

Cs L-Edge EXAFS Atomic Absorption Background

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Abstract

X-ray absorption coefficient of Cs in the energy region of L edges has been measured on a 1 : 9 alloy of Cs and Na at room temperature. The absorption spectrum is virtually free of the structural signal. EXAFS oscillations are visible only in a ~ 70 eV wide interval immediately above the edges. The short range of the signal is attributed to a strong disorder of the alloy introduced by the complete miscibility of the constituents and the large difference of their metal radii. The spectral regions above three L-edges exhibit the same pattern of sharp multielectron photoexcitation features involving electrons from outer subshells 6s to 4p as in the adjacent element xenon. The segment above the L_3 edge can be used as the atomic absorption background for the standard EXAFS structural analysis of Cs compounds.

1. Introduction

X-ray atomic absorption can be measured either directly on a monatomic gas sample [1–5] of an element or derived from an X-ray absorption spectrum of a compound sample after removal of the structural signal [6–10]. The tiny sharp features on the smooth energy dependence of the photoabsorption cross section are fingerprints of multielectron photoexcitations (MPE). These weak processes arise from the inter-electron interactions in the target atom.

The atomic absorption spectrum is a very good approximation to the atomic absorption background (AAB) in the XAFS structural analysis of a substance containing the target element. Since the structural signal and MPE occupy the same spectral region above a major absorption edge, their interference, if unrecognized, impedes the interpretation of the structural signal leading to errors in the structure parameters determined in the XAFS analysis [8, 9].

For Cs, only the most prominent resonant MPE feature has been extracted from the L-edge EXAFS spectra of amorphous materials containing Cs [11–13]. Complete atomic Cs L-edge absorption has not been determined: apparently, an experimentally demanding and costly heat-pipe cell [4] would be required. In a substitute experiment we measured Cs absorption on a thin layer of Cs/Na alloy expecting to remove the weak EXAFS signal numerically. Surprisingly, the experiment showed that the strong disorder in the alloy produces a practically pure Cs atomic absorption spectrum almost without an EXAFS component.

To assess the purity of the measured AAB a comparison with older absorption data on gaseous Xe [2] can be used. Recent studies in K-edge absorption of noble-gas/alkali-metal neighbor pairs Ar/K and Kr/Rb [4, 5] have proven that the MPE features in a pair differ only in details while following the same overall pattern.

2. Experiment

Cs/Na alloy with a concentration ratio of 1 : 9 was prepared. A small amount of the alloy was placed, together with a drop of paraffin oil to prevent oxidation, into a small lucite container between two kapton foils and squeezed into a thin layer. The container and the oil kept the metal perfectly stable for several hours of the experiment: no sign of oxidation was observed after demounting. The stability of the sample was confirmed also by the perfect reproducibility of the scans that were recorded in sequence at each of the L subshell edges.

The absorption experiment was performed at the E4 station of the DORIS ring at HASYLAB synchrotron facility, DESY (Hamburg, Germany). The beamline provides a focused beam from Au-coated mirror and a Si(111) double-crystal monochromator with 0.8 eV resolution at the Cs L_3 -edge. Harmonics are effectively eliminated by a plane Au coated mirror and by detuning the monochromator crystal using a stabilization feedback control. Exact energy calibration was established with a simultaneous measurement on a Ti metal foil ($E_K = 4966$ eV) between the second and the third ionization cell.

3. Results

A compound picture of the L edges (Fig. 1) is obtained as a superposition of three scans per subshell region. Each of the edges is preceded by a resonance due to the excitation of the 2p or 2s electron to the unoccupied bound states just below the continuum.

The spectra above each of the edges are remarkably flat, almost without oscillatory EXAFS signal characteristic of solid

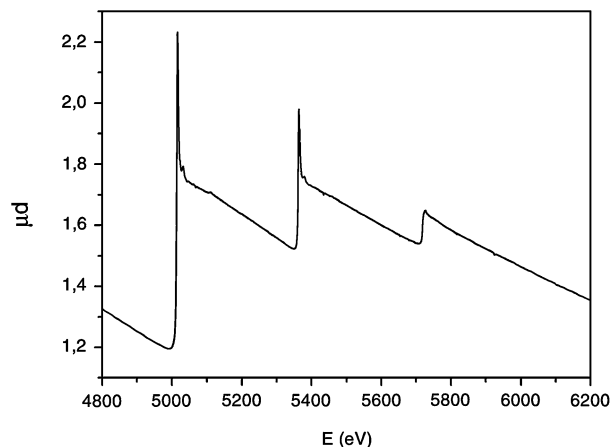


Fig. 1. The L-edge absorption spectrum of Cs measured on a thin layer of the Na/Cs alloy.

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samples. A slight convexity of the spectrum above the L_3 and L_2 edge, observed already in the L absorption spectra of some heavy elements, has been explained as a consequence of subshell polarization [14].

The strongest of the sharp MPE features are just barely visible in the spectrum. To expose the details, the average trend of each subshell region is removed from the relative cross section (Fig. 2). Several groups of MPE can be clearly discerned above each absorption edge. The groups can be identified by their energy as multiple excitations involving electrons in consecutively deeper subshells from $6s$ to $4p$, in complete analogy with the MPE groups in the neighboring Xe [2], shown below. Hartree-Fock estimates [15] of the threshold energies of the corresponding double excitations are indicated by arrows.

Even at this level of magnification the oscillatory structural signal is visible only close to the edge. The amplitude of EXAFS oscillations is smaller than the MPE features and vanishes in the noise level about 70 eV above each edge. A more definite estimate of the EXAFS amplitude and range can be obtained from the comparison with the absorption spectrum of the cooled

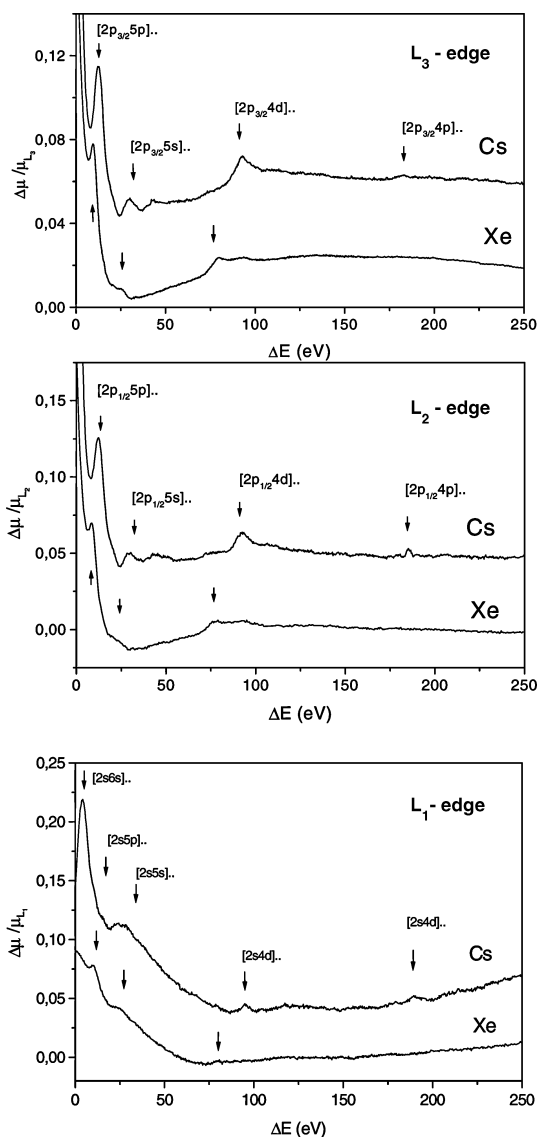


Fig. 2. The comparison of the absorption in the L subshell regions of Cs and Xe after removal of the average trend to enhance the detail. Theoretical estimates of the energy of double excited states are shown by arrows. For each subshell, the origin of the energy scale is shifted to the respective ionization threshold.

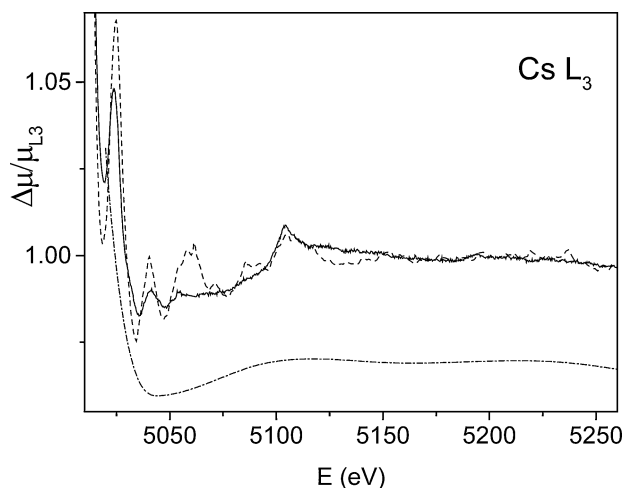


Fig. 3. The comparison of Cs/Na alloy L_3 absorption spectra at room temperature (solid line) and at liquid nitrogen temperature (dashed line). Note the contraction of the structural signal so that the atomic absorption is clearly exposed in the room-temperature spectrum from 70 eV above the edge on. Below, a standard spline background of the liquid-nitrogen spectrum is shown, shifted for -0.03 for clarity.

sample (Fig. 3). It shows that only the first two periods of the structural signal are retained in the room-temperature spectrum, further oscillations being suppressed by the Debye-Waller factor.

Incidentally, the comparison in Fig. 3 also illustrates the importance of using the proper AAB in the analysis of a weak structural signal. The XAFS and MPE are so intimately intertwined even in the low-temperature spectrum that the separation by the standard approach of the spline background constructed from the lowermost Fourier components cannot be reliable. The AAB extracted from the room-temperature spectrum, on the other hand, reproduces fully also the sharp non-structural features of the signal, as e.g. the $[2p4d]$ edge and resonance at 5105 eV.

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