

X-ray Absorption Near-Edge Spectroscopy of the P *K*-edge of Transition-Metal Phosphides M_2P

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Introduction

First-row transition-metal phosphides, M_2P (where $M = Cr$ to Ni) form an important class of materials having diverse magnetic properties and that crystallize in three closely related structures: hexagonal Fe_2P -type ($M = Fe, Mn, Ni$), orthorhombic Co_2P -type ($M = Co$), and tetragonal Cr_2P -type ($M = Cr$) [1,2]. They have been found to exhibit potential catalytic activity in hydrosulphurization and hydronitrogenation processes [3]. The

electronic structure of metal phosphides has not been well studied, but trends in the bonding character have recently been deduced in the related MP series [4,5]. The shifts in the P *K*-edge absorption energy of several M_2P compounds are discussed herein, and distinctive features in selected P *K*-edge XANES spectra are highlighted.

Experimental

Cr_2P , Mn_2P , Fe_2P , Co_2P , and Ni_2P were prepared by stoichiometric reaction of the elements at 1050 °C over 7 days, and their identities were confirmed by powder X-ray diffraction patterns collected on an Inel powder diffractometer.

Total X-ray fluorescence yield (FLY) P *K*-edge spectra were measured from 20 eV below the edge to 40 eV above the edge at 0.1 eV per step on the SGM beamline. The spectra were calibrated against a sample of $Na_2P_2O_7$, with the P *K*-edge peak maximum set to 2152.4 eV [6]. All edge energy values reported herein were located from the maximum of the first-derivative peak, which removes the influence of high-energy surface phosphates. A precision of ± 0.1 eV was estimated. A dark current correction was applied to each FLY spectrum.

Results and Discussion

Figure 1 shows P *K*-edge XANES spectra for several M_2P compounds. Peak A represents the P *K*-edge absorption energy, arising from the excitation of an electron from the 1s orbital to a nonbonding 3p orbital in P. Figure 2 shows a plot of the P *K*-edge absorption energy versus the difference in electronegativity (ΔX) between P and M for several M_2P compounds. As is the case for MP (whose energies [4] are also plotted in Figure 2 for comparison), the absorption energy decreases with increasing, consistent with an increase in ionic character in the M–P bond from Ni_2P to Cr_2P . Each P atom is surrounded by nine M atoms in M_2P , in contrast to only six M atoms in MP . Because the positively charged M atoms poorly screen the nuclear charge, the absorption energy should

be increased in the case of M_2P . However, the absence of P–P bonding in M_2P , in contrast to MP , should lead to greater ionic character in the M–P bond. The net result of these competing effects is that the P *K*-edge absorption energies are similar in M_2P and MP for a given M.

A second peak (B) observed above the P *K*-edge is apparent in each of the spectra (Figure 1). This may arise from phosphates formed at the surface, or from a multiple-scattering resonance (MSR) process similar to that observed in other nickel phosphides [7]. Consistent with expectations, as the M–P bond length increases in the isostructural series Mn_2P , Fe_2P , and Ni_2P , the difference in absorption energy between P *K*-edge peaks A and B diminishes.

The P *K*-edge XANES spectrum of Fe_2P reveals a pre-edge peak (C) just below the onset of the edge. This pre-edge peak arises from mixing of the P 3p and M 3d states with unoccupied states. Pre-edge peaks have been observed in P and S *K*-edge XANES spectra for phosphates and sulphates [8].

Conclusion

The decrease in P *K*-edge absorption energy from Ni_2P to Cr_2P indicates an enhancement of ionic character in the M–P bond. However, increased screening by the greater number of M atoms in M_2P and the absence of P–P bonding result in absorption energies that are nearly similar to the MP counterparts. Features such as MSR and pre-edge peaks were clearly visible, indicating that spectra can be obtained on the SGM beamline of high quality beyond its design range.

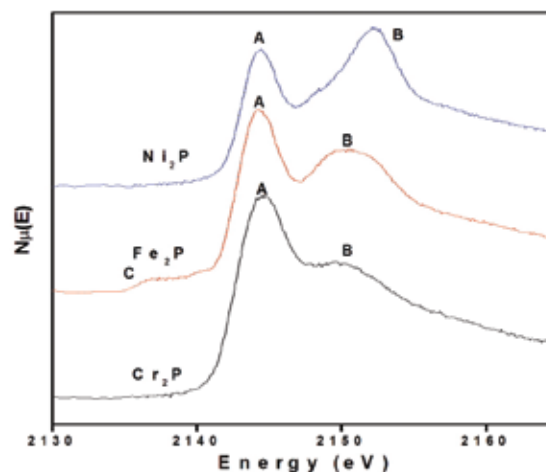


Figure 1. Representative P *K*-edge XANES spectra collected on the SGM beamline.

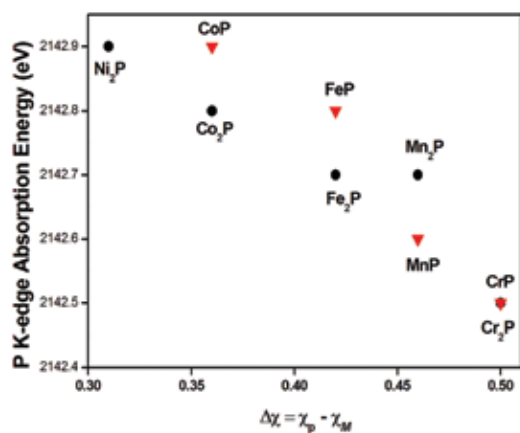


Figure 2. Plot of P K-edge absorption energies versus difference in electronegativity between P and M in M_2P and MP compounds. P K-edge absorption energies for MP were taken from reference 5.

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