

This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in Applied Surface Science, copyright © Elsevier Online after peer review. To access the final edited and published work see <https://www.sciencedirect.com/science/article/pii/S0169433216001872> (<https://doi.org/10.1016/j.apsusc.2016.01.150>)

Surface studies of praseodymium by electron spectroscopies

Mirosław Krawczyk*, Marcin Pisarek, Wojciech Lisowski, Aleksander Jablonski

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52,

01-224 Warszawa, Poland;

*Corresponding author: Tel.: +48-22-3433403; Fax: +48-22-3433333; E-mail address:

mkrawczyk@ichf.edu.pl

Abstract

Electron transport properties in praseodymium (Pr) foil samples were studied by elastic-peak electron spectroscopy (EPES). Prior to EPES measurements, the Pr sample surface was pre-sputtered by Ar ions with ion energy of 2-3 keV. After such treatment, the Pr sample still contained about 10 at.% of residual oxygen in the surface region, as detected by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) analyses. The inelastic mean free path (IMFP), characterizing electron transport within this region (4 nm – thick), was evaluated from EPES using both Ni and Au standards as a function of energy in the range of 0.5 - 2 keV. Experimental IMFPs, λ , were approximated by the simple function $\lambda = kE^p$, where E is energy (in eV), and $k = 0.1549$ and $p = 0.7047$ were the fitted parameters. These values were compared with IMFPs for the praseodymium surface in which the presence of oxygen was tentatively neglected, and also with IMFPs resulting from the TPP-2M predictive equation for bulk praseodymium. We found that the measured IMFP values to be only slightly affected by neglect of oxygen in calculations. The fitted function applied here

was consistent with the energy dependence of the EPES-measured IMFPs. Additionally, the measured IMFPs were found to be from 2% to 4.2% larger than the predicted IMFPs for praseodymium in the energy range of 500-1000 eV. For electron energies of 1500 eV and 2000 eV, there was an inverse correlation between these values, and then the resulting deviations of -0.4% and -2.7%, respectively, were calculated.

Keywords: praseodymium; elastic-peak electron spectroscopy; electron inelastic mean free path; surface composition; x-ray photoelectron spectroscopy; Auger electron spectroscopy

1. Introduction

Praseodymium belongs to the light rare earth elements (REEs) which find applications in a wide range of industries. These applications range from permanent magnets, metal alloys, catalysts, polishing, to glass additives and others [1]. Praseodymium is primarily used in high-power magnets; it can also be combined with neodymium, another REE, to form rare earth alloy magnets [2]. These constructions are very powerful permanent magnets which are particularly useful in the automotive and wind power generation industries due to their light weight compared to magnetic strength. The application of rare earth permanent magnets in wind turbines is expected to be another major growth factor for the global REEs market over the long term [3,4]. In addition, these magnets are also used in computer disc drives, mobile phones, iPods, etc. Praseodymium is also applied as an alloying agent with magnesium to create high-strength metals used in aircraft engines [1,2]. Moreover, it is a component of mischmetal, a material that is used to make flints for lighters, and in carbon arc lights used in

the motion picture industry for studio lighting and projector lights. Praseodymium is often added to fiber optic cables as a doping agent to help amplify a signal.

Quantification of Pr-containing materials can be performed using AES and XPS. However, for both techniques, knowledge of the electron inelastic mean free path (IMFP) value for praseodymium is required. Presently, this value can only be estimated with unknown accuracy from the TPP-2M predictive equation [5], which is implemented in the NIST Database SRD 71 [6]. Importance of the IMFP in quantitative Auger electron spectroscopy (AES) and XPS has been extensively discussed by Jablonski [7]. In addition, Powell and Jablonski [8] have been provided an extensive evaluation of the published IMFPs in elements, and selected inorganic and organic compounds. IMFP values can be also determined from elastic-peak electron spectroscopy (EPES) [9,10] measurements of the intensity of electrons elastically backscattered from a surface at various energies. Such measurements were recently performed to estimate IMFPs for two metal oxides: zinc oxide [11], and cerium dioxide [12].

In this work, the IMFPs of 0.5–2 keV electrons from the relative EPES measurements for Pr foil material are evaluated. These measurements were preceded by XPS-AES examination of the Pr surface composition.

2. Introduction

2.1. Samples

Small pieces (5x5 mm) of praseodymium foil (0.25 mm-thick, 99.5%), purchased from Alfa Aesar GmbH (Karlsruhe, Germany), were used for electron spectroscopies (XPS, AES, EPES) studies described in more detail below.

In the EPES studies, nickel sheet (0.1 mm-thick, 99.999%, Alfa Aesar, A Johnson Matthey Comp., Heysham, UK) and gold foil (0.1 mm-thick, 99.9975+ %), Alfa Aesar GmbH & Co KG, Karlsruhe, Germany) were used as standard materials.

2.2. XPS studies

Surface composition of the Pr sample was determined by XPS and AES. High-resolution (HR) XPS measurements were performed using a PHI 5000 VersaProbe™ (ULVAC-PHI) spectrometer with microfocused and monochromatic Al K α radiation. The spectrometer was equipped with a spherical capacitor energy analyzer with multi-channel detection with a 100 x100 μm area for XPS analysis. The X-ray beam was incident on the sample surface at an angle of 45° with respect to the surface normal, and the analyzer axis was located at 45° with respect to the surface. HR XPS spectra of Pr (Pr 5p, Pr 5s, Pr 4d, Pr 4p, Pr 4s, Pr 3d, Pr 3p_{3/2}, Pr 3p_{1/2}) and O 1s photoelectron lines were recorded with the energy step of 0.1 eV at the analyzer pass energy of 23.5 eV. All XPS spectra were recorded on the Pr foil sample pre-sputtered by 2 keV argon ions (at angle of incidence of 35° with respect to the surface normal, rastered over a 2 x 2 mm² surface area; a maximal ion current of 1.1 μA) for 5 min. The Ar⁺ sputtering rate was 7 nm/min, as measured using a SiO₂/Si reference sample.

ULVAC-PHI MultiPak software (ver. 9.6.0.15) was used to evaluate the XPS data. Deconvolution of XPS spectra were performed using a Shirley background and a Gaussian peak shape with 30% Lorentzian character. The binding energies (BE) of all detected spectra were calibrated with respect to the BE of C 1s at 285.0 eV. Atomic concentration (AC) of praseodymium and oxygen at the Pr sample surface was quantified using the multiline software [13].

2.3. AES studies

The AES measurements were carried out using the MICROLAB 350 spectrometer (Thermo VG Scientific) with a spherical sector analyzer. The Auger spectra were taken at the normal incidence of the primary electron beam of 5 keV. AES quantification was based using the software Avantage (ver. 4.88, Thermo Fisher Scientific) on the Pr MNN (696 eV) and O KLL (510 eV) peak intensities [14].

The Auger spectra were obtained from the samples which were initially sputter-cleaned by 3 keV Ar⁺ ions rastered over a 3 x 3 mm² surface area for 5 min at an incidence angle of 30° with respect to surface normal. A maximal ion current was about 1.3 μA.

2.4. EPES studies

Elastic-peak intensities for the Pr sample surface were also recorded using the MICROLAB 350 spectrometer. During the measurements, the electron gun was located at the normal to the surface and the analyzer axis was located at 60° to the surface normal. The acceptance half-angle of the analyzer was 6° . Relative EPES measurements were performed using two standard materials, nickel and gold, for comparison. For both these metals, the IMFP values are known as the recommended IMFPs [8]. Furthermore, the gold sample has been recently indicated as the best standard material [15].

Principles of relative EPES measurement procedures have already been described in Refs. [10,12]. Measurements of the elastic-peak intensity were performed for the Pr sample with respect to both the Ni and Au standards at electron energies of 500, 700, 1000, 1500 and 2000 eV. The electron energy dependence of the IMFP for the surface composition of the analyzed Pr samples was determined using the software package EPES [16] without corrections for surface-excitation effects. This software package allows elastic-peak spectra processing and Monte Carlo simulations of electron trajectories in solids; the two options were recently described in Ref. [12].

Before the EPES measurements, the surfaces of all samples were also cleaned by sputtering with 3 keV argon ions to remove surface contamination. After 5 min sputtering, oxygen and carbon contaminants were entirely removed from the surface region of nickel and gold; however, some residual oxygen contamination at the praseodymium surface was still detected by XPS/AES analysis.

3. Results and discussion

3.1. XPS-AES analysis of Pr surface composition

Fig. 1 shows a survey XPS spectrum from the surface area of the Pr sample after 2 keV Ar-ion sputtering. Praseodymium and oxygen were detected at the sample surface. The surface composition was evaluated using the multiline method [13], taking all detected Pr signal intensities and the O 1s XPS peak intensity for calculation. The atomic concentrations of Pr and O were found to be 90 at.% and 10 at.%, respectively.

Fig. 2 shows the Auger spectrum from the Pr surface after 3 keV Ar-ion sputtering and before EPES measurements. The oxygen surface concentration determined by quantitative AES analysis was found to be about 8 at.%, which was close the value obtained from XPS. Practically all surface contamination was removed from the praseodymium surface by argon ion sputtering. However, the relatively small amount of oxygen (8-10 at.%) was still detected on the sputter-cleaned Pr surface (see Figs. 1 and 2).

The O 1s photoelectrons have a kinetic energy of 949 eV corresponding to an IMFP value in Pr of about 1.9 nm. Taking this value, we can roughly estimate the corresponding sampling depth to be about 4 nm. This value is determined by the information depth, S , for the O 1s photoelectrons in the Pr sample. Jablonski and Powell [17] proposed a simple analytical expression describing the S for all photoelectron and Auger-electron signals:

$$S = -\lambda \cos \alpha \ln \left(1 - \frac{P}{100} \right) \quad (1)$$

where λ is the IMFP for the signal electrons in the sample material, α is the electron emission angle measured with respect to the surface normal, and P is a selected percentage of the total signal-electron intensity originating from the sample surface. We selected $P = 95\%$ in Eq. (1)

to calculate the S here. Influence of surface oxygen on the determined energy dependence of IMFP for praseodymium will be considered later.

3.2. EPES analysis: determination of the energy dependence of IMFP

In order to evaluate the IMFPs and their energy dependence, the intensity of the measured elastic peaks were determined using the software EPES [16], which does not account for the surface electron excitations. Fig. 3 shows the ratios of measured elastic-peak intensities I_{Pr} for oxygen-containing praseodymium to the corresponding intensities for both nickel I_{Ni} and gold I_{Au} standards, as functions of electron energy. The intensity ratios for the Ni standard are larger than for the Au standard at all examined energies. The minimum values of the intensity ratio were found at 1500 eV for both Au and Ni standards. Finally, we used the measured elastic-peak intensities for determination of the IMFP values in the surface region of praseodymium.

Fig. 4 and Table 1 show comparison of the EPES IMFPs obtained assuming the Pr surface with the oxygen content taken into account and the oxygen content neglected, and the values resulting from the TPP-2M predictive formula [5] for pure Pr. In addition to these values, Fig. 4 shows the fit to the EPES IMFPs using both Ni and Au standards with the simple function [8]

$$\lambda_{fit} = kE^p \quad (2)$$

where λ_{fit} is the IMFP obtained from the fit (in angstroms), E is the electron energy (in eV) and k and p are the fitted parameters. The resulting values of k and p are 0.1549 and 0.7047, respectively.

The following set of six equations represent the TPP-2M formula [5] for estimating the IMFP, λ , as a function of electron energy and material properties, for each material

$$\lambda = \frac{E}{E_p^2[\beta \ln(\gamma E) - (C/E) + (D/E^2)]} \quad (3a)$$

$$\beta = -0.10 + \frac{0.944}{\sqrt{E_p^2 + E_g^2}} + 0.069\rho^{0.1} \quad (3b)$$

$$\gamma = 0.191\rho^{-0.5} \quad (3c)$$

$$C = 1.97 - 0.91U \quad (3d)$$

$$D = 53.4 - 20.8U \quad (3e)$$

$$U = \frac{N_v\rho}{M} = \frac{E_p^2}{829.4} \quad (3f)$$

where $E_p = 28.8(N_v\rho/M)^{1/2}$ is the free-plasmon energy (in eV), N_v is the number of valence electrons per atom (for elemental solids) or molecule (for compounds), ρ is the density (in g cm⁻³), M is the atomic or molecular weight and E_g is the band-gap energy (in eV). For pristine praseodymium, values of E_g , E_p , and ρ are 0 eV, 18.94 eV and 6.77 g cm⁻³ [18], respectively, and $N_v = 9$ [19].

We see from Fig. 4 and Table 1 that the IMFPs measured using the Au standard are appreciably larger than the corresponding IMFPs measured using the Ni standard. The largest

difference between these values is observed at 500 eV and it is systematically smaller for energies between 500 and 2000 eV.

In order to provide a quantitative description of the fit shown in Fig. 4, both the percentage deviation Δ_j from the fitted function and the mean percentage deviation R from the fitted function were calculated from

$$\Delta_j = \frac{100(\lambda_j - \lambda_{fit})}{\lambda_{fit}} \quad (4)$$

$$R = 100 \frac{1}{r} \sum_{j=1}^r \left| \frac{\lambda_j - \lambda_{fit}}{\lambda_{fit}} \right| \quad (5)$$

where λ_j is a measured IMFP for the Pr_{0.9}O_{0.1} surface at a particular energy, and r is the number of IMFP measurements. Fig. 5 shows the percentage deviations Δ_j between the measured and fitted IMFPs using Eq. (2), as a function of electron energy for the Pr_{0.9}O_{0.1} surface with respect to both Ni and Au standards. The mean percentage deviation R from the fitted function, evaluated from Eq. (5) (12.4%), is also shown in this figure. The smallest Δ_j values for Au and Ni standards were found for electron energies of 2000 eV (+4.6%) and 1000V (-5.5%), respectively, while the largest deviations of -26.6% and +21.8% appear for Ni and Au standards, respectively, at the energy of 500 eV. The value of R (12.4%) was close to the average value of R (13.2%) reported previously [8] for seven elements (Al, Si, Ni, Cu, Ge, Ag and Au). This value can be considered acceptably small, so that the fitted function (Eq. (2)) was generally consistent with the energy dependence of the EPES IMFPs.

To analyze the measured and approximated by Eq. (2) IMFPs for Pr_{0.9}O_{0.1} (solid line

in Fig. 4) and the IMFPs resulting from the TPP-2M predictive formula [5] for Pr (dashed line in Fig. 4), we calculated the percentage deviation Δ_f from

$$\Delta_f = \frac{100(\lambda_{fit} - \lambda_{TPP})}{\lambda_{TPP}} \quad (6)$$

where λ_{TPP} denotes the IMFP value estimated from the TPP-2M equation (Eq. (3)) [5] for praseodymium at a particular electron energy. Energy dependence of this deviations is plotted in Fig. 6. Close inspection of this figure reveal the deviation Δ_f to be below 5% and the largest value of this deviation is equal to 4.2% at the electron energy of 500 eV. The deviations evaluated for energies 1500 and 2000 eV were found to be -0.4% and -2.7%, respectively. Generally, good agreement is found between the measured and approximated by Eq. (2) IMFPs and those predicted from the TPP-2M formula [5]. The EPES results prove the high reliability of this formula for praseodymium.

The IMFPs data for oxygen-containing praseodymium seem to be reliable since they are obtained from measurements involving two standards. The deviation of the measured IMFPs from the predicted IMFPs can be largely ascribed to uncertainties of the TPP-2M predictive formula [5]. One should stress the fact that in derivation of the TPP-2M (Eq. (3)), the IMFP data for elemental solids and organic compounds were used. There is still controversy in determining the parameter N_v for REEs elements [19]. In the present IMFP calculations, we used the recommended value of 9 for praseodymium [19], however, the recommendation for the N_v values may not be of universal validity. Therefore, the change of the N_v value would affect the shape of IMFP energy dependence for praseodymium.

The EPES IMFP values obtained assuming presence of oxygen and neglect of its presence on the surface of praseodymium are compared in Table 1. As can be seen, the differences between the corresponding IMFPs related to clean (oxygen-free) and oxygen-containing Pr surfaces are very low (0.01 - 0.05 nm) for the whole energy range (0.5 - 2 keV) and the largest value of this difference is equal to 2.6%. Therefore, the influence of surface oxygen on the EPES IMFPs for praseodymium can be considered negligibly small.

4. Conclusions

Electron transport in Pr foil samples, pre-sputtered by 3 keV argon ions, was studied using relative EPES measurements with both nickel and gold standards. The surface composition of this material was found to be formed by oxygen-containing praseodymium (up to 10 at.% of oxygen), as detected by XPS-AES analysis.

It was found that EPES, applied without corrections for surface excitations, can be an useful method for determination of reliable IMFPs within the 4 nm – thick surface oxygen-containing layer of Pr. The experimentally determined IMFP values for the $\text{Pr}_{0.90}\text{O}_{0.10}$ surface were well fitted using Eq. (2) with the parameters $k = 0.1549$ and $p = 0.7047$ within the energy range 500 - 2000 eV. Good agreement was found between the fitted EPES IMFPs and the IMFPs obtained from the TPP-2M predictive formula [5]. Experimental IMFPs values were found to be only 2% - 4.2% larger than those estimated from the TPP-2M in the energy range of 500 - 1000 eV. For electron energies of 1500 eV and 2000 eV, we observed an inverse correlation between these values, and then the differences of -0.4% and -2.7%,

This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in Applied Surface Science, copyright © Elsevier Online after peer review. To access the final edited and published work see <https://www.sciencedirect.com/science/article/pii/S0169433216001872> (<https://doi.org/10.1016/j.apsusc.2016.01.150>)

respectively, were calculated. Influence of surface oxygen on the EPES-measured IMFPs for praseodymium was found to be negligibly small for the whole energy range considered.

References

- [1] J. Lucas, P. Lucas, T. Le Mercier, A. Rollat, W. Davenport. Rare Earths, Science, Technology, Production Use, first ed., Elsevier, Amsterdam, Boston, Heidelberg, London, New York, Oxford, Paris, San Diego, San Francisco, Singapore, Sydney, Tokyo, 2015.
- [2] P. C. Dent, Rare earth elements and permanent magnets (invited), J. Appl. Phys. 111 (2012) 07A721-07A726.
- [3] <http://www.marketsandmarkets.com/Market-Reports/rare-earth-metals-market-121495310.html>
- [4] I. Öhrlund, Future Metal Demand from Photovoltaic Cells and Wind Turbines – Investigating the Potential Risk of Disabling a Shift to Renewable Energy Systems, Science and Technology Options Assessment (STOA), European Parliament, 2011.
- [5] S. Tanuma, C. J. Powell, D. R. Penn, Calculations of electron inelastic mean free paths. V. Data for 14 organic compounds over the 50-2000 eV range, Surf. Interface Anal. 21 (1994) 165-176.
- [6] C. J. Powell, A. Jablonski, NIST Electron Inelastic-Mean-Free-Path Database SRD 71, version 1.2, National Institute of Standards and Technology, Gaithersburg, 2010.
- [7] A. Jablonski, Quantification of surface-sensitive electron spectroscopies, Surf. Sci. 603 (2009) 1342-1352.
- [8] C. J. Powell, A. Jablonski, Evaluation of calculated and measured electron inelastic mean

- free paths near solid surfaces, *J. Phys. Chem. Ref. Data* 28 (1999) 19-62.
- [9] A. Jablonski, P. Mrozek, G. Gergely, M. Menyhard, A. Sulyok, The inelastic mean free path of electrons in some semiconductor compounds and metals, *Surf. Interface Anal.* 6 (1984) 291-294.
- [10] A. Jablonski, Determination of the electron inelastic mean free path in solids from the elastic electron backscattering intensity, *Surf. Interface Anal.* 37 (2005) 1035-1044.
- [11] M. Krawczyk, W. Lisowski, J. W. Sobczak, A. Kosiński, A. Jablonski, Elastic-peak electron spectroscopy (EPES) studies of ZnO single crystals, *J. All. Comp.* 590 (2014) 553-556.
- [12] M. Krawczyk, M. Holdynski, W. Lisowski, J. W. Sobczak, A. Jablonski, Electron inelastic mean free paths in cerium dioxide, *Appl. Surf. Sci.* 341 (2015) 196-202.
- [13] A. Jablonski, Determination of surface composition by x-ray photoelectron spectroscopy taking into account elastic photoelectron collisions, *Anal. Sci.* 26 (2010) 155-164.
- [14] K. D. Childs, B. A. Carlson, L. A. LaVanier, J. F. Moulder, D. F. Paul, W. F. Stickle, D. G. Watson, Ed. C. L. Hedberg, *Handbook of Auger Electron Spectroscopy, A Book of Reference Data for Identification and Interpretation in Auger Electron Spectroscopy, Third Edition*, Physical Electronics, Inc., 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344, 1995.
- [15] A. Jablonski, J. Zemek, Remarks on some reference materials for applications in elastic peak electron spectroscopy, *Anal. Sci.* 26 (2010) 239-246.
- [16] A. Jablonski, M. Krawczyk, Determination of the Electron IMFP from Elastic Peak Electron Spectroscopy, Users' Guide, Version 1.0, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, 2014; http://ichf.edu.pl/mcap/software_pl.html;

This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in Applied Surface Science, copyright © Elsevier Online after peer review. To access the final edited and published work see <https://www.sciencedirect.com/science/article/pii/S0169433216001872> (<https://doi.org/10.1016/j.apsusc.2016.01.150>)

http://ichf.edu.pl/mcap/software_en.html.

- [17] A. Jablonski, C. J. Powell, Information depth and the mean escape depth in Auger electron spectroscopy and x-ray photoelectron spectroscopy, *J. Vac. Sci. Technol. A* 21 (2003) 274-283.
- [18] W. M. Haynes, *CRC Handbook of Chemistry and Physics*, 91st ed., CRC Press, Boca Raton-London-New York, 2010.
- [19] S. Tanuma, C. J. Powell, D. R. Penn, Calculations of electron inelastic mean free paths (IMFPs). VII. Reliability of the TPP-2M IMFP predictive equation, *Surf. Interface Anal.* 35 (2003) 268-275.

Figure captions

Fig. 1. (color online). Survey XPS spectrum of the sputter-cleaned (2 keV Ar⁺ ions, 5 min) praseodymium specimen.

Fig. 2. (color online). The AES spectrum of the sputter-cleaned (3 keV Ar⁺ ions, 5 min) praseodymium specimen.

Fig. 3. (color online). Energy dependence of the measured elastic-peak intensity ratios, I_{Pr}/I_{Ni} (full circles), I_{Pr}/I_{Au} (full triangles), recorded from oxygen-containing praseodymium, nickel and gold surfaces. $\alpha_{in} = 0^\circ$, $\alpha_{out} = 60^\circ$ measured from the surface normal.

Fig. 4. (color online). Energy dependence of the IMFP determined using nickel and gold standards for the Pr_{0.9}O_{0.1} surface. For comparison, the IMFP from the TPP-2M formula [5] for Pr is shown. Symbols: the EPES IMFPs; solid line: the fitted function (Eq. (2) with the parameter values shown in text) to EPES IMFPs; dashed solid: the IMFPs predicted from the TPP-2M formula [5] for Pr.

Fig. 5. (color online). Percentage deviations Δ_j of the measured IMFPs from the function (Eq. (2)) fitted to these IMFPs (solid line in Fig. 4) as a function of electron energy for the $\text{Pr}_{0.9}\text{O}_{0.1}$ surface. The symbols (■, ▲) indicate the deviations obtained using nickel and gold standards, respectively. The solid line indicates zero deviation.

Fig. 6. Percentage deviations Δ_f of the measured and approximated by Eq. (2) IMFPs for $\text{Pr}_{0.9}\text{O}_{0.1}$ from the TPP-2M IMFPs (dashed line in Fig. 4) for Pr as a function of electron energy. The solid line indicates zero deviation.

Table 1. Values (in angstroms) of the EPES IMFPs determined using nickel and gold standards for both $\text{Pr}_{0.9}\text{O}_{0.1}$ and Pr surfaces, and the IMFPs estimated from the TPP-2M formula (Eq. (3)) [5] for Pr.

E (eV)	Surface composition				
	Oxygen content taken into account		Oxygen content neglected		
	EPES (Ni)	EPES (Au)	EPES (Ni)	EPES (Au)	TPP-2M
500	9.1	15.1	9.0	14.9	11.9
700	14.4	18.6	14.3	19.0	15.1
1000	19.0	23.1	19.5	23.6	19.7

This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in Applied Surface Science, copyright © Elsevier Online after peer review. To access the final edited and published work see <https://www.sciencedirect.com/science/article/pii/S0169433216001872> (<https://doi.org/10.1016/j.apsusc.2016.01.150>)

1500	24.9	28.8	25.2	28.6	26.9
2000	29.6	34.3	29.5	34.5	33.7

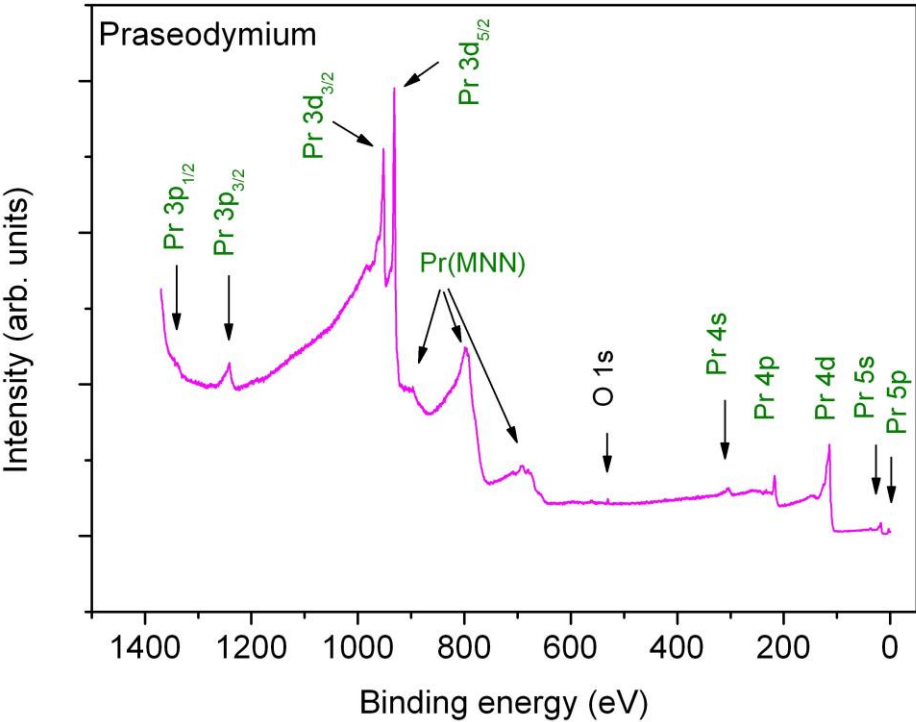


Fig.1.

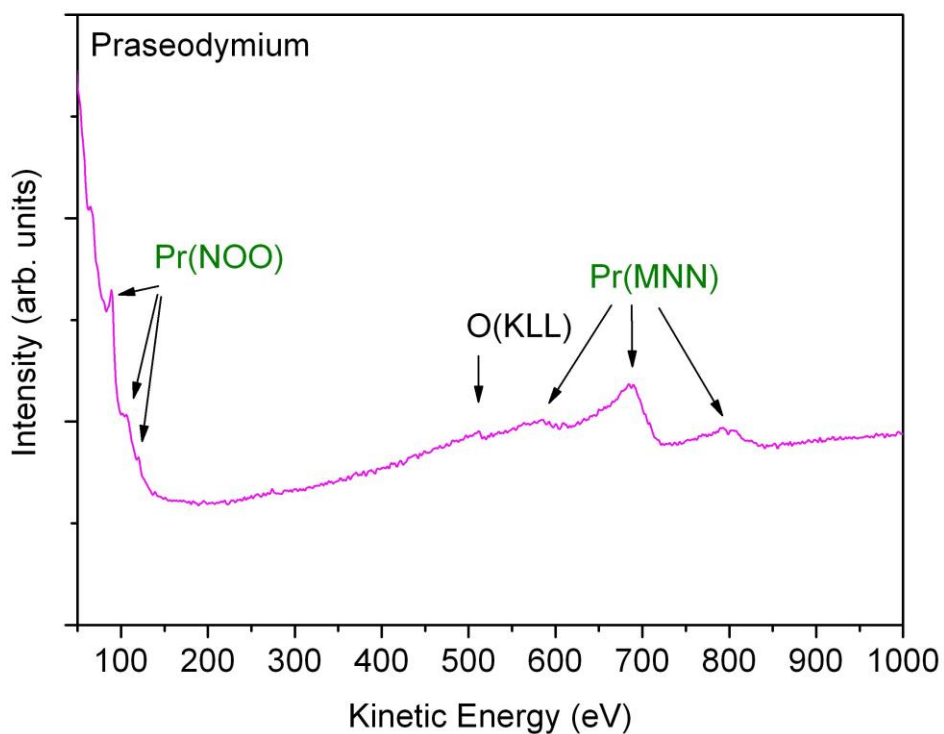
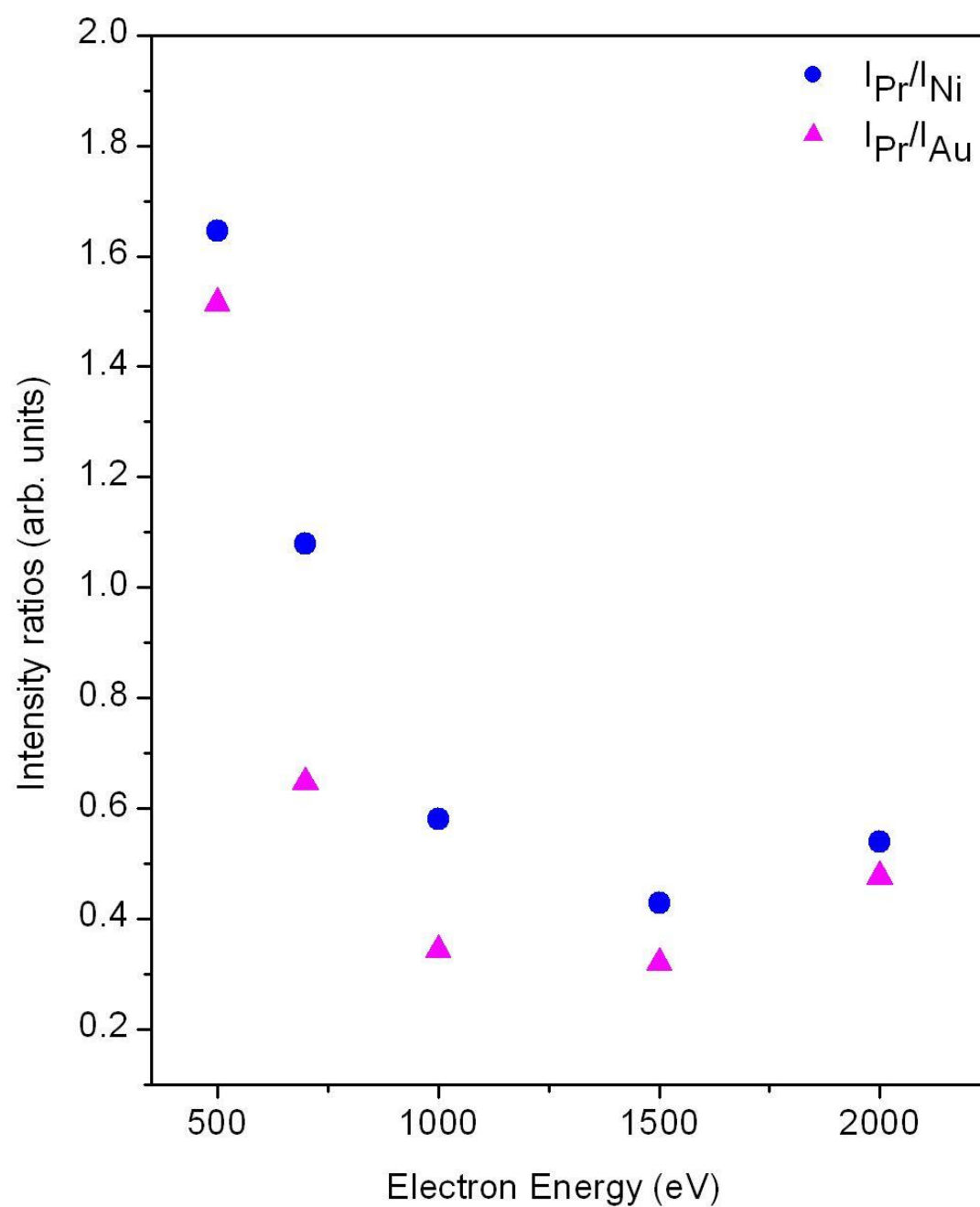


Fig.2.



This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in Applied Surface Science, copyright © Elsevier Online after peer review. To access the final edited and published work see <https://www.sciencedirect.com/science/article/pii/S0169433216001872> (<https://doi.org/10.1016/j.apsusc.2016.01.150>)

Fig.3.

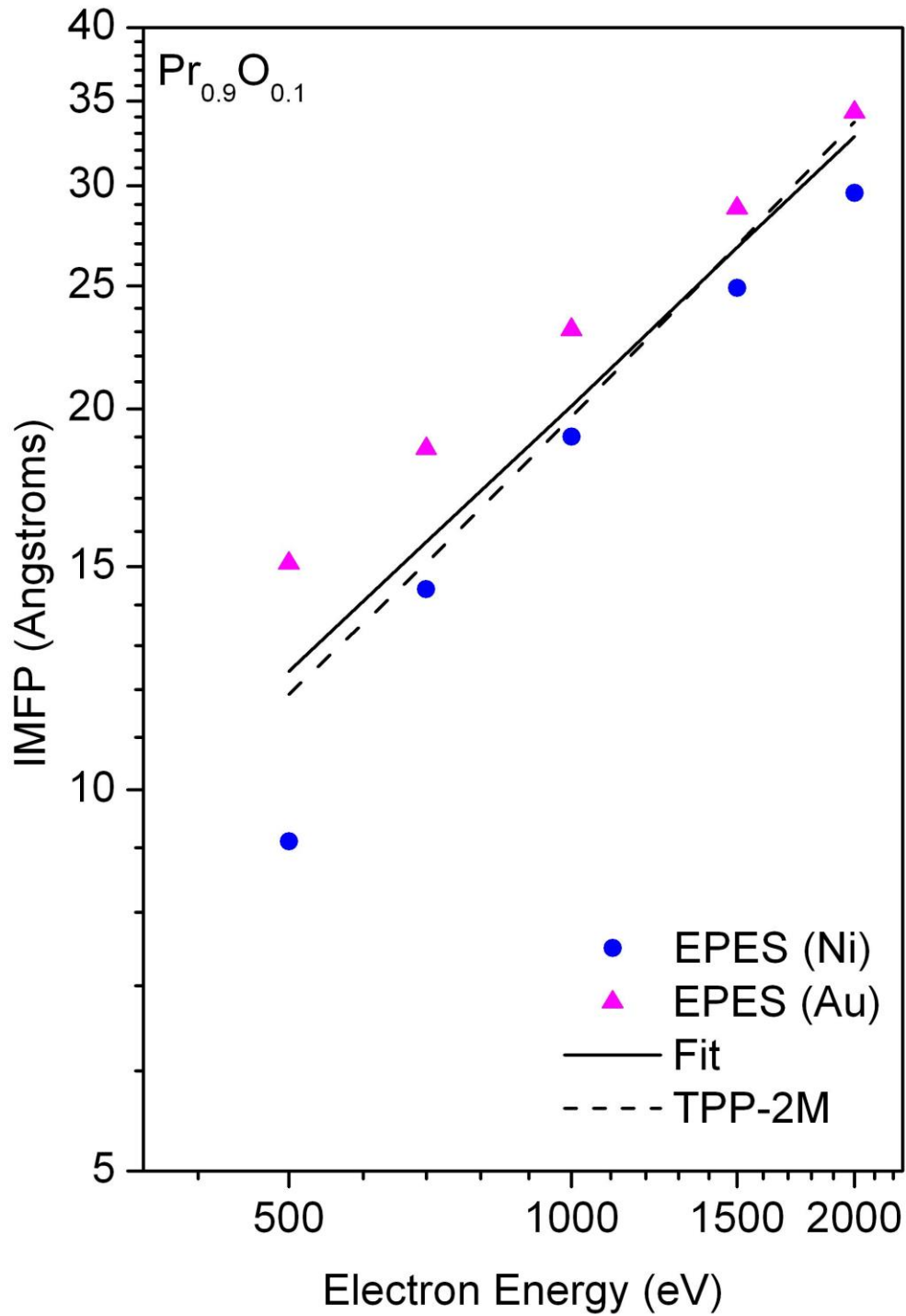


Fig.4.

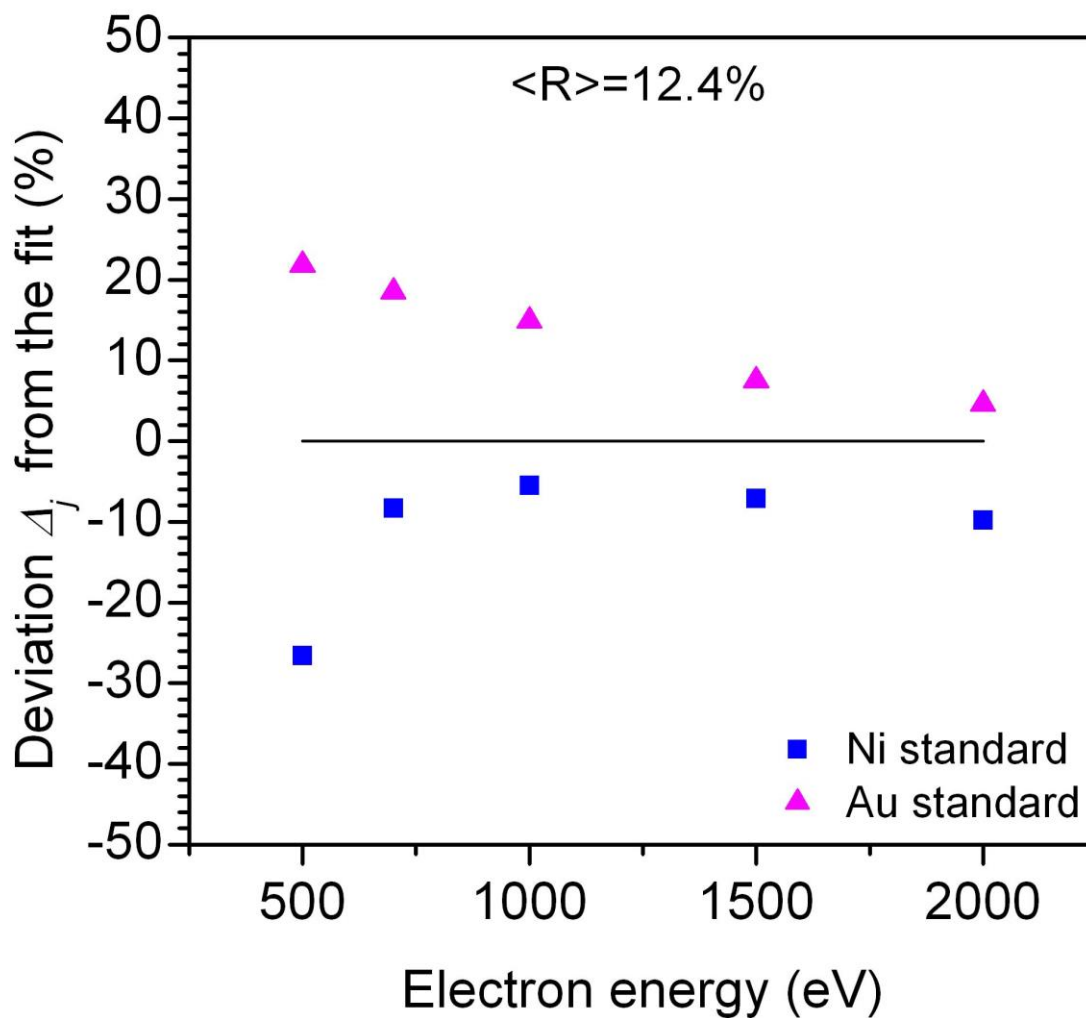


Fig.5.

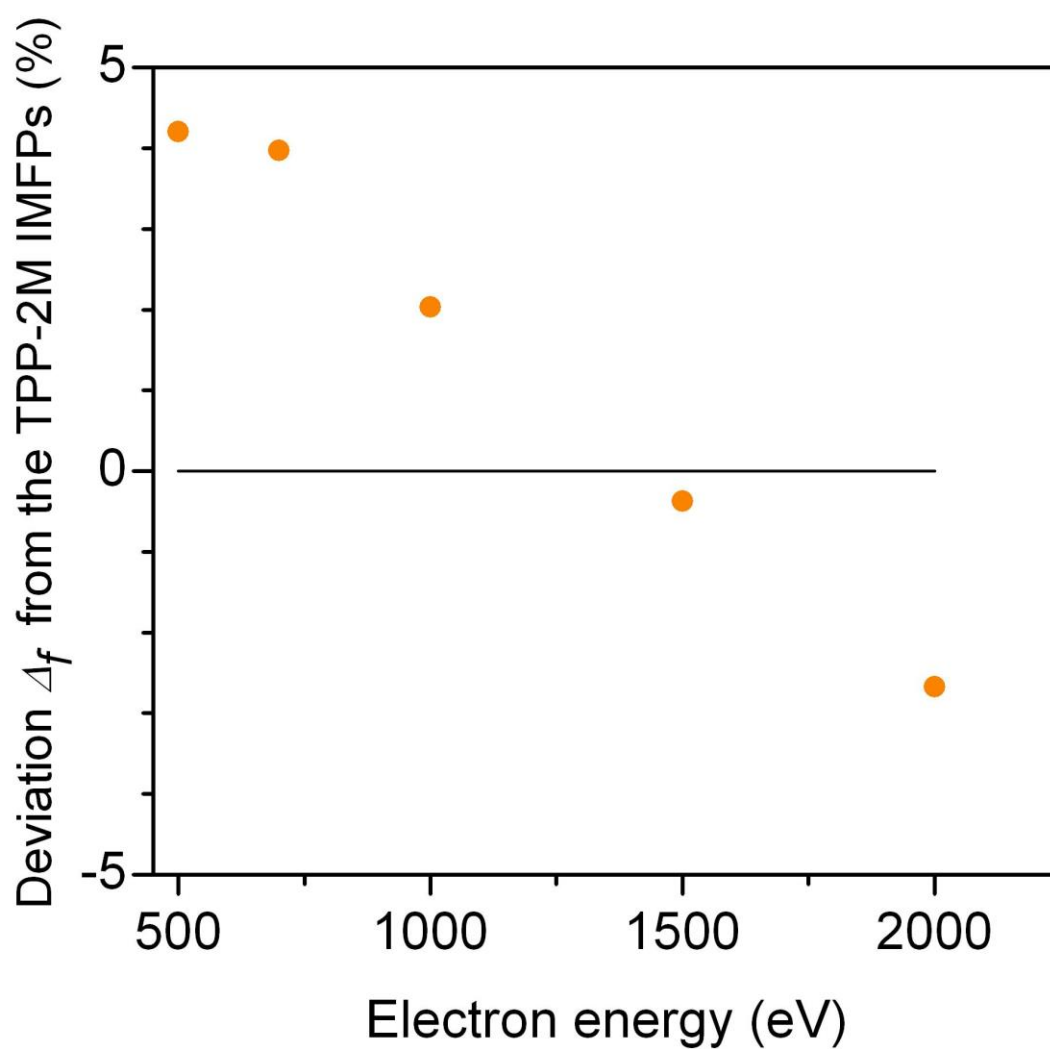


Fig.6.