $k$  ( $\text{\AA}^{-1}$ ) for the FT performed on  $(\chi(k)*k)$  function. The onset of the  $L_1$ -edge is just before  $k = 6.4\text{\AA}^{-1}$ .

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