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## Surface studies of praseodymium by electron spectroscopies

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### 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,  $\lambda$ , 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.

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### 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 disk 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.

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## 2. Experimental

### 2.1. Samples

Small pieces (5 mm × 5 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 $\alpha$  radiation. The spectrometer was equipped with a spherical capacitor energy analyzer with multi-channel detection with a 100  $\mu$ m × 100  $\mu$ m 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<sub>3/2</sub>, Pr 3p<sub>1/2</sub>) 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 mm × 2 mm surface area; a maximal ion current of 1.1  $\mu$ A) for 5 min. The Ar<sup>+</sup> sputtering rate was 7 nm/min, as measured using a SiO<sub>2</sub>/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<sup>+</sup> ions rastered over a 3 mm × 3 mm surface area for 5 min at an incidence angle of 30° with respect to surface normal. A maximal ion current was about 1.3  $\mu$ A.

### 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

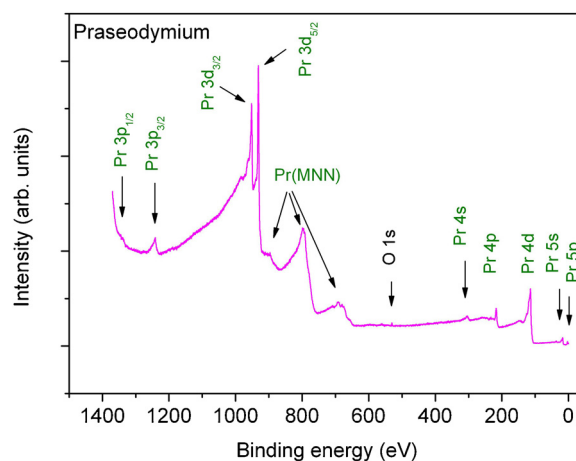


Fig. 1. Survey XPS spectrum of the sputter-cleaned (2 keV Ar<sup>+</sup> ions, 5 min) praseodymium specimen.

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