Fast Numerical Calculations of Ion-Atom Collisions

by

J. F. Reading, A. L. Ford

Texas A&M University, College Station, Texas 77843

R. L. Becker, Oak Ridge National Laboratory,* Oak Ridge, TN 37830

When an ion impinges on an atom, the cross sections for electronic transitions can be described in the independent electron model by functions of single electron amplitudes. A single centered expansion of the time-dependent wave function of an electron about the heavier nucleus, with charge Z_N, is shown to be moderately successful in explaining the dependence of K-shell hole production on the charge, Z_p, of the projectile. However, capture of electrons by the projectile is important for a complete understanding and can be incorporated, in principle, in the single-center approach by evaluation of a transition matrix element involving a final state on the projectile. This is not an easy theoretical problem even in an asymmetric ($Z_p \ll Z_N$) collision, because long times are involved which aggravate the inadequacies of a coupled-state calculation where the continuum is replaced by a discrete set of pseudostates. Nevertheless a method has been devised which allows convergence in the truncated expansion of Hilbert states. Comparisons are made to experiment. Future developments are discussed.

*Research sponsored by the Division of Basic Energy Sciences, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

Fast Numerical Calculations of Ion-Atom Collisions

by

J. F. Reading, A. L. Ford

Texas A&M University, College Station, Texas 77843

R. L. Becker, Oak Ridge National Laboratory*, Oak Ridge, TN 37830

When an ion impinges on an atom, the cross sections for electronic transitions can be described in the independent electron model by functions of single electron amplitudes. A single centered expansion of the time-dependent wave function of an electron about the heavier nucleus, with charge Z_N, is shown to be moderately successful in explaining the dependence of K-shell hole production on the charge, Z_p, of the projectile. However, capture of electrons by the projectile is important for a complete understanding and can be incorporated, in principle, in the single-center approach by evaluation of a transition matrix element involving a final state on the projectile. This is not an easy theoretical problem even in an asymmetric ($Z_p \ll Z_N$) collision, because long times are involved which aggravate the inadequacies of a coupled-state calculation where the continuum is replaced by a discrete set of pseudostates. Nevertheless a method has been devised which allows convergence in the truncated expansion of Hilbert states. Comparisons are made to experiment. Future developments are discussed.

13 references

*Research sponsored by the Division of Basic Energy Sciences, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

Introduction

By using bare ionic projectiles of different charge, Z_p, to ionize and excite target atoms, Brandt et al demonstrated experimentally that the first-order Born approximation was invalid, i.e. that the cross section did not vary proportional to Z_p^2. They also gave a very reasonable physical explanation for the real Z_p behavior of the ionization cross section, σ, by semi-quantitative calculations of "increased binding" and "polarization" effects.[1] This powerful new experimental test of scattering from a bound system was shown[2] to demonstrate also the inadequacy of the Glauber and Cheshire (distorted wave) approximations; see Fig. 1, where the ratio $r_{12} = \sigma_\alpha/4\sigma_d$ is plotted as a function of projectile energy for alpha and deuteron projectiles.

A rigorous way to test the validity of Brandt's ideas is to perform a converged coupled state calculation numerically after the fashion of Bates, Wilets, Cheshire or Shakeshaft.[4] Unfortunately, those methods "fail" in a very real sense, in that to demonstrate anything like convergence in this type of calculation, one needs to use a large number of basis states. The calculations are therefore slow to perform on a computer and very very expensive.

We wish to describe here a new fast method of performing this type of numerical calculation and to compare results of many different experiments with such calculations. While a great deal of progress has clearly been made, it would be wrong to give the impression that we have "solved" all the problems of ion atom collisions. New experiments are constantly being performed which test the ingenuity of the theorist. Altogether, ion-atom collision theory is a very active and exciting area to be working in; there are many years of work ahead still.

The single electron theorem: single vs. multiple hole production.

If the first Born approximation is invalid, higher order terms in the Born series must be important. We take for granted here that we are in a region of parameters where there is no appreciable difference between the wave picture and the semiclassical impact parameter treatment of the scattering process. We thus equate n^{th} order time-dependent perturbation theory in the impact parameter method with the n^{th} Born approximation in the wave method for the scattering amplitude and use the concepts interceably. It is the wave picture of course that is strictly correct, but the classical trajectory approach is much more convenient for doing calculations.

In the Born approximation only one interaction is allowed and, therefore, must perturb the "active K-electron" to create a K-shell hole, i.e. the K-shell electron must be lifted above the passive Fermi sea. If we wish to calculate to a higher order accuracy, however, it is not clear that this prescription is correct, because now the projectile may interact with more than one electron, e.g. may excite an L-shell electron first and then excite the K-shell electron to this vacancy or, alternatively, having made a K-shell hole, might fill it by demoting an L-shell electron into it. The single electron theorem[5] says that in the independent particle model these processes cancel, so that the correct prescription is to ignore the "~~inactive~~ passive" electrons and to calculate to all orders the amplitude for the electron to be lifted above the Fermi sea initially occupied in the target-projectile system. It is interesting to note that this is what was assumed by most workers anyway; most theories of vacancy production have ignored the other electrons. It is well, though, to be able to prove these things rigorously, as it turns out[5] that to produce two holes the passive electrons may <u>not</u> be ignored.

Mathematically expressed, the single-electron theorem states that the inclusive probability, ρ_1, for making a hole in state 1 is given by

$$\rho_1 = 1 - \sum_k |a_{k1}|^2$$

where a_{kj} is the amplitude for excitation of an electron from state j to k. Here k is taken over all target and projectile states originally occupied before the collision. On the other hand, even in the independent particle model, it is not true that the probability for making two holes ρ_{12} is $\rho_1\rho_2$, as has been commonly assumed; rather, it is given by the determinant

$$\rho_{12} = \begin{vmatrix} 1 - \sum_k |a_{k1}|^2 & -\sum_k a^*_{1k} a_{2k} \\ -\sum_k a^*_{2k} a_{1k} & 1 - \sum_k |a_{k2}|^2 \end{vmatrix} \leq \rho_1\rho_2 .$$

That these "cross terms" are by no means neglible in a collision is demonstrated by another "two state" process, K-shell hole production accompanied by capture of an electron by the projectile, see Table 1. The table demonstrates the role the other electrons play i.e. factors of two or more in the probability. That ρ_{12} is rigorously always less than $\rho_1\rho_2$ for two hole production is a mathematical consequence of a "hidden" degree of freedom, in this case spin, entirely in correspondence to Bell's theorem[6] proved for "hidden variables". It is interesting to speculate that by measuring ρ_1, ρ_2, and ρ_{12} the existence of a "hidden degree of freedom", i.e. spin, could have been deduced without the spectroscopic evidence that was actually used. It might also be noted that if ever an experiment was performed in which "hidden variables" were "discovered", the possibility of a degree of freedom previously unsuspected might also provide an explanation completely within the framework of quantum mechanics.

With the single electron theorem many ion-atom processes can be calculated, but how are we to obtain accurate values for a_{kj}?

A single-centered expansion

Coupled-state calculations with a two-centered expansion of the wave function are slow because, amongst other things, the overlap integrals are difficult to work out because some of the basis states have good angular momentum about the target, others good angular momentum about the moving projectile. A one-centered expansion about the target would be much easier and quicker to use except that, in the traditional formulation, a prohibitively large number of angular momentum states would be needed whenever electron capture was important. This is because here the electron cloud divides into two pieces as the target and projectile separate, a difficult thing to describe in a one-centered expansion. For example, we plot in fig. 2 a calculation of excitation to the n-2 state, and in fig. 3 ionization in a proton-hydrogen collision, using a single-centered expansion. Above 30 keV the agreement with experiment is excellent, below 30 keV where charge transfer is important, the calculation has simply not converged with only S, P, and D states in the basis.

However, as Professor Brandt has reminded us, most collisions of interest to this conference are of the type $Z_p << Z_N$ or $Z_p >> Z_N$. Here Z_N is the target nuclear atomic number. In these cases charge transfer is not important, and we can use a one-centered expansion about the biggest charge (Z_N, say). We have applied this method with a U-matrix approach in which all terms in the Born series are included. The target atom is described in a Hartree-Fock model.

In fig. 4 we plot the differential cross section for ionization as calculated and compared to experiment for 0.5 MeV protons on copper. The agreement is excellent. However, such tests are not really definitive, and much poorer agreement is obtained between theory and experiment at somewhat higher energies, as shown in fig. 5. We can always talk ourselves out of such disagreement with absolute measurements by slyly adjusting the fluorescence yield. This, in fact, is the whole

point of a Brandt type experiment. By measuring the Z_p dependence of the cross section and comparing results with different projectiles one gets a much more powerful test of the theory. In fig. 6 we show such a test. The single-centered expansion, extremely cheap and simple to calculate with, works very well.[10] In fact it is so well converged that one can now assign with confidence a completely different reason to the fact that the ratio r_{12} does rise above unity at high energies, namely, a small amount of charge transfer is present. To calculate this accurately is then our next task. But how can we do this without going back to a two-centered approach and losing all the advantages we have gained?

Charge Transfer in a target-centered expansion.

Charge transfer is another mechanism by which the projectile can create a K shell hole. It was first brought to the attention of people working in this area by G. Doolen,[11] and many other authors have since pointed out its possible importance. A way to calculate charge transfer is to use a single centered expansion to obtain a good wave function ψ in the potential region of the target and then use a t-matrix expression $(\phi_{CT}, U\psi)$ to obtain the desired transition. This approach is along the lines suggested by Glauber over twenty years ago. Unfortunately, without further refinement it does not work very well in the asymmetric collisions of interest here. The reason is that charge transfer in such a collision takes a "long time", compared say to the typical interaction time for ionization, which is the time taken to cross the target K-shell radius (a_o/Z_N). For charge transfer we need the time taken for the target to cross the radius (a_o/Z_p). For $Z_p \ll Z_N$ this can be a very large time indeed.

Coupled state methods fail for large times because the real continuum of the target system is replaced by a discrete finite spectrum $E = \lambda$. It has been shown recently[12] that this is equivalent to replacing an integral over the continuum by a discrete integration rule with abscissae $E = \lambda$ and weights Δ_λ. This rule fails for large times because $\exp(iH_e t/\hbar)$ is rapidly varying and cannot be correctly integrated. The correct integration rule, i.e. the correct spectral representation of $P \exp(iH_e t/\hbar)P$, is

$$P\exp(iH_e t/\hbar)P = \sum_\lambda \phi_\lambda(r)\phi_\lambda(r')\exp(i\lambda t/\hbar)\sin x/x,$$

$$x = \Delta_\lambda t/2\hbar.$$

where ϕ_λ are the discrete eigenvectors of $P H_e P$, the Hamiltonian of the target system projected onto the basis space, P. With the new sin x/x term, the integration rule works for large times, and the method does now give convergence.[13]

The great advantage of this refined single-centered-expansion approach is that it takes minutes of computer time, not hours, to calculate cross sections. How does it work when compared to experiment?

Comparison of this new method to experiment

We have used the method described above to calculate many different processes where charge transfer is measured directly or where it is thought to contribute to a particular process. In fig. 7 we compare to total charge transfer from an argon atom to a proton. The closed triangles represent an expansion keeping S, P and D states centered around the argon nucleus; the crosses represent an S, P expansion. The agreement with experiment is fair.

In fig. 8 we compare calculations with experimental results for a "two state" process, where a K-shell vacancy (X-ray) is produced in coincidence with an electron being captured by the proton. This is another

example where the "cross terms" discussed above are correctly incorporated, though their effect here is small (~ 10%). The theoretical results have the right energy dependence as compared to experiment, but are consistently too high. The simplest explanation of this, in order of decreasing probability, are that:

(a) The theoretical calculation even with S, P, D states has not converged.

(b) The experimental normalization is incorrect.

(c) We are seeing a new phenomena of great future interest for this area, namely inelastic electron-electron interactions beyond the independent particle model: the K- electron moving up to the speed of the projectile in order to be captured has some finite probability of interacting with and exciting the L and M shell electrons; if this happens, it may not be captured, but left behind. Auger electrons should exhibit a similar behavior, though this process does not seem to have been considered by people measuring fluorescence yields. We do not know why.

In fig. 9 we return to K-shell hole production with C^{+6} and C^{+4} ions. We already can fit protons and alphas on argon, but with such heavily charged projectiles, charge transfer plays a much more important role and becomes appreciable when compared to direct ionization, i.e. here once again we are back to testing the Z_p dependence of the cross section. An interesting result of the single electron theorem is that, apart from a small screening correction, the only difference between K-shell vacancy production with C^{+6} and C^{+4} ions is that the C^{+4} ion forbids charge transfer to the K-shell of carbon. It should be understood that

the theorem applies even though, in any particular collision, all the K-shell electrons might be removed from the projectile; it is only the initially occupied Fermi sea that matters. However, the theorem depends on the assumption that the effective projectile-electron potential is independent of attaching or detaching "passive" electrons. In fig. 9 we present the results of a calculation of a C^{+6} ion incident on argon where we have included charge transfer to all shells and ionization (closed circles), and ionization alone (open circles). The experimental data for C^{6+} and C^{4+}, respectively are in very good agreement with these two calculated quantities. In identifying the lower curve with the C^{+4} data, we have assumed charge transfer to the K-shell is not allowed and charge transfer to the higher shells of C^{+4} is negligible. The C^{+4} theory could presumably be improved by using a screened C^{+4} Coulomb potential to ionize the argon. As the ionization cross section goes roughly like Z_p^2, presumably the cross section could be reduced in principle by a factor up to $(4/6)^2$! However, the electron is ejected from the argon only when it is inside the K-shell radius of the carbon, and the screened effective nuclear charge is much closer to 6 than 4. The Slater rule would give 5.7, i.e., a 12% decrease in the lower circles. This estimate is most probably near the answer that a non-hydrogenic potential would give, but our code, as presently written, can only treat hydrogenic projectiles. We have, of course, treated argon in a full Hartree-Fock model.

Further Experiments & Theoretical Problems

For the past five years, our group at Texas A & M has been trying to provide ab initio, realistic, cheap, accurate calculations of ion-atom collisions. Our success for ionization has been so marked that we now have available for general use a fairly straightforward computer code, that we can provide for experimentalists to use themselves. It includes

Coulomb deflection, all orders of perturbation theory and full Hartree-Fock treatment of the atom.

An additional package added to this code allows us to calculate charge transfer; it is more difficult to run and so far does not include Coulomb deflection. Work before us concerns the inclusion of relativistic effects, and of deflection effects in charge transfer. However, these could not be described as theoretical problems; their inclusion is now straightforward. Real theoretical problems that must be tackled with new ideas are:

(1) Removal of the $Z_p \ll Z_N$ or $Z_p \gg Z_N$ restriction.

(2) Removal of the independent particle model approximation, i.e. inclusion of inelastic final-state many-electron interactions.

(3) Wave packet effects where the "classical projectile" is not moving with a large coherence length, but with one short compared to the interaction distance.

With regard to the third problem, it is important here to understand the difference between "coherence length" and "de Broglie wave-length". Spectacular nuclear-atomic interference effects are possible with time delay in compound nucleus formations. A great deal of theoretical work still needs to be done which may throw light on the fundamental meaning of time and collapse of wave packets.

To experimentalists it may seem impertinent for the theorist to suggest experiments. And most of them that spring to mind as useful for the theorist are "impossible". However, we should remind ourselves that the calculations we have heard described here by Dr. Trautman were characterised as "impossible" five years ago by quite competent theorists. So if theorists can respond to the experimentalists' extravagant

demands, why not they to ours.

Experiments that we think should be performed are:

(a) *definitive absolute measurements of proton, deuteron, and* alpha cross sections on light atoms, $Z_p \leq Z_N$;

(b) experiments with negatively charged projectiles such as pions or muons, when no charge transfer is present and Coulomb deflection is interestingly different,

(c) measurements of atomic-nuclear interference effects, and

(d) study of inelastic electron-electron effects.

In conclusion: there is certainly more to be done than has been done.

References

1) W. Brandt, R. Laubert and I. Sellin, Phys. Rev. 151 (1966) 56; G. Basbas, W. Brandt and R. Laubert, Phys. Lett. 34A (1971) 277.

2) J. Binstock and J. F. Reading, Phys. Rev. A 11 (1975) 1205; J. F. Reading and E. Fitchard, Phys. Rev. A 10 (1974) 168.

3) C. W. Lewis, R. L. Watson and J. B. Natowitz, Phys. Rev. A 5 (1971) 1773; R. L. Watson and L. H. Toburen, Phys. Rev. A 7 (1973) 1853.

4) D. R. Bates, R. McCarroll, Adv. Phys. 11 (1962) 39; D. F. Gallaher and L. Wilets, Phys. Rev. 169 (1968) 139; I. M. Cheshire, D. F. Gallaher and A. J. Taylor, J. Phys. B 3 (1970) 813; R. S. Shakeshaft, Phys. Rev. A 14 (1976) 1626.

5) J. F. Reading, Phys. Rev. A 8 (1973) 2760; J. F. Reading and A. L. Ford, ibid. (in press).

6) J. S. Bell, Physics 1, (1965) 195. For a recent review, see J. F. Clauser and A. Shimony, Rep. Prog. Phys. 41 (1978) 1881.

7) (a) E. Fitchard, A. L. Ford and J. F. Reading, Phys. Rev. A 16 (1977) 1325; (b) J. T. Park, J. E. Aldag, J. M. George, J. L. Peacher and J. H. McGuire, Phys. Rev. A 2 (1977) 508.

8) G. L. Swafford, J. F. Reading, A. L. Ford and E. Fitchard, Phys. Rev. A 16 (1977) 1329.

9) J. U. Andersen, E. Laegsgaard, M. Lund, C. D. Moak, L. Kocbach, J. Phys. B 9 (1976) 3247; J. U. Andersen, E. Laegsgaard, M. Lund and C. D. Moak, Nucl. Instrum. Meth. 132 (1976) 507.

10) A. L. Ford, E. Fitchard and J. F. Reading, Phys. Rev. A 16 (1977) 133.

11) G. Doolen (private communication).

12) J. F. Reading, A. L. Ford, J. Phys. B 12 (1979) 1367.

13) J. F. Reading, A. L. Ford, G. L. Swafford and A. Fitchard, Phys. Rev. (in press).

References (Continued).

14) J. R. MacDonald, C. L. Cocke and W. W. Edison Phys. Rev. Lett. 32 (1974) 648. M. Rodbro, E. H. Pedersen, C. L. Cocke, J. R. MacDonald Phys. Rev. A (In press).

15) C. D. Lin, S. C. Soongand, L. N. Tunnell, Phys. Rev. A 17 (1978) 1646.

16) D. Belkic, and R. McCarroll, J. Phys. B: Atom. Molec. Phys. 10 (1977) 1933.

17) H. Tawara, Y. Awaya, Y. Tendow, T. Katow, M. Akiba, and M. Tonuma, Phys. Lett. 59a (1976) 14.

Table 1. Cross sections for K-shell electron capture in Ar by C^{+6} projectiles in units 10^{-19} cm^2.

E(MeV/amu)	σ_{CK} [a]	$\sigma_{C,VK}$ [b]
1.0	0.16	.54
2.5	0.95	1.86
5.0	0.93	1.22
9.0	0.43	0.48

[a] σ_{CK} is single electron capture from the K-shell, with no regard to the presence of the passive electrons; i.e., the contribution charge transfer makes to the total K-shell vacancy production (see fig. 9 also).

[b] $\sigma_{C,VK}$ is evaluated for capture while producing a K-shell vacancy including the cross terms due to spin and antisymmetry of the "passive" electrons on the argon target; i.e., the cross section obtained experimentally by observing simultaneously a captured electron and a K-shell hole.

Captions for figures

Fig. 1. Cross section ratio r_{12} for K-shell vacancy production. The experiments are from ref. 3. The dotted curve represents a Glauber calculation, the broken curve a Cheshire calculation, and the solid curve a more elaborate approximation, Binstock and Reading (see ref. 2).

Fig. 2. Cross section for proton-hydrogen, n=2 excitation (in units 10^{-16} cm^2) from ref. 7a, experiments from ref. 7b.

Fig. 3. Cross section for proton-hydrogen ionization (in units 10^{-16} cm^2). Upper curve B SPD target centered basis. Lower curve a SP target centered basis. From ref. 7a, experiments from ref. 7b.

Fig. 4. Ionization probability of K-shell electrons of copper by 0.5 MeV protons as a function of impact parameter. Solid curve ab initio calculation including deflection of projectile. Broken curve: rectilinear trajectory. From ref. 8. Data from ref. 9.

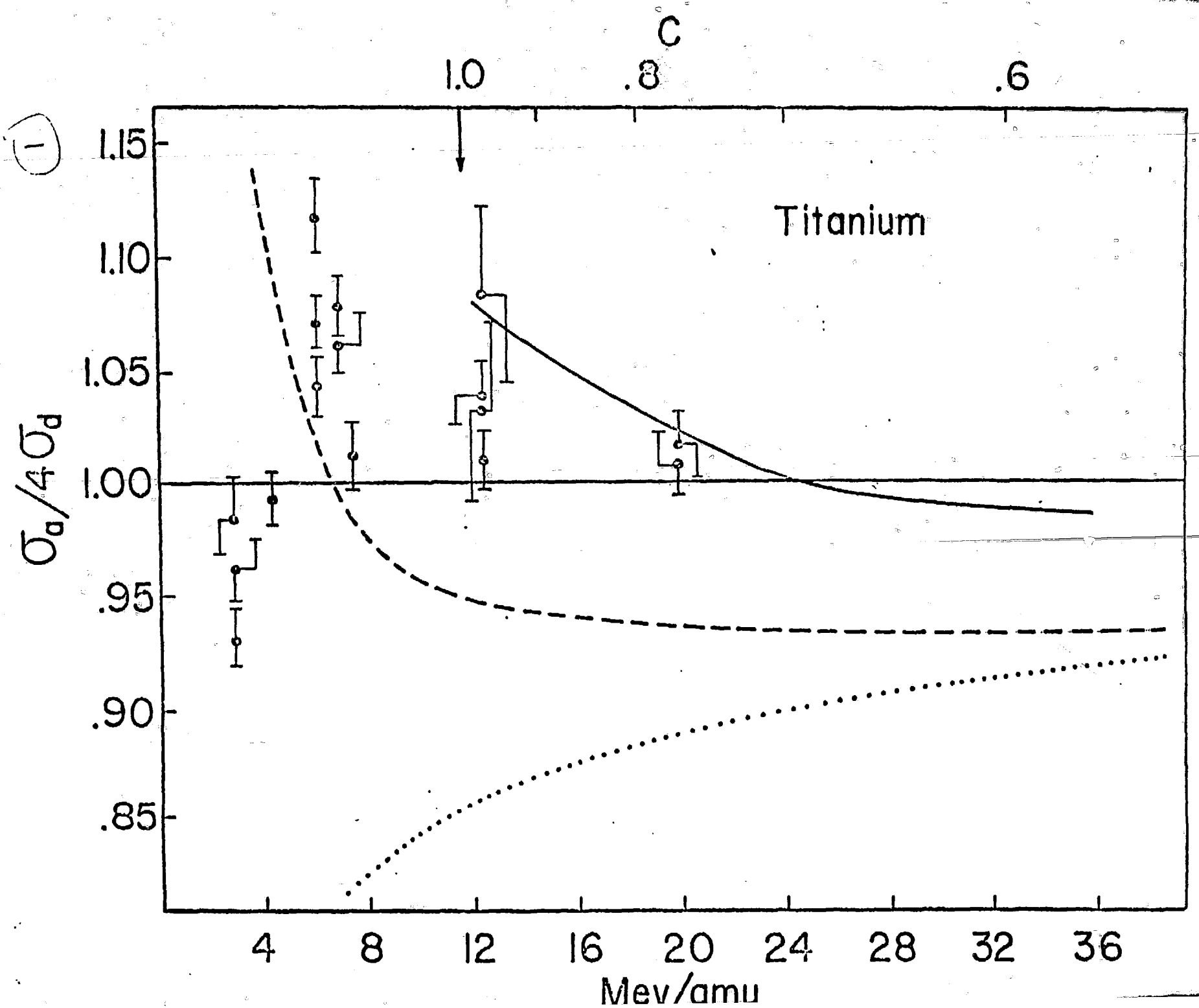
Fig. 5. Lack of agreement between ab initio theory and absolute measurement. Calculation ref. 8. Data ref. 9.

Fig. 6. Here we plot $r_{12} = \sigma_\alpha/4\sigma_d$ as in fig. 1. The upper curve includes an estimate of charge transfer effects in r_{12}. The lower curve is ionization only. From ref. 10.

Fig. 7. Total charge transfer for protons on argon. The crosses and triangles are theory by present authors to be published in J. Phys. B. The data are from ref. 14.

Fig. 8. K-shell charge transfer $\sigma_{C,VK}$ for protons on argon. Experiments are from ref. 14. The solid line is from ref. 15; the dashed line from ref. 16. The solid triangles (S,P,D states) and the crosses (S,P states) are by the present authors to be published in J. Phys. B.

Fig. 9. Cross sections for K-shell vacancy production in Ar by C^{+6}, C^{+4} projectiles. The C^{6+} and C^{4+} projectile K-shell vacancy production cross sections plotted as solid curves are the smooth curves through experimental data presented by Tawara et al. (ref. 17). The closed circles (to be compared with upper curve) are our calculated K-shell vacancy production cross sections (ionization plus charge transfer), whereas the open circles (to be compared with lower curve) are the K-shell ionization cross sections. The calculations were carried out for a bare C^{6+} projectile, and are to be published in J. Phys. B.


C
1.0
.8
.6
Titanium
1.15
1.10
1.05
1.00
.95
.90
.85
$\sigma_a/4\sigma_d$
4
8
12
16
20
24
28
32
36
Mev/amu

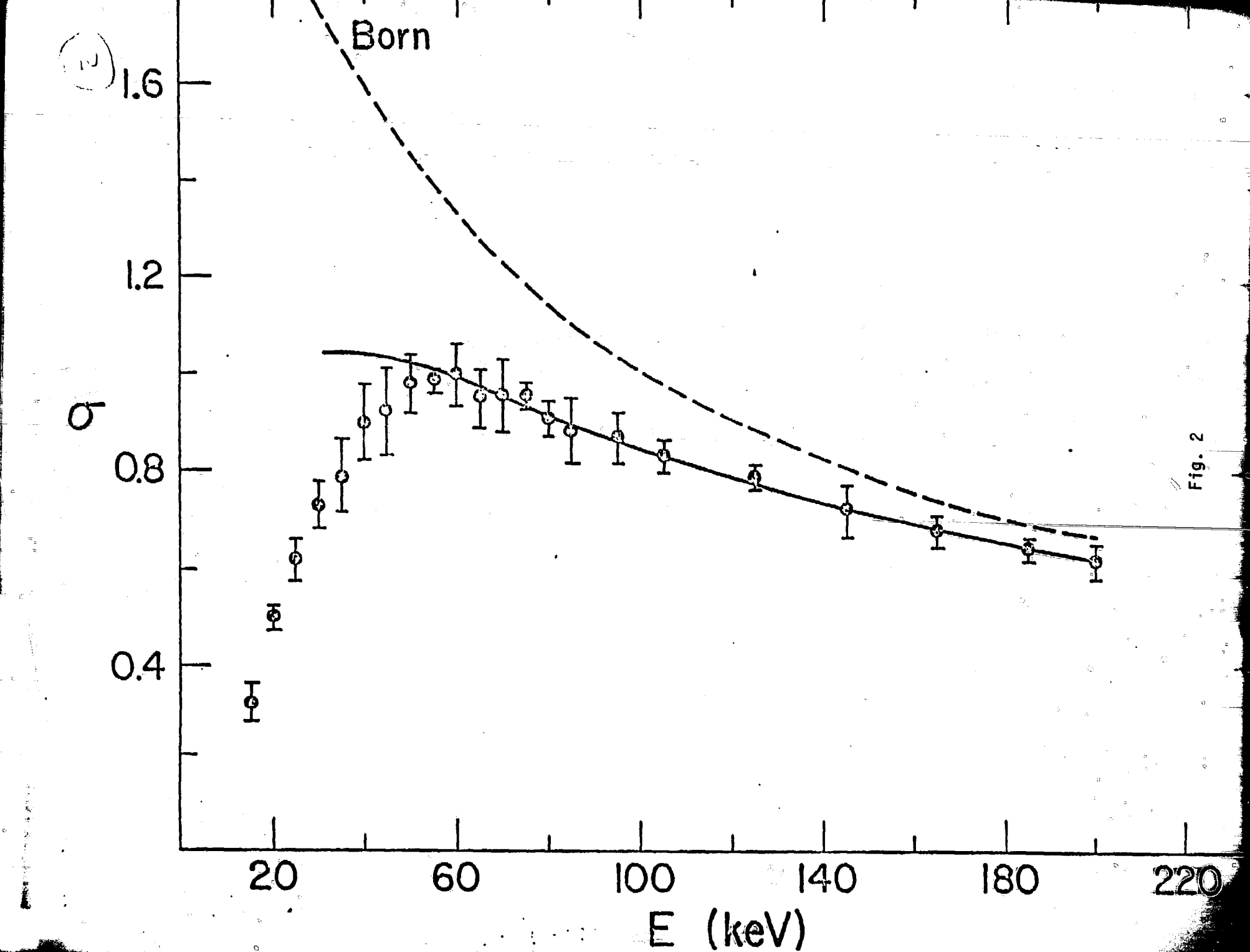


Fig. 2

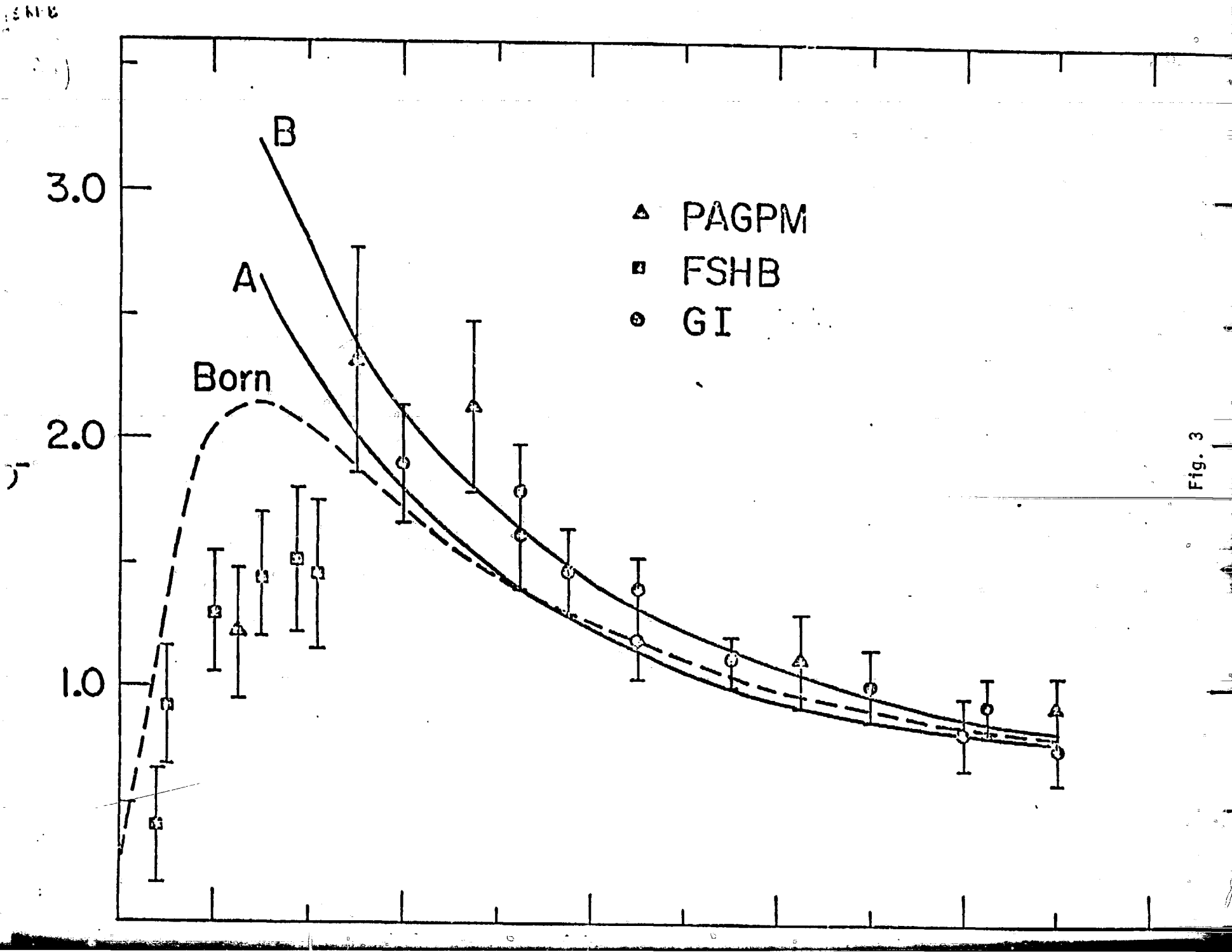


Fig. 3

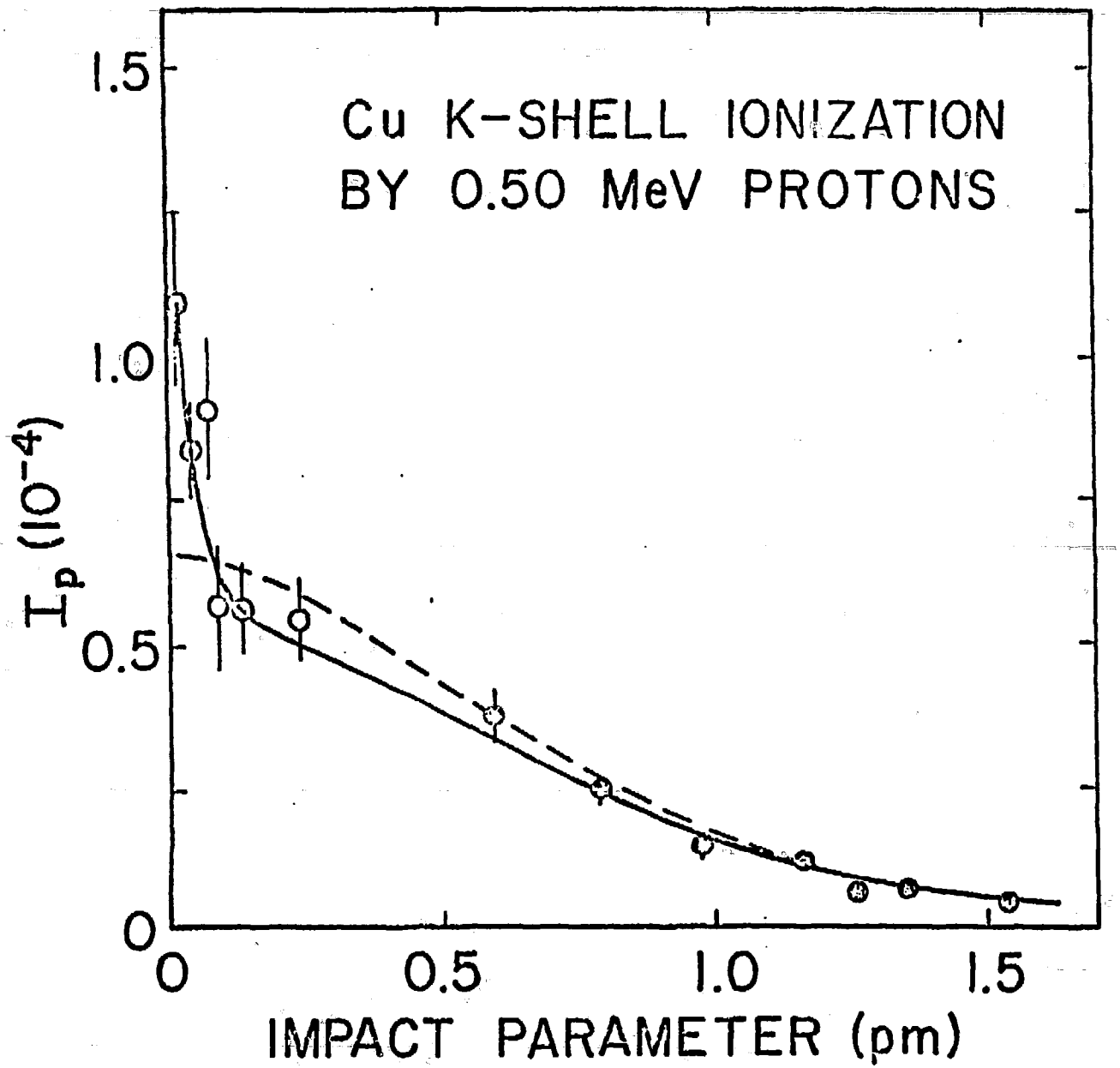
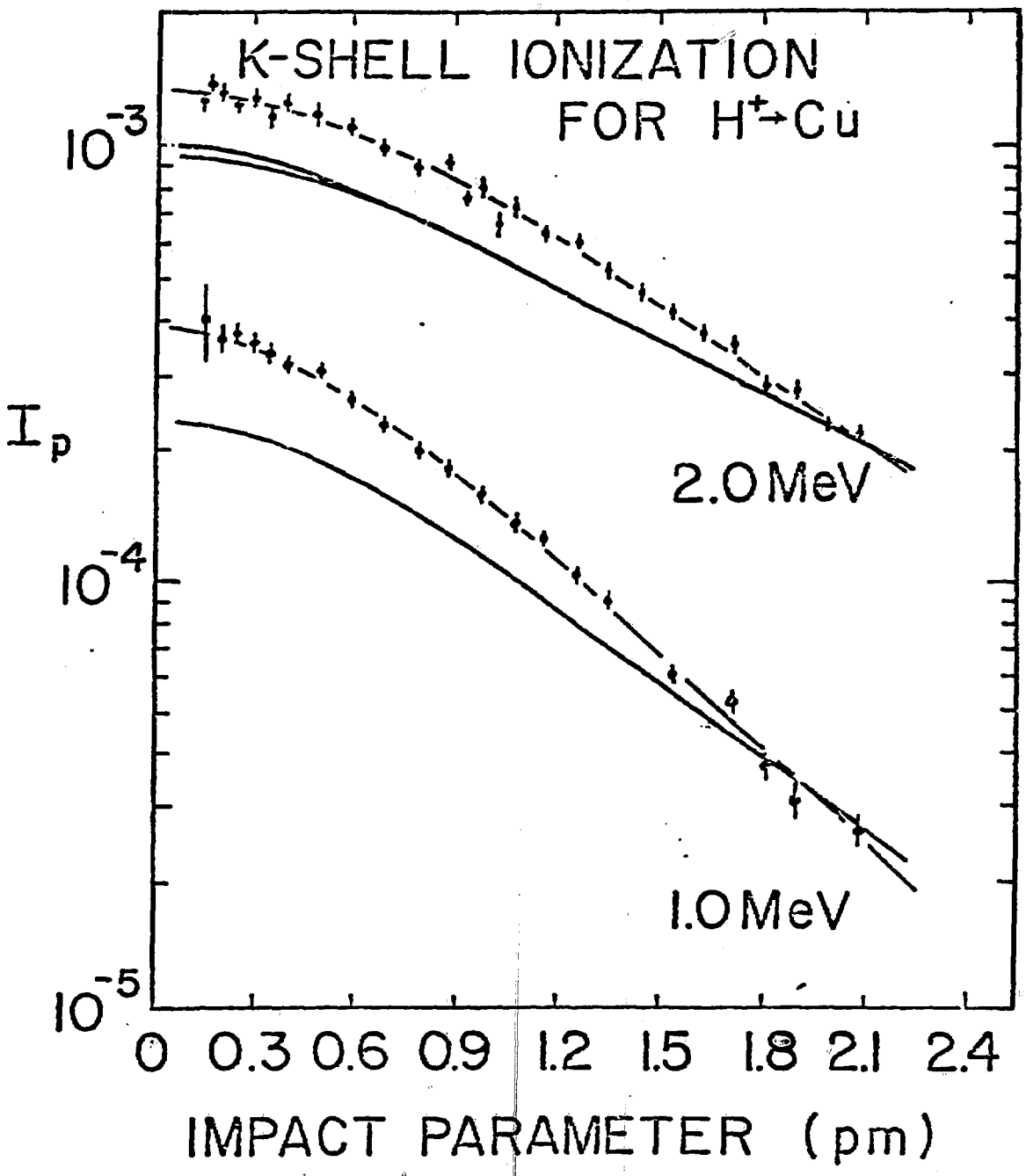

Cu K-SHELL IONIZATION
BY 0.50 MeV PROTONS
I_p (10^{-4})
1.5
1.0
0.5
0
0
0.5
1.0
1.5
IMPACT PARAMETER (pm)

Fig. 4

Fig 5. R.T.D



PR-A—June—AA1011W—Fig 3—45%

Fig. 5

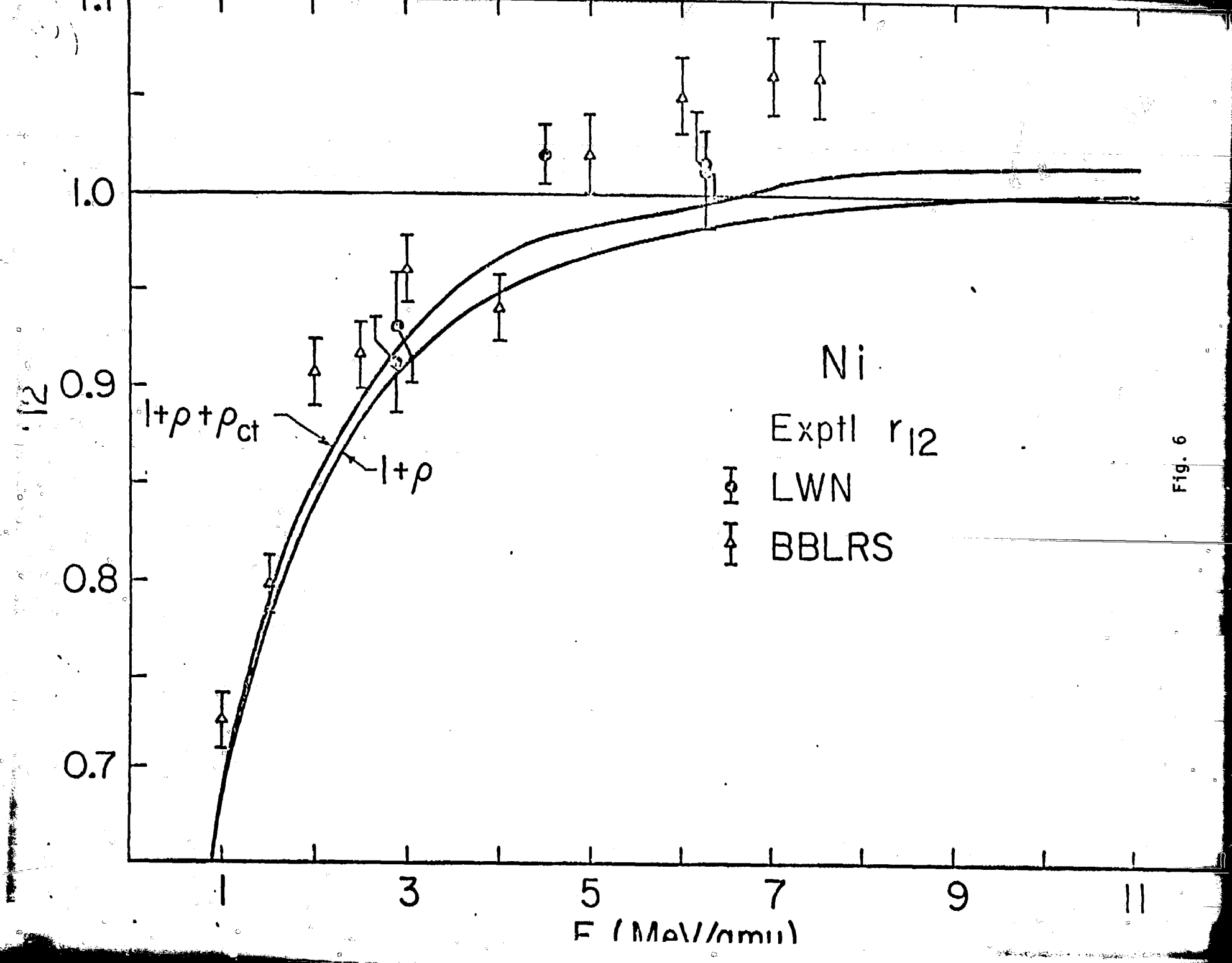
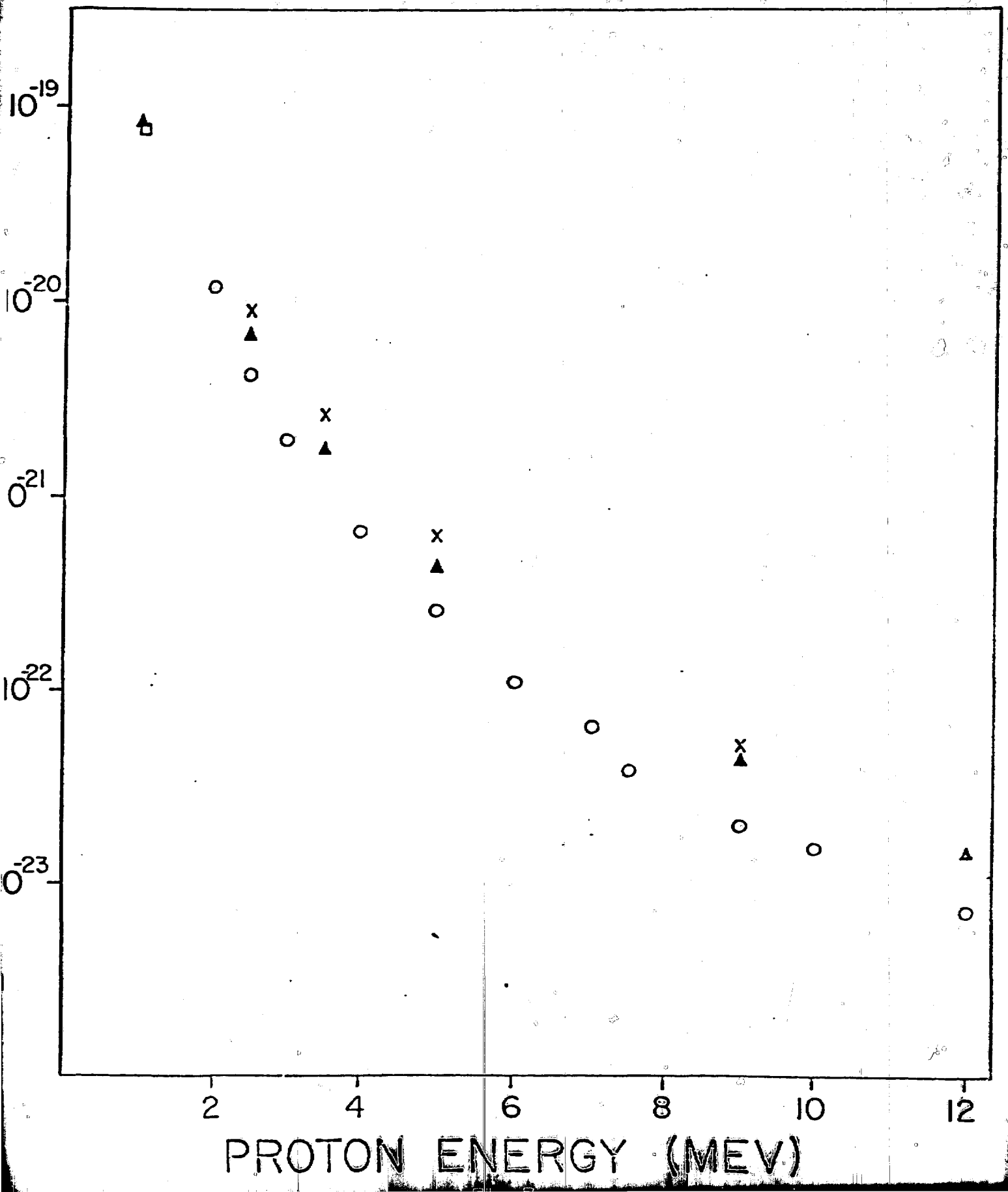

1.0
0.9
0.8
0.7
r_{12}
$1+\rho+\rho_{ct}$
$1+\rho$
Ni
Exptl r_{12}
LWN
BBLRS
1
3
5
7
9
11
E (MeV/amu)

Fig. 6


10-19
10-20
10-21
10-22
10-23
2
4
6
8
10
12
PROTON ENERGY (MEV)

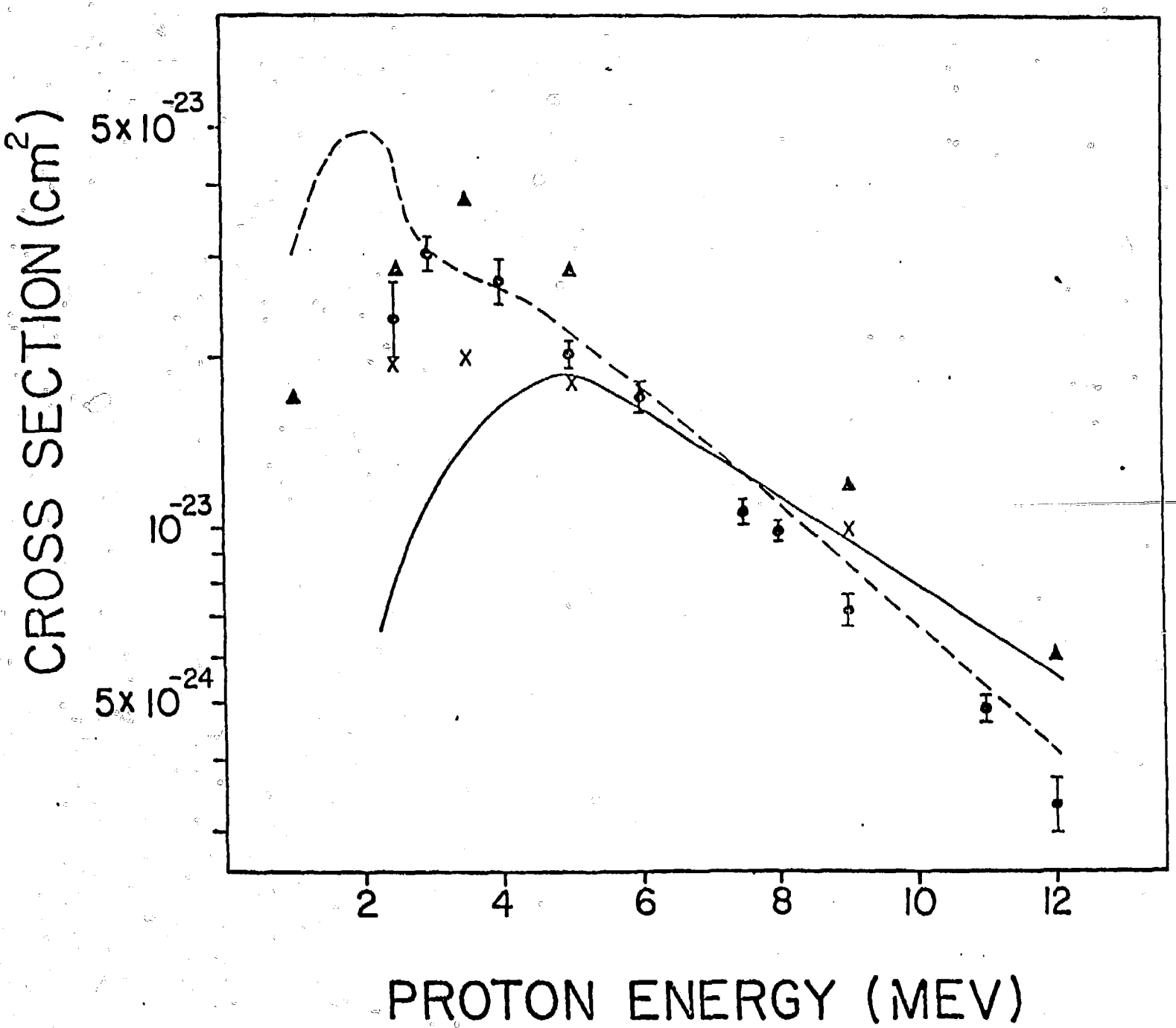

CROSS SECTION (cm²)
5x10⁻²³
10⁻²³
5x10⁻²⁴
2
4
6
8
10
12
PROTON ENERGY (MEV)

Fig. 8

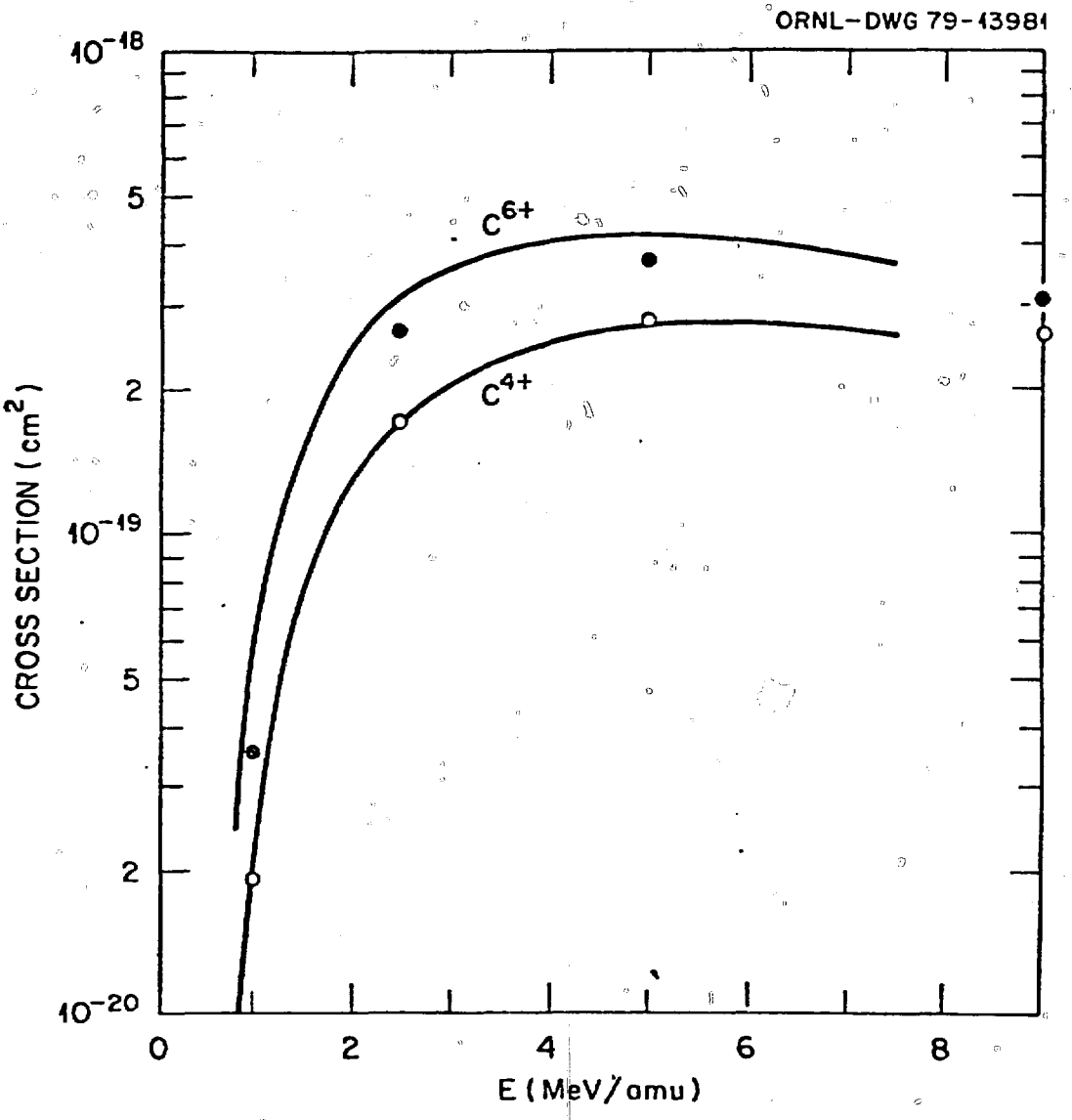

ORNL-DWG 79-13981
CROSS SECTION (cm²)
10⁻¹⁸
5
2
10⁻¹⁹
5
2
10⁻²⁰
C⁶⁺
C⁴⁺
0
2
4
6
8
E (MeV/amu)

Fig. 9