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A LOCAL PROBE INTO THE ATOMIC STRUCTURE OF METALLIC GLASSES USING EELS

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Abstract

Electron energy loss spectroscopy (EELS) is used to extract information on the topological arrangement of atoms around Pd in the bulk-glass-forming $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$. It is found that the environment around Pd in the glass is only a slight modification of the Pd crystalline structure. However, the modification is enough to allow this alloy to form a glass in bulk. In examining the differences between the structure of crystalline Pd and glassy $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ it is concluded that incorporation of Ni and P into the structure frustrates the structure enough that glass formation becomes easy.

Introduction

The discovery of alloys that form bulk metallic glasses^{1,2} (BMGs) has rejuvenated interest in these systems in recent years. Since the "bulk" nature of these BMGs is central to the new-found scientific interest in them, a basic question need to be answered: what governs their easy glass forming ability? This has been explained to some extent by different criteria that are based on the suppression of the nucleation of crystals³, the suppression of the kinetics via the "confusion principle"⁴, and atomic size effects of the constituent elements⁵. The experimental data in this case are profuse but structural models that tie together all the evidence are lacking.

A major reason for the lack of structural models for glass-formability and glass stability is that little information is available on the atomic structure for these glasses. Scattering experiments using neutrons, X-rays or electrons can provide total radial distribution function (RDF), but the interpretation of RDFs become difficult for BMGs, which contain many different elements, often five or more. It is much more useful to obtain a partial radial distribution function (PRDF), the RDF around a individual elements. Extended X-ray absorption fine structure (EXAFS) and anomalous X-ray scattering provides PRDFs directly but these techniques require a synchrotron light source. Only for selected elements is it possible to obtain PRDFs from neutron scattering using isotopic substitution. All these techniques give structural information with poor spatial resolution. By comparison, the electron analog of EXAFS, extended electron energy loss fine structure (EXELFS), provides a much higher spatial resolution (a sampling volume of $\sim 50 \text{ nm}^3$, and a sampling area of $\sim 1 \text{ nm}^2$ are attainable). Also the image and diffraction pattern from the sampling area may be monitored at all times during the experiment. In general, EXELFS provides supporting, and complementary structural information to EXAFS. This technique, however, is still under development.

EXELFS refers to the fine structure that appears at energies $>30 \text{ eV}$ above the ionization edge in an EELS spectrum. Incident electrons are scattered inelastically as they pass through the sample and on to an energy-loss detector, producing an EELS spectrum. If a scattering event causes an ionization event in the sample material then the ionized electron

wave sets up a standing wave between the central atom and a neighboring atom from which it is elastically backscattered. It does so with all its neighbors. This standing wave modulates the energy loss characteristics of the incident electrons and shows up as the fine structure (EXELFS) beyond the ionization edge of the EELS spectrum. It is obvious that this modulation function contains information on the distribution of atoms around the parent atom in reciprocal space. The Fourier transform of this function is proportional to the PRDF.

$\text{Pd}_x\text{Ni}_{(80-x)}\text{P}_{20}$ is a prototypical BMG family. In a recent study⁶ Egami *et al.* found using anomalous X-ray scattering the structure of $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glasses to be best described by the dense random packing (DRP) model⁷. The DRP model has already been shown to work well for binary transition metal-metalloid (TM-M) glasses⁸. It was found that the total RDF for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ are almost identical. However, in the Pd PRDFs for the two compositions the shapes of the well-known "split" second peak (characteristic of the DRP structure) in this case were different. If the local atomic structure in these glasses have an important bearing on the glass-formability of these alloys, then it is the PRDFs that will indicate this.

The goal of our work is to develop EXELFS for the study of BMGs using the $\text{Pd}_x\text{Ni}_{(80-x)}\text{P}_{20}$ family as our case study. The viability of using EXELFS for the study of BMGs is examined in a separate paper⁹. In this paper, we present the initial results of using EXELFS in determining the structure of $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$. For comparison we also measured the RDF of crystalline Pd.

Experiment

The specimens are $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ BMG and Pd pure metal foil (99.95%, Goodfellow metals). The glass was formed by water quenching of the melt. The details of the processing of the alloys can be found elsewhere¹⁰. These specimens were pre-thinned by mechanical polishing and finished with Precision Ion Polishing System (PIPS, Gatan Inc.). The samples in each case was placed on a cold stage and cooled with $\text{N}_2(\text{l})$ to eliminate contamination buildup under the high electric field of the electron probe. The thickness of the analyzed area was in the range of 30 - 40 nm thick.

The Philips EM400 120 keV conventional transmission electron microscope (CTEM) with a single crystal LaB_6 thermionic emission gun was used. The microscope is equipped with Gatan 666 Parallel Electron Energy-Loss Spectrometer (PEELS). The spatial resolution of the electron probe used was ~ 50 nm and its effective collection semi-angle for EELS was 8 mrad. The energy dispersion of the PEELS system was set to 1 eV per channel for EXELFS analysis.

The data reduction steps involve first the removal of dark-current noise from a raw spectrum, the pre-edge background and the contribution of plural scattering by the application of the Fourier-ratio deconvolution¹¹. The resulting Pd M-edges for crystalline Pd and glassy $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ are shown in Fig. 1.

The PRDFs were extracted using the WinXAS package¹². The data processing using WinXAS involved the isolation of the oscillations beyond $M_{3,2}$ (Fig. 1), their conversion to oscillations in k-space, correction for termination broadening by the modulation of the k-space oscillation by a Bessel function, and the Fourier transform into radial space.

Results and Discussion

In practice, a PRDF thus obtained may need further correction since a phase shift is possible for the ionized electron between its outgoing and backscattered waves. If one

assumes that the phase shift to be a as a linear function of k , then the effect upon Fourier transform into

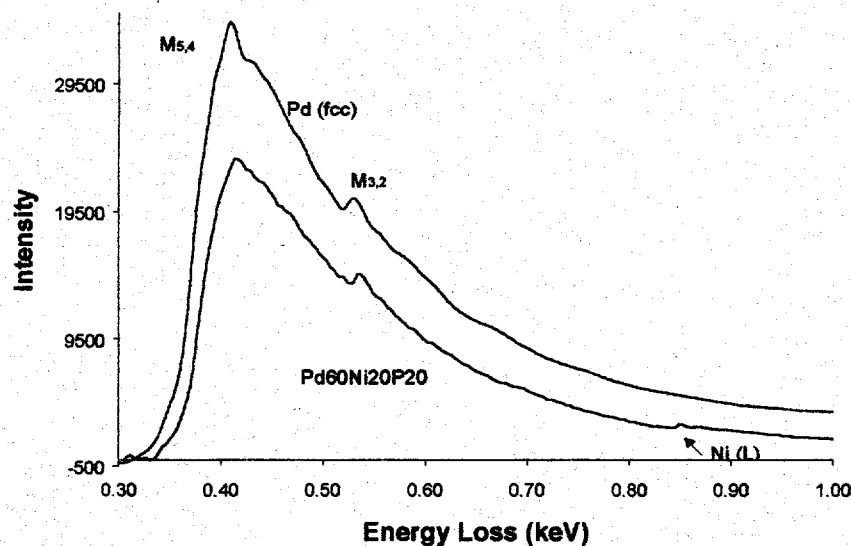


Fig1: EELS M edges of Pd (fcc) and glassy $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$. The $M_{5,4}$ and $M_{3,2}$ are separate ionizations. EXELFS was carried out beyond $M_{3,2}$. $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ shows a small Ni L-transition.

real space is simply a constant shift in r . The abscissa in the RDF of Pd was thus shifted so that the first peak matches a calculated RDF of crystalline Pd and the heights of the first peaks are scaled to be equal (Fig. 2). The comparison between the calculated and phase-shifted experimental RDFs of Pd shows us that the phase shift correction assuming a linear dependence of k is accurate in matching the position of the second major peak at $\sim 4.5 \text{ \AA}$ and its pre-peak at $\sim 3.9 \text{ \AA}$. However, the peak at 6 \AA does not line up perfectly. What is more interesting is that heights of the peaks in the range of 4 \AA and 6 \AA are underdetermined in the experimental RDF. This may be explained by the fact that the probing electrons were sampling along a specific crystallographic direction within a single crystal grain, and therefore had "seen" more of certain radial distances and less of others. This beam orientation dependence of EXELFS in crystals has been observed by others¹³. This should not be a problem in the random structure of glass.

The same rigid phase shift was applied to the PRDF of $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ and it was scaled vertically so that the height of the first peak matched that of the calculated one (Fig.3). The position of the first peak in the two cases match quite well, as should be expected since they both correspond to the Pd-Pd bond distance. The distribution of distances around this first maximum in glassy $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ is wider than in Pd (fcc). This is also expected since there are Pd-Ni and Pd-P bonds within the first coordination shell of the glass, and each of these bonds may have a distribution of distances from the inherent disorder of the glass.

The second peak in the Pd (fcc) PRDF is at $\sim 3.9 \text{ \AA}$ and corresponds to $\sqrt{2} * d$, where $d=2.75 \text{ \AA}$ (the first peak position). This is, of course, the diagonal distance in a square plane, and characteristic of an octahedron. The following two peak positions correspond to $\sqrt{3} * d$ and $2d$ respectively.

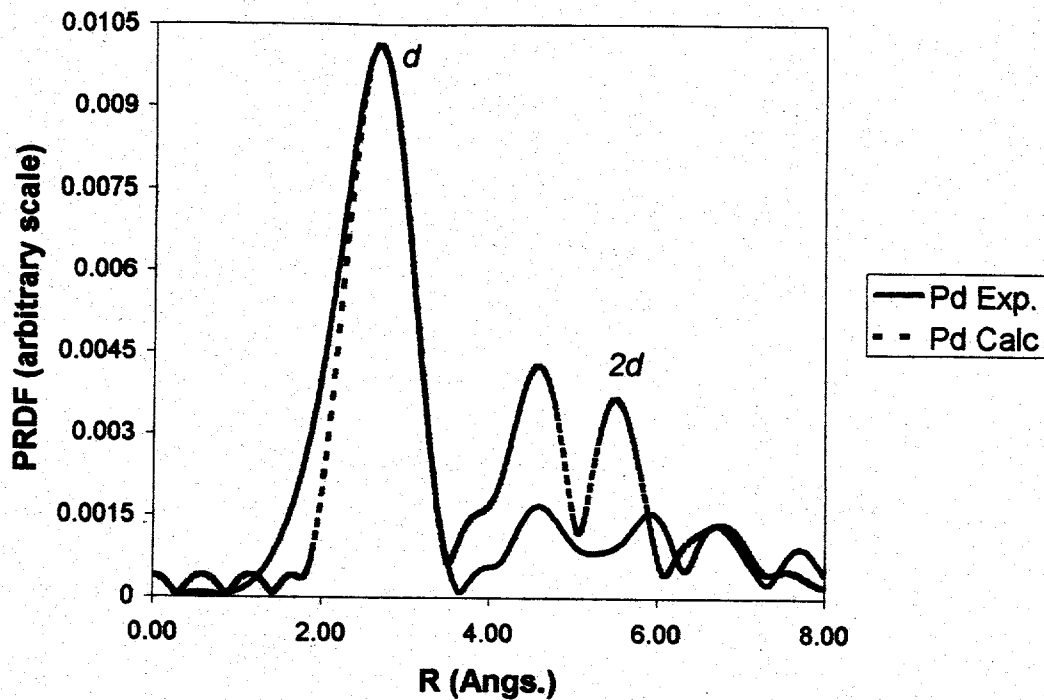


Fig. 2: Experimental and calculated RDFs of crystalline Pd. The distance d corresponds to the Pd-Pd bond distance.

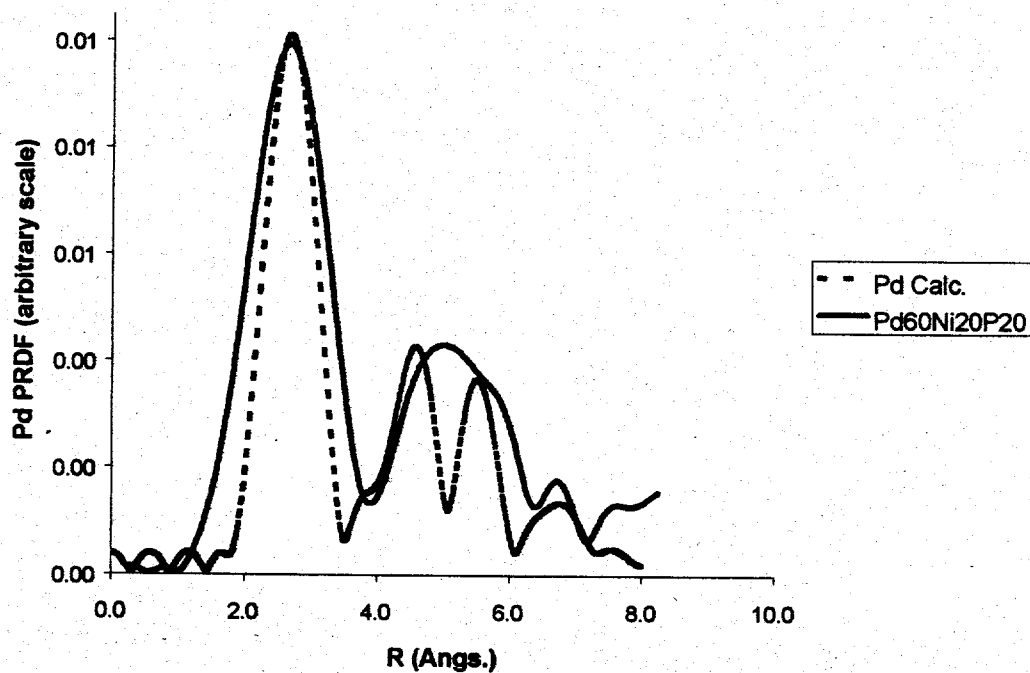


Fig 3: Pd PRDF in $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ glass compared to the calculated RDF of Pd (fcc).

In the region between d and $2d$ we have an interesting correlation between the glass and Pd (fcc). The average height of broad peak between 4 Å and 6 Å in this case is close to that from the Pd (fcc) structure. Moreover, the shape of this broad peak is such that the ratio

of height at the maximum ($\sim 5 \text{ \AA}$) to that at the shoulder ($\sim 6 \text{ \AA}$) is the same as that of the two peaks in Pd (fcc) in this region. The full-width-at-half-max (FWHM) of this broad "split" peak is slightly broader as the combined FWHM of the $\sqrt{3} * d$ and $2d$ peaks in Pd. However, in the glass, between $\sqrt{3} * d$ and $2d$ there is in the glass a broad distribution of bonds instead of the two well-defined peaks of Pd. This tells us that the atomic environment around Pd in the second coordination shell is similar as that of Pd (fcc) but with many types of bond distances. It can be suggested that it is in through such a distribution of distances that this system is able to incorporate enough "confusion" within its atomic structure and thus form a glass.

In their work Egami *et al.*⁶ showed that the total RDF for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ are almost identical. It is well known that the $x=40$ composition in the $\text{Pd}_x\text{Ni}_{(80-x)}\text{P}_{20}$ family is the best glass-former. It was thus concluded in their study that the chemical substitution of Ni with Pd has minimum effect on the total atomic structure which resembles, in any case, the DRP structure commonly found in other TM-M glasses. In the same study, however, the Pd PRDFs were presented for the two compositions and, in fact, the shape of well-known "split" second peak (characteristic of the DRP structure) in this case were different. It was found that the split in peak between $\sqrt{3} * d$ and $2d$ for Pd PRDF in the $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ glass is sharper than in the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass. It is worth investigating whether or not this splitting is correlated to glass-formability.

If the local atomic structure in these glasses have an important bearing on the glass-formability of these alloys, then the PRDFs will indicate this. For this it would be necessary to look not only at the Pd PRDFs over a composition range in this family, but also the Ni PRDFs. EXELFS of Ni is, however, still problematic⁹. We therefore have plans to carry out Ni EXAFS.

Conclusions

It is concluded from the EXELFS study of $\text{Pd}_{60}\text{Ni}_{20}\text{P}_{20}$ that the structure around Pd in this BMG is very similar to that of Pd (fcc) with slightly broader distribution of distances in the first and second coordination shells. The broader distributions can be understood from the fact that in the glass Pd-Ni and Pd-P bond distances need to be incorporated into the structure. The structure in the second coordination shell around Pd in this BMG family has been observed by others to change as Pd is substituted with Ni. The effect of structure in the second coordination shell has not been examined yet for this BMG family. EXELFS of Pd has been found, from this study to be a viable technique for this investigation.

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