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THE MAGNITUDE AND EXTENDED ENERGY RANGE OF X-RAY K-ABSORPTION
FINE STRUCTURE FOR Ti, Fe, Co, Ni, Cu and Zn

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Other results of current interest are multiple excitation processes which involve inner and outer shell electrons. Double excitation is observed in the absorption fine structure of Ne, Ar and Kr²⁰⁻²³ and occurs with a probability of 21% per photo-absorption event for Ar K α excitation.²¹ Peaks which occur 21.8 eV and 33.8 eV above the initial K-excitation peak (i.e., $1s \rightarrow 4p$)²² are due to the respective double excitation of $1s$ and $3p$ (i.e., $KM_{II} III$) and $1s$ and $3s$ (i.e., KM_I)²⁰ electrons. Theoretical explanations of double excitation, excitation plus ionization (i.e., shakeup) and double ionization (i.e., shakeoff) suggest that they result due to the localized ionization potential created by the deep K-shell hole.²⁴⁻²⁸ The probability of exciting outer shell electrons (i.e. $3d$ and $4s$ electrons to regions of d-like or s-like symmetry, since $\Delta L = 0, \pm 2$) is $\approx 25\%$ for a metal such as iron, based on previous calculations.²¹ Shakeup and shakeoff processes may be responsible for narrow (e.g., d-like) peaks which we will show occur at energies greater than the $1s$ ionization energy, $E_F + 10$ eV, associated with the transition metals.¹⁰

We hope that our detailed measurements of the magnitude and extent of fine structure for six pure transition metals will inspire calculations such as those undertaken by Bagus²⁹ whose inclusion of dipole transitions between Hartree-Fock states has enabled a nearly-complete semi-quantitative interpretation of the argon K-absorption spectrum.⁹ He observes that many electron matrix elements are often larger than those obtained using the one-electron approximation. This may account for the as yet unexplained high continuum slope just above the argon K-edge^{9,22,30} which we will report occurs also for the iron-group transition metals with an argon-like core of inner-shell electrons. Whether obtained as a result of emission or absorption spectroscopy, direct measurements, appropriately identified, for: (1) the mode of decay and final configuration resulting from atomic readjustment to inner shell vacancies;²² (2) multiplet splittings in core-level peaks;³¹ (3) rearrangement energies and relaxation times;^{32,33} (4) quasi-stationary bound states;^{5,24,34,35} or (5) collective oscillations of free electrons in a solid³⁶⁻³⁹ provide valuable information for evaluating the methods and approximations used by theoreticians.

II. EXPERIMENTAL PROCEDURES AND RESULTS

Previous qualitative experimental results exist of x-ray K-absorption fine structure for the iron-group metals.^{7,9,14-19,35,39-45} High resolution double-crystal spectrometers have revealed details in the vicinity of their respective K-absorption edges. However, experimental K-edge energies (i.e. those which refer to the onset of allowed transitions to unoccupied levels for ejected $1s$ electrons) indicate differences which depend on the experimental measurements and methods used. For Iron, discrepancies as large as 2.4 eV exist between corrected x-ray values and those obtained from electron spectroscopy.⁴⁶ This discrepancy is inconsistent with the estimated experimental errors of each of the high resolution systems. We, for reasons of convenience, avoid this issue by relating all energy measurements to the centroids of tungsten L emission lines, the values of which were obtained from Bearden.⁴⁷ For consistency, we use Bearden's value based on x-ray measurements (i.e. 7111.2 eV) rather than the more recent values based on electron or soft x-ray appearance potential spectroscopy for the Iron K-edge. The reader may make reasonable adjustments for the location of peaks relative to the values which we have selected, in recognition of the above discrepancies.

Our experimental measurements of fine structure for titanium, iron, cobalt, nickel, copper and zinc were taken with a micro-focus x-ray generator that provided a source of continuous radiation from 1 to 45 keV. A single (LIF) crystal spectrometer with narrow slits produced a monoenergetic x-ray beam that was detected with a flow proportional counter (i.e. 90 percent argon with a mixture of 10 percent methane) as shown in Figure 1. The measured resolution was ~ 7 eV at 7 keV with a few exceptions which will be noted accordingly. The centroids of emission lines due to impurities on the Ag target (e.g. Fe, Ni, Cu and W)⁴⁷ provided both a convenient means of locating the positions of fine structure peaks (see Figure 2) and of measuring the system resolution. Published values for the corrected line widths were available based on precise, high-resolution, double-crystal measurements.⁴⁸ The system resolution

- g — X-Ray Generator**
- t — Ag Target**
- c — Soller Slit Collimators**
- m — Monitor Assembly**
- a — Absorber Foil**
- d — Detector**
- s1,s3 — Scatter Slits**
- s2 — Defining Slit**
- s4 — Acceptance Slit**

FIGURE 1. The single crystal spectrometer.

FIGURE 2. The diffracted spectrum from 7-8 keV.

was obtained by subtracting in quadrature the true width from the measured width assuming a Gaussian distribution for the measured line shapes. The true line shapes are Lorentzian. However, for lines which appear nearly symmetric (e.g. $W L\beta_1$) the upper half of the measured peak is not very different from that of a Gaussian, due to the convolution of the true line shape with the instrumental response of the experimental system.

A motorized gear system controlled changes in θ and 2θ , the respective incident and Bragg diffracted angles. A precise crystal oscillator furnished periodic signals which allowed the motor to advance one turn (thus changing the 2θ angle .003 degrees), and the system to accumulate the desired number of counts during a predetermined interval. After repeating this process several times the total accumulated counts were then stored (e.g. every 2 eV as shown in Figure 2) in successive channels of a multichannel analyzer. The continuous scans were taken at intervals which varied from sixteen hours to several days depending on whether or not the filter was in the x-ray beam. The incident beam was continuously monitored. Counting times were selected to obtain optimum counting statistics according to the methods discussed by Nordfors.⁴⁹ Corrections were made for dead time counting losses. These corrections, though for the most part less than 1 percent, varied in the vicinity of $W L$ emission lines where in a few instances they were as high as 5 percent. In these instances, some of the data were deleted.

The data shown in Figures 3 and 4 were taken in the manner discussed above. The energy scale was established on the basis of $W L$ lines observed in the first and second order. The latter was used to align the system for the Ti measurements, after which second order effects were removed by lowering the target voltage. The data were taken first with no filter in the beam and repeated with the filter in position for the same range of energies. Monitor counts were compared to check the incident beam stability. Precise measurements were taken at selected energies, in a manner to be described below, and used to

make corrections for dead time, trace impurities and background effects which varied with energy in the region of fine structure. These measurements are indicated by the open circles in Figures 3, 4 and 5. The continuous scans were taken from ~ 100 eV below to ~ 900 eV above the respective x-ray K-absorption edges of the elements Ti, Co, Ni, Cu, and Zn at intervals of ~ 5 eV. The data for Fe shown in Figure 3 were taken at intervals of ~ 2 eV. The narrow slit used for the above measurements provided a system resolution which varied from less than 5 eV at the Ti K-edge to about 12 eV at the Zn K-edge. The experimental values other than our present measurements were obtained from the experimental compilation by McMaster et al.⁵⁰⁻⁵⁷ reviewed recently by Hubbell.⁵⁸

Measurements of the attenuation coefficient, μ_{TOTAL} , are straightforward. The ratio of the transmitted to incident x-ray flux (represented by I and I_0 respectively) obeys the simple classical absorption equation whereby the x-ray beam is attenuated exponentially. It follows that:

$$\mu_{\text{TOTAL}} = -\frac{1}{\rho x} \log_e \frac{I}{I_0}$$

where ρ is the density and x is the thickness of the foil to be measured.

The theoretical values given in Figures 3 and 4 were based on self-consistent relativistic Hartree-Fock-Slater central potential models for the atomic photoeffect,^{1,2} reviewed recently by R. H. Pratt.³ A small scattering contribution was added (i.e. less than 1 percent, based on calculations by Cromer)² for purposes of comparison with the experimental data. The dotted line represents a least squares fit to the log of the total attenuation coefficient, $\log \mu_{\text{TOTAL}}$ versus $\log E$ where E represents the incident photon energy. Data taken below the edge were extrapolated to the edge energy⁴⁷ and taken in a manner described below, with thicker samples. The dashed line represents the theoretical atomic behavior based on one-electron transitions.^{1,2} This agrees to 3 percent or better with our experimental data at higher energies, which were >1 keV above the K-edge (e.g., 15 keV).

THEORY		EXPERIMENTAL DATA	
◆ SCOTFIELD	△ DEL GRANDE, OLIVER	△ DALTON, GOLDBAR	○ MORSE, WOODHOUSE
◆ STORM COMPILATION	▽ DESLATTES	× CARTER et al.	□ EMMENHOFER, DOROS
	◆ BOH, WENRICH	● McMASTER COMPILATION	◆ DOCKINS

FIGURE 3. The behavior of total attenuation coefficients above the respective K-edges of titanium, iron, and cobalt, at 297°K.

FIGURE 4. The behavior of total attenuation coefficients above the respective K-edges of nickel, copper and zinc at 297°K.

The energy scale is adjusted in Figure 5 to show the similarities of the fine structure for fcc Co, Ni and Cu which have respective lattice constants: 3.545 Å, 3.524 Å and 3.615 Å.⁵⁹ The spacings between maxima and minima are inversely proportional to the square of the lattice constant, a feature of many proposed models^{6-9,24,35} which agrees with our experimental results. We note that the energy scale was expanded roughly 5 percent in order to line up the peaks of Cu with those of Ni and Co, since the latter two have smaller lattice constants.

The values of the total attenuation coefficients, μ_{TOTAL} , were measured to ± 1 percent at selected energies known to ± 0.5 eV. The electronic block diagram (see Figure 6) describes the procedure used for these point calibrations. Methods discussed by Nordfors⁴⁹ were used to measure backgrounds (which involved rocking the crystal) and obtain optimum statistics. The sample ρx values were respectively: 2.72, 4.53, 7.18, 5.41, 4.70 and 6.21 milligrams per cm^2 for measurements taken above the K-edge of Ti, Fe, Co, Ni, Cu and Zn. Measurements taken below the edge were made with longer counting intervals and with thicker samples. The value of ρx , the weight per unit area, was measured to ± 0.4 percent. The sample uniformity was checked by making separate measurements at various positions. Corrections for trace impurities (which included measurements for both high Z elements and surface oxides) were in all cases less than 1 percent for the regions above the K-absorption edge. Dead time corrections were kept below 1 percent by adjusting the counting rates. External errors were calculated from the mean value determined from about twenty pairs of consecutive measurements with the filter inserted in and out of the beam. These were compared with the statistical value and the larger of the two was combined in quadrature with other uncertainties generated from the corrections and measurements mentioned above. In all cases, the resulting total error was less than 1 percent.

FIGURE 5. The fine structure behavior for face centered cubic metals cobalt, nickel and copper from the data taken by Del Grande and Oliver. The energy scale for copper is expanded about 5 percent to line up the peaks.

Electronic Block Diagram

FIGURE 6. A block diagram describing the electronic system used to obtain precise attenuation coefficients at selected energies.

The diffractometer was carefully aligned at a prominent peak (e.g. the $W\text{ }L_{\alpha_1}$ line). Adjustments in θ and 2θ were made using an iterative process which optimized the peak counting rate and located the position of the centroid. Fine adjustments could be made in the position of the receiver slit. The precision of the energy measurements relative to the $W\text{ }L_{\alpha_1}$ line (i.e. 8.3976 keV)⁴⁷ was ± 0.5 eV. This was determined by taking repeated measurements of μ_{TOTAL} at critical energies (e.g. on the rise of the Fe K-edge and in the vicinity of the absorption peak at 7.2208 keV) under different conditions, at different times, with different slits, different sample thicknesses, different crystals and a separate spectrometer. The errors in μ_{TOTAL} for the Fe data shown in Figures 7 through 9 were ± 1 percent as discussed above.

A Gaussian fitting procedure was used to locate centroids for the overlapping peaks in Figure 8. The first five peaks for Fe had a corrected F.W.H.M. value: $\Gamma \approx 3.2 \pm 0.5$ eV and occurred at 7.1238 keV, 7.1315 keV, 7.1439 keV, 7.1516 keV, and 7.1592 keV with respective areas which were 5%, 21%, 10%, 27%, and 18% of the largest peak. The following three peaks had a corrected F.W.H.M. value: $\Gamma \approx 13 \pm 1$ eV and occurred at 7.1683 keV, 7.1938 keV, and 7.2208 keV with respective relative areas which were 40%, 50%, and 100%. The area of the major peak was 112 barn-keV, as shown in Figure 8. The total attenuation coefficients at 7.221 keV based on the extrapolated results from previous experiments⁵⁰ and the calculations of Scofield¹ are respectively: $400\text{ cm}^2/\text{g}$ and $398\text{ cm}^2/\text{g}$, when a small theoretical scattering contribution² is added to the theoretical atomic photoeffect value. The peak height from our present measurement after corrections are made for the system resolution is $488 \pm 2\text{ cm}^2/\text{g}$.

The 7.221 keV peak was considered in detail, using two different slits (i.e. .106mm and .245mm). The peak height was $\sim 2\%$ higher for the narrow slit, where the system resolution was 6.9 eV, than for the wider slit where the system resolution was 11 eV. To test for a thickness effect, three sample thicknesses: $.00453\text{ g/cm}^2$, $.0109\text{ g/cm}^2$ and $.0150\text{ g/cm}^2$ were measured with respective μ_{TOTAL} values: $478 \pm 2\text{ cm}^2/\text{g}$,

FIGURE 7. The measured and corrected behavior of total attenuation coefficients for body centered cubic iron at 297°K using a narrow slit system with a F.W.H.M. of 6.9 eV at 7.221 keV.

FIGURE 8. Fine structure peak locations relative to 7.1112 keV for iron at 297°K. Iterative procedures were used to unfold overlapping Gaussian peaks and corrections were made for the system resolution.

FIGURE 9. A series of overlapping Gaussian peaks which empirically fits the fine structure behavior for Iron at 297°K as predicted by Hayasi.³⁵ Corrections for the wide slit system resolution with a F.W.H.M. of 11 eV at 7.221 keV will reduce the peak widths to 13 eV.

$481 \pm 5 \text{ cm}^2/\text{g}$ and $506 \pm 31 \text{ cm}^2/\text{g}$ at 7.221 keV. Corrections were made for backgrounds but not for resolution. The results were the same within error limits. The narrow slit was used for these measurements and the measured background corrections⁴⁹ varied respectively: $(0.7 \pm 0.1)\%$, $(5.7 \pm 1.0)\%$, and $(22 \pm 6.1)\%$. We did not observe a thickness effect⁶⁰ under the above circumstances. The data in Figure 9 were measured using the wide slit, and corrections were not made for the system resolution, which would sharpen the overlapping peaks at 7.363 keV from about 11% to about 15%.

III. SUMMARY AND CONCLUSIONS

We have shown a systematic high continuum slope in the behavior of total x-ray cross sections at energies approaching the K-absorption edge from the high energy side for six metals: Ti, Fe, Co, Ni, Cu and Zn. The experimental cross sections are on the average $\sim 10\%$ higher than the one-electron calculations as shown in Figures 3 and 4. The theoretical calculations were obtained numerically beginning with relativistic Hartree-Fock-Slater screened central potentials. At higher energies greater than 1 keV above the K-edge our experimental data agrees to 3% or better and has the same energy dependence as given by the calculations.^{1,2} The details of this comparison will be published elsewhere, and agree with the conclusions of Pratt.³

The 10% discrepancy between theory and experiment for six of the iron-group metals indicates a breakdown in the suitability of one-electron approximations near the K-absorption edge. Many-electron effects associated with atomic rearrangement have contributed as much as 30% to the dipole length form of the transition matrix element²⁹ (e.g., for the $1s\text{-hole} \rightarrow 3p\text{-hole}$ transition of Ar^+). For metals however, the calculations are less complete. Nozières attributes K-edge singularities to the scattering of conduction electrons by the attractive transient potential of the deep lying core hole. Unfortunately, he

discards a multiplicative constant, presumed to have no physical significance (i.e. see Equations 64 through 66 of Reference 27), which would determine the enhancement associated with this effect.²⁸

Fine structure undulations above the Fe K-absorption edge were fit to $\pm 1/2\%$ by overlapping Gaussian peaks with narrow (corrected) widths: $\Gamma = 3.2 \pm 0.5$ eV within 50 eV of the K-edge and broader (corrected) widths: $\Gamma = 13 \pm 1$ eV from 50 eV to 600 eV above the K-edge, which is identified with the Fermi energy. Recent energy band calculations locate the bottom of the d-band, the Fermi energy, and the top of the d-band at respective energies: ~ 14 eV, ~ 10 eV and ~ 9 eV below the "vacuum" level (i.e. the energy necessary to remove the 1s electron from the atom in a gaseous phase) for bcc Fe as shown in Figure 14 of Reference 10.

We note that the details of absorption fine structure undulations provide a means by which we may: (1) determine the final configuration resulting from atomic readjustment to inner shell vacancies; (2) investigate atomic rearrangement energies, relaxation times, core level splittings and atomic core relaxation processes; (3) observe excitations of inner and outer shell electrons (e.g. double excitation, excitation plus ionization or double ionization of 1s and 3d or 4s electrons) due to shakeoff processes; (4) locate an upward shift of the Fermi energy for fcc Co, Ni and Cu relative to the bottom of the d-band due to increased occupation and compare with the results of recent APW calculations; (5) evaluate the relative merits of conflicting explanations for the origin of the extended fine structure: one which considers it to result from partial scattering of the ejected electron by neighboring atoms in the crystal lattice^{7,8} and the other which considers a positive ion produced by electron shakeoff to exist for about 10^{-15} sec and provide extra bound states for the ejected electron,²⁴ which is otherwise trapped in the vicinity of the absorbing atom; (6) investigate the possibility of quasi-stationary bound states (e.g. exciton states); and (7) determine the importance of collective oscillations (e.g. plasma oscillations) of free electrons in a solid.

A detailed evaluation of the above models as they relate to our experimental data is beyond the scope of the present paper. We expect however, that further investigations of the striking similarities and small differences in the behavior of the extended fine structure for fcc metals Co, Ni and Cu, and of the detailed location of peaks for bcc Fe, will clarify our understanding of the electronic structure of matter.

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