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Gamma spectra resulting from the annihilation of positrons with electrons in single, selected core levels of Cu, Ag, and Au

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Abstract

The γ -ray energy spectra due to positron annihilation with the 3p core-level of Cu, the 4p core-level of Ag, and 5p core level of Au were obtained separately from the total annihilation spectrum by measuring the energies of γ -rays time coincident with Auger electrons emitted as a result of filling the core-hole left by annihilation. The results of these measurements are compared to the total annihilation spectra and with LDA based theoretical calculations. A comparison of area normalized momentum distributions with the individual cores extracted from the Doppler measurements shows good qualitative agreement, however, in all three spectra, the calculated values of the momentum density appears to fall below the measured values as the momentum increases. The discrepancies between theory and experiment are well outside the statistical uncertainties of the experiment and become more pronounced with increasing Z going down the column from Cu to Ag to Au. The comparison with the experimental results clearly indicates that the calculations are not predicting the correct ratio of high momentum to low momentum spectral weight and suggest the need to improve the treatment of many body electron-positron correlation effects in annihilation as they pertain to core levels.

Introduction

Spectroscopies based upon the detection and analysis of the γ -rays emitted when a positron becomes trapped and annihilates in a defect are among the most sensitive probes of open volume or charged defects in metals and semiconductors.[1-3]. In addition, the tendency of positrons to become trapped at open volumes in polymers, at surfaces, at interfaces and within nano-particles has allowed positron-annihilation spectroscopy to be used as a highly selective probe of these systems [4-7]. The contributions to the Doppler-broadened annihilation spectra due to core electrons has become a subject of increased interest as the result of recent applications of the coincidence Doppler broadening (CDB) technique that have demonstrated that it possible to identify the elements in the vicinity of the positron at the time of annihilation [3,8] from a chemically distinct spectral signature in the region of the spectra with large Doppler shifts due to annihilation with the fast moving core electrons. In CDB two Ge detectors are used to measure both the red and blue shifted annihilation γ -rays in coincidence. The use of two detectors in coincidence has made it feasible to extract a statistically significant core annihilation contribution from the background resulting from the large valence contribution [9]. The CDB technique has been extensively applied in studies of vacancy-impurity complexes [1-3] and quantum-dot nano-particles and nano-precipitates [5-7].

In order to be confident in the elemental identification made from coincidence-Doppler technique it is important to understand the spectral contributions of the

annihilation with core electrons in detail. However the core contributions constitute only a small fraction of the total spectrum due to the fact that, typically, more than 90% of the annihilation events occur with the valence electrons due to the repulsion of positron from the positive core. This makes it impossible, using only γ -detection, to uniquely identify the core contributions to the spectra. Recently, Eshed et al. reported the first measurements of the Doppler-broadened γ -ray energy spectra associated with the annihilation of a positron with single selected core levels of Cu and Ag.[10] using a new technique in which γ -rays are detected in coincidence with Auger electrons. In this paper we report research expanding on this previous work and report new data on the Doppler-broadened γ -ray energy spectra associated with the annihilation of a positron with the core levels of Au. The core annihilation spectra for Au is compared to data obtained for Cu and Ag and to LDA based calculations of the core momentum densities. We also present a detailed discussion of the experimental system used in the γ -Auger coincidence measurements and the methods used in extracting in the pair momentum densities from the Doppler broadened γ -spectra together with details of the model calculations of the projected 1-D pair momentum densities.

The experimental measurements of the annihilation γ -spectra for individual core levels reported in this paper provide a stringent test of theoretical calculations of core annihilation momentum distributions, and a guide to the construction of improved descriptions of the electron-positron correlation effects as they pertain to annihilation with core electrons. The addition of the Au data to that obtained for Cu and Ag has allowed us to both confirm that the LDA based theory does not adequately account for

the ratio of high momentum to low momentum spectral weight in the extracted momentum densities and to establish that the disagreement between theory and experiment becomes larger with increasing Z . Attempts to improve upon the agreement using currently available higher order approximation schemes did not yield positive results. Possible reasons for the disagreement between theory and experiment are discussed. In addition, the experimental method for separating out the core contribution to annihilation spectra, described in detail in this paper, can be applied in other types of momentum measurements including Angular Correlation of Annihilation Radiation (ACAR) and to study the effects of adsorbates and reduced coordination on the core level momentum densities of atoms at the surface.

Background

Positrons in solids annihilate predominantly into two γ -rays. In the center of mass frame these γ -rays are emitted equal in energy and opposite in propagation direction. In the laboratory frame, the center of mass motion of the positron-electron pair results in a Doppler shift of magnitude, $(P_L c)/2$, yielding energies, $E_{\gamma 1}$ and $E_{\gamma 2}$ for the two annihilation γ -rays:

$$\begin{aligned}
 E_{\gamma 1} &= m_0 c^2 - E_B/2 + (P_L c)/2 \\
 E_{\gamma 2} &= m_0 c^2 - E_B/2 - (P_L c)/2
 \end{aligned}
 \tag{1}$$

Where m_0 is the rest mass of the electron (positron), c is the speed of light, E_B is the binding energy of the electron, and P_L is the component of the center of mass momentum of the electron-positron pair along the direction of the γ -ray emission.

Equation 1 can be inverted to obtain the momentum of the electron-positron pair at the time of annihilation in the direction of the HPGe γ -detector[15-17]

$$\mathbf{P}_L = \frac{2E_{\gamma_i} - 2\mathbf{m}_0\mathbf{c}^2 + E_B}{\mathbf{c}} \quad (2).$$

As a consequence, a histogram of the energy of detected annihilation γ 's can be used to obtain a one-dimensional projection of the momentum distribution of annihilating electron-positron pairs. This distribution can be modeled by appropriate two dimensional integration of a calculated momentum distribution given by:

$$\rho(\mathbf{p}) = \pi r_0^2 c \sum_i \left| \int d\mathbf{r} e^{i\mathbf{p}\cdot\mathbf{r}} \Psi_+(\mathbf{r}) \Psi_{-,i}(\mathbf{r}) \sqrt{\Gamma_i(\mathbf{r})} \right|^2 \quad (3)$$

where r_0 is the classical electron radius, \mathbf{p} is the total momentum of the annihilation pair and $\Psi_+(\mathbf{r})$ is the positron wave function, $\Psi_{-,i}(\mathbf{r})$ is the wave function for the i^{th} electron and $\sqrt{\Gamma_i(\mathbf{p},\mathbf{r})}$ is a weighting function that models “enhancement” i.e. electron-positron correlation affects which lead to an annihilation rate higher than that predicted in the independent particle approximation [11].

Calculations of the annihilation γ -spectra with sufficient accuracy to extract chemical information in positron defect studies require detailed understanding of the enhancement factor, $\Gamma(\mathbf{p},\mathbf{r})$, for core levels. Conventional measurements (including those using γ - γ coincidence techniques [3,8,9]) probe the total momentum density of the system including both core and valence electrons. In modeling this data, Eq. 3 must be summed over all occupied electron states. Thus conventional spectra must be

compared with calculations of sums of individual level momentum densities weighted by momentum dependent enhancement factors that introduce uncertainties that seriously limit the reliability of the comparison.

The γ -spectra of individual core levels obtained using the γ -Auger technique make it possible to compare the measured and model momentum distributions term by term and provide a unique means to test theoretical efforts to go beyond the local density approximation (LDA), (which can be expected to break down for the core levels because of their wide range of momenta and large electron density gradients [12]), such as the generalized gradient approximation (GGA) [13] and explicitly non-local treatments [12] such as the weighted density approximation (WDA). In addition, the γ -Auger coincidence measurements provide the only means available, to date, of measuring the low momentum part of the annihilation spectra for cores (the low momentum contribution of the cores is swamped by the low momentum contribution of the valence band in the total annihilation spectrum). The measurement of the low momentum part of the spectra of the cores makes it possible, for the first time, to determine the ratio of the high momentum to low momentum contributions providing a test of attempts to model the momentum dependence of Γ [14].

Experimental

The method of selecting γ -rays associated with the annihilation with individual core levels relies on the fact that annihilation with a core electron results in an energetic core hole which can decay via the almost simultaneous emission of an Auger electron

whose energy is characteristic of the core level [15,16]. For the outer core levels (the levels of most relevance to Doppler broadening measurements) almost all of core hole excitations decay via an Auger process[17,18], typically a core-valence-valence Auger process, in which one valence electron carries off the energy made available when another valence electron fills the core-hole left by annihilation. Previous measurements have demonstrated that it is possible to detect annihilation induced Auger electrons with high efficiency and with an energy resolution sufficient to infer the energy-level of the initial core hole.[15,16] As a result, γ -spectra associated with positron annihilation with electrons in a particular core level can be obtained by measuring the energies of γ 's detected in coincidence with annihilation-induced Auger electrons of the appropriate energy.

The γ -Auger coincidence data were collected using a magnetically guided positron beam system described previously [19]. The measurements were performed using a positron beam energy of 12 eV and a flux of $\sim 2 \times 10^4$ positrons/second. The beam system is equipped with a trochoidal energy analyzer which is used for Positron annihilation induced Auger spectroscopy, an ion-sputter gun and a conventional electron stimulated Auger system (PHI – 1100) (the later two systems are operated with the magnetic field of the positron beam turned off). The previous configuration of the beam system was augmented with the addition of a HPGe detector (ORTEC-GEM-30185P, 58.6mm diam. x 54.8mm, relative efficiency 32% at 1.33 MeV), which was mounted perpendicular to the positron beam, 0.058 m from the sample, and behind a 0.0016 m stainless steel vacuum window. The full width at half maximum (FWHM) of

the detector resolution was measured to be 1.23 keV at 514 keV using a ^{85}Sr calibration source.

The samples were cut to a size of 20 mm x 20 mm from pure Ag, Cu and Au foils, etched in a 48% solution of Hydrofluoric acid and rinsed in Acetone and Ethyl alcohol before loading into the vacuum chamber which was evacuated and baked to obtain UHV conditions. The samples were initially cleaned by repeated sputter-anneal cycles (30 minutes sputtering by Neon (Ag) or Argon (Cu, Ag, Au) ions followed by annealing at ~ 150 °C. The sample was maintained under UHV conditions $P < 5.0 \times 10^{-5}$ Torr sputtered for 3 hours two times a week during the period of data acquisition (~ 20 days per sample). Surface cleanliness was monitored throughout the ~ 20 day period required for data accumulation by conventional electron stimulated Auger spectroscopy (EAES) and contamination levels were observed to be below 1% except for O, C for which the surface concentration stayed below 10% during the data collection period. We note that the spectral weight in the energy range of interest from the low energy tails of the annihilation induced C (O) Auger lines for 100% C (50% O) surfaces are only a few percent of the PAES signals from Cu, Ag, and Au [20]. Consequently, we estimate that less than 0.2% of the γ -Auger coincidence signal is from the C and O cores.

Annihilation (core) γ -energy spectra were obtained in coincidence with the detection of annihilation-induced Auger electrons by gating the input of the MCA with a pulse resulting from the detection of electron in the selected energy range within 600 ns of the detection of the γ -ray (see figure 1.). Conventional "non-coincidence"

γ -spectra (containing contributions from both core and valence electrons) were obtained by setting the gate input high allowing all of the HPGe pulses into the MCA.

The annihilation γ -spectra of the 3p level of Cu were obtained by requiring coincidence with electrons in the energy range 57-59 eV. This range spans the peak of the energy distribution of the $M_{23}VV$ Auger transition in the valence electron fills a $3p_{1/2}$ (N2) or $3p_{3/2}$ (N3) hole. Similarly the annihilation γ -spectra of the 4p level of Ag and the spectra for the 5p level of Au were obtained by requiring coincidence with electrons in the energy range 35-38 eV for Ag [corresponding to Ag $N_{23}VV$ Auger transition with initial states of holes in the $4p^{1/2}$ or $4p^{3/2}$ levels) and electrons in the range 38-40 eV for Au (corresponding to Au $O_{23}VV$ Auger transition with initial states of holes in the $5p^{1/2}$ or $5p^{3/2}$ levels).

A small background (accounting for 5.4% of the total intensity for Cu, 11.6% for Ag, and 5.5% for Au) due to accidental coincidences between the γ -signal and uncorrelated MCP pulses was determined directly from a measurement of the integrated intensity of the γ -signal taken in coincidence with electrons detected in an energy range where no true coincidences are present (20 eV above the annihilation induced Auger peak). The accidental contribution was then removed by subtracting a high statistics, non-coincidence γ -spectra scaled to match the measured intensity of the accidental contribution to the spectra. Figure 2 shows a comparison of the γ -Auger coincidence data associated with the annihilation of positrons with Cu 3p electrons before and after subtraction of the accidental background.

We note that the kinetic energy of the positrons hitting the surface at 12 eV, was below the impact-ionization threshold for all of the core levels studied. This was important to ensure that the Auger electrons detected resulted from annihilation with core-electron and not from Auger electrons resulting from impact ionization. If a positron beam-energy higher than the core ionization energy were to be used, it would excite Auger electrons both by positron annihilation with core electrons and by impact ionization. The use of too high a positron-beam energy would also result in positron induced secondary electrons with energies in the range of the Auger electrons[21]. Since the positrons that cause impact ionization or impact induced secondaries are free to annihilate with valence electrons after the impact, the presence of Auger electrons (or secondary electrons) in the Auger energy range from impact excitation would result in an undesirable valence background in the coincidence measurements. Note also that a large fraction of the positrons injected into the samples at 12 eV diffuse back to the surface and become trapped in an image-correlation well before they annihilate. This greatly increases the escape probability of the Auger electrons and implies that the positron-Auger coincidence technique predominantly samples atoms in the topmost atomic layer.

Theoretical Calculations

The calculations were based on an atomic code using a local-density form for the electron-positron correlation function, with no explicit momentum- or density-dependent enhancement.[22] The calculations include appropriate integration of the 3-D radial momentum distribution to correspond to the 1-D Doppler measurements. We

use an approach in which the momentum integration is performed analytically using a delta-function identity, thereby reducing the expression for the 1D momentum density to real-space integrals over well-behaved radial functions. As a result of the integration, nodes in the radial momentum distributions result in breaks in momentum that appear as shoulders in the 1-D momentum distribution.

The calculations use a generalized-gradient approximation for the electron-positron enhancement.[23] Separate calculations have been performed using state-dependent and r-dependent enhancement. State-dependent enhancement uses a constant (momentum-independent) enhancement factor equal to the average enhancement of the individual atomic state, while r-dependent enhancement multiplies the 3-dimensional electron-positron momentum by the square root of the density-dependent enhancement factor, $\gamma(n(r))$ prior to performing the radial integrations to produce the 1D momentum density, resulting in a momentum-dependent enhancement function.

The electron-positron enhancement function $\gamma(n(r))$ becomes very large when the density becomes small. In our atomic calculation, the electron charge density drops off rapidly at large radii, while in a real solid the charge density from the neighboring atoms would maintain a much larger charge density. For this reason, we limit the enhancement to a value determined by the interstitial charge density in each of the elements we consider here, with r_s values of 2.67, 3.02 and 3.0 respectively for Cu, Ag and Au.

Results and Discussion

Figure 3 (a) shows a comparison of the energy distribution of annihilation γ -rays from positrons incident on Cu measured in coincidence with an Auger electron emitted as a result of filling the 3p core hole in Cu with a spectra obtained without the requirement of coincidence. Similarly, panels 4 (b) and 4 (c) show comparisons of the energy spectra of annihilation γ -rays obtained with and without the requirement for coincidence with Auger electrons emitted as a result of filling the 4p level in Ag and the 5p level in Au respectively. The curves were all scaled to have the same maximum.

In all three cases widths of the coincidence spectra are significantly larger than those of the non-coincidence spectra. The FWHM of the non-coincidence spectra are 2.24 keV, 2.73 keV and 2.38 keV from Cu, Ag, and Au respectively while the corresponding FWHM of the coincidence spectra are 5.5 keV, 4.6 keV and 4.4 keV respectively. This is consistent with the fact that the non-coincidence data are dominated by γ 's resulting from annihilation with the relatively low momentum valence electrons and the coincidence data characterizes the energy spectra of γ - rays emitted as a result of annihilation with relatively high momentum core electrons.

A qualitative understanding of the spectral widths of the non-coincidence spectra can be obtained by estimating the width of the momentum distribution of the valence electrons alone. To the lowest approximation this contribution can be modeled by a parabola representing annihilation with free conduction electrons. The parabola cuts off at an energy ΔE_{\max} :

$$\Delta E_{\max} = m_o c^2 \frac{V_F}{2c} \approx 1KeV \quad (3)$$

where V_F is the Fermi velocity of an electron (10^{-6} ms^{-1}).[15-17]

The larger width of the coincidence spectra is due to the relatively large Doppler shift associated with the core electrons which are the sole contributors to the coincidence spectra. As noted above, the FWHM of the coincidence spectra are 5.5 keV, 4.6 keV and 4.4 keV from the Cu 3p, Ag 4p, and Au 5p levels respectively. The ratios of these widths, 1.25:1.05:1, correspond approximately to the ratios of the square root of the binding energies of the $p^{3/2}$ levels (a rough estimate of the average magnitude of momentum of these levels) 1.15:1.01:1. The fact that the Au 5p is less tightly bound than the Ag 4p which in turn is less tightly bound than the Cu 3p implies that the Au 5p is wider in real space than the Ag 4p which is again wider than the Cu 3p and hence their widths in momentum space are reversed Ag level.

We note that the use of γ -Auger coincidence, like the use of γ - γ coincidence eliminates background due to Ps, nuclear decay and cosmic ray γ 's etc. However, only γ -Auger coincidence is capable of separating the core part of the annihilation spectra from the much larger (20 times at the peak) valence contribution.

Figure 4. shows a comparison between the first principles theoretical calculation and the one-dimensional momentum distribution of the electron-positron pairs. The momentum is expressed in dimensionless atomic units, where q is the wave vector and a_0 is the Bohr radius.

The Cu 3p curve has a shoulder starting at $4.5 qa_0$. As in the case of Ag when both theory and experiment are area normalized, the calculation for Cu lies consistently

below the experimental values from a qa_0 of ~ 3 to ~ 6 . The Ag 4p curve has a shoulder starting at $3.8 qa_0$ and the Au 5p curve has a shoulder starting at $3.0 qa_0$. As in the case with Ag and Cu when both theory and experiment are area normalized, the calculated momentum density for Au lies consistently below the experimental values for momenta $qa_0 > 2$.

The agreement between the theory and experiment is remarkable given the complexities of both the experiment and theory and the fact that the calculations were done independently with no adjustable parameters aside from the overall normalization. However, referring to Fig. 4 it may be seen that there are differences with theory that are well outside of the statistical uncertainties of the experiment. Specifically, when both theory and experiment are area normalized, the calculation for Ag lies consistently below the experimental values for $qa_0 > 3$ and the calculation for Au falls below the experiment for $qa_0 > 2$. Because the area-normalization procedure tends to make the measured and theoretical values coincide in the low momentum part of the spectra due to its much larger intensity and hence larger contribution, some care should be taken in assuming the comparison indicates that the discrepancy between theory and experiment is only at high momentum. However, the comparison clearly indicates that the calculations are not predicting the correct ratio of high momentum to low momentum spectral weight. It should be noted that the γ -Auger coincidence measurements were the first to allow such a comparison of high and low momentum contributions to the core since it was capable of separating the low momentum contributions of the core from the much larger signal from annihilation with valence electrons.

There are a number of possible explanations for the discrepancies between theory and experiment: 1. The LDA-based calculation of the core electron momentum distribution may underestimate the high momentum tails. However, while the LDA is known to give the wrong core level binding energies, the charge densities from which the momentum distributions are calculated are believed to be accurate. 2. The discrepancies may be due to the level of approximation used in modeling the positron wave function in which only an s-like state was included. While s-states have appeared to be adequate for approximating the positron state in bulk calculations, it is likely that a mixed s-p state may be more appropriate for the overlap of a positron in a surface state with a surface atom. We note however, that the observed discrepancies appear to be in the high momentum region in which the positron's contribution to the total pair momentum could be expected to be small due to the fact that, on the average, the positrons are at thermal energies at the time of annihilation. 3. The discrepancy may reflect inadequacies in the treatment of electron-positron correlation effects and the need for an enhancement term with an explicit momentum dependence that increases at higher momentum. We note, however, that current treatments of the momentum dependence of the LDA based theories predict the opposite momentum dependence, and our r-dependent enhancement factor calculations, which introduce a momentum-dependent enhancement factor, in fact showed a preferential enhancement of the low-momentum electrons, worsening the agreement with experiment.

CONCLUSION

The data presented in this paper represents the results of the first measurements of the Doppler-broadened γ -ray spectra resulting from the annihilation of positrons with individual core levels. Annihilation γ spectra from the 3p core-level of Cu, the 4p core-level of Ag, and 5p core level of Au were obtained by measuring the energies of γ -rays time coincident with Auger electrons emitted as a result of positrons annihilating with the selected core level. A comparison with calculations of the annihilation spectra for these core levels shows excellent qualitative agreement with no adjustable parameters aside from the overall normalization. However, differences with theory are well outside of the statistical uncertainties of the experiment and become more pronounced with increasing Z going down the column from Cu to Ag to Au. Specifically, when both theory and experiment are area normalized, the calculation for Cu lies consistently below the experimental values from a qa_0 of ~ 3 to ~ 6 while that for Ag there is a shift of about 1 unit in the position of the shoulder at $qa_0 \approx 3.8$ and the calculations fall well below the experiment in for values of qa_0 above ~ 4 . For Au the disagreement is even larger with the suggestion of additional shoulder at a value of $qa_0 \approx 2.8$ in the experimental momentum density at a momentum where the calculation indicates a dip

In all three spectra, the calculated value of the momentum density appears to fall further below the measured value as the momentum increases. We note that our measurements are the first to directly separate the low momentum contributions of the core from the much larger signal from annihilation with valence electrons.

The method of using coincidence with the detection of Auger electrons to select core annihilation events, while used in this study to measure the Doppler broadened γ -spectra, is of general applicability in studies of core annihilation. Future γ -Auger coincidence measurements could be used to measure the core spectra of impurity atoms at the surface. The core-signatures of impurities thus obtained could then be used to provide confirmation of the signatures of vacancy-impurity complexes in the bulk as seen in Doppler spectra obtained using γ - γ coincidence. The Auger coincidence technique can also be used in conjunction with the measurement of the Angular Correlation of Annihilation Radiation, (ACAR), in high-resolution fundamental studies of core electron momentum distributions.

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Figure Captions

Fig. 1. Details of the experimental set up. A low energy positron beam is used to place positrons at the sample surface. The γ -energy was measured using a HPGe detector. The signal from the preamp of the HPGe detector is amplified and connected to the ADC of a multichannel analyzer (MCA). The Auger electrons were energy selected using an $\mathbf{E} \times \mathbf{B}$ filter and detected using a microchannel plate. The Doppler-broadened γ -spectrum for a selected core level was acquired by using a fast coincidence circuit to open the gate to the MCA only after the simultaneous detection of a γ -ray and an electron from an Auger transition resulting from the annihilation of the selected level. Conventional Doppler-broadened spectra were acquired by holding the MCA gate open.

Fig 2. Comparison of the γ -ray –Auger electron coincidence data associated with the annihilation of positrons with electrons in the Cu 3p level as collected and the same data with a small accidental background subtracted.

Fig. 3. Comparison of the “core + valence” and “core” annihilation γ -ray energy spectra resulting from the bombardment of polycrystalline Cu (a), Ag (b) and Au (c) foils with a 12 eV positron beam. The core + valence spectra (open symbols) were acquired without a coincidence requirement. The core spectra (solid symbols) were acquired in time coincidence with the detection of an electron in the range of the peaks of the energy distribution of Auger electrons emitted as a result of the annihilation of a positron with the Cu 3p (M_{23}), Ag 4p (N_{23}), and Au 5p (O_{23}) electrons for (a), (b), and (c) respectively.

Fig. 4. Momentum distribution of positron-electron pairs for the Cu 3p, Ag 4p, and Au 5p core states. The experimental distributions (solid squares) were extracted from Doppler-broadened-spectra by using Eq. (2) to convert the annihilation γ energy to electron-positron pair momentum (given in dimensionless units, qa_0 , where q is the wave vector and a_0 is the Bohr radius). The measured distributions (solid squares) are compared to LDA-based calculations, normalized to have the same area as the measured curves, shown as solid lines (see text).

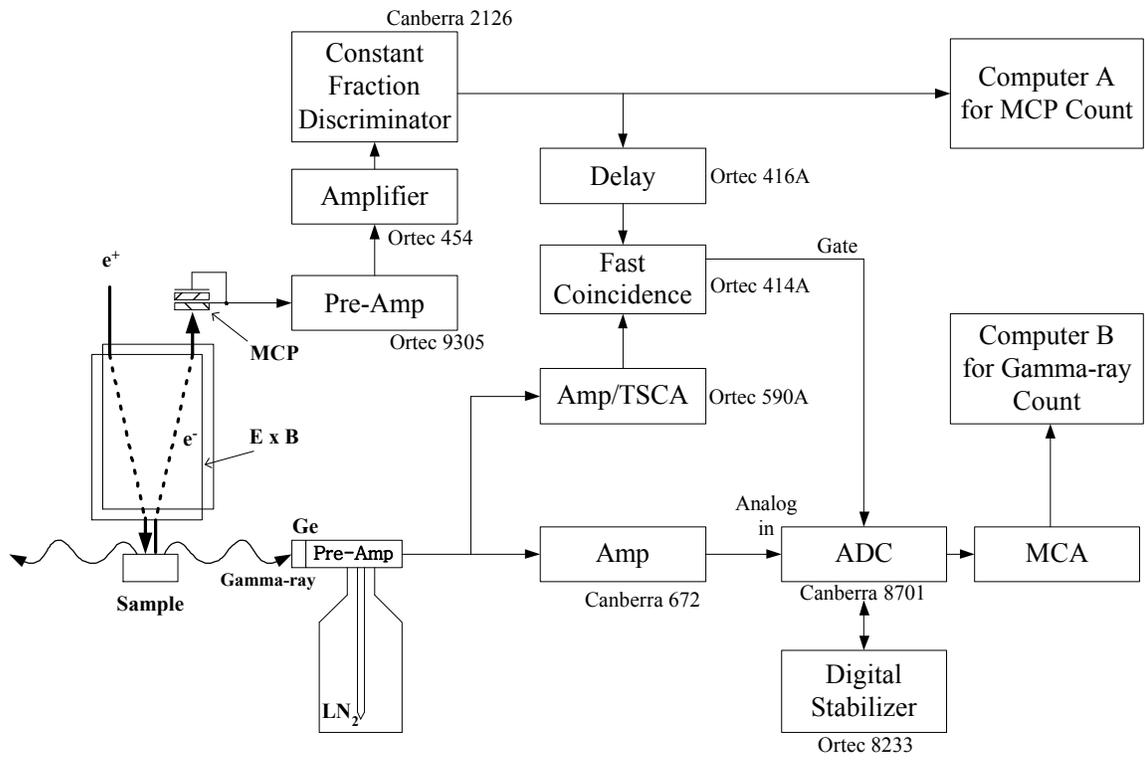


Fig. 1.

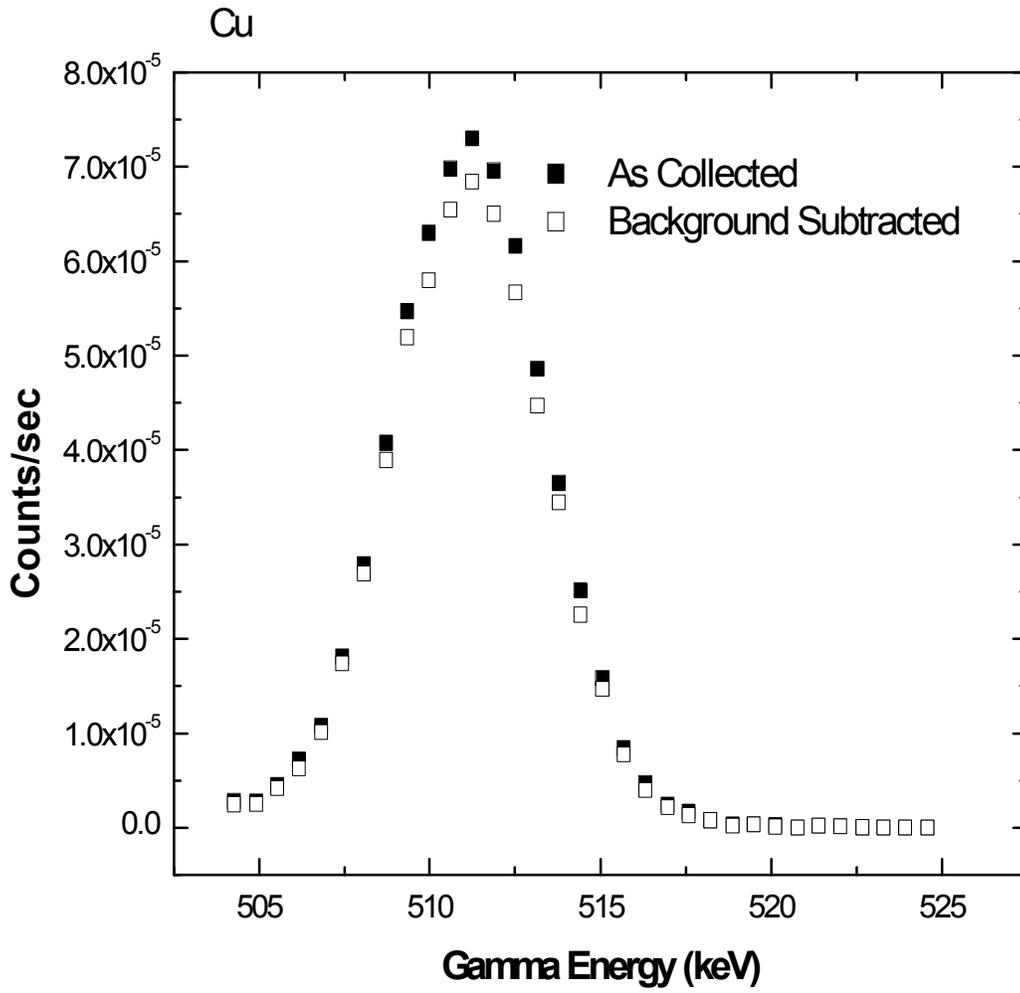


Fig 2.

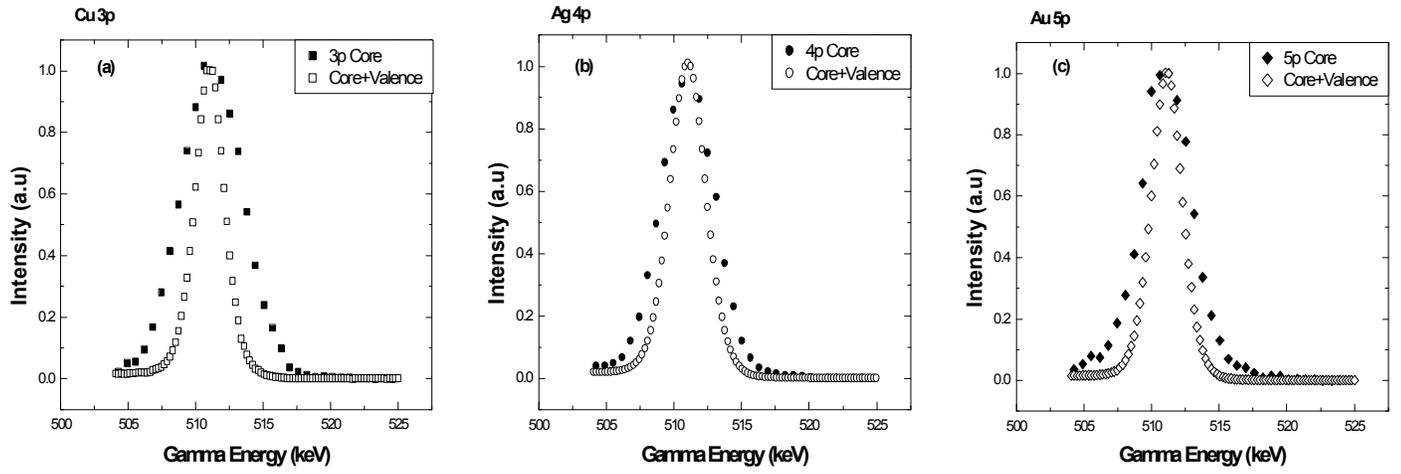


Fig. 3.

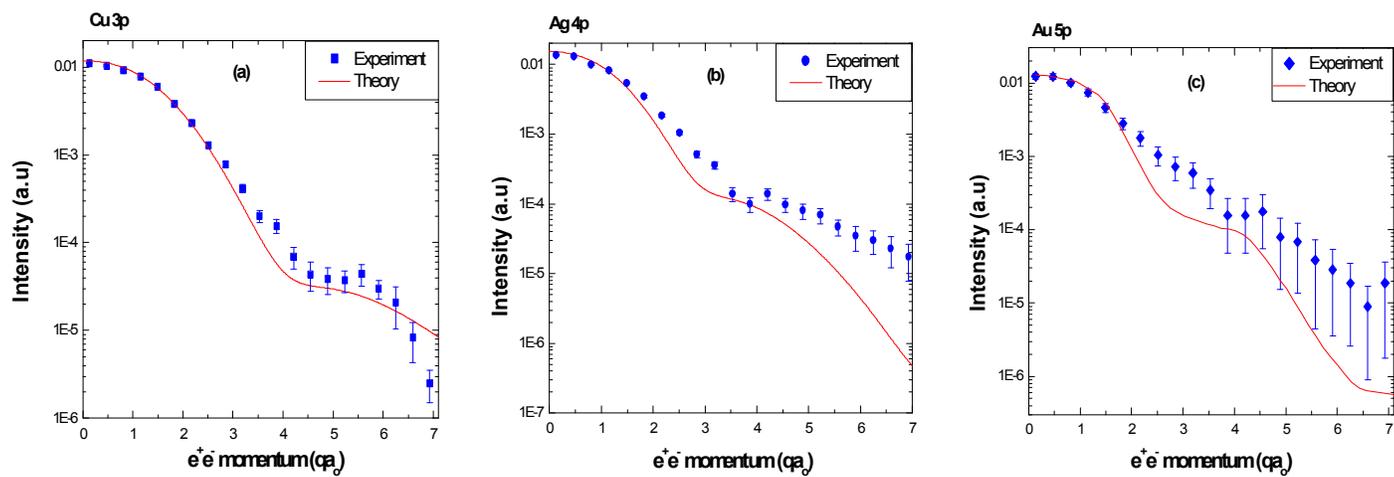


Fig.4.