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X-Ray Determination of Charge States of Ions Moving in Solids

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Introduction

One problem area in atomic physics is the study of charge states of ions moving in solids. The particular electronic configuration of the ion influences the dynamic interaction of the projectile in the solid and will determine such quantities as stopping powers, ranges and distributions of implanted ions. Previous attempts to measure these charge state distributions incorporate the use of thin foils and measurements of emergent charge states. However, the logical extension of those previous measurements of charge states of ions outside the foil to the identification of charge states of ions in the foil has led to divergent pictures of ions moving in solids.¹ Work recently completed by our group^{2,3} has concentrated on the use of x rays (both total yield and high resolution spectra) emanating from projectiles moving in solids as a practical tool for investigating the equilibrium states of ions traversing a solid. Two rather important conclusions were obtained from these original studies; first, the number of vacancies determined in the valence and inner shells from x-ray measurements while the ion is in the solid are much greater than the total number of vacancies in the atom as determined from thin foil charge state measurements performed outside the solid; second, large numbers of inner shell vacancies can be produced in the projectile beam. These large numbers of inner shell vacancies have led to the proposal^{4,5} that thin foil excitation of inner shell vacancies in an ion beam could provide a source of population inversion for the production of amplified stimulated x-ray emission (x-ray laser).

This proposal will be in two parts. In the first part our previous measurements of x-ray spectra and thick target yield for argon ions moving in solid graphite targets will be discussed. We will see that these data are strongly influenced by "solid target effects," for example, carbon K x rays are observed to be produced copiously in these solid target measurements, however, similar spectral measurements using carbon gas targets⁶ indicate no detectable carbon K yield. In this work a simple model based on the assumption of "swapping of energy levels" due to excitation of the moving argon projectile is found to accurately explain the observed thick target yield data. The model indicates that the carbon K-shell vacancies are produced primarily by a substantial steady state fraction of the argon projectiles which have one argon L-shell vacancy. Parametric fits of the data enable us to determine the mean fluorescence yields and total decay rates of these argon L-shell vacancies.

The mean fluorescence yields (and therefore lifetimes) of the argon L-shell vacancies is found to be much smaller for the argon ions moving in the solid than for argon ions moving in gas targets. A model based upon redistribution of the argon projectile among various multiplet states in the solid by subsequent collisions within the lifetime of the inner shell vacancy is used to explain this decreased L-shell fluorescence yield (i.e. lifetime). The effect of this multiplet redistribution on projectile x-ray spectra is also considered. Gross estimates of the M-shell vacancy distribution based on projectile x-ray spectra are found to be in reasonable agreement with the model.

Finally, the excitation states of the argon projectiles moving in the graphite target as determined from the x-ray data are compared with equilibrium beam foil charge state measurements.^{7,8} Large differences are observed.

In the second part of the proposal a more detailed presentation of three types of measurements which we are proposing will be given. In the measurements mentioned above we will see some rather serious limitations. The purpose of this proposal is to solicit funds which will enable us to expand our program to eliminate the limitations in our previous measurements.

The first types of measurements proposed involve the extension of our $\text{Ar} \rightarrow \text{C}$ work to other collision systems. In this section the general theoretical formulation for handling many collision systems is discussed and some preliminary data showing the importance of multiple collision effects is shown.

The second set of measurements involves the development of an Auger electron spectrometer. This device will be used to measure total ionization cross sections for inner shells using gas targets. In our analysis, discussed below, known ionization cross sections must be used. Presently we use x-ray cross sections and x-ray spectral measurements to infer ionization cross sections. Due to large uncertainties in fluorescence yield this technique is susceptible to large errors. Direct measurements of total cross sections will eliminate this uncertainty.

The third set of measurements will eliminate the most serious limitation. This limitation in our measurements involves the resolution attainable in our x-ray spectrometers. Our current measurements use crystal spectrometers. These measurements are unable to resolve any structure. In our analysis we are forced to unfold the x-ray spectra using questionable x-ray centroid energies. It appears that the limitations in our spectral measurements is a fundamental limitation induced on us by the crystals available for soft x-ray spectroscopy. The third program we propose involves the use of a 7m grazing incidence spectrograph. It will be possible with this instrument to measure the intrinsic linewidths (see below) of the relevant x-ray transition and

thus resolve the spectra whose envelopes are presented in Figs. 4 and 5. Our theoretical model for the lifetime of inner shell vacancies, below, in ions moving in solids can be tested directly with this instrument (see Appendix 1).

These measurements will enable us to test current pictures describing ions moving in solid and test the feasibility of producing a beam of ions which could give rise to amplified stimulated x-ray emission.

1. Discussion of Previous Measurements

In Appendix 1, our measurements and analysis of the x-ray spectra and yield for the argon-solid carbon collision are presented. In this section we will discuss the conclusion drawn from these measurements.

The agreement between the thick target yield data and the simple theoretical model, described in Appendix 1 substantiate the importance of "swapping" of argon 2p and carbon 1s binding energies in the inner shell vacancy production process. This analysis demonstrates that a large fraction of the argon beam has an L-shell vacancy (see Fig. 1). These large fractions are consistent with the observations of quasi-molecular x rays from similar collision systems.^{9,10} Finally, the mean fluorescence yield determined from this analysis indicates that the average fluorescence yield associated with an electronic configuration of an ion moving in a solid is going to be very different from the average fluorescence yield associated with the same electronic configuration for an ion moving in a gas.

Analysis of the x-ray spectra enabled us to determine the equilibrium distribution of the M-shell vacancies in the moving argon ion (Fig. 2). It is interesting to compare our distributions of M- and L-shell vacancies with

measurement of equilibrium charge states as determined from beam foil measurements.^{7,8} In Fig. 3 the number of composite vacancies in the L and M shell for a 90-keV argon ion as determined from our data is presented. In this analysis we have assumed the M-shell vacancy distribution in an ion with or without an L-shell vacancy is the same, and then used the sequential stripping assumption (see Appendix 1) for reasons which are discussed in Appendix 1. In Fig. 3 the charge state distribution for beam foil measurements is also presented. As can be seen from the figure the beam foil charge state distributions are skewed to fewer vacancies. For example, the charge state data indicate that for ion energies <100 keV, less than 6% of emerging ions are found to be in charge states greater than +2. This is to be contrasted with our results which indicate that a 90-keV argon ion moving in a carbon solid has a 15% probability of having one L-shell vacancy (Fig. 1) and at least 30% probability of having more than two M-shell vacancies (Fig. 2). The uncertainties discussed below are unlikely to be able to account for this large discrepancy. The disparity could be reasonably explained by assuming the ion moving in the solid has associated with it electrons in highly excited states. X-ray measurements are not sensitive to these electrons because they only weakly affect the L-shell x-ray energies. If this were the case, the charge state of the ion moving in the solid would be smaller than the emergent beam-foil charge state, thus, the final charges are determined, under this assumption, by subsequent autoionizing transitions which take place after the ion and attendant electrons leave the foil. Other explanations of the differences shown in Fig. 3 are also possible; for example, a large probability of electron capture at the exit surface could also account for the differences.

No conclusions distinguishing between these two possibilities can be drawn from our data.

The role of inner shell vacancies in determining the emergent charge state distributions has received almost no attention in the literature. This study, by providing an estimate of the beam fraction having an inner shell vacancy at a given distance into the target, indicates that it is possible to pursue this subject quantitatively. Equilibrium charge state measurements for argon ions emerging from carbon foils with energies of 70 keV and 180 keV have mean charges of 0.5 and 1.25, respectively.⁸ Our analysis indicates that for argon ions emerging with these energies, the fractions having an L-shell vacancy would be 0.1 and 0.3, respectively. Since the predominant vacancy filling mode is by Auger emission, increasing the charge of the ion by one (though Coster-Kronig transitions may increase it by one more) we may conclude that about 20% of the mean change at 70 keV and 25% of the change in mean charge is due to inner shell processes. Within the sensitivity of our measurements, the x-ray spectra (and thus the M-shell populations) don't change in going from 70 to 180 keV ion energy. This implies that the remainder of the change is due to changes in the outer shell mechanisms, i.e., processes involving excited states or capture at the last surface. This area of investigation appears promising and should be pursued further.

The large fractions of inner shell vacancies attainable in the projectile beam has lead to a proposal that ion-atom collisions could be used in the production of amplified spontaneous x-ray emission.^{4,5} In one proposal a carbon foil is used to induce L-shell vacancies in an argon beam and amplified spontaneous emission takes place on the back side of

the carbon foil. Concerning this proposal we can make several comments. First, the argon-carbon system can give rise to large numbers of L-shell vacancies in the argon beam. The maximum value of 0.3 obtained in our experiments (at 200 keV) will undoubtedly continue to increase as the projectile energy increases. The argon carbon system has the property that multiple collisions are not expected to produce multiple L-shell vacancies in the same atom. This is due to the swapping of the argon 2p and carbon 1s levels previously discussed. Similar measurements² using chlorine and sulphur projectiles on carbon demonstrate that multiple L-shell vacancies are produced and hence introduce an additional complication in the design of an amplified x-ray emitter.

Other interesting questions concern the L-shell lifetimes (fluorescence yields) and charge state distribution of the argon beam at the time of x-ray emission. In the foil excitation proposal the lifetimes (and fluorescence yields) will be more consistent with the gas target values, as discussed previously. The redistribution among the multiplet states which reduced the mean lifetimes (and fluorescence yields) in the solid will no longer be operational once the beam leaves the foil. Concerning the distribution of charge states at the time x-ray emission we can also offer the following comments. Neither distribution in Fig. 3 is appropriate for these considerations. The charge-state distribution measured in the solid is not appropriate because autoionizing transitions or electron capture at the back surface are expected to take place before x-ray emissions. Likewise, the beam-foil charge-state measurements which are measured after the decay of the inner shell vacancies will not be appropriate. The actual charge-state distributions (and therefore numbers of lines) which are present at the time of x-ray emission will be important in

determining the feasibility of these schemes. The differences in the two distributions in Fig. 3, one measured in the foil, the other measured long after the atom has relaxed indicates that a dramatic redistribution of the ion near the back surface of the foil.

While additional work is necessary to test the various assumptions and details of our analysis, the present results indicate that x rays can be used as a practical tool for investigating equilibrium excitation states of ions traversing a solid.

However, several questions still remain. The resolution used in the present experiments was insufficient to resolve any significant structure in the spectra. This difficulty seems to be universally true for all measurements of soft L x-ray spectra using crystal spectrometers. For example, similar measurements using extremely high resolution¹¹ crystal spectrometers still fail to resolve any structure. If any progress is to be made here, different energy dispersive techniques (such as grazing incidence spectrometers, see next section) will be needed.

This poor resolution results in several ambiguities in our analysis of the observed x-ray spectra. Multiplet splittings of x-ray transition energies can cause overlaps between x rays from different charge states (see Table 1). In our analysis we assumed that, by simply using centroid energies, these effects would cancel. The M-shell distribution we presented in Fig. 2 is sensitive to these assumptions. We believe our assumptions to be reasonable; however, large errors are possible. This technique to determine charge-state distributions requires higher resolution measurements. However until these measurements are available, the sequential distribution presented in Fig. 2 can be considered as our best estimates based on the x-ray spectra presented in Fig. 1. Indeed, the argument between the mean lifetimes and mean fluorescence yields determined

from this M-shell distribution and those same numbers obtained from our analysis of the thick target yields (see Appendix) suggest that the M-shell distribution is, at least, approximately correct.

The purpose of this proposal is to solicit funds to expand our current program. The expanded program will enable us to eliminate the ambiguities in our previous measurements and to look at other projectile target systems.

2. Proposed Measurements

In this section our proposals for expanding the current program are presented. Three specific types of measurements will be discussed in varying detail. All the equipment necessary to perform these experiments is on hand or presently being constructed.

I. Studies of Different Projectiles

The studies presented in the previous section were for argon projectiles. Due to the swapping of the argon 2p and carbon 1s energy levels in an argon projectile with one 2p vacancy this is a rather special case. Extension of this work to other projectiles is very important. One particularly interesting set involves projectiles whose Z differs from argon by only a few units (such as, chlorine and sulphur). For these projectiles the swapping of the 2p energy level with the 1s level of the carbon target does not take place until multiple L-shell vacancies are produced in the projectile. For example, consider the L x-ray spectra for sulphur projectiles moving in carbon gas (CH_4) and solid (graphite) targets presented in Fig. 4. The spectra for solid targets are seen to extend over a much broader energy range and indeed with x-ray energies are consistent with as many as three L-shell vacancies in the sulphur projectile.

These multiple L-shell vacancies can be produced in the projectile due to multiple collisions in the solid within the lifetime of an inner shell hole. The lifetime of a ground state sulphur L-shell vacancy is 5×10^{-14} sec.¹² This can be compared with the mean free time for producing an L-shell vacancy, $1/N\sigma v$, where N is the number of carbon atoms per cm^3 , σ is the L-shell vacancy production cross section (in cm^2) and v is the velocity of the projectile in cm/sec . The cross section can be estimated¹³ to be $\sim 10^{-17} \text{ cm}^2$. This leads to a mean free time for producing an L-shell vacancy in 90 keV $\text{S}^+ \rightarrow \text{C}$ collisions of about 10^{-14} sec. Thus, each ion having an L-shell vacancy undergoes several collisions of this type during the lifetime of the vacancy. L-shell vacancies are not expected to be produced in the projectile when the 2p binding energy of projectile exceeds the 1s binding energy of carbon. This is due to changes in the molecular orbital diagrams⁷ which are normally used to describe these collisions (see Fig. 4). The changes result in the inner shell vacancies being produced in the carbon K shell rather than the projectile. This results in a limitation in the number of L-shell vacancies of 3, 2 and 1 for S, Cl, and Ar, respectively.

The formulation of the problem presented in Appendix 1 do not apply to cases involving multiple inner shell vacancies. However, the general theoretical formulation of this problem is straightforward. Let f_i be the fractional probability of beam having i inner shell vacancies and let q be the maximum number of vacancies determined by the discussion above. Assuming thin targets and neglecting double electron processes,

the production and decay of inner shell vacancies in any thickness dx of the solid is determined by the following equations.

$$f_0 + f_1 + \dots + f_q = 1$$

$$\frac{df_0}{dx} = f_1/v\tau_1 - N\sigma_0 f_0$$

$$\frac{df_1}{dx} = N\sigma_0 f_0 - f_1/v\tau_1 + f_2/v\tau_2 - N\sigma_1 f_1$$

$$\frac{df_{q-1}}{dx} = N\sigma_{q-2} f_{q-2} - f_{q-1}/v\tau_{q-1} + f_q/v\tau_q - N\sigma_{q-1} f_{q-1}$$

$$\frac{df_q}{dx} = N\sigma_{q-1} f_q/v\tau_q \quad (1)$$

where N is number of target atoms per cubic centimeter, v is the velocity of the projectile, τ_i is the lifetime of the projectile having i inner shell vacancies and σ_i is the cross section for i to $i+1$ inner shell vacancies. For $q=1$ the equations are shown in Appendix 1. For $q>1$ solutions can be obtained but, the more relevant quantities, the equilibrium fractions can be determined simply by setting the derivatives equal to zero. When this is done, Eq. (1) yields

$$f_i = \frac{\prod_{j=1}^i (N\sigma_{j-1}v\tau_j)}{[1 + \sum_{k=1}^q \prod_{j=1}^k (N\sigma_{j-1}v\tau_j)]}$$

or

$$f_i = N\sigma_{i-1}v\tau_i f_{i-1} \quad (2)$$

Equation (2) can be used to estimate equilibrium fractions of projectile inner shell vacancies.

For the measurements we are proposing thick target yields will be determined for each inner shell vacancy. The equations above are for thin targets. A series of equations analogous to those in Appendix 1 can be developed for the multiple inner shell vacancy systems. Our thick target yield data, these general equations and total cross section measurements (see next section) will be used in a method analogous to that discussed previously to determine the distributions of inner shell vacancies for the projectiles.

The instrumentation necessary for these measurements is the same as used previously. X-ray spectra using a crystal spectrometer and thick target yield measurements using a proportional counter will be performed.. The spectra will be used to determine the relative yield of x rays from each number of L-shell vacancies in the projectile and carbon K x rays from the targets.

Other collision systems will be considered. Specifically projectiles such as boron will be used where K-shell vacancies become an important consideration. In addition a special ultra-high vacuum (10^{-9} Torr) system is being constructed which will enable us to study targets other than carbon without concern for the standard carbon contamination problem which occurs on other targets.

II. Measurements of Total Cross Sections Using Gas Targets

Studies of the states of projectiles moving in solids using x-ray emission requires substantial data analysis. One very important input into this analysis is the total ionization cross sections. Measurements of these cross sections requires gas targets so as to eliminate the so-called solid target effects that we are studying. In our previous work these cross sections were inferred from x-ray spectra and x-ray production cross section measurements. Very serious errors can result from this type of a study since x-ray emission is a very low probability event and since the probability of x-ray emission can be very projectile energy dependent. Greater than 99% of inner shell vacancies decay by emission of an Auger electron. Thus by measuring the total Auger electron cross section, one determines to high accuracy the total cross section. An Auger electron spectrometer of our own design is presently being constructed which will enable us to make these measurements. The spectrometer is a parallel plate type, capable of measuring Auger electron spectra at a wide variety of emission angles. These types of measurements are described in detail elsewhere¹⁴ and so no elaborate discussion will be presented here.

III. High Resolution X-Ray Measurements with a Grazing Incidence Spectrograph

In Appendix 2 we demonstrate that by using a grazing incidence spectrograph we can improve our resolution by a factor of ~ 20 and still maintain reasonable data collection times. This improvement in resolution is very important in that we will be able to measure the intrinsic linewidths and study effects such as collision and Stark broadening in solids. Of course, the limitations imposed by using low resolution crystal spectrometers will be eliminated.

Appendix 1

Determination of Charge States of Argon Projectiles

Moving in Solid Targets Using X-Ray Spectra

1. Experimental Data

A. X-Ray Spectra

The experimental technique has been described in detail elsewhere.¹⁵ A Bragg spectrometer with a lead stearate film ($2d = 100.4\text{\AA}$) as the diffracting element was used for observing the x rays emitted at 90° to the direction of the incident beam; the detector was a flow-mode proportional counter with a parylene window approximately $3000\text{\AA}$ thick.

The resultant x-ray spectra was found to be extremely sensitive to the amount of incident beam used to obtain the spectra. An x-ray peak at approximately 230 eV was found to grow in relative intensity as the amount of beam was increased. This peak was attributed to L x rays from implanted argon projectiles produced in subsequent $\text{Ar}^+ \rightarrow \text{Ar}$ collisions. To eliminate these effects a special procedure for obtaining the data was established. The method involves a rapid movement of the target to expose a clean target spot, followed by automatic, rapid, sequencing of short counting periods. The "clean target" x-ray spectra is obtained by extrapolating the observed yields to "zero incident beam." The procedure is described in more detail elsewhere.¹⁶

The resultant clean target x-ray spectra are presented in Fig. 5. The differences between these spectra and similar spectra obtained using gas

targets is very dramatic. There are three principal differences; first, the argon L x-ray spectra for solid targets extends over a much broader energy range (from 200 to 260 eV) supposedly indicating a broader distribution of M-shell vacancies associated with the ion in the solid target as compared to the ion in the gas target; second, carbon K x rays are clearly observed in the solid target spectra where as in the gas target spectra little or no carbon K x-rays are observed. Finally, the argon L x-ray spectral distribution for solid targets (that is, the resultant x-ray spectra obtained after stripping of the carbon K x-ray, see discussion below) appears not to change with projectile energy.

In subsequent analysis it will be necessary to estimate the relative intensities of the photon yield. To do this the x-ray spectra in Fig. 5 must be corrected for window transmission¹⁷ and crystal reflectivity.¹⁸ In Fig. 6 these corrections as a function of photon energy are presented.

B. Thick Target Yield.

The thick target x-ray yield for $\text{Ar}^+ \rightarrow \text{C}$ collisions has been previously reported.¹⁹ In these early measurements a 6×10^{-6} m mylar window was used to filter the argon L x rays and thus the reported yields were attributed to carbon K x rays. However recent measurements²⁰⁻²² of x-ray cross sections for $\text{Ar}^+ \rightarrow \text{Ar}$ collisions using a wide variety of proportional counter windows indicate that the transmission of 6×10^{-6} m mylar is much higher than originally estimated and in fact these measurements substantiate the measured absorption coefficients of Spivak.¹⁷ In reanalyzing the previously reported thick target yields it was determined that the previously reported yields were in fact a mixture of argon L and carbon K x rays. To determine the correct thick target yields the x-ray spectra were corrected for window transmission¹⁷ and crystal reflectivity.¹⁸ The relative carbon

yield was determined using the carbon K x-ray profile obtained from proton bombardment. All the remaining x-ray intensity was attributed to argon L x rays. The total yield of argon L and carbon K x rays was then obtained from the previous thick target yield measurements,¹⁹ the absorption characteristics of 6×10^{-6} m mylar as measured by Spivac¹⁷ and finally the corrected x-ray spectra from Fig. 5. These thick target yields are presented in Fig. 7.

2. Thick Target Yield

Since the production of characteristic x rays involves vacancies in inner shells of an atom, the object of primary interest in yield analysis is the occupancy of the inner shells. These inner shell electrons are sufficiently tightly bound that the rate of change of occupation number is not very large, even for ions moving in a solid. It is this circumstance which makes a meaningful analysis of the x-ray data possible. We will see in the next section that M-shell vacancy distributions can be extracted.

In this section we construct a model for analysis of both projectile and target atom x-ray yields. The proposed model permits a number of consistency checks to be made, and the results in values for the average L-shell vacancy lifetime of the projectile moving in the solid, as well as mean value for the fluorescence yield. In the next section these values will be compared to semi-empirical theoretical values which have been arrived at on the basis of spectral information.

It should be made clear at the outset that the "standard" thick target yield analysis, in which the slope of the yield as a function of incident energy is proportional to the x-ray cross section,²³ is not applicable to the present experiment.²⁴ To understand this, we note that in gas target

experiments, with either argon projectiles and a carbon gas target or carbon projectiles and an argon target, no carbon x rays are observed,⁶ at least at the relative velocities of interest here. This implies that the observed of carbon x rays in the thick target data are a result of multiple collisions of an Ar projectile. Thus, the carbon x-ray yield will depend on the fraction of the projectiles in certain excited states. The change with incident energy of this yield must now also reflect the change in this fraction with energy, thus necessitating an analysis more detailed than standard thick target yield analysis.

In our formulation of the problem, we utilize the fact that inner shell vacancy production is well described by considering the transient molecule formed by the collision partners.^{25,26} The processes we include are consistent with the guidelines given by a molecular orbital (MO) description. In this description, the correlation diagram (see Fig. 8a) for an Ar-C collision indicates^{6,25} that the carbon K-shell electrons should not be promoted in such a collision, consistent with the gas target data mentioned above, while the Ar 2p subshell electrons may be promoted via level crossing which involve the 3d σ MO.

The x-ray and vacancy-production cross sections for this process has been measured²⁰ for gas targets. Total cross section is estimated to be $2.8 \times 10^{-18} \text{ cm}^2$ for Ar projectiles incident at 90 keV. If this ion is traveling in a graphite target, the time between inner shell vacancy creating collisions, $1/N\sigma v$, is approximately 4×10^{-14} sec which is very nearly the same as the theoretical lifetime¹² for a ground state argon atom with an L-shell vacancy. Though, as we indicate below, we expect

some shortening of the mean life of the vacancy for the ions traversing the solid. This estimate shows that collisions will not in general override the normal vacancy filling processes, so that the concept of a lifetime will remain well defined. This conclusion is strengthened within the molecular orbital description of these collisions by consideration of a subsequent collision of an argon ion which has an L-shell vacancy with a carbon atom. The correlation diagrams are sensitive to the binding energies of the electrons in question.^{6,25} The increase in binding energy for the Ar ion electrons due to the L-shell vacancy is sufficient to make the L-shell electrons become more tightly bound than the carbon 1s electrons in the latter collision, as illustrated in Fig. 8b. These orbitals do not cross any orbitals having vacancies during this collision, so the probability of additional vacancy creation becomes negligible, completely analogous to the lack of carbon K x rays in the gas target case. This correlation of electrons indicates that the carbon K-shell electrons now become 3d σ electrons so that carbon K-shell promotions are expected instead, while the inner shell occupation number in the argon projectile is unaltered.

The filling of L-shell vacancies in argon involves the outer shell. While a detailed description of the events attendant the M shell for argon projectiles in solid is at this time impossible, some general considerations are helpful. As the ion with an inner shell vacancy continues to move through the solid, it will undergo many long range interactions which can affect the M-shell population, such as ionization, charge exchange, etc. Using a nominal cross section of 10^{-16} cm² for these processes,¹ we estimate that the mean time between such events to be approximately 10^{-15} seconds. Thus, the ion will experience at least 40 such events prior to the filling of the L-shell vacancy. We expect, on this basis, that the M-shell population will reach an equilibrium distribution prior to the filling of the

vacancy. The mean life and fluorescence yield associated with the vacancy should then reflect this equilibrium distribution, as should the x-ray spectral distribution (see below).

The above considerations indicate that we may consider the vacancy distribution for the inner shells as a problem in binary collisions between target and projectile atoms, if we treat the internal (i.e., inner shell) states of the projectile and consider the filling process as arising from some sort of "equilibrium" outer state. We will neglect processes involving 2 or more inner shell electrons, as the existing data² confirm the notion that these are small compared to the one-electron processes.

We assume a steady state situation in which a beam of projectiles is incident on a solid. If we denote by f_i the fraction of the projectiles having i inner shell vacancies, the production and decay of inner shell vacancies leads to the following equations for the f :

$$\frac{df_1}{dx} = N\sigma f_0 - \frac{f_1}{v\tau} \quad (3)$$

$$f_0 + f_1 = 1 \quad (4)$$

where N is the target atom number density, v is the velocity of the projectile, τ is the mean life of the projectiles inner shell vacancy, and σ is the cross section for production of an argon L-shell vacancy in an Ar-C collision. These equations are truncated versions of a more general set which allows for the possibility of several inner shell vacancies to be created by multiple collisions in the solid which will be discussed in a later section. In the Ar-C case, we have seen that the existence of one vacancy in Ar produces a "swapping" of energy levels which results in suppression of

further argon vacancy production. The production of several L-shell vacancies in other ions by multiple collisions when this suppression does not occur has been verified experimentally; for such cases the larger set of equations must be used. This will be discussed in more detail later.

For ions moving in solids, v is a function of the distance x , and since the cross sections are functions of velocity, σ also depends upon x . We can, however, obtain a qualitative understanding of the x dependence of the f_1 by examining the above equations at a position x in the solid which is small compared to the total range, so that energy loss is negligible. The solution for Eq. (3) under these restrictive conditions is

$$f_1 = \frac{N\sigma v_0\tau}{1 + N\sigma v_0\tau} \left[1 - \exp \left(-\left(N\sigma + \frac{1}{v\tau} \right) x \right) \right] \quad (5)$$

This solution obeys the boundary condition $f_1(x = 0) = 0$ and shows normal curve growth to an equilibrium value of $N\sigma v_0\tau / (1 + N\sigma v_0\tau)$ where v_0 is the initial velocity.

For any real solid we know that the stopping power cross section is large compared to inner shell excitation cross sections, and that these latter are sensitive functions of the velocity, so that the growth rate will be smaller than anticipated on the basis of σ evaluated at v_0 , and the maximum value will be less than the equilibrium value anticipated on the above basis. (It should be obvious that f_1 will eventually decrease from its maximum as the velocity decreases.)

Equation (1) was formulated with the assumption that collisions of a projectile having no inner shell vacancies with a target atom resulting in excitation of the projectile, leaving the C K-shell unexcited. This was predicted on the basis of the gas target data discussed earlier. However, it has been suggested⁶ that simple outer shell stripping alone will change

the binding energies sufficiently that the molecular orbital model will predict a "swapping." Hartree-Fock-Slater calculations confirm that the removal of 4 or more electrons from the argon M shell will cause the argon 2p binding energy to be equal to or larger than the carbon K-shell binding energy. For projectiles in these stages of ionization, a collision with carbon would result in carbon K-shell excitation instead. In our model, we have allowed for this possibility by including a term which accounts for a fraction α of the projectiles having no inner shell vacancies as being able to excite the carbon K shell, and therefore, with no argon L-shell excitation for this fraction.

A calculation of the projectile inner shell population fractions f_i as outlined above requires a knowledge of the argon L-shell vacancy production cross sections for all velocities between the incident velocity and zero. While there are no direct total cross section measurements or theoretical estimates known to us at this time, the argon L-shell x-ray production cross sections in gas target Ar-C collisions have been measured, and an empirical approach used to estimate the total cross section σ .²⁰ We have used those values in the following calculations. The velocity as a function of distance was found by using the stopping power, both nuclear and electronic; these are conveniently tabulated in Ref.¹⁹

Of the quantities needed to calculate the f_i we still lack α and τ . Examination of the spectral data (see the following section) from the thick target experiments shows that the spectral features associated with argon emission show essentially no variation with incident energy. We thus assume the average values to be constant, but unknown, parameters in this calculation.

We are now ready to outline our model. We modify Eqs. (3) and (4)

as indicated above to read:

$$\frac{df_1}{dx} = N\sigma(x) (1-\alpha)f_0(x) + f_1(x)/v(x)\tau \quad (5)$$

$$f_0(x) = 1-f_1(x) \quad (6)$$

Equations (3) and (4) were solved numerically for various values of α and τ . The resultant f_0 and f_1 were used to predict both target and projectile x-ray yields, T_x and P_x , respectively, from the equations:

$$T_x = \omega_t N \int_0^{x_0} (\alpha f_0 + f_1) \sigma e^{-\mu_t x} dx \quad (7)$$

$$P_x = \bar{\omega}_p \left\{ \int_0^{x_0} (f_1/v\tau) e^{-\mu_p x} dx + f_1(x_0) e^{-\mu_p x_0} \right\} \quad (8)$$

Here ω_t is the carbon K-shell fluorescence yield taken to be 2.1×10^{-4} ,²⁷ x_0 is the total range, $\bar{\omega}_p$ is the argon L-shell mean fluorescence yield, as yet unknown but assumed constant, as with α and τ , because of the constancy of the spectral features with energy. We note that T_x depends on α and τ , while P_x depends on $\bar{\omega}_p$, α and τ . We thus fitted the experimental carbon K-shell yield, T_x , by varying α and τ . This fit was found to be essentially unique because while α seriously affected the low energy data, the higher energy values were only sensitive to τ .

The values of α , τ , and $\bar{\omega}_p$ which resulted from the above analysis are:

$$\begin{aligned} \tau &= 0.95 \times 10^{-14} \text{ sec} & \alpha &= 0.06 \\ \bar{\omega}_p &= 1.3 \times 10^{-03} \end{aligned} \quad (9)$$

The values of T_x and P_x , i.e., Eqs. (7) and (8) were generated using values expressed in Eq.(9). The results are shown as the solid lines in Fig. 7. The fit to the data is seen to be everywhere within 15%.

The values of $f_1(x)$ from the integration of equation (3), and using (1), are shown in Fig. 1 for several values of incident energy. Notice in Fig. 1 the rapid rise to maximum value and the gradual drift to zero thereafter. The distance required for this rapid growth was found to be about 200 Å, almost independent of incident energy. However, the maximum value of f_1 is energy dependent.

We see from Fig. 7 that our analysis of the yield data is consistent with the assumption of constant values of ω_p , α , and τ . We will also see in the next section that the fraction $\alpha = 0.06$ is consistent with a spectral analysis of the charge state fractions for large numbers of M-shell vacancies.

While we have seen that the production of additional argon 2p electrons, we know that the 3dσ orbital contains 2 electrons when filled. This brings up the possibility of producing two argon L-shell vacancies directly in the first collision. We have modified our analysis to allow for this possibility as follows: the cross section for this event, assuming independent probabilities, is proportional to the square of the probability for single electron transfer. In Ref. 20, the "maximum total cross section, πr_x^2 for the Ar-C system is estimated. This was used to approximate a two-electron transfer cross section. An equation for f_2 similar to Eq. (5) results, with the addition of a term. The resultant coupled equations were solved numerically as above. The maximum value of f_2 did not exceed 0.02 even for the largest energy of interest here and was totally negligible for most energies. The resultant x-ray yields differed insignificantly from those shown in Fig. 7. The experimental results²⁰ for gas targets confirm

that these events cannot contribute more than about 10% to the x-ray yield. Only an upper limit can be extracted, however, because of the existence of a 3d-2p transition in the same spectral region. At higher energies, we expect such events to play a more important role.

B. Spectra

In the previous section we have used measurements of total x-ray yield and a simple model to determine three important quantities associated with the moving argon ion; the mean lifetime of an L-shell vacancy; the mean fluorescence yield of the L-shell vacancy and finally the fraction of the argon ions having no L-shell vacancies but sufficient M-shell vacancies to "swap" the argon 2p binding energy and the carbon 1s ground state energy. In this section the measured x-ray spectra from the moving argon ion are analyzed to determine if the three parameters obtained are reasonable. Since the observed projectile x-ray spectra is quite broad and essentially unresolved, straightforward analysis of the spectra is virtually impossible. This is because we cannot separate the different multiplet states or even determine if M-shell vacancies are in the 3s or 3p subshells. Since any of these different possibilities can have widely differing fluorescence yields, unique analysis of the spectra is discounted. Our approach here will be to make certain assumptions concerning distribution of ions among the multiplet states and distribution of M-shell vacancies among 3s and 3p levels and then determine a fluorescence yield. If that fluorescence yield appears in reasonable agreement with the value determined from the thick target yield then the assumptions are considered reasonable. Fortunately, the fluorescence analysis yield is found to be very sensitive to the assumptions used, thus, this procedure provides a strong test of these

possible assumptions.

The first problem we consider is distribution of the ions among the multiplet states. Previous calculations of fluorescence yield²⁸ have assumed

$$\bar{\omega} = \frac{\bar{T}_x}{\bar{T}_x + \bar{T}_A} \quad (10)$$

where ω is the fluorescence yield corresponding to a particular configuration (that is, a given number of vacancies in the various sub shells) and $\bar{T}_x$ and $\bar{T}_A$ are the x ray and Auger transition rates, respectively, averaged over the possible multiplet states in that configuration. Our experiments have shown that these fluorescence yields do not agree with measurements using gas targets.^{20,29} Recent calculations³⁰ of fluorescence yields for particular multiplet states have shown that a different definition of $\bar{\omega}$ removes this discrepancy between theory and experiment. In order to determine the fluorescence yield associated with the multiplet and then weigh these individual multiplet fluorescence yields by some distribution, such as statistical population of multiplets. In Table 1 these two types of averaging are illustrated for a single configuration, the $1s^2 2s^2 2p^5 3s^2 3p^5$ initial state. Presented in the table are the multiplet calculations of Chen and Craseman³⁰ and the calculations of the average transition rates of Bhalla.²⁸ The table includes the calculations of the Auger transition rates. Within the dipole approximation of the x-ray transition rate is independent of the multiplet state. To determine the fluorescence yields a value of $T_R = 8.8 \times 10^{-7}$ a.u. was used.³⁰ The fluorescence yield is determined for each multiplet and also using the average values (i.e. Eq. 10).

The average fluorescence yield for a configuration is found by assuming each state has equal probability of being populated and thus

$$\bar{\omega} = \frac{\sum \omega_i (2L_i + 1)(2S_i + 1)}{\sum (2L_i + 1)(2S_i + 1)} \quad (11)$$

where the sums are overall the multiplet states in a given configuration. As can be seen from the table the two ways of averaging give entirely different results. We have also included in the table the x-ray transition energies associated with each multiplet. The x-ray transition energies were calculated by using measured Auger electron transition energies involving the same initial states^{31,32} and accounting for differences in the final state configuration.³³ Notice that the x-ray transition energies depend on the quantum number J. The fluorescence yield calculations exhibit no J dependence because they were calculated in an LS coupling scheme.

In Fig. 9 the fluorescence yields determined by both types of averaging for several different electronic configurations are presented. It is seen from this figure that large differences are observed except for the ground state which involves one multiplet.

Previous checks of the fluorescence yield calculations involved gas targets. In the case of solid targets discussed in this paper, the use of the fluorescence yields determined from gas targets is not justified. For example, in the case considered in Table 1 the final average fluorescence yield was influenced strongly by the ³D state. This is because the state had a large multiplicity [(2L + 1)(2S + 1)] and a small Auger transition rate (relative to the other multiplet states in that configuration). If this ³D state were produced in

an argon ion moving in the solid the probability of that state being maintained for its normal lifetime unaffected by subsequent collisions is essentially zero. This fact is appreciated when one realizes that the lifetime of state is approximately the same as the time it takes a 90-keV Ar projectile to come to the end of its range (approximately $1000 \text{ \AA}$) in a graphite target. This state differs in total energy by only a few eV from the other multiplet states in that configuration thus even a very large impact parameter collision can cause remixing of the multiplet states. One would expect the fluorescence yield of an ion moving in a solid to be smaller since the decay would be more probable due to the redistribution of the multiplet states in the high transition probability and thus reduce the average lifetime of the state.

Rate equations can give some insight to the problem of an ion moving in a general medium with redistribution among the multiplets. As the projectile moves through the medium it will have collisions with target atoms. These collisions can produce inner shell vacancies, produce different outer shell configurations or redistribute the ion among the multiplet states. Let M_i be the number of ions in a particular configuration and in the i^{th} multiplet at any time t . The time rate of change of this number is given by

$$\frac{dM_i}{dt} = S_i - \frac{M_i}{t_i} - \frac{M_i}{t_i^c} + \sum_j R_{ij} M_j \quad (12)$$

where S_i is the number of M_i being created per unit time, $(1/t_i)$ is the total vacancy filling rate, $(1/t_i^c)$ is the rate of the collisional transfers out of the i^{th} multiplet and R_{ij} is the rate at which collisions are transferring projectile atoms from the j^{th} into the i^{th} multiplet.

In the subsequent analysis we will make the following assumption: in any collision the probability that a particular multiplet state, within a specific configuration, be produced is proportional only to its multiplicity and thus each substate of the multiplet after a collision is equally likely produced. For a given configuration the total number of states, T , is simply $(2L_i + 1)(2S_i + 1)$. The fraction of states associated with the i^{th} multiplet, s_i is $(2L_i + 1)(2S_i + 1)/T$. The above assumption enables the following designations

$$\begin{aligned} S_i &= K s_i T \\ R_{ij} &= s_i \left(\frac{1}{t_j^c} \right) \\ \frac{1}{t_j^c} &= \frac{1}{t_i^c} \end{aligned} \tag{13}$$

where K is some constant which depends only upon the electronic configuration. This assumption is consistent with detailed balance and is based on the fact that the multiplet splittings are only a few eV.

The solutions to Eq. (12) for steady state, $\frac{dM_i}{dt} = 0$ are

$$M_i = \frac{s_i}{\Gamma_i} [TK + \beta m] = C \frac{s_i}{\Gamma_i} \tag{14}$$

where

$$\Gamma_i = \frac{1}{t_i} + \frac{1}{t_i^c}, m = \sum_j M_j, \beta = \frac{1}{t_j^c} = \frac{1}{t_i^c} \tag{15}$$

and C is some constant which depends only upon the configuration.

Given the steady state populations M_i , the mean fluorescence yield

$\bar{\omega}$ is given by

$$\bar{\omega} = \frac{\text{total x-ray count rate}}{\text{total vacancy filling rate}} = \frac{\sum T_i^X M_i}{\sum (1/t_i) M_i} \quad (16)$$

where T^X is the radiative decay rate of the i^{th} multiplet. Within the dipole approximation the radiative rates depend only on configuration,

$T_j^X = T_i^X = T_X$. Thus,

$$\bar{\omega} = \frac{T_X (s_i / \Gamma_i)}{(s_i / \Gamma_i t_i)} \quad (17)$$

We can now explore the various limits as the collisional transfer rate β changes. In a diffuse medium, such as a gas, the collisional frequency, β , is small compared to the lifetime of the inner shell vacancy. Thus

$$\Gamma_i \approx \frac{1}{t_i} \quad (18)$$

and

$$\bar{\omega} \approx \frac{\sum s_i [T_X / (1/t_i)]}{\sum s_i} = \sum s_i \omega_i \quad (19)$$

This is just the averaging described in Eq. 11 and indeed this is the expected gas target limit (assuming production is statistical).

The other extreme which might be represented by solid targets is

$$\beta \gg 1/t_i \quad (20)$$

thus

$$\Gamma_i \approx \beta \quad (21)$$

and

$$\bar{\omega} = \frac{T_x s_i}{s_i/t_i} = \frac{\bar{T}_x}{\bar{T}_x + \bar{T}_A} \quad (22)$$

which is just the averaging described by Eq. 10. The conclusion then is that two types of averaging represented by Eqs. (10) and (11) correspond to two different physical limits. The high density limit where many multiplet changing collisions take place within the lifetime of the inner shell vacancy is described by Eq. (10) and the low density limit where the multiplets are unaffected by subsequent collisions is described by Eq. (11). It can be seen by comparing the two averages presented in Table 1 that the difference between these two limits is very large. In order to convince ourselves that the limit described by Eq. (10) is appropriate for the systems discussed in this paper remember the previous discussion concerning the $3D$ state of the configuration discussed in Table 1. The lifetime of this state is sufficient to allow a 90-keV argon projectile to traverse a few hundred lattice parameters in the graphite target. Since only a small amount of energy transfer is required to rearrange the multiple structure the quantity β will be approximately the inverse of the transit time for one lattice parameter. Clearly in this case $\beta \gg \frac{1}{t_i}$. The same conclusions can be obtained from the arguments presented in the previous section which indicate that the M-shell is in equilibrium prior to the filling of the L-shell vacancy. Based on the arguments present above we have elected to refer to the two types of fluorescence yield numbers as gas target fluorescence yields for those obtained from Eq. (11) and solid target fluorescence yields for those obtained from Eq. (10). We emphasize that these designations are relevant to the collision systems being studied here. Which value of fluorescence yield should be used will depend on the specific collision system being studied.

The distribution of x rays among the multiplets will also be different for the two limiting cases. The average x-ray energy for a particular configuration is

$$\bar{E} = \frac{T_x \sum M_i E_i}{T_x \sum M_i} = \frac{\sum s_i E_i / \Gamma_i}{\sum s_i / \Gamma_i} \quad (23)$$

In the gas target limit ($\Gamma_i = 1/t_i$) is

$$\bar{E} = \sum s_i \omega_i E_i / \sum s_i \omega_i$$

In the solid target limit ($\Gamma_i = \beta$) is

$$\bar{E} = \sum s_i E_i$$

Thus, in the gas target limit the mean configuration energy is found by weighting the individual multiplet energies with the individual fluorescence yields and multiplicities. However, in the solid target limit the mean x-ray energy is independent of the individual fluorescence yields but found by weighting the multiplet energies with the multiplicities only. These two limits are demonstrated graphically using the x-ray transition energies from Table 1 for the $1s^2 2s^2 2p^5 3s^2 3p^5$ configuration in Fig. 10. It can be seen from this figure that the spectra are quite different, however, very high resolution is required to resolve these differences. The arrows in the figure indicate the positions of x-ray transition observed in proton and α -particle excitation of argon gas.³⁴

Due to a lack of resolution, detailed analysis of the argon L x-ray spectra presented in Fig. 5 is virtually impossible. However, we have attempted to estimate the relative probabilities of the projectile having a given number of M-shell vacancies from the x-ray spectra. This was done by unfolding the spectra using line shapes determined from gas target

spectra, centroid energies obtained from average adiabatic Hartree Fock (AHF) calculations and fluorescence yields obtained from the averaging described by Eq.(10). (Note that the spectra in Fig. 5 are slowly varying functions of photon energy; small errors in line position will not produce significant changes in individual intensities.) Since the x-ray data cannot differentiate between them, some assumption must be made concerning the relative probabilities of 3s and 3p vacancies. In Fig. 2 the resultant M-shell distributions using both sequential and statistical stripping are presented. Here sequential stripping means that the electrons in the M-shell are removed in order of increasing binding energy; i.e., no 3s electrons are removed until all 3p electrons are gone. Statistical stripping means that the probability of removing an electron from a subshell is proportional to the statistical weight of that subshell. Note the sequential stripping assumption is skewed to lower numbers of M-shell vacancies.

Fortunately our M-shell distribution must be consistent with the parameters $\bar{T}$, $\bar{\omega}_p$ and α determined in the previous section. First we observe that $\bar{\omega}_p$ is much too small to be consistent with the fluorescence yields determined by the averaging described in Eq.(11). For example, the majority of x rays observed are from charge states with 1 or more M-shell vacancies. However, $\bar{\omega}_p$ is smaller than the fluorescence yield for all charge states except the ground state (see Fig. 9). Indeed the use of the solid target fluorescence yields present in Fig.10 are necessary to obtain reasonable agreement. Using these values and both the sequential and statistical stripping assumptions presented in Fig. 9 we obtain values of $\bar{\omega}_p$ of 9.0×10^{-4} and 6.0×10^{-4} , respectively. The sequential stripping assumption agrees best with the value of 1.3×10^{-3} obtained in the previous section. The

30% discrepancy between the two values is consistent with the spread in calculations for the ground state of 1.5 and 1.9×10^{-4} , and their discrepancy with the measured³⁵ ground fluorescence yield of 2.4×10^{-4} . Likewise the mean average lifetime ($1/\bar{T}$) determined from the thick target yield data and the sequential stripping assumptions, 0.95×10^{-14} and 0.61×10^{-14} sec, respectively are in reasonable agreement. Finally, we consider the value of α as determined from the thick target yield. AHF calculations suggest 4 M-shell vacancies can cause a match of the argon 2p levels and carbon 1s levels. Thus α should be half the fraction of ions having 4 M-shell vacancies plus all ions having 5 or more vacancies. Using the sequential stripping assumption presented in Fig. 6 we get a value of 0.09 in reasonable agreement with the value of 0.06 obtained in the previous section.

To summarize, the values of $\bar{\omega}_p$, $\bar{T}$ and α can be obtained from thick target yield data of Ar_L and C_K x rays obtained from solid target measurements. These values of $\bar{\omega}_p$, $\bar{T}$ and α are in reasonable agreement with the observed argon L x-ray spectral data, only when an appropriate set of fluorescence yields are used in the solid to account for redistribution of the moving ions among the various multiplet states during the lifetime of the inner shell vacancy.

Appendix 2

Feasibility Analysis of Grazing Incidence Spectrograph

The purpose of this section is to demonstrate the feasibility of using a concave grating spectrograph operated at grazing incidence to resolve the multitude of x-ray lines produced when ions traverse a solid or gas.

The resolving power $R = \lambda/\Delta\lambda$ of a typical Bragg crystal spectrometer such as we have been using is typically about 200 when using a lead stearate soap film crystal. For the wavelength range of interest, $\lambda > 44 \text{ \AA}$, this resolving power is not large enough to separate x-ray lines from different multiple states of a specific atomic configuration (see Table 1) nor is it sufficient to measure spectral line widths. In contrast we will see below that a grazing incidence spectrograph can easily provide an order of magnitude in resolving power. In this section how much time is necessary and what resolving powers are feasible to credibly measure L x rays with a grazing incidence spectrograph will be determined. We will demonstrate that the measurements we propose are easily feasible.

Much background into the theory and operation of grazing incidence spectrographs can be found by reading relevant sections in Refs. 36-40. The grating equation $m\lambda = \sigma(\sin\alpha - \sin\beta)$ illustrates how an x ray of wavelength λ is diffracted to an order m by a ruled grating of σ grooves/mm. The incident x ray is diffracted from an incident angle α to a final angle β as measured from a normal to the grating surface. For maximizing resolving power the most important characteristics of the spectrograph are the entrance slit widths, the grating spacing σ and the grating radius ρ . Mack et al.⁴⁰ derived an expression for the slit limited resolving power as

$$R_{\text{slit}} = \frac{0.91 \rho \lambda m}{S \sigma} \quad (24)$$

which emphasizes the importance of the various parameters mentioned previously as well as the significance of looking at higher order diffracted rays ($m > 1$) in order to enhance resolution. In the spectrometer we have $\rho = 7 \text{ m}$, S for example can be $10 \text{ } \mu\text{m}$, $\sigma = 1200 \text{ } \text{\AA}/\text{mm} = 8.3 \times 10^3 \text{ } \text{\AA}$ so if $m = 1$ and we look at Ar L_m x rays at $\lambda = 55 \text{ } \text{\AA}$

$$R_{\text{slit}} \sim 4200 \quad (25)$$

therefore a resolving power greater than 3000 can be readily achieved. However, we must consider the impact of high resolving power on spectrograph efficiency. Most importantly a large R indicates we must use photographic film for x-ray detection. With film the entire x-ray spectrum is automatically accumulated at once and therefore time consuming scanning techniques are unnecessary.

With the spectrograph parameters fixed to give high resolving power we can now use the results of papers by Morgan et al.⁴¹ and Hobby and Peacock⁴² to obtain an estimate of the time necessary to collect a reasonable spectrum. They⁴¹ derive an expression for the photographic density D_λ at a given λ that one can expect to receive from a source radiating into a spectrograph whose entrance slit collimates the impinging radiation such that all radiation passing the slit strikes the grating. This can be expressed as

$$\int D_\lambda dx = \frac{S_\lambda}{r_1 r_2} t \int F_\lambda d\lambda \quad - - - \quad (26)$$

where $\int D_\lambda dx$ is the integrated peak strength along a width x of the photographic plate, t is the time duration of irradiation, r_1 is the source

to slit distance, r_2 is the source to film plate distance and $\int F_\lambda d\lambda$ is the integrated strength of the radiated x-ray line in ergs. S_λ is the spectrograph sensitivity which is defined as $S_\lambda = SG_\lambda P_\lambda$ where S_λ is the slit width in cm, G_λ is the grating reflectivity⁴² at wavelength λ and P_λ is the film response $\frac{(\text{density-cm}^2)}{\text{erg}}$. Using a $p = 2$ m spectrograph with a $\sigma = 600$ $\text{\AA}/\text{mm}$ platinum coated blazed grating, $10 \mu\text{m}$ slit widths and Ilford Q2 x-ray film S_λ has been determined⁴⁰ for λ from 10 - $120 \text{ \AA}$. We can also use the S_λ numbers since our spectrograph uses the same Bausch and Lomb grating though with $1200 \text{ \AA}/\text{mm}$ (which does not affect G_λ appreciably) provided we use Ilford Q2 film or another of similar response and use 10 mm slit widths. Figure 12 gives the Morgan et al. S_λ values vs λ . At $55 \text{ \AA}$ (Ar L x rays) S_λ is $5 \times 10^{-4} \frac{\text{density-cm}^3}{\text{erg}}$. Reasonable values for r_1 , and r_2 in Eq. 25 are 1 cm and 30 cm , respectively, thus giving

$$\int D_\lambda dx = 1.6 \times 10^{-5} \cdot t \cdot \int F_\lambda d\lambda \quad (27)$$

Now to obtain $\int F_\lambda d\lambda$ we use some of our previous work¹⁶ for $\text{Ar}^+ + \text{C}$ (solid target) collisions. Yields of 10^{-3} L x rays/incident ion in a typical $100 \text{ keV } \text{Ar}^+ + \text{C}$ collision system have been measured. Thus for $10 \mu\text{A}$ of Ar^+ and 250 eV Ar L x rays

$$\int F_\lambda d\lambda = 5.5 \frac{\text{ergs}}{\text{sec-sr}} \quad (28)$$

which gives

$$\int D_\lambda dx = 8.8 \times 10^{-5} t (\text{sec}^{-1}) \quad (29)$$

or

$$t = 1.1 \times 10^4 \int D_\lambda dx \text{ sec} \quad (30)$$

A reasonable value for $\int D_{\lambda} dx$ is 0.1 density above gross fog thus yielding $t \sim 20$ min. This estimate is too low, however, since the value we obtained for $\int F_{\lambda} d\lambda$ is for all emitted x rays. A more conservative estimate reflecting the strength in a given line (representing a unique atomic state) might be 1/10 or 1/100th of this value. Even at the resulting 3-1/3 or 30-1/3 hour exposure times the experiments are still feasible. The value of $\int D_{\lambda} dx = 0.1$ is also quite conservative and can easily be pushed to 0.01 thus demonstrating that this experiment is easily accomplishable in $t \lesssim 24$ hours. For a gas target say Ar at 0.1 Torr we still get a reasonable t , largely because the x-ray production cross section is higher for projectiles in a gas than in a solid (fluorescence yields higher for projectiles moving through a gas than in a solid). For 90 keV $\text{Ar}^+ + \text{Ar}$ collisions we get a $\int F_{\lambda} d\lambda \sim \frac{0.04}{\text{sec-sr}}$ for a given line which yields $t < 24$ hours which is still achievable by multiply exposing the film (in case the accelerator fails to operate for 24 consecutive hours).

Should our experimental results demonstrate that these preliminary calculations are indeed conservative then we will definitely decrease the slit width which will raise the resolving power thus extending the range of line widths we can study.

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Figure Captions

Fig. 1 The fraction of argon projectile having L-shell vacancies plotted as a function of depth into the solid for several different initial projectile energies.

Fig. 2 The equilibrium M-shell distributions deduced from the x-ray spectra for argon ions moving in solid targets. For details, see text.

Fig. 3 The charge distributions for 90 keV argon ions emerging from a carbon foil compared with number vacancies in the M and L shells of same ion in the solid as deduced from x-ray measurements (see text).

Fig. 4 X-ray spectra for S + C collisions in solid (graphite) and gas (methane) targets. The arrows in the figures indicate the positions of the normal ground state x-ray transitions. In the case of the solid target data the large number of sulphur L x rays above 168 eV are attributed to x-ray transitions in atoms having more than one L-shell vacancy. These are attributed to multiple collisions in the solid (see text).

Fig. 5 Relative efficiency of the lead-stearate crystal spectrometer plotted as a function of photon energy. It includes corrections for crystal reflectivity and proportional counter window transmission.

Fig. 6 X-ray spectra for Ar + C collisions in solid (graphite) targets for various bombarding energies, which are indicated in the figure.

Fig. 7 Absolute thick target yields for Ar_L and C_K x rays deduced from x-ray spectral measurements (Fig. 2) and total thick target yield measurements (Ref. 11). The solid curve represents the fit of our theoretical model described in the text.

Fig. 8 Diabatic molecular-orbitals diagrams for the $\text{Ar} \rightarrow \text{C}$ collision. For simplicity only inner shells are included. The upper figure, designated a, is ground state atoms; the lower figure, designated b, is for systems where the excitation in the argon atom is sufficient to cause a "swapping" in the relative position of the carbon 1s and argon 2p levels.

Fig. 9 Comparison of fluorescence yield values of ω_L for highly ionized argon obtained by the two averaging methods described in the text.

Fig. 10 Different L x-ray spectra expected for argon ions in the $1s^2 2s^2 2p^5 3s^2 3p^5$ configuration moving in solid and gas targets.

The lines indicate the total relative intensities and do not correct for the different widths of the lines.

Fig. 11 Sensitivity of the grazing incidence spectrograph plotted as a function of wavelength.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Distribution

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