Excitation Potentials and Shell Corrections for the Elements $Z_2=20$ to $Z_2=30$

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Excitation potentials and shell corrections for the elements $Z_2=20$ to $Z_2=30$ are evaluated from experimental stopping-power data for 5–12-MeV protons and deuterons. Use is made of Walske's K- and L-shell corrections and shell corrections calculated by Bonderup on the basis of the Thomas-Fermi model. It is suggested that Cu be used rather than Al as a standard for stopping-power measurements. I_{Cu} is deduced to be 320.8 ± 3.8 eV. Relative stopping-power measurements by Bakker and Segrè, by Teasdale, by Burkig *et al.*, and by Nakano *et al.* are normalized to Cu, and mean excitation potentials are found by means of Bonderup's shell corrections. With only a few exceptions, they agree with the I values obtained from our measurements. Within the Z_2 interval treated here, it is found that I/Z_2 increases with increasing Z_2, contrary to the general trend through the periodic system of elements.

I. INTRODUCTION

THE theory of penetration of heavy charged particles through matter has recently been reviewed by Fano,[1] and an entire publication has been devoted to the analysis of the theoretical and experimental situation within this field.[2] It appeared there that the situation was quite satisfactory for a few materials (e.g., Al and Cu) which have often been studied experimentally. The basic parameters in the theory were known well enough to make it possible to calculate the proton stopping powers of these materials to within approximately 1% throughout the MeV range and well into the BeV region. For many other materials the situation was very unsatisfactory, mainly because of poor knowledge of the mean excitation potentials. Nevertheless, many tabulations have been published for different materials. As shown in Ref. 3, they often disagree with new experimental results.

Since the appearance of Refs. 1 and 2, the accuracy of stopping-power measurements has been considerably improved,[3–5] and there has also been progress on the theoretical side.[6,7] It thus appears feasible to try an evaluation of the basic parameters of stopping-power theory from the recently published experimental data for the elements from $Z_2=20$ to $Z_2=30$.[3]

In Sec. II, the present status of the Bethe stopping-power theory is reviewed in some detail, especially the attempts to make theoretical calculations of mean excitation potentials and shell corrections. In Sec. III, this material is used for an evaluation of these from our own experimental data, and in Sec. IV, published relative stopping-power measurements are used for the evaluation of mean excitation potentials for the same elements. Finally the results obtained are discussed in Sec. V.

II. REVIEW OF THEORY

The stopping power of a swift charged particle is given by the expression

$$-\frac{dE}{dx}=\frac{4\pi e^4 Z_1^2}{mv^2}\frac{N_0}{A}Z_2L(v,Z_2), \tag{1}$$

where m and $-e$ are the electron mass and charge, respectively. Z_1e and v are the charge and the velocity of the incoming ion, N_0 is Avogadro's number, and A and Z_2 are the atomic weight and number of the target material. Note that the dimension of dx is mass/area. At energies of interest to us the dimensionless function $L(v,Z_2)$ is given by the Bethe expression

$$L(v,Z_2)=\ln\frac{2mv^2}{I}+\ln\frac{1}{1-\beta^2}-\beta^2-\frac{C}{Z_2}, \tag{2}$$

where I is the mean excitation potential of the target material, C/Z_2 are the so-called shell corrections, and β is the ratio of the projectile velocity to the velocity of light. Equation (2) may also be written in the form

$$L(v,Z_2)=f(\beta)-\ln I-C/Z_2, \tag{3}$$

where the velocity dependence of Eq. (2) is contained in $f(\beta)$. A detailed derivation of Eqs. (1) and (2) may be found in Fano's review article.[1]

Until some years ago the importance of the shell corrections was often underestimated, and I was evaluated from experiments disregarding these corrections altogether; thus velocity-dependent values of I given by[8]

$$\ln I'=\ln I+C/Z_2 \tag{4}$$

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[1] U. Fano, Ann. Rev. Nucl. Sci. **13**, 1 (1963).

[2] Natl. Acad. Sci. Natl. Res. Council Publ. 1133 (1964).

[3] H. H. Andersen, C. C. Hanke, H. Simonsen, H. Sørensen, and P. Vajda, Phys. Rev. **175**, 389 (1968).

[4] H. H. Andersen, C. C. Hanke, H. Sørensen, and P. Vajda, Phys. Rev. **153**, 338 (1967).

[5] H. H. Andersen, A. F. Garfinkel, C. C. Hanke, and H. Sørensen, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **35**, No. 4 (1966).

[6] J. Lindhard and Aa. Winther, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **34**, No. 4 (1964).

[7] E. Bonderup, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **35**, No. 17 (1967).

[8] Note that the expression (4) is the reduced variable X_{expt} used in Ref. 3.

were obtained. The proper theoretical definition of I is

$$\ln I=\sum_n f_n \ln E_n. \tag{5}$$

Here E_n are all possible transition energies of the target electron system and f_n the corresponding dipole oscillator strengths. The main concern of this paper will be to try to separate the two terms in Eq. (4).

Equation (5) is of little use for a direct calculation of $\ln I$ because the oscillator strengths are not known accurately enough in the most important energy-transition range from 10 to 1000 eV. A direct calculation has only met with success for the very simplest target atoms. On the other hand, I is the main nontrivial factor in the theoretical evaluation of the stopping power of a given element. Thus it appears reasonable to demand that any theory of the stopping power of specific materials should also yield a value for I. This requirement appears only to be met by statistical calculations of Thomas-Fermi nature. The simplest result of this type of approach is Bloch's rule

$$I=I_0 Z_2, \tag{6}$$

where $I_0\approx 10$ eV. From the evaluation of experimental data it has been clear for a long time that I_0 is not a constant, but decreases with increasing Z_2 (see e.g., Turner[9]). Brandt[10,11] argued from Thomas-Fermi-Dirac arguments that

$$I_0=I_0'(1+k_0 Z_2^{-2/3}), \tag{7}$$

with $I_0'=9.5$ eV and $k_0=0.70$ (the actual value of I is then $I=I_0 Z_2 F$, where F is a so-called valence factor), while Lindhard[12] and Bonderup[7] advocate the view that it is possible to account for the decrease in I_0 within the Thomas-Fermi theory. They give a Thomas-Fermi equivalent of Eq. (5) in the form

$$\ln I_0=\int_0^\infty g\left(\frac{\omega}{Z_2}\right)\ln\left(\frac{\hbar\omega}{Z_2}\right)d\left(\frac{\omega}{Z_2}\right), \tag{8}$$

where $g(\omega/Z_2)$ is the density of dipole oscillator strengths, and they argue that there will be a gap in the distribution g at low energies, causing I_0 to decrease with increasing Z_2.

The relative stopping-power measurements of Burkig and McKenzie[13] at 19.8 MeV show considerable fluctuations in $\ln I+C/Z_2$, as illustrated clearly by Bichsel.[14] Substantial oscillations occur around the smooth decrease, presumably connected with the shell structure of the target atoms. As the amplitude of these oscillations is larger than the total shell corrections, within the Z_2 interval treated here, the fluctuations in $\ln I+C/Z_2$ must be due mainly to I and not C/Z_2. Lindhard and Scharff[15] showed that the statistical model also indicated these oscillations if distributions more realistic than the Thomas-Fermi one were used for the outermost electrons. For instance, they obtained a considerably lower I_0 for Ar than for Cu.

The term C/Z_2, representing the so-called shell corrections, describes the nonparticipation of some of the electrons in the stopping process. The corrections reach maximum values of the order of 0.1 for light and 0.3 for heavy elements at proton energies of a few MeV and decrease rapidly at higher energies. To neglect them in the evaluation of I from Eq. (4) will thus give errors of the order of 10 to 30%. The correction due to a given shell, i, vanishes asymptotically for $v\gg v_i$,[16] where v_i is the orbital velocity of the bound electrons. Because of the relativistic velocities of inner-shell electrons in heavy elements, the condition $v\gg v_i$ will never be fulfilled, and the shell corrections for these elements will not disappear even for $\beta\rightarrow 1$. It is somewhat misleading to call C/Z_2 a correction because its evaluation abandons the method used in the derivation of Eqs. (1) and (2).[1] The name "shell correction" has nevertheless been retained here because it is customary to use it.

The first attempts to calculate C/Z_2 were made by a shell-by-shell approach. The appropriate matrix elements for the energy transfers were calculated by means of hydrogenic wave functions to describe the electrons. This was done for the K-[17] and L-electrons[18] by Walske. The L-shell corrections are only claimed to be valid for $Z_2>30$, and the whole scheme is dubious at high Z_2 because the inner electrons are treated as nonrelativistic.

Bichsel noted[14,19] that the K- and L-shell corrections as calculated by Walske were quite similar in shape, and proposed to obtain higher shell corrections by scaling the L-shell correction in energy and amplitude. He treated the scaling factors as fitting parameters and obtained a good fit to experimental data. Janni[20] lowered the number of free parameters by demanding the scaling factors to vary slowly with Z_2. It was then possible to fit all data in a single computation because faster computers had appeared. The fit for a specific element might not be as good as Bichsel's, but it will be more reliable to extrapolate to elements where the experimental material is scarce. Bichsel has recently abandoned the use of a separate correction for each subshell.[21]

[9] J. E. Turner, Ref. 2, p. 99.
[10] W. Brandt, Phys. Rev. **112**, 1624 (1958).
[11] W. Brandt, Natl. Acad. Sci. Natl. Res. Council Publ. 752, p. 56 (1960).
[12] J. Lindhard, Ref. 2, p. 1.
[13] V. C. Burkig and K. R. McKenzie, Phys. Rev. **106**, 848 (1957).
[14] Hans Bichsel, Ref. 2, p. 17.
[15] J. Lindhard and M. Scharff, Natl. Acad. Sci. Natl. Res. Council Publ. 752, p. 49 (1960).
[16] U. Fano and J. E. Turner, Ref. 2, p. 49.
[17] M. C. Walske, Phys. Rev. **88**, 1283 (1952).
[18] M. C. Walske, Phys. Rev. **101**, 940 (1957).
[19] Hans Bichsel, Linear Accelerator Group, University of Southern California, Technical Report No. TR-3, 1961 and 1963 (unpublished).
[20] J. F. Janni, Report No. AFWL-TR 65-150, 1966 (unpublished).
[21] Hans Bichsel, University of California Lawrence Radiation Laboratory Report No. UCRL-17538, 1967 (unpublished).

TABLE I. Mean excitation potentials for the elements $20 \leq Z_2 \leq 30$ as obtained by asymptotic and relative fitting to the stopping-power data of Ref. 3. The first two columns include only the fitting uncertainty, while the experimental errors are also included in the average values.

Element	Z_2	I(eV) Asymptotic	I(eV) Relative	I(eV) Average	I/Z_2 (eV)
Ca	20	193.6±1.6	196.0±1.2	194.8±3.4	9.74±0.17
Sc	21	216.2±1.8	217.5±1.1	216.8±3.6	10.32±0.17
Ti	22	228.6±1.8	229.7±1.0	229.8±2.6	10.44±0.12
V	23	239.4±1.9	238.9±0.7	239.2±2.8	10.40±0.12
Cr	24	258.5±2.1	257.5±1.0	258.0±4.4	10.75±0.17
Mn	25	273.2±2.2	273.1±0.5	273.1±5.4	10.93±0.20
Fe	26	280.0±2.2	281.2±0.8	280.6±3.1	10.79±0.12
Co	27	299.0±2.4	298.7±0.9	298.8±3.7	11.06±0.12
Ni	28	302.9±2.4	303.5±0.9	303.2±3.7	10.83±0.12
Cu	29	320.8±2.5	···	320.8±3.8	11.06±0.12
Zn	30	322.8±2.5	323.0±1.0	323.1±3.8	10.77±0.12

Khandelwal and Merzbacher[22] have extended the shell-by-shell calculations to the M shell. The calculations are extremely laborious, and the deduced corrections do not agree well with the M-shell corrections obtained by Janni by the scaling method (Ref. 20, Fig. 6).

The problem of obtaining theoretical shell corrections has been treated in an entirely different way by Bonderup.[7] Lindhard and Winther[6] derived an expression for the stopping power of a gas of free electrons as a function of the density of the gas. Bonderup assumed that this would still hold locally in an inhomogeneous electron gas. He then obtained the stopping power by an integration over the electron distribution of the target atoms, using the Lenz-Jensen expression for this distribution.[23] The theory is nonrelativistic in its treatment of both projectile and target electrons. The excitation potentials are still given by $I=I_0Z_2$, with I_0 constant [cf. Eq. (8)]. One great uncertainty in such a calculation is that I will be greatly influenced by the detailed distribution of the outermost electrons as shown specifically for C.[7] Theoretical shell corrections were then obtained as $X(v,Z_2)_{\text{theor}}-\ln I_0Z_2$, whereby the influence of uncertainties in the calculation of I was eliminated. (The definition of X_{theor} is equivalent to that of X_{expt}[9]).

As is the case with the shell-by-shell computations, these calculations may need corrections for high Z_2 because of the nonrelativistic treatment of the target electrons. For low and intermediate Z_2 they yield shell corrections for all elements.

Fano (Ref. 1, p. 37) pointed out that shell corrections obtained by either of the above-mentioned approaches behave like $av^{-2}+bv^{-4}$ for $v\rightarrow c$. Fano and Turner[10] calculated C/Z_2 at these high velocities, and their asymptotic values have been tabulated by Turner.[9] Bonderup found that the statistical model yielded numerical values in good agreement with this.[24] For low and intermediate values of Z_2 the two approaches thus yield a common asymptote at high velocities.

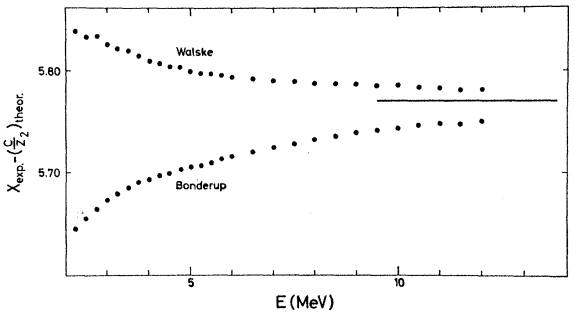

FIG. 1. Asymptotic fitting of the mean excitation potential to experimental stopping-power data for Cu by means of Walske's and Bonderup's shell corrections. The result is $\ln I=5.770\pm0.008$ and $I=320.8\pm2.5$ eV (fitting error only).

III. EVALUATION OF I AND C/Z_2 FROM EXPERIMENTAL DATA

To obtain experimental values of I we use two different approaches, "asymptotic fitting" and "relative fitting."

The first approach is defined as follows: We calculate

$$\ln I_{\text{expt}}'=X_{\text{expt}}-(C/Z_2)_{\text{theor}}, \tag{9}$$

where

$$X_{\text{expt}}=f(\beta)-L_{\text{expt}}; \tag{10}$$

L_{expt} is calculated from experimental stopping-power data by means of Eq. (1). If the theoretical shell corrections are not entirely correct, $\ln I_{\text{expt}}'$ will be found to be energy-dependent. If, however, an asymptote at high energies is observed for $\ln I_{\text{expt}}$, a well-defined value of $\ln I_{\text{expt}}$ may be obtained. As pointed out in the preceding section, Walske's and Bonderup's shell corrections have the same asymptotic values at high velocities (apart from the very small contribution of the M-shell correction to the asymptotic value). $\ln I_{\text{expt}}'$ as calculated from Eq. (10) by means of Walske's and Bonderup's shell corrections must thus have the same asymptotic value.

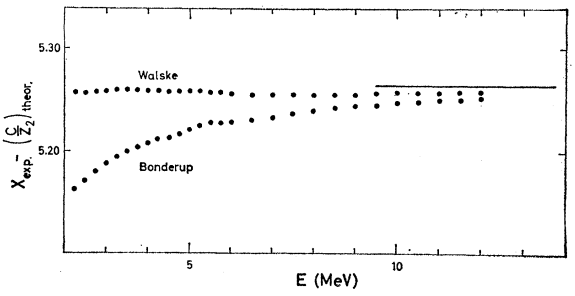

FIG. 2. Asymptotic fitting of the mean excitation potential to experimental stopping-power data for Ca by means of Walske's and Bonderup's shell corrections. The result is $\ln I=5.265\pm0.008$ and $I=193.6\pm1.6$ eV (fitting error only).

[22] G. S. Khandelwal and E. S. Merzbacher, Phys. Rev. 144, 349 (1966).
[23] H. Jensen, Z. Physik 77, 722 (1932).
[24] E. Bonderup (private communication).

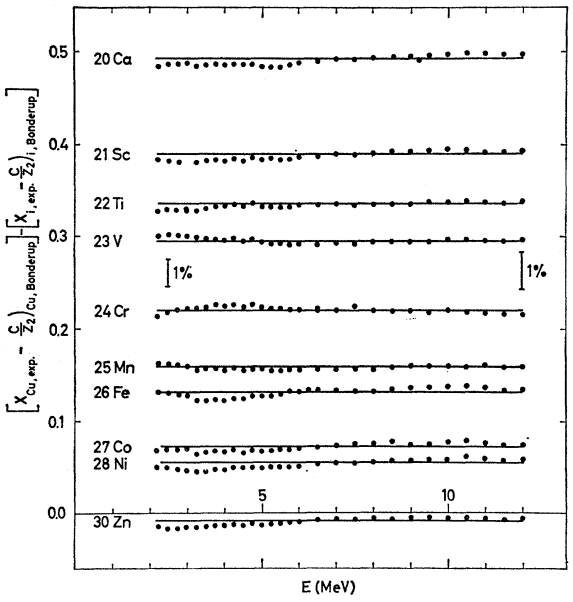

FIG. 3. Relative fitting of excitation potentials to that of Cu. The differences $\ln I_{Cu}-\ln I_i$ are shown as a function of energy, where $\ln I_i$ is found as $(X_{expt}-C/Z_2)_{Bonderup,i}$. The energy variation of the difference curves is seen to be small. The displacement of the curves which would be caused by a 1% change in the experimental stopping powers is also shown.

Figure 1 shows $\ln I_{expt}'$ for Cu as an example. Here it is rather easy to estimate the position of the asymptote. To make certain that the asymptote is placed consistently in all cases, we use the following procedure: The distances of the two curves from the asymptote at 12 MeV are determined to be directly proportional to the slopes of the curves at the same energy. The feasibility of this scheme is recognized from Fig. 2, where the curves for Ca are shown. The asymptote is no longer squeezed between the two curves, and it might be difficult to estimate the position of the asymptote without a definite procedure. For the intermediate elements, a gradual transition from the behavior shown in Fig. 1 to that in Fig. 2 is observed. The result of the

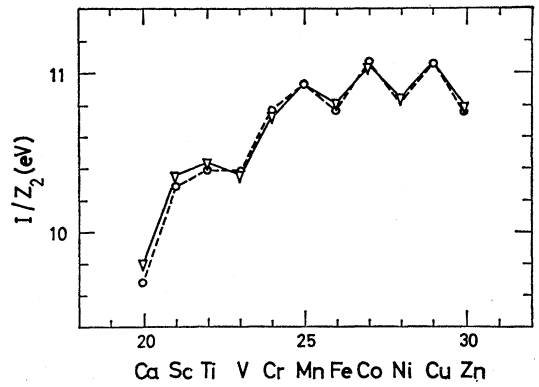

FIG. 4. Excitation potentials evaluated by means of asymptotic Δ and relative 0 fitting.

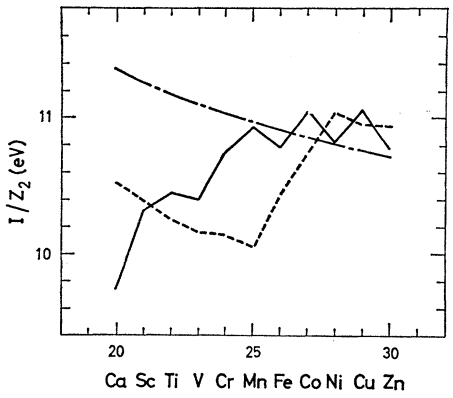

FIG. 5. Experimental values of I/Z_2 (solid) as compared with those proposed by Janni (Ref. 20) (dashed) and Turner and Sternheimer (Refs. 9 and 25) (dot-dashed).

fitting for all elements in the interval $20\leq Z_2\leq 30$ is given in Table I.

In the second approach we assume that the theoretical shell corrections vary slowly with Z_2 at fixed velocities. Then

$$\Delta \ln I_{expt,i}'=\ln I_{expt,Cu}'-\ln I_{expt,i}' \qquad (11)$$

varies very little with v and yields the ratio between I_{Cu} and I_i. If the shell corrections are approximate, this will only work for elements with not too different atomic numbers. On the other hand, most of the systematic errors, both in the shell corrections and in the experimental data, will disappear in the difference equation (11). Especially worth mentioning is that systematic errors in the energy determination of the projectile will be completely eliminated. Finally, while the asymptotic fitting only makes use of the high-energy trend of the data, the relative fitting uses the entire energy interval. Agreement between the results obtained by the two methods is thus a check on the consistency of the schemes.

Figure 3 shows the result of the relative fitting by means of Bonderup's shell corrections. It is seen that the

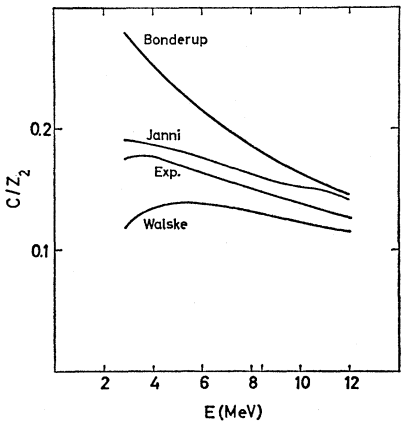

FIG. 6. Comparison of experimental to theoretical shell corrections in Cu.

TABLE II. Experimental shell corrections as determined from the experimental stopping-power data of Ref. 3 and the mean excitation potentials of Table I.

E (MeV)	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
3.00	0.142	0.145	0.146	0.139	0.145	0.157	0.168	0.170	0.180	0.176	0.188
3.50	0.141	0.143	0.142	0.142	0.143	0.160	0.173	0.172	0.182	0.178	0.189
4.00	0.137	0.139	0.137	0.140	0.139	0.158	0.171	0.170	0.178	0.176	0.187
4.50	0.132	0.132	0.132	0.137	0.136	0.155	0.164	0.166	0.172	0.172	0.183
5.00	0.128	0.128	0.128	0.133	0.133	0.150	0.158	0.161	0.168	0.169	0.178
5.50	0.124	0.123	0.123	0.130	0.130	0.146	0.152	0.155	0.164	0.165	0.174
6.00	0.119	0.119	0.120	0.127	0.127	0.143	0.146	0.151	0.159	0.162	0.168
6.50	0.114	0.115	0.116	0.124	0.123	0.138	0.141	0.146	0.154	0.159	0.163
7.00	0.110	0.111	0.113	0.121	0.122	0.135	0.137	0.141	0.150	0.156	0.159
7.50	0.107	0.108	0.110	0.118	0.119	0.132	0.134	0.136	0.145	0.152	0.155
8.00	0.104	0.105	0.107	0.115	0.117	0.129	0.131	0.132	0.142	0.149	0.151
8.50	0.103	0.102	0.105	0.112	0.115	0.125	0.127	0.129	0.139	0.146	0.148
9.00	0.099	0.099	0.103	0.110	0.113	0.122	0.125	0.126	0.134	0.144	0.145
9.50	0.096	0.097	0.100	0.107	0.111	0.119	0.122	0.124	0.130	0.140	0.141
10.00	0.094	0.095	0.099	0.105	0.109	0.118	0.120	0.122	0.128	0.138	0.138
10.50	0.092	0.093	0.096	0.102	0.108	0.114	0.117	0.119	0.125	0.136	0.136
11.00	0.090	0.092	0.095	0.100	0.106	0.112	0.115	0.117	0.123	0.131	0.133
11.50	0.088	0.091	0.093	0.097	0.105	0.110	0.114	0.116	0.121	0.128	0.130
12.00	0.087	0.090	0.092	0.095	0.104	0.108	0.112	0.114	0.119	0.126	0.128

assumption that $\Delta \ln I_i$ is energy-independent is very well fulfilled. As the missing M-shell corrections vary rapidly with Z_2 the condition for the use of relative fitting is not fulfilled in connection with Walske's shell corrections.

The result of the relative fitting to $I_{Cu}=320.8$ eV (as found by asymptotic fitting) is given in Table I, and the results of the two fitting procedures are compared in Fig. 4. The agreement is seen to be good.

Table I also gives average values of I and I/Z_2. They represent the final result of the present evaluation and are displayed in Fig. 5 together with values proposed by Janni,[20] Turner,[9] and Sternheimer.[25] Within the Z_2 interval considered here, Turner's and Sternheimer's values have a wrong trend, but the numerical agreement is quite good for $Z_2 \geq 24$. Janni's values are seen to agree well where measurements have been made before (Ti,Fe,Ni,Cu), but where no measurements have been made until now (Cr,Mn), or where existing results have not been considered reliable (Ca), the agreement is very bad. It is possible to obtain values of I/Z_2 by interpolation if they are known for the neighbors on both sides, but interpolation over wider spacings to obtain I is very uncertain.

As I has now been found, it is possible to find the shell corrections C/Z_2. They are obtained as

$$(C/Z_2)_{\text{expt}}=X_{\text{expt}}-\ln I_{\text{expt}}. \tag{12}$$

As an example, experimental values for (C/Z_2) for Cu are shown in Fig. 6 together with the theoretical values by Walske $[(C_K+C_L)/Z_2]$ and Bonderup and the semiempirical ones by Janni. The shell corrections as determined from Eq. (12) are tabulated in Table II. The accuracy is difficult to estimate, but is of the order of ± 0.008. A discussion is given in Sec. V.

[25] R. M. Sternheimer, Phys. Rev. **164**, 349 (1967).

It is difficult to find published experimental results directly comparable to those obtained here. Cu appears to be the only element for which a sufficient number of good data have been used to evaluate I; but although they are stated as recommendations for future use in Ref. 2, these authors obtain different results. Care must be taken in such comparisons. Some authors use

$$\ln I_{\text{adj}}=\ln I+(C/Z_2)_{\beta=1} \tag{13}$$

instead of I. Where this is the case, values have been converted to I. For I_{Cu} Bichsel[14] gives 326 eV, Fano[1] 315 eV, and Turner[9] 314 eV. Janni uses 318 eV, while Bichsel (Ref. 2, p. 28) states that $I=320\pm 2$ eV is the best existing fit to all data below 30 MeV. Recently a high-energy result has been obtained from a new measurement by Vasilievskii and Prokoshkin.[26] They find that $I=318\pm 6$ eV. It is seen that the agreement between our value (320.8 ± 3.8 eV) and the two last-mentioned ones is very good. As the other data are not as accurate, we see no serious discrepancy and will use $I=320.8$ eV in the following.

IV. COMPARISON WITH RELATIVE STOPPING-POWER MEASUREMENTS

It is only possible to compare a few of the results obtained in the preceding section with other absolute measurements, but there exist some relative measurements of high quality. To obtain excitation potentials from these measurements it is of course necessary to normalize to a fixed material. We choose the value found for Cu above. The method is then essentially the same as that used for relative fitting in the last section.

Let ϵ be the stopping power per electron. If the relative stopping per electron is given as $r_i=\epsilon_i/\epsilon_{Cu}$,

[26] I. M. Vasilievskii and Yu. D. Prokoshkin, Yadern. Fiz. 4, 549 (1966) [English transl.: Soviet J. Nucl. Phys. 4, 390 (1967)].

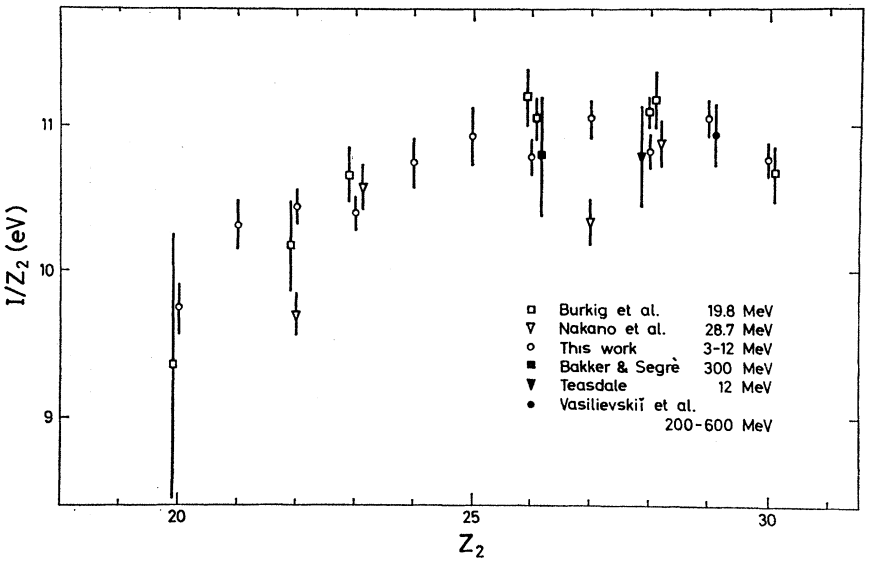

FIG. 7. Excitation potentials calculated from the measurements of several authors. Error indications in all cases as stated by authors, i.e., the uncertainty in the normalization value $I_{Cu}=320.8$ eV, have not been included for relative measurements.

we have

$$\ln I_i = f(\beta) - (C/Z_2)_i - r_i[f(\beta) - \ln I_{Cu} - (C/Z_2)_{Cu}]. \quad (14)$$

If only Z_2 is not widely different from 29, the results do not depend very much on the choice of the shell corrections because they vary slowly with Z_2, i.e., the results do not depend on whether we use Bonderup's or Walske's shell corrections.

The measurements evaluated here are those of Teasdale[27] for 12-MeV protons, of Burkig and McKenzie[13] for 19.8-MeV protons, of Nakano *et al.*[28] for 28.7-MeV protons, and of Bakker and Segrè[29] for 300-MeV protons. Not all of these measurements were made relative to Cu. Where this is not the case, two ratios have been combined to yield the ratio relative to Cu although this lowers the accuracy of the results. Apart from the use of different fixed points, the result of this evaluation is in very good agreement with a recent calculation by Dalton and Turner,[30] who used still another approach to the shell corrections. The outcome of our evaluation is shown in Fig. 7. Although the agreement is generally very good, the authors concerned must sometimes have underestimated their errors.

V. DISCUSSION

Figure 7 shows that the oscillatory tendency of I/Z_2 is so strong that in the region $20 \leq Z_2 \leq 30$ the general decreasing trend of I/Z_2 is reversed. Furthermore, a fine structure in I/Z_2 is seen. Elements of even Z_2 appear to have lower I/Z_2 than their neighbors with odd Z_2. It is, however, doubtful whether this is of statistical significance, especially because some of the relative measurements indicate the opposite tendency (cf. Fig. 7). Fano states (Ref. 1, p. 25) that interpolation should be dependable to a few per cent of the value of I in the range $Z_2 > 20$. This appears to be a dubious procedure in regions where the positions of the oscillations have not yet been established.

The shell corrections as given in Table II are quite close to those of Janni, but they are in some cases smaller than the sum of Walske's K- and L-shell corrections. It is thus not possible to find empirical M-shell corrections by means of Table II, and care must in any case be recommended if these tabulated values are fitted to theory. The evaluation as presented here will classify all energy-dependent corrections to the simple Bethe formula as shell corrections. These deviations might be of different nature, e.g., deviations from the Born approximation and errors caused by joining of the different regions of approximation.[1] This might explain why the tabulated shell corrections are lower than Walske's K- plus L-shell corrections for lower Z_2. Another explanation might of course be that Walske's values are too large in this region (where they are not claimed to be valid). In any case this shows that it is very questionable to use Walske's L corrections at still lower Z_2 values. Recent measurements with single- and double-charged ions at equal velocities have shown that other velocity-dependent corrections are important and have to be taken into account if Table II is compared with theoretical estimates.[31]

It remains to be discussed what policy to choose for future experimental work to obtain maximum information about shell corrections and excitation potentials. It is apparent from Fig. 7 that our experi-

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mental method is not more accurate for obtaining excitation potentials than the best relative measurements, especially not when they are made directly relative to a close neighbor, see e.g., the points for Fe and Ni by Burkig *et al.* taken directly relative to Cu. The best thing to do thus appears to be to establish a few key elements throughout the periodic system, viz., Al, Cu, Ag, one of the rare earths, Au or Pb, and U. The shell corrections and excitation potentials for these six elements should be determined by careful absolute measurements over a wide suitably chosen energy interval, and excitation potentials for intermediate elements should be found from measurements relative to the nearest key element, which, with the same accuracy, are considerably faster performed than absolute measurements. This program has probably been fulfilled for Al and, in the light of the results of Ref. 3, probably also for Cu.

Until now Al has been considered some sort of standard for all stopping-power measurements. This is unfortunate for several reasons, from the theoretical standpoint partly because Walske's L corrections are not valid for this element and one has to extrapolate from higher Z_2 values to use Bichsel's scaling procedure, and partly because Z_2 is a little too low to make the statistical method really work. From the experimental standpoint it is very inconvenient that all relative measurements are made with an element at the lower end of the periodic system as a standard. Replacing it by Cu would mean that the stopping powers of materials as important for experimental nuclear physics as Fe and Ni would be known with higher accuracy. Furthermore, and this is very important, the excitation potential of Cu is very close to that of nuclear emulsion. The main difficulty for Cu appears to be the discrepancy between existing data. As mentioned above, the value $I=320.8$ eV proposed here is in perfect agreement with all low-energy data.[14] Apart from the recent result discussed above,[26] the high-energy data disagree with this, but they also disagree mutually. As will be shown in the next paragraph, it is not always profitable to go to high energies to obtain excitation potentials, and it appears that a check on the 320.8 eV should be made by high-precision measurements in the energy range of 20 to 100 MeV.

It is often assumed that since the influence of shell corrections on the determination of I vanishes at high energies, and since shell corrections are only incompletely known, it pays to measure at very high energies. This is only true with modifications. It is seen from Eq. (1) that $L(v,Z_2)$ is known with the same relative accuracy as dE/dx. From Eq. (2), it is further seen that if

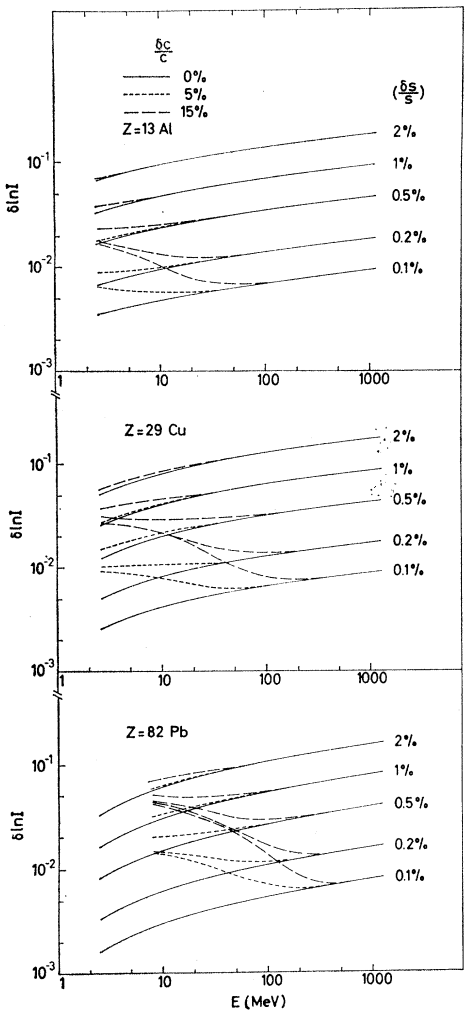

FIG. 8. Attainable accuracy in $\ln I$ as a function of energy for Al, Cu, and Pb. Parameters are the relative accuracy of stopping-power measurements and the relative accuracy in the knowledge of shell corrections.

shell corrections were perfectly known, measurement at very low energies would yield the most accurate determination of I. The result of these competing influences is shown in Fig. 8. The accuracy with which $\ln I$ (and thus approximately the relative accuracy of I) is determined is shown as a function of energy with the measuring accuracy and the uncertainty of the knowledge of shell corrections as parameters. It is seen that at the present state of the art, for Al (0.3%, ~10%) it does not pay to measure beyond 40 MeV; for Cu (0.3%, ~5%) the limit is about the same, while for Pb (0.3%, ~15%) it lies about 300 MeV. For the heavy elements an accuracy better than 2% in I cannot be hoped for at present. Here a combination of theoretical progress and careful experimental work over a broad energy range is

especially urgent. It should also be noted that when measurements are made relative to close-lying elements, the influence of uncertainties in the shell corrections is very much reduced, and in these cases it is best to measure at energies considerably below the minima of Fig. 8.

VI. CONCLUSION

The analysis of stopping-power measurements for the series of metals from Ca to Zn has shown that it is possible to separate the influence of shell corrections from that of the excitation potentials also at the relatively low energies (3–12-MeV protons) in question here. The excitation potential for Cu has been found to be 320.8±3.8 eV. This value is proposed as a future standard for relative stopping-power measurements.

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Electron Paramagnetic Resonance of NpO_2^{2+} in $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$†

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The EPR spectra of NpO_2^{2+} in $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$ have been observed at liquid-helium temperature. The Np^{6+} in its host crystals has been assumed to have an axial symmetry due to the strong NpO_2^{2+} complex. The resonances have been identified and fitted with the axial spin Hamiltonian

$$\mathcal{H}=g_{\parallel}\beta H_z S_z+g_{\perp}\beta(H_x S_x+H_y S_y)+AI_z S_z+B(I_x S_x+I_y S_y)+P[I-\tfrac{1}{3}I(I+1)].$$

For NpO_2^{2+} in $Cs_2UO_2Cl_4$, the parameters are $g_{\perp}=1.32\pm0.02$, $|A|=0.009\pm0.005$ cm^{-1}, $g_{\parallel}=1.3\pm0.3$, $P=-0.016\pm0.005$ cm^{-1}, and $B=0.0880\pm0.005$ cm^{-1}; for NpO_2^{2+} in $CsUO_2(NO_3)_3$ they are $g_{\parallel}=3.36\pm0.04$, $A=0.166\pm0.003$ cm^{-1}, $g_{\perp}=0.20\pm0.20$, $P=-0.030\pm0.003$ cm^{-1}, and $|B|=0.20\pm0.20$ cm^{-1}. The nuclear moment of Np^{237} has been calculated as $2.1\mu_B$ and $2.9\mu_B$ for Np^{6+} in $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$, respectively.

INTRODUCTION

TWO values of the nuclear moment of Np^{237} have been reported by Bleaney and co-workers[1] and by Hutchison and Weinstock.[2] Bleaney and co-workers calculated a nuclear moment of $6.0\mu_B$ from their EPR spectrum of NP^{6+} in $RbUO_2(NO_3)_3$. A value of $2.7\mu_B$ was reported by Hutchison and Weinstock based on their EPR data on NpF_6. The discrepancy of the reported nuclear moments was later resolved by Eisenstein and Pryce.[3] By choosing a ground state different from the one used by Bleaney and co-workers, Eisenstein and Pryce were able to calculate a nuclear moment of $3.2\mu_B$ for Np^{237} from the EPR data on NpO_2^{2+} in $RbUO_2(NO_3)_3$. The value of 40×10^{24} cm^{-3} for $\langle r^{-3}\rangle$ used by Eisenstein and Pryce in their calculation was different from the value of 50×10^{24} cm^{-3} used by Hutchison and Weinstock. If 50×10^{24} cm^{-3} were used as the value of $\langle r^{-3}\rangle$ in Eisenstein and Pryce's calculation, a nuclear moment of $2.6\mu_B$ would be obtained. In essence, the two reported values of the nuclear moment of Np^{237} are in agreement. We are reporting two more measurements of the nuclear moment of Np^{237} from our EPR data on Np^{6+} in $Cs_2UO_2Cl_4$ and in $CsUO_2(NO_3)_3$.

PREPARATION OF CRYSTALS

The samples were prepared by slow evaporation of water from the salts in an acidic solution. The neptunium was obtained from Union Carbide in the form of NpO_2. The dioxide was oxidized to NpO_2^{2+} in a solution of $6M$ H_2SO_4 and $0.1M$ $KBrO_3$.[4] The NpO_2^{2+} was precipitated as neptunyl hydroxide. This hydroxide was redissolved in solution of $Cs_2UO_2Cl_4$ with HCl and in the solution of $CsUO_2(NO_3)_3$ with HNO_3. The mole

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