

The electronic state of cerium in two palladium alloys by energy loss spectroscopy

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1. Introduction

Early work on the Pd-Ce system [1] showed that there is a significant range of solid solution of cerium in palladium despite the large size factor in the system. Lattice spacing and magnetic susceptibility measurement indicated that the cerium atoms are in a 4-valent state in the solid solution alloys but the valence decreases towards 3.0 in the ordered, Cu₃Au type Pd₃Ce compound [1, 2]. Subsequent work [3] showed that large range ordering occurred at the Pd₇Ce composition (Pt₇Cu type super lattice) and this alloy underwent an order-disorder transition on heating to 735±6°C. The present work was undertaken to see if the proposed different valence state for Ce in Pd₇Ce and Pd₃Ce could be detected by energy loss spectroscopy in the TEM.

2. Experiment

The palladium (99.98%) used in the present work was kindly loaned by Johnson Matthey and Co. Ltd. The Pd₃Ce and Pd₇Ce alloys were prepared by argon arc melting and then air-cooling to room temperature after the alloys had been heat treated at 1000°C for a week for homogenization. The specimens for transmission electron microscopy were prepared by conventional mechanical polishing followed by ion beam milling (GATAN PIPS) for a short time to electron transparency. In order to collect standard spectra of 3-valent Ce and 4-valent Ce, we used CePO₄.xH₂O (59.4% Ce) and CeO₂ powder (99.9%) from Strem Chemicals. The purity was given as 99.9%. The measurement was performed with a Gatan666 Digital PEELS spectrometer attached to a FEI Tecnai F20 Schottky field emission gun transmission electron microscope operating at 200 keV, which offers an energy resolution of 0.8–0.9 eV. The spectra were corrected for dark current, readout noise and channel-to-channel gain variation.

3. Results and discussion

For Ce the core-loss edges include the O_{2,3}, O₁, N_{4,5}, N_{2,3}, N₁, M_{4,5}, M_{2,3} and M₁ edges. Of these, the M_{4,5} edge is best suited for studying Ce because it exhibits distinct valence-specific shapes which are separated in energy. The M₅ and M₄ edges arise from the two ways in which the spin quantum number, *s*, couples to the orbital angular momentum, *l*, giving a total angular momentum, *j*=*l*+*s*. This coupling gives two peaks; M₅ from the 3d_{5/2} (*j*=5/2) level and M₄ from the 3d_{3/2} (*j*=3/2) level. The M_{4,5} edges reflect transitions of 3d core electrons to unoccupied states of p- and f-like symmetry. The sharp M₅ and M₄ peaks near the edge onsets arise from quasiautomatic, dipole-allowed transitions from an initial 3d¹⁰4f^{*n*} state to final states of the form 3d⁹4f^{*n*+1}[5]. The transitions mask the much weaker 3d→p edge. The edge shapes are also little affected by the crystal field and other bonding effects.

The Ce M_{4,5} edges of CeO₂ have shapes characteristic of Ce⁴⁺ and distinct from those of the Ce³⁺ in CePO₄.xH₂O (Fig.1). The Ce⁴⁺ M₅ and M₄ edges are separated by 17 eV and consist of two

main symmetrical maxima at 884 and 901eV followed by lower intensity, broader maxima Y and Y' at 889 and 906eV. The main M_5 and M_4 maxima of CeO_2 result from transitions from an atomic-like f^0 ground-state configuration [4]. The Y and Y' maxima also occur in other rare-earth dioxides and are thought to originate from transitions to 4f states in the conduction band [5]. Finazzi et al. [6] refer to Y and Y' as the f^0 satellites and relate their intensities to the degree of delocalization of the f-electrons. The Ce^{3+} $M_{4,5}$ edge shapes, intensities, and energies differ from those of Ce^{4+} . The Ce^{3+} M_4 edge has a weak peak, E, at 896eV.

From Fig. 2, we see that the Ce spectrum from $CePd_3$ behaves more like 3-valent Ce: we can clearly see the small edge just before the main M_4 edge. The spectrum from $CePd_7$ indicates a nearly 4 valent state for the Ce atoms. Since the intensity ratio M_5/M_4 is sensitive to the valence state of Ce, we intend in the future to determine the exact valence of Ce via the M_5/M_4 ratio.

4. Conclusion

PEELS is suitable for the analysis of the oxidation state of Ce using the Ce $M_{4,5}$ edges. The Ce atom in $CePd_7$ alloy is close to 4-valent Ce because of the strong hybridization of the 4f state of Ce with the 4d state of Pd. The Ce atom in $CePd_3$ behaves more like 3-valent Ce since the Ce spectrum looks very like the Ce spectrum from $CePO_4 \cdot xH_2O$.

Reference

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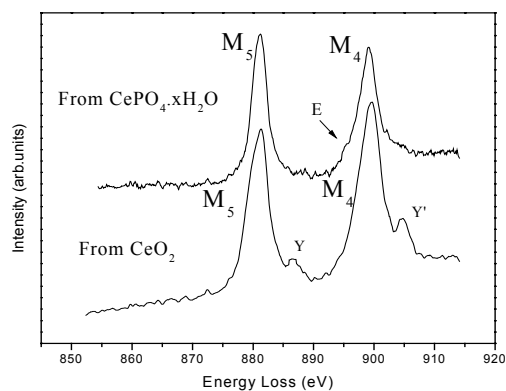


Fig.1. Ce $M_{4,5}$ edges of Ce^{4+} and Ce^{3+} from CeO_2 and $CePO_4 \cdot xH_2O$.

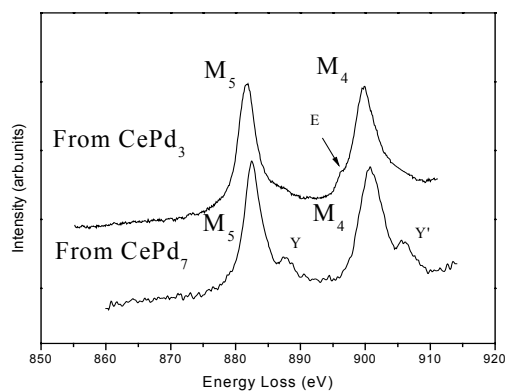


Fig.2. Ce $M_{4,5}$ edges from $CePd_3$ and $CePd_7$.