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Ionization of silicon, germanium, tin and lead by electron impact

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Abstract

Cross sections for electron impact ionization of neutral atoms are important in modelling of low temperature plasmas and gases. Cross sections for ionization have been calculated for ionization from ground levels and low-lying metastable levels of Si, Ge, Sn and Pb. We use the binary-encounter-Bethe approximation (BEB) for direct ionization and the scaled plane-wave Born approximation for excitations to autoionizing levels. Multiconfiguration Dirac–Fock wavefunctions have been used for the atomic structure. We have also employed a technique to accurately determine the range of excitation energies of the dominant autoionizing levels. It is clear that autoionization is important in these elements and must be included to obtain accurate total ionization cross sections. The calculated ionization cross sections are in good agreement with experimental measurements.

1. Introduction

Cross sections for ionization of atoms by electron impact are essential input data in the modelling of low-temperature plasmas used in industrial applications such as semiconductor fabrication and material coating. Atoms commonly used in such applications, such as silicon and germanium, are open-shell atoms that pose challenges to both experimental and theoretical studies of collision cross sections. Experimentally, it is not easy to prepare a large quantity of these atoms in their ground states in gaseous forms. Theoretically, extensive configuration mixing is needed to accurately describe their electronic structure, which in turn makes it difficult to obtain reliable cross sections with advanced collision theories.

In the early 1990s, Freund *et al* [1] published experimental cross sections for total ionization of many neutral atoms by electron impact. Most of these target atoms were prepared by neutralizing singly charged ions by charge transfer. For open-shell atoms such as those treated in this paper, the charge transfer process tends to produce the neutralized atoms not only in their ground state but also in low-lying metastable states. Although the presence of metastable target atoms in the measurements is easy to see from the threshold energies at

which ions begin to emerge, the fraction of the atoms in each low-lying state is usually not known.

The carbon-like structure of the atoms treated in this paper have electron configurations of closed shells plus a ns^2np^2 valence shell, with $n = 3$, 4, 5 or 6 for Si, Ge, Sn and Pb, respectively. These configurations give rise to ground levels of ^3P_j with $j = 2$, 1, 0, and low-lying metastable levels $^1D_2$ and $^1S_0$. In addition to direct electron impact ionization of the valence shell, ioniztion can be caused by impact ionization of an inner shell. The threshold energy for ejection of an inner shell electron is large for these atoms, however, and so the cross section for direct ionization of an inner shell is small for most of the incident electron impact energies that we consider. Direct inner shell ionization is, therefore, not included in our calculations.

A second mechanism for ionization is important, however. This is excitation to an excited bound level in the continuum followed by autoionization. This process of excitation–autoionization, EA, occurs most easily to excited levels of the $nsnp^3$ configuration, where one of the valence shell 's' electrons is excited. Levels that are easily excited are levels that are permitted by electric dipole-allowed and spin-allowed selection rules in the LS coupling scheme. Excitation cross sections for levels that are not connected by these selection rules have much smaller values and are not included in our calculations.

Levels permitted by the selection rules for excitation from the ground levels are $nsnp^3\ ^3S_1$, $^3P_{0,1,2}$ and $^3D_{1,2,3}$. Levels permitted for excitation from the low-lying metastable levels are $nsnp^3\ ^1D_2$ and $^1S_0$. We include excitations to these levels when the levels are in the continuum and when autoionization to the corresponding ion levels does not require a parity change. More specification of the relevant levels for each target atom are discussed in the sections on results. We assume, when autoionization is allowed, that it occurs with 100% probability rather than decaying radiatively.

Quantum-mechanical Born approximation ionization calculations for these elements have been done by McGuire [2] and by Bartlett and Stelbovics [3] using modifications to reduce the well-known overestimation of the Born approximation at low energies. McGuire's scaled Born approximation gave cross sections for Sn that are high compared to measurements of Freund *et al* [1] by about 5% in the peak region of the cross section, and high by more than 30% for Ge. The Bartlett and Stebovics Born calculation includes a Coulomb wave for the ejected electron that is made orthogonal to the occupied atomic orbitals. Their cross sections for Ge and Sn are generally low compared with the measurements at energies below the energy of the peak cross section but agree with the measurements in the peak region. For Si, their peak cross section is too high by about 8% compared to the measurements of Freund *et al* [1] and occurs at too high an energy, while the values are too low at energies below the peak.

Neither of these two quantum-mechanical calculations allows for the target atom to be in a metastable state and neither includes EA. Including EA would increase their calculated cross sections, giving even less agreement with the measurements.

The theoretical models we have used enable us to calculate separate ionization cross sections for the target atoms in the ground and metastable states. Such separate cross sections in turn enable plasma modellers to use arbitrary mixtures of ground-state and metastable atoms to improve agreement with observations and to test the sensitivity of plasma characteristics to external paramaters. The binary-encounter-Bethe (BEB) [4] model provides accurate cross sections for the direct ionization of neutral target atoms by electrons. It is a simple, easy to use formula without adjustable parameters. Numerous applications of the method have established its accuracy for both atoms and molecules [5–8].

Ionization by EA events is included by calculating excitation cross sections to autoionizing levels by the scaled plane-wave Born (scaled PWB) procedure developed earlier by Kim [9].

2. Theory

The BEB model is a simplified version of the more detailed binary-encounter-dipole (BED) model of Kim and Rudd [4]. The BED model combines a modified form of the Mott cross section [10, 11] with the Bethe theory [12, 13]. The BED model calculates the singly differential cross section, or the energy distribution of secondary (ejected) electrons, and requires the continuum oscillator strength, $\mathrm{d}f/\mathrm{d}E$, where E is the photon energy, for each atomic orbital. To cover a wide range of incident electron energy T, the BED model requires $\mathrm{d}f/\mathrm{d}E$ for each orbital from the threshold to over 1000 eV in E.

The exact form of the $\mathrm{d}f/\mathrm{d}E$ for H-like ions is known from theory [14], while one can sometimes deduce $\mathrm{d}f/\mathrm{d}E$ from either theoretical or experimental photoionization cross sections for other atoms. The BEB model uses a simple form for $\mathrm{d}f/\mathrm{d}E$ for each initial state orbital when accurate $\mathrm{d}f/\mathrm{d}E$ for each orbital is not available. The expression for total ionization cross section in the BEB method is based on equation (57) of Kim and Rudd [4] and given explicitly as equation (5) in Hwang, Kim and Rudd [5]. The cross section for the ionization of each orbital by an incident electron of energy T is

$$\sigma_{\mathrm{BEB}} = \frac{S}{t+u+1}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right], \tag{1}$$

where $S = 4\pi a_0^2 N(R/B)^2, t = T/B, u = U/B, a_0 = 0.529$ Å (Bohr radius), and $R = 13.61$ eV (Rydberg energy). The constant N is the number of electrons in the orbital, B is the orbital binding energy, and $U = \langle p^2/2m\rangle$ is the orbital kinetic energy of the target electron. In general, U and B are calculated from an atomic or molecular wavefunction code, except that B for the valence electron is obtained from the experimental ionization energy. The orbital cross sections equation (1) are summed over all the electron orbitals to get the total ionization cross section for the atom or molecule.

The BEB theory is an impact theory for an incident electron interacting with a bound target electron. As such, it cannot account for multiple ionization of the target by a single encounter. At high energies, where multiply ionized targets might be expected, the theory only accounts for the production of singly ionized targets. Our comparison with experiments is, therefore, only for singly ionized targets. Inner shell orbitals below the valence shell usually contribute little to the total ionization cross section because of their large binding energies, and so we include only the valence orbitals in our calculations.

An estimate of doubly ionized target cross sections can be made from the BEB theory by summing twice the cross section for ionization from an inner shell electron when the binding energy of the inner shell is sufficient to release a second electron by the Aujer effect. Similarly, triply ionized cross sections could be obtained by summing the BEB cross section three times for an inner shell orbital with sufficient binding energy to release two additional electrons, and so forth for higher multiple ionizations. We have not included these estimates in this work.

We obtained U and B for each orbital using a Dirac–Fock wavefunction code [15]. A modification has been introduced into equation (1) to reduce $u + 1$ in the denominator for atomic orbitals with the principal quantum number $n \geqslant 3$. In earlier applications of the BEB model, Hwang *et al* [5] found that the cross sections for these orbitals at energies below the energy of the peak cross section are reduced too much by the $u + 1$ term because the kinetic energy of valence orbitals with many radial nodes becomes very high (e.g., $U = 97.03$ eV, $B = 14.86$ eV for Pb 6s). The large value is related to the contraction of the radial wavefunctions as the charge increases and larger orbitals are introduced. The denominator on the right-hand side of equation (1) is therefore replaced by $t + (u + 1)/m$ where $m = 1$ when $n = 1, 2$ and

$m = n$ when $n \geqslant 3$. The BEB cross section becomes

$$\sigma_{\mathrm{BEB}} = \frac{S}{t + (u+1)/m}\left[\frac{\ln t}{2}\left(1 - \frac{1}{t^2}\right) + 1 - \frac{1}{t} - \frac{\ln t}{t+1}\right]. \tag{2}$$

This expression is used for all the BEB cross sections in this work. The success of the BEB model over earlier ionization theories can be attributed to two features of the BEB approach. First, the expression $t + u + 1$ in the denominator in equation (1) reduces the cross section noticeably between the threshold and the peak. The expressions in conventional classical and quantum-mechanical cross section theories have only the kinetic energy t of the incident electron in the denominator. The $t + u + 1$ denominator occurs naturally in the development of the BEB model but a similar denominator was introduced by Burgess in 1964 [16]. His argument was that the average kinetic energy of the incident electron during the collision process as seen by the target (bound) electron was effectively the incident kinetic energy plus the potential energy of the ionized target electron. The second factor that contributes to the success of the BEB model is the way the Mott cross section is combined with the leading dipole part of the PWB cross section at high energies. The BED theory, on which the BEB model is based, requires both the ionization cross section and the stopping cross section (the ionization cross section multiplied by the energy transferred to the target from the incident electron) to have the correct high-t asymptotic forms as determined by the Bethe theory [12]. These two features have produced much better agreement with experiments at all t than previous ionization theories.

The largest excitation cross sections for excitation to autoionizing levels occur when a core electron of the initial atom is excited to an orbital with the same principal quantum number. For silicon, for example, the ground state is $3s^2 3p^2\ ^3P_0$ and an easily excited level above the ground state is $3s3p^3\ ^3S_1$. One of the two 3s core electrons has been excited to 3p, an orbital with the same $n = 3$ principal quantum number. Excitations to other levels with different principal quantum numbers have smaller cross sections and are not included in this paper.

We calculate the excitation cross sections by the scaled plane wave Born method, scaled PWB, developed by Kim [9]. The expression for this cross section is

$$\sigma_{\mathrm{excitation}} = \sigma_{\mathrm{pwB}}\left[\frac{t}{t + E/B + 1}\right], \tag{3}$$

where σ_{pwB} is the plane wave Born (PWB) cross section for the transition, $t = T/B$ is the incident electron energy normalized to the binding energy, B is the orbital binding energy, and E is the excitation energy of the transition. Our determination of σ_{pwB} is done with a Dirac–Fock code in a single configuration calculation [15]. The PWB cross section is well known to be accurate at high energies and to greatly overestimate excitation of neutral atoms at low energies. The fraction in equation (3) accurately scales the PWB cross section at low energies to give results that agree well with experiments in nearly all neutral atoms calculated so far by this method [9, 17, 18]. The scaling denominator is similar to the denominator for direct ionization in the BEB cross section, equation (1). It reduces the cross section magnitude at low energies and shifts the peak to a higher energy while keeping intact the high-energy validity of the PWB approximation.

3. Results

The direct electron impact ionization cross sections are calculated with the BEB formula, equation (1). The results for Si, Ge and Sn are shown in tables 3–7 and in the plots of figures 1–4.

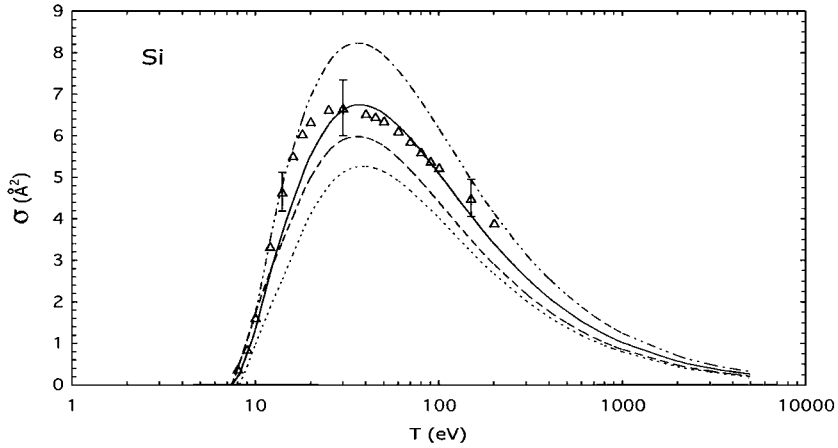

Figure 1. Ionization cross section 's' of Si. BEB cross section for $^3P_2$ direct ionization (· · · · · ·); $^1D_2$ cross section for direct ionization (– – –) and direct plus EA (— · · —); experimental data by Freund *et al* [1] (△); a mixture of equal parts $^3P_2$ and $^1D_2$ (——). Ionization from the other states in the ground level term, $^3P_0$ and $^3P_1$, are nearly identical to $^3P_2$ and are not shown. No autoionization is included from the ^3P ground term (see text). The experimental measurements at the threshold show that ionization occurs close to the ionization energy of the $^1D_2$ metastable level and well below the threshold for ionization of the ^3P_j levels, indicating that some of the target atoms in the experiment were in the metastable level. Calculated cross sections for a mixture of equal parts $^3P_2$ and $^1D_2$ fit the data throughout the energy range and especially in the peak cross section region.

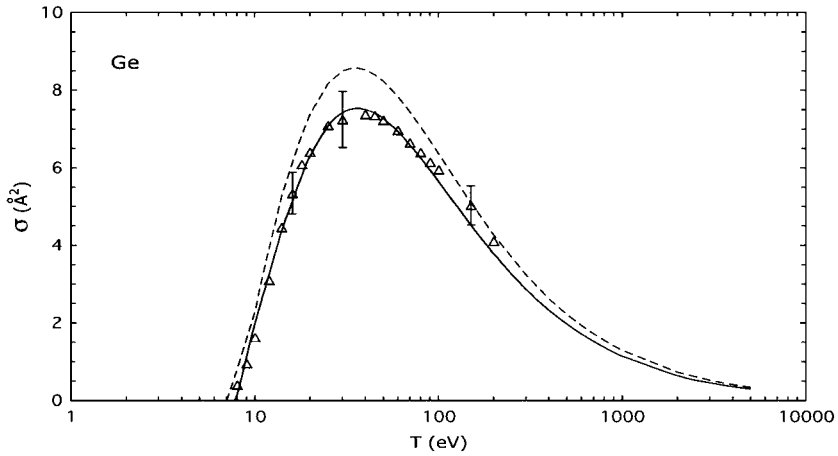

Figure 2. Ionization cross sections 's' of Ge. Cross sections for $^3P_2$ direct ionization plus EA (——); $^1D_2$ direct plus EA (– – –); experimental data by Freund *et al* [1] (△). The calculated values for the target in the $^3P_2$ level agree well with the experimental data. The other $^3P_0$ and $^3P_1$ ground term levels differ noticeably from $^3P_2$ (see table 4) and do not agree as well with experiment, especially in the peak and high-energy regions.

The indirect ionization EA process is calculated by the scaled plane wave Born formula, equation (3). The direct plus indirect total ionization cross sections are also shown in the tables and the figures. It is clear that autoionization significantly increases the ionization cross sections for each of these elements except for silicon.

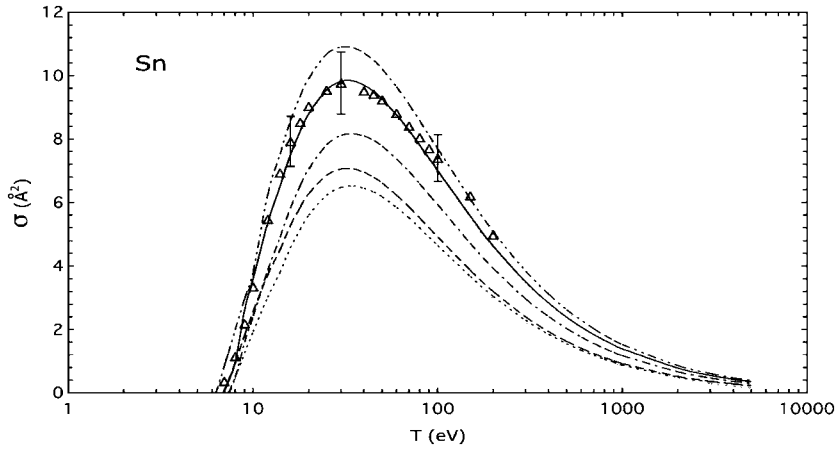

Figure 3. Ionization cross sections 's' of Sn. Cross sections for $^3P_0$ direct ionization (· · · · · ·) and direct plus EA (— · —); cross sections for $^3P_2$ direct (- - - -) and direct plus EA (——); cross sections for $^1D_2$ direct plus EA (— · · —); experimental data by Freund *et al* [1] (△). The calculated values for the target in the $^3P_2$ level agree well with the experimental data.

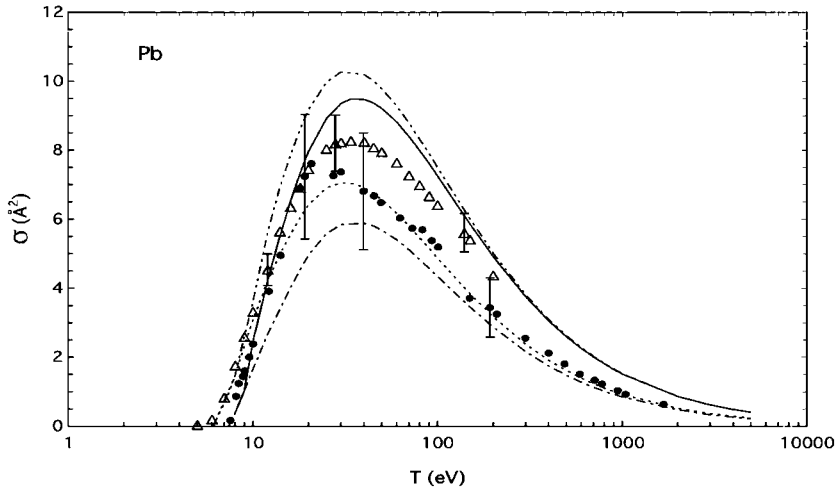

Figure 4. Ionization cross sections 's' of Pb. Cross sections for $^3P_0$ direct ionization (— · —) and direct plus EA (——); cross sections for $^3P_2$ direct ionization (· · · · · ·) and direct plus EA (— · · —); experimental data by Freund *et al* [1] (△) and McCartney *et al* [21] (●). The calculated values for $^3P_2$ fit the experimental data of Freund *et al* at the threshold while the $^3P_0$ values fit the data of McCartney *et al* The calculated values do not agree very well with either experiment in the peak and high energy regions. The experimental uncertainties are, however, large in the peak region.

There are generally several autionizing levels of importance for these elements. These are the levels that are allowed by electric dipole excitation and have the same spin and where one of the electrons in the outer s orbital is excited to the 'p' orbital of the same principal quantum number. For example, the ground terms are $ns^2np^2\,{}^3P_j$ with $j = 0$, 1 and 2, where $n = 3$ is the principal quantum number for silicon and $n = 4$, 5 or 6 for germanium, tin and lead respectively. The dominant autoionizing levels for excitation from the ground terms are $nsnp^3\,{}^3P_{0,1,2}$, $^3S_1$ and $^3D_{1,2,3}$. Lead is the heaviest element we consider and all these levels

Table 1. Experimental excitation energies, E, for equation (3).

Target	n	Experimental E	Calculated E
Si	3	15.7483	15.2933
Ge	4	15.9281	15.4135
Sn	5	15.1603	14.2714
Pb	6	16.1335	15.2041

Table 2. Orbital parameters U, B and constant N. Energies are in eV. The np B values are the experimental ionization energy.

Element	Orbital	j	U	B	N
Si	3s	1/2	14.743	37.921	2
	3p	1/2	8.124	25.691	0.345
	3p	3/2	8.124	25.543	1.655
Ge	4s	1/2	56.374	15.373	2
	4p	1/2	32.966	7.899	1.44
	4p	3/2	32.746	7.899	0.56
Sn	5s	1/2	64.153	13.686	2
	5p	1/2	37.183	7.344	1.586
	5p	3/2	36.059	7.344	0.414
Pb	6s	1/2	97.029	14.8591	2
	6p	1/2	53.071	7.4167	1.856
	6p	3/2	47.312	7.4167	0.144

make a contribution. The lighter elements have some of these excited levels as bound and do not autoionize. In particular, the ^3D_j levels are calculated as bound for Si, Ge and Sn and the ^3P_j levels are bound for Si. The $nsnp^3\,^5S_0$ level is bound for all these elements and, in any case, is not easily excited because of the change in spin.

Different autionizing levels are important for ionization of the metastable levels. There are two metastable levels for each of the elements, $ns^2np^2\,^1D_2$ and $^1S_0$ where n is the appropriate principal quantum number. In each case, the autoionizing levels are $ns^2np^2\,^1D_2$ and $^1S_0$.

The excitation cross sections calculated by equation (3) are dependent on an accurate value for the excitation energy, E. The multiconfiguration Dirac–Fock wavefunction code [15] that we use for the electronic structure of the target atoms does not give very accurate excitation energies to high excited states unless an inordinate number of configurations is included. We have instead relied upon measured spectroscopic data to determine an upper limit to the excitation energy. The energy levels for excited levels of the singly charged ions with an electron configuration of $nsnp^2$ are generally known [19] for the target elements we consider. These levels are the resulting levels of the autoionization processes we wish to calculate. Accordingly, the energy of these levels above the neutral atom initial level is an uper limit to the excitation energy. There are, however, many $nsnp^2$ ion levels with term designations of ^4P, ^2D and ^2S. As an upper limit, we have used the energy of the term that differs most from our calculated estimates.

Table 1 shows the experimental excitation energies we have used for the four targets of this paper in calculating the scaled PWB cross sections by (3).

Table 2 provides the orbital parameters in the calculation of the direct ionization cross section by BEB formula, equation (2). The values are calculated by the Dirac–Fock wavefunction code [15].

Table 3. Silicon direct ionization and total ionization (direct+excitation autoionization) cross sections. Energy T is in eV. Cross sections are in units of Å^2 (10^{-16} cm^2).

T	$^3P_2$ Dir.	$^1D_2$ Dir.	$^1D_2$ Total	$^1S_0$ Dir.	$^1S_0$ Total	50% $^3P_2$ + 50% $^1D_2$
6.243				0	0	
7				0.8120	0.8120	
7.371		0	0	1.2096	1.2096	0
8		0.4303	0.4303	1.8547	1.8547	0.2152
8.124	0	0.5164	0.5164	1.9761	1.9761	0.2582
8.142	0.0093	0.5289	0.5289	1.9936	1.9936	0.2691
8.152	0.0141	0.5356	0.5356	2.0029	2.0029	0.2749
9	0.4616	1.1117	1.1117	2.7707	2.7707	0.7866
10	0.9803	1.7334	1.7334	3.5420	3.5420	1.3568
12	1.8718	2.7396	3.5093	4.7037	5.7575	2.6905
14	2.5445	3.4622	4.8282	5.4797	6.9356	3.6863
16	3.1555	4.0669	5.6925	6.0513	7.7747	4.4240
18	3.6982	4.6035	6.4091	6.5540	8.4697	5.0536
20	4.1216	5.0131	6.9491	6.9190	8.9772	5.5353
25	4.7950	5.6376	7.7685	7.4157	9.6937	6.2818
30	5.1180	5.9069	8.1257	7.5580	9.9406	6.6219
35	5.2457	5.9834	8.2328	7.5185	9.9424	6.7393
40	5.2627	5.9536	8.2009	7.3853	9.8138	6.7318
45	5.2160	5.8649	8.0909	7.2052	9.6161	6.6535
50	5.1327	5.7441	7.9374	7.0035	9.3836	6.5351
60	4.9143	5.4619	7.5732	6.5855	8.8836	6.2438
70	4.6744	5.1703	7.1919	6.1850	8.3907	5.9331
80	4.4384	4.8918	6.8244	5.8174	7.9300	5.6314
90	4.2160	4.6337	6.4815	5.4852	7.5082	5.3488
100	4.0101	4.3976	6.1660	5.1865	7.1251	5.0880
150	3.2094	3.4958	4.9461	4.0765	5.6735	4.0777
200	2.6776	2.9063	4.1372	3.3691	4.7282	3.4074
300	2.0248	2.1897	3.1419	2.5224	3.5773	2.5834
400	1.6390	1.7689	2.5513	2.0308	2.8993	2.0951
500	1.3829	1.4907	2.1580	1.7076	2.4494	1.7704
600	1.1998	1.2921	1.8760	1.4779	2.1277	1.5379
700	1.0620	1.1429	1.6633	1.3058	1.8853	1.3626
800	0.9542	1.0264	1.4966	1.1715	1.6957	1.2254
900	0.8675	0.9327	1.3623	1.0638	1.5430	1.1149
1000	0.7960	0.8556	1.2515	0.9753	1.4171	1.0238
2000	0.4466	0.4791	0.7072	0.5443	0.7996	0.5769
3000	0.3159	0.3386	0.5023	0.3842	0.5677	0.4091
4000	0.2464	0.2640	0.3930	0.2993	0.4441	0.3197
5000	0.2029	0.2174	0.3245	0.2463	0.3666	0.2637

3.1. Silicon results

The calculated silicon cross sections for direct and indirect EA are presented in table 3 and plotted in figure 1.

Silicon is a sufficiently low mass target that LS coupling gives an accurate description of the electronic structure. The only autoionizing level that is reached by an electric dipole-allowed and spin-allowed excitation from the $3s^2 3p^2\ ^3P_j$ ground terms is a $^3S_1$ level at 9.877 08 eV above the ground state. Energetically, this level cannot decay into any excited Si^+, and does not easily autoionize because of the parity selection rule. To autoionize, the

excited triplet S (odd parity) must decay into $Si^+3s^23p\,^2P$ (odd) plus a free electron. To keep the total orbital angular momentum to be zero of an S state, the free electron must be a p electron. This makes the total parity even, while the triplet S state is odd. The triplet S state cannot, therefore, autoionize easily and must decay by photoemission. Accordingly, there is no significant autoionization of the ground terms of silicon and only direct impact ionization is important.

On the other hand, the silicon metastable states $3s^23p^2\,^1D_2$ and $^1S_0$ do have $3s3p^3\,^1D_2$ and $^1S_0$ autoionizing levels. These levels can autoionize without violating the no spin change selection rule.

The three states of the ground term, $^3P_{0,1,2}$, have binding energies so close that their direct ionization cross sections given by equation (2) are nearly identical. Only values for the $^3P_2$ state are shown in table 3.

The experimental data near the threshold energy [1] show ionization occurring at energies below the ^3P_j states. The first experimental ionization energies are, in fact, nearly coincident with the threshold energy for ionization of the $^1D_2$ metastable state, suggesting that some target atoms in the experiment were in this metastable state. It is likely that the experiment included some mixture of target atoms in the ground and first metastable state $^1D_2$. The cross sections for a mixture of equal concentration of atoms in these two states is shown in figure 1 and agree well with the experimental data at all energies, especially allowing for the $\pm 10\%$ uncertainty quoted by the experimenters [1].

3.2. Germanium results

Germanium autoionizing levels reached by electric dipole- and spin-allowed excitations include ^3P_j and the $^3S_1$ state. In contrast to the situation for silicon, the $^3S_1$ level is not so well described by the LS coupling but is mixed with other configurations sufficiently that it has a significant probability for autoionizion. We accordingly include it as an autoionizing level in the calculations.

The ^3D_j excited levels are calculated to be just below the ionization limit and therefore not autoionizing. Spectroscopic measurements agree that the ^3D_j levels are bound, but the levels interact with other odd-parity levels of the same J and the identification is somewhat arbitrary [20]. We have excluded these levels from autoionization.

The experimental measurements show ionization beginning in the threshold region at the onset of ionization from the $^1D_2$ metastable level, suggesting, as with silicon, that some of the target atoms were in the metastable level. Nevertheless, at higher energies, and especially in the peak cross section region, the experimental measurements are in best agreement with calculations for atoms in the $^3P_2$ level. Perhaps the experiment had about 90% of the atoms in the $^3P_2$ level and about 10% in the $^1D_2$ level.

The calculated germanium results for direct and indirect EA are presented in tables 4 and 5, and plotted in figure 2.

3.3. Tin results

As with germanium, the autoionizing levels that are reached by dipole- and spin-allowed excitations are the ^3P_j levels and the $^3S_1$ state. The $^3D_2$ level is bound.

The atom is sufficiently massive that the three j levels of the ^3P ground term have easily observed separate threshold ionization energies. The experimental measurements, as with the other targets in this study, show ionization occurring at the threshold for ionization of the $^1D_2$ metastable level, suggesting that some of the target atoms were in the metastable level. The

Table 4. Germanium direct ionization and total ionization (direct+excitation autoionization) cross sections, Part A. Energy T is in eV. Cross sections are in units of Å^2 (10^{-16} cm^2).

T	$^3P_0$ Dir.	$^3P_0$ Total	$^3P_1$ Dir.	$^3P_1$ Total	$^3P_2$ Dir.	$^3P_2$ Total
7.725					0	0
7.830			0	0	0.0522	0.0522
7.899	0	0	0.0207	0.0207	0.1085	0.1085
8	0.0584	0.0584	0.0730	0.0730	0.1718	0.1718
9	0.6553	0.8846	0.6754	0.9606	0.8074	1.1587
10	1.2273	1.6826	1.2510	1.7697	1.4047	2.0087
12	2.1855	2.8612	2.2134	2.9693	2.3909	3.2604
14	2.8920	3.9214	2.9217	4.0532	3.1094	4.3938
16	3.4512	4.6538	3.4792	4.7923	3.6670	5.1480
18	3.9803	5.3009	4.0076	5.4446	4.1941	5.8097
20	4.3901	5.7954	4.4167	5.9425	4.6003	6.3121
25	5.0313	6.5613	5.0557	6.7115	5.2289	7.0810
30	5.3260	6.9099	5.3484	7.0591	5.5103	7.4204
35	5.4298	7.0295	5.4504	7.1760	5.6014	7.5260
40	5.4267	7.0208	5.4457	7.1637	5.5870	7.5013
45	5.3631	6.9393	5.3808	7.0781	5.5133	7.4033
50	5.2656	6.8165	5.2821	6.9512	5.4068	7.2644
60	5.0249	6.5147	5.0394	6.6413	5.1509	6.9322
70	4.7684	6.1930	4.7813	6.3121	4.8822	6.5833
80	4.5197	5.8803	4.5315	5.9927	4.6236	6.2466
90	4.2874	5.5873	4.2982	5.6936	4.3829	5.9322
100	4.0736	5.3168	4.0835	5.4176	4.1621	5.6429
150	3.2496	4.2674	3.2568	4.3477	3.3147	4.5243
200	2.7067	3.5697	2.7124	3.6367	2.7586	3.7829
300	2.0435	2.7103	2.0475	2.7613	2.0808	2.8712
400	1.6527	2.2002	1.6558	2.2416	1.6820	2.3305
500	1.3937	1.8605	1.3963	1.8956	1.4180	1.9706
600	1.2088	1.6170	1.2110	1.6476	1.2296	1.7127
700	1.0696	1.4334	1.0716	1.4605	1.0879	1.5181
800	0.9609	1.2895	0.9626	1.3140	0.9771	1.3658
900	0.8734	1.1736	0.8750	1.1958	0.8881	1.2430
1000	0.8014	1.0780	0.8028	1.0985	0.8148	1.1418
2000	0.4493	0.6085	0.4501	0.6201	0.4566	0.6446
3000	0.3177	0.4319	0.3183	0.4402	0.3228	0.4577
4000	0.2478	0.3378	0.2482	0.3443	0.2518	0.3580
5000	0.2041	0.2788	0.2044	0.2842	0.2073	0.2955

best calculated cross sections are for target atoms in the $^3P_2$ level of the ground term. As with germanium, perhaps the experiment had about 90% of the atoms in the $^3P_2$ and about 10% in the $^1D_2$ levels.

The calculated tin results for direct and indirect EA are presented in tables 6 and 7, and plotted in figure 3.

3.4. Lead results

The Pb target atom is more massive than the others in this study and, as a consequence, the calculated energies of the ^3D_j levels lie above the ionization limit and are autoionizing. Spectroscopic measurements support this conclusion in the sense that bound ^3D_j levels are

Table 5. Germanium direct ionization and total ionization (direct+excitation autoionization) cross sections, Part B. Energy T is in eV. Cross sections are in units of Å^2 (10^{-16} cm^2).

T	$^1D_2$ Dir.	$^1D_2$ Total	$^1S_0$ Dir.	$^1S_0$ Total	90% $^3P_2$ + 10% $^1D_2$
5.870			0	0	
7			1.4920	1.4920	
7.016	0	0	1.5127	1.5127	0
7.725	0.5811	0.5811	2.3891	2.3891	0.0581
7.830	0.6686	0.6686	2.5123	2.5123	0.1138
7.899	0.7257	0.7257	2.5917	2.5917	0.1702
8	0.8084	0.8084	2.7056	2.7056	0.2355
9	1.5954	1.5954	3.7314	3.7314	1.2024
10	2.2897	2.2897	4.5730	4.5730	2.0368
12	3.3793	3.9228	5.8036	6.4645	3.3267
14	4.1376	5.2809	6.5956	7.6402	4.4825
16	4.6862	6.1219	7.0980	8.3865	5.2454
18	5.1998	6.8375	7.5572	9.0207	5.9125
20	5.5856	7.3711	7.8790	9.4734	6.4180
25	6.1520	8.1668	8.2749	10.0766	7.1896
30	6.3695	8.4980	8.3306	10.2380	7.5282
35	6.4016	8.5809	8.2180	10.1747	7.6315
40	6.3341	8.5274	8.0234	9.9959	7.6039
45	6.2134	8.3983	7.7913	9.7590	7.5028
50	6.0651	8.2280	7.5451	9.4954	7.3607
60	5.7389	7.8358	7.0557	8.9502	7.0226
70	5.4136	7.4321	6.6005	8.4270	6.6682
80	5.1086	7.0463	6.1897	7.9453	6.3266
90	4.8294	6.6882	5.8228	7.5087	6.0078
100	4.5759	6.3597	5.4954	7.1147	5.7146
150	3.6197	5.0959	4.2947	5.6388	4.5815
200	3.0018	4.2610	3.5390	4.6876	3.8307
300	2.2558	3.2355	2.6415	3.5372	2.9076
400	1.8199	2.6274	2.1232	2.8626	2.3601
500	1.5323	2.2225	1.7835	2.4162	1.9958
600	1.3275	1.9323	1.5425	2.0974	1.7346
700	1.1737	1.7134	1.3621	1.8575	1.5377
800	1.0536	1.5418	1.2216	1.6699	1.3834
900	0.9572	1.4036	1.1089	1.5190	1.2591
1000	0.8779	1.2895	1.0163	1.3947	1.1566
2000	0.4910	0.7290	0.5664	0.7857	0.6530
3000	0.3469	0.5180	0.3995	0.5574	0.4637
4000	0.2704	0.4054	0.3111	0.4357	0.3627
5000	0.2226	0.3348	0.2560	0.3596	0.2994

not observed [22]. The experimental measurements of Freund *et al* [1] show an ionization threshold at the $^1D_2$ metastable ionization energy. The measured cross section agrees well, however, with the calculated cross section at the threshold for ionization of the $^3P_2$ ground state. This suggests that some, but only a few, target atoms in the Freund *et al* experiment populated the metastable level.

The j-states of the ground term ^3P_j of Pb have easily observed separate threshold energies for ionization. Additional experimental measurements for ionization of Pb by McCartney *et al* [21] show ions appearing in their experiment at the threshold for ionization of the $^3P_0$ ground

Table 6. Tin direct ionization and total ionization (direct+excitation autoionization) cross sections, Part A. Energy T is in eV. Cross sections are in units of Å^2 (10^{-16} cm^2).

T	$^3P_0$ Dir.	$^3P_0$ Total	$^3P_1$ Dir.	$^3P_1$ Total	$^3P_2$ Dir.	$^3P_2$ Total
6.919					0	0
7					0.0720	0.0720
7.134			0	0	0.1926	0.1926
7.344	0	0	0.1720	0.1720	0.3839	0.3839
8	0.5028	0.5028	0.7219	0.7219	0.9825	0.9825
9	1.2577	1.6116	1.5256	2.1032	1.8367	2.6265
10	1.9378	2.4346	2.2368	3.0072	2.5798	3.6113
12	3.0205	3.8757	3.3518	4.5906	3.7273	5.3639
14	3.8194	4.9198	4.1535	5.6876	4.5318	6.5249
16	4.5880	5.8497	4.9202	6.6512	5.2954	7.5283
18	5.1702	6.5471	5.4964	7.3677	5.8643	8.2674
20	5.6025	7.0637	5.9207	7.8936	6.2791	8.8049
25	6.2321	7.8185	6.5275	8.6478	6.8594	9.5606
30	6.4757	8.1157	6.7486	8.9272	7.0548	9.8220
35	6.5178	8.1727	6.7704	8.9596	7.0535	9.8284
40	6.4528	8.1007	6.6875	8.8606	6.9503	9.7005
45	6.3308	7.9589	6.5498	8.6917	6.7948	9.5023
50	6.1795	7.7806	6.3848	8.4869	6.6141	9.2687
60	5.8451	7.3816	6.0274	8.0388	6.2309	8.7670
70	5.5113	6.9794	5.6754	7.5929	5.8583	8.2734
80	5.1985	6.5997	5.3477	7.1748	5.5140	7.8131
90	4.9123	6.2503	5.0492	6.7915	5.2018	7.3926
100	4.6526	5.9318	4.7793	6.4430	4.9203	7.0111
150	3.6752	4.7210	3.7679	5.1231	3.8709	5.5707
200	3.0452	3.9314	3.1188	4.2648	3.2006	4.6364
300	2.2862	2.9708	2.3390	3.2221	2.3975	3.5027
400	1.8434	2.4055	1.8849	2.6090	1.9309	2.8364
500	1.5516	2.0309	1.5859	2.2028	1.6240	2.3950
600	1.3439	1.7632	1.3733	1.9126	1.4058	2.0796
700	1.1880	1.5616	1.2137	1.6941	1.2422	1.8422
800	1.0664	1.4040	1.0893	1.5232	1.1147	1.6565
900	0.9687	1.2771	0.9894	1.3856	1.0124	1.5071
1000	0.8884	1.1726	0.9073	1.2723	0.9282	1.3839
2000	0.4968	0.6605	0.5071	0.7170	0.5185	0.7804
3000	0.3509	0.4685	0.3581	0.5087	0.3661	0.5539
4000	0.2735	0.3662	0.2791	0.3978	0.2852	0.4332
5000	0.2252	0.3021	0.2297	0.3283	0.2348	0.3576

state. The experiment of McCartney *et al* was done with a pulsed crossed-beam technique and the authors are confident that, indeed, their target atoms were in the ground state.

Our calculated cross sections at the threshold bear out both of the experimental measurements. That is, we calculate cross sections for ionization of the $^3P_2$ in good agreement at threshold with the measurements of Freund *et al* and calculated cross sections at the threshold for ionization of the $^3P_0$ ground state agree with the measurements of McCartney *et al*. At energies above about 20 eV incident electron energy, however, the calculated cross sections are not in good agreement with the experiments, and the experiments are not in good agreement with each other. The measurements of McCartney *et al* peak at about 22 eV and drop rapidly with increasing incident energy. The measurements of Freund *et al* peak at about 35 eV and

Table 7. Tin direct ionization and total ionization (direct+excitation autoionization) cross sections, Part B. Energy T is in eV. Cross sections are in units of Å^2 (10^{-16} cm^2).

T	$^1D_2$ Dir.	$^1D_2$ Total	$^1S_0$ Dir.	$^1S_0$ Total
5.216			0	0
6			1.5169	1.5169
6.276	0	0	2.0425	2.0425
6.919	0.7600	0.7600	3.1921	3.1921
7	0.8566	0.8566	3.3283	3.3283
7.134	1.0157	1.0157	3.5491	3.5491
7.344	1.2619	1.2619	3.8827	3.8827
8	1.9981	1.9981	4.8348	4.8348
9	2.9912	2.9912	6.0369	6.0369
10	3.8189	3.8189	6.9812	6.9812
12	5.0458	6.2533	8.2893	9.4244
14	5.8483	7.5337	9.0684	10.6112
16	6.5923	8.5987	9.7022	11.5327
18	7.1303	9.3696	10.1428	12.1869
20	7.5091	9.9220	10.4190	12.6246
25	7.9946	10.6766	10.6539	13.1151
30	8.1010	10.9122	10.5364	13.1247
35	8.0207	10.8841	10.2625	12.9058
40	7.8484	10.7191	9.9235	12.5793
45	7.6327	10.4840	9.5638	12.2063
50	7.3992	10.2149	9.2052	11.8187
60	6.9283	9.6478	8.5281	11.0584
70	6.4862	9.0967	7.9235	10.3568
80	6.0855	8.5859	7.3916	9.7258
90	5.7266	8.1210	6.9245	9.1625
100	5.4058	7.7002	6.5129	8.6598
150	4.2267	6.1167	5.0357	6.8104
200	3.4835	5.0918	4.1258	5.6392
300	2.6005	3.8487	3.0605	4.2382
400	2.0905	3.1181	2.4517	3.4230
500	1.7561	2.6340	2.0550	2.8856
700	1.3413	2.0273	1.5653	2.2153
800	1.2031	1.8234	1.4026	1.9908
900	1.0921	1.6592	1.2722	1.8103
1000	1.0010	1.5240	1.1653	1.6617
2000	0.5581	0.8604	0.6475	0.9351
3000	0.3938	0.6111	0.4561	0.6632
4000	0.3067	0.4782	0.3549	0.5184
5000	0.2523	0.3949	0.2918	0.4278

drop more slowly at higher energies, consistent with their measurements of the other targets. The McCartney measurements do not seem to include autoionization at the higher energies, approaching our calculated cross sections for direct ionization alone. These comments cannot be taken with much confidence, however, as the error bars quoted by the experimenters are quite large [1, 21].

Our calculated cross sections seem to overestimate the contribution of autoionization of Pb. This might be caused by the more complex electronic structure of Pb that is not calculated well with our single configuration Dirac–Fock calculation of the plane wave Born

cross sections used in (3). It might also be caused by a breakdown of the scaling procedure of (3) for heavy atoms.

The calculated results for lead for direct and indirect EA are shown in figure 4. We have not included a table of the numerical values because the calculations do not seem to be reliable, as evident by figure 4.

4. Conclusion

The rather good agreement with experiments suggests two conclusions. First, autoionization is significant for these open-shell structure atoms and should be included. Previous theoretical calculations have not included autoionization. Second, the targets in the series of experimental measurements of Freund *et al* [1] included many atoms in the excited states of the ground term. In the case of silicon, some atoms are in the $^1D_2$ metastable state, as evident by comparison of our calculated cross sections for Si with the threshold measurements. Population of targets in excited states and metastable states is reasonable because of their use of charge transfer to prepare the atoms. Our calculations suggest that it is mostly the $^3P_2$ excited state that is populated.

The experimental measurements of McCartney *et al* [21] for lead appear to have the target atoms in the $^3P_0$ ground state owing to their use of an oven source for the atoms. The agreement of our calculated cross sections with the measurements for lead is not as good as for the other elements, and the two sets of experimental measurements for lead have rather large error bars and differ significantly from each other.

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References

[1] Freund R S, Wetzel R C, Shul R J and Hayes T R 1990 *Phys. Rev.* A **41** 3575
[2] McGuire E J 1977 *Phys. Rev.* A **16** 62
[3] Bartlett P L and Stelbovics A T 2002 *Phys. Rev.* A **66** 012707
[4] Kim Y-K and Rudd M E 1994 *Phys. Rev.* A **50** 3954
[5] Hwang W, Kim Y-K and Rudd M E 1996 *J. Chem. Phys.* **104** 2956
[6] Kim Y-K, Hwang W, Weinberger N M, Ali M A and Rudd M E 1997 *J. Chem. Phys.* **106** 1026
[7] Ali M A, Kim Y-K, Hwang W, Weinberger N M and Rudd M E 1997 *J. Chem. Phys.* **106** 9602
[8] Nishimura H, Huo W, Ali M A and Kim Y-K 1999 *J. Chem. Phys.* **110** 3811
[9] Kim Y-K 2001 *Phys. Rev.* A **64** 032713
[10] Mott N F 1930 *Proc. R. Soc.* A **126** 259
[11] Vriens L 1969 *Case Studies in Atomic Physics* vol 1, ed E W McDaniel and M R C McDowell (Amsterdam: North-Holland) p 335
[12] Bethe H 1930 *Ann. Phys.* **5** 325
[13] Inokuti M 1971 *Rev. Mod. Phys.* **43** 297
[14] Bethe H A and Salpeter E E 1957 *Quantum Mechanics of One- and Two-Electron Atoms* (Berlin: Springer) p 304

[15] Desclaux J P 1993 *Methods and Techniques in Computational Chemistry: METECC-94, Vol. A: Small Systems* ed E Clementi (Cagliari: STEF) chapter 5
[16] Burgess A 1964 *Proc. 3rd Int. Conf. on Electronic and Atomic Collisions* ed M R C McDowell (Amsterdam: North-Holland) p 237
[17] Kim Y-K and Stone P M 2001 *Phys. Rev.* A **64** 052707
[18] Stone P M and Kim Y-K 2004 *J. Res. Natl Inst. Stand. Technol.* **109** 505
[19] NIST Physical Reference Data 2006 http://physics.nist.gov/PhysRefData/Handbook/index.html
[20] Brown C M, Tilford S G and Ginter M L 1977 *J. Opt. Soc. Am.* **67** 584
[21] McCartney P C E, Shah M B, Geddes J and Gilbody H B 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 4821
[22] Wood D R and Andrew K L 1968 *J. Opt. Soc. Am.* **58** 818