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Determination of s and d contributions to the $L_{2,3}$ extended x-ray absorption fine structure*

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An analysis of the extended x-ray absorption fine structure (EXAFS) on the $L_{2,3}$ edges of Au shows significant contributions from both the d- and s-symmetric final states. The contribution to the EXAFS of the final s states relative to the final d states decreases as the energy increases past the edge. Local structure can be determined by Fourier transforming L-edge EXAFS data, similar to the case of the K edge.

A renewal of interest in extended x-ray absorption fine structure (EXAFS) has occurred because of the realization that quantitative information on the short-range environment around each type of atom, separately, can be obtained by an appropriate Fourier transformation of the K-edge data.[1-4]

The EXAFS of K edges has become reasonably understood in recent years.[2-7] Applying similar concepts, L-edge theories have been proposed.[5,8,9] Previous studies[10] of the L edges of materials have shown that the EXAFS is dependent on the symmetry of the initial state. These differences are qualitatively understood since the initial state in the L_1 edge has s symmetry and therefore can make only a dipole transition to p-symmetric final states, while the initial states in the $L_{2,3}$ edges have p symmetry, and can have both s- and d-symmetric final states. In earlier studies it was incorrectly assumed for the $L_{2,3}$ edges that the transition to the d final states dominated the observed structure.[8,9] We show for the first time that by use of Fourier-transform techniques it is possible to experimentally determine not only structural information as in the case of the K edges, but also the ratio of the s to d contributions in the $L_{2,3}$ edges as a function of energy above the edge.

Figure 1(a) illustrates the $L_{1,2,3}$ edges absorption spectra for a 2.5 μm thick gold foil. Data were obtained at 120 °K on the Stanford Synchrotron Radiation Project EXAFS spectrometer.[11] Similar results have also been obtained on a more conventional apparatus by Lytle.[10]

When the edge structure is omitted and the EXAFS separated from the smoothly varying background and normalized,[4] the L_3-edge results $\chi(k)$ for gold are illustrated in Fig. 1(b) (over its energy range the L_2-edge EXAFS is identical). Fourier transforms of $k^n\chi(k)$, $n=0, 1, 2, 3$ with respect to the photoelectron wave number k give peaks which can be interpreted in terms of the structure in the vicinity of the type of atom whose EXAFS is being studied.[2,3] The magnitude of the $k^1\chi(k)$ transformed data from Fig. 1(b) over the range in k space of 3.8–20.8 Å^{-1} is shown in Fig. 2(a). In Fig. 2(a) note that the transform is dominated by two peaks at about 2.7 and 2.4 Å and that the peaks to the right of the main peaks arising from the other coordination shells are also doubled with a roughly similar ratio of the smaller peak to the larger peak and with the same relative positioning. Other transforms weighted by different powers of k produced similar results but with different relative amplitudes of paired peaks which we develop later as evidence of a differing k dependence for the probability of making transitions to final s- or d-symmetric states. Contrast Fig. 2(a) with the $k^1\chi(k)$ transform of the K edge of metallic Cu shown in Fig. 2(b) where there is no evidence of double peaks at each lattice position. Note that both Au and Cu are fcc with interatomic spacings of Au-Au = 2.884 Å and Cu-Cu = 2.556 Å. Thus the transforms should be similar. The Cu peaks are broader because the EXAFS drop off more rapidly at high energy because of the smaller nuclear charge of Cu. There is a small (10%) side-lobe structure symmetric to each peak which is a natural consequence of the finite EXAFS transform. This undulation is clearly seen on the low-r side of the main Cu peak. This same structure is present in the Au transform and produces the shoulders on the two largest peaks of interest here. Once the effect is recognized as an unavoidable artifact of the transform it need not be confusing.

We interpret these results with arguments similar to those used in explaining the EXAFS of K edges. For polycrystalline samples, neglecting multiple scattering between atoms and assuming $kR_j \gg 1$, the EXAFS, $\chi(k)$, will be of the form

$$\chi(k)=[\mu_s(k)\chi_s(k)+\mu_d(k)\chi_d(k)]\,[\mu_s(k)+\mu_d(k)]^{-1}\,, \tag{1}$$

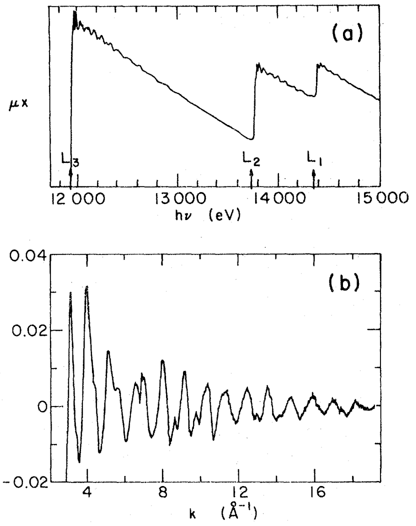

FIG. 1. (a) X-ray absorption μx (x is the sample thickness of 2.5μm) vs x-ray energy for Au at 120°K, in the vicinity of the L edges. The arrows show the expected positions of each L edge according to the tabulated values of Bearden and Burr (Ref. 12). (b) The L_3 EXAFS of Au, χ, vs k, the photoelectron wave number, normalized as described in Ref. 4.

where

$$\chi_l(k) = \sum_j A_j(k)\sin[2kR_j + 2\delta_l(k)],$$

$$A_j(k) = \frac{m}{4\pi\hbar^2 k}\,\frac{N_j t_j(2k)}{R_j^2}\, e^{-R_j/\lambda}\, e^{-2\sigma_j^2 k^2},$$

and l is either s or d. The sum is over shells containing N_j atoms at a distance R_j from the absorbing atom. $t_j(2k)$ is the magnitude of the backscattering from the jth atom, λ is the mean free path for electron-electron scattering and other inelastic processes, σ_j^2 is the mean square relative displacement between the absorbing atom and the atoms in the jth shell, and δ_l is a phase shift of the electron which will be discussed below. In contrast to the K edge, $\chi(k)$ for the $L_{2,3}$ edges has two contributions, one for the final d state, χ_d, and the other for the final s state, χ_s, each weighted by its respective $\mu_l(k)$.

The major difference between χ_d and χ_s comes from the phase shifts δ_s and δ_d in the sine function which are introduced to the excited photoelectron wave function as it both interacts with the excited atom and scatters from the surrounding atoms. In general the phase shift introduced by the excited atom will be different for the s and d states; however, the scattering of both the s and d waves from the surrounding atoms will be similar since they will have, throughout most of the range of EXAFS, wavelengths small compared to the interatomic spacing.

We have shown that the effect of this phase shift on the Fourier transform of the EXAFS is to shift all of the peaks to smaller r by an amount $|\alpha_l|$, where α_l is approximately the average derivative of δ_l over the k-space range of the transform.[3] The peaks may also be skewed a small amount by a nonlinear behavior of δ_l as a function of k. The double peak behavior shown in Fig. 2(a) is caused by the difference between α_d and α_s in gold. By comparing the positions from the transforms of EXAFS with the known positions of the atoms in gold it is possible to determine that $|\alpha_s| = 0.48$ Å and $|\alpha_d| = 0.13$ Å. The relative values for α are consistent with the calculations by Lee and Pendry[5] on Cu and by us on Ta which showed that the slopes of phase shifts decreased with increasing angular momentum l. We associate the large and small peaks with d and s final states, respectively, because of the phase shifts and because theoretically the d contribution is expected to be larger.

A theoretical estimate of $\bar{\mu}_d/\bar{\mu}_s$, the average relative contribution of s and d to the EXAFS follows. The dipole matrix element can be divided into contributions from separable angular and radial portions. The ratio of the d to s angular portions of the square of the dipole matrix element is 2. Since the peaks in r space are obtained by integrating over all available k space, the ratio of the radial parts is roughly given by

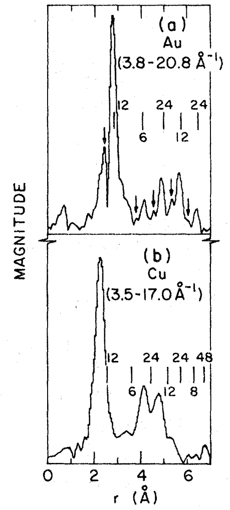

FIG. 2. (a) Magnitude of the $k^1\chi(k)$ Fourier transform of the data from Fig. 1(b) over the range $3.8 < k < 20.8$ Å^{-1}. The lines and numbers across the middle of the figure denote the positions and coordination numbers in metallic gold. The arrows indicate the s peaks. (b) The magnitude of the $k^1\chi(k)$ Fourier transform of Cu K-edges EXAFS over the range $3.5 < k < 17.0$ Å^{-1}. Coordination numbers and positions are indicated as in (a). In Cu the peaks are shifted 0.22 Å by the phase shift.

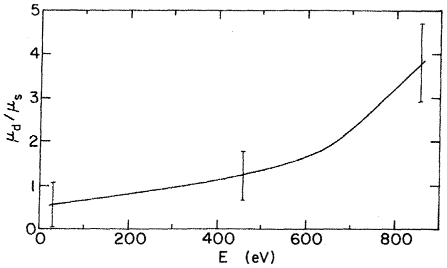

FIG. 3. μ_d/μ_s vs photon energy above the edge. The error bars are estimates of the uncertainty introduced by the measurement and analysis.

$$\sum_d |\langle\beta_d|r|p\rangle|^2 \Big/ \sum_s |\langle\beta_s|r|p\rangle|^2,$$

where β_s and β_d are unoccupied final states of s and d symmetry, respectively. If we change the sum to be over all states of the same final angular momentum, not just the unoccupied ones, and use the fact that both β_s and β_d are complete sets,[13] the ratio of the radial parts becomes $\langle p|r^2|p\rangle/\langle p|r^2|p\rangle = 1$. Thus we find approximately $\mu_d/\mu_s \approx 2$ as the ratio of the d peak to the s peak in the Fourier transform of $\chi(k)$, in rough agreement with the result of 2.5 of Fig. 2. When the transform is weighted by k^n, $n=0,1,2,3$, the effect is to weight the higher k values of $\chi(k)$, giving in effect the nth moment of $\chi(k)$. We have used this effect to evaluate the k dependence of μ_d/μ_s. The values at the peaks in the 1st shell in r space are then proportional to the nth moment of the functions

$$\frac{\mu_s(k)A_1(k)}{\mu_s(k)+\mu_d(k)} \text{ and } \frac{\mu_d(k)A_1(k)}{\mu_s(k)+\mu_d(k)},$$

integrated over the range 3.8–20.8 Å^{-1} for the s and d final states, respectively. By assuming a polynomial expansion of these functions in k it is straightforward to determine the coefficients of this expansion by requiring that they give the measured moments. As can be seen above, the ratio of these functions is equal to μ_d/μ_s. The results are plotted versus k in Fig. 3. Note that the final s state dominates at low k while at higher k the final d state dominates. This low-k behavior is consistent with the expectation that in Au the angular momentum barrier will repel d states.

In summary, by Fourier transforming the EXAFS of the L_3 edges of Au the contributions of the final d and s states were separately discerned for the first time, and the ratio μ_d/μ_s was obtained from the data as shown in Fig. 3. Contrary to what was believed previously, the s contribution is not negligible. The phase shifts of the final s and d states are different with an average slope over the range of the transform in k space of $\alpha_d = 0.13$ Å and $\alpha_s = 0.48$ Å. Similar results have been obtained for W, Ta, and Pt and will be presented elsewhere. The discussion here indicates that in Eq. (1) we have the basic understanding of EXAFS at L edges, and can obtain information about the short-range order structure about atoms in condensed matter similar to the case for the K-edge data.

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[13] We are indebted to Professor R. E. Peierls for suggesting this argument.