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FIELD ION ENERGY DEFICITS IN THE ATOM PROBE FIM

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Resumé — Nous re-examinons la théorie des énergies d’apparition et de déficits d’énergie s’appliquant aux mesures de résolution à haute énergie dans la sonde à atomes pulée par laser. Des commentaires sur quelques récentes études sont présentés.

Abstract — The theory of appearance energies and energy deficits, as it applies to pulsed laser atom probe measurements in the limit of high energy resolution, is reviewed, and comments are made on some recent work.

In recent papers [1-3] Tsong has reported elegant time-of-flight measurements, and uses these to discuss energy deficits for field-desorbed gaseous ions and field-evaporated metal ions.

Amongst other things, he has suggested that:

1) The critical energy deficit of field-desorbed or field-evaporated ions can, in principle, be determined to ±0.1 eV.

2) His data are accurate enough to confirm the validity of a formula for the "critical energy deficit" $\Delta E_C$ of a field-evaporated ion that travels down the atom-probe flight-tube in an $r$-fold charged state. This formula has the form:

$$\Delta E_C = A^0 + \sum_{i=1}^{r} I_i - Q - r\phi E$$

where: $A^0$ is the sublimation energy of the atom, $I_i$ is the $i$-th free-space ionization energy, $\phi E$ is the local emitter work function, and $Q$ is the relevant field evaporation activation energy. (My notation differs slightly from that of ref.[1], for reasons that will become clear later.)

However, if this $\Delta E_C$ is meant to be interpreted as $\Delta E_C$, where $e$ is the elementary charge and $\delta E$ is a critical voltage difference that would be necessary to bring the ion to a halt outside a retarding electrode, and if by "critical" energy deficit is meant the "standard" energy deficit $D_{\text{stand}}$ as defined in the Appendix, then this formula is certainly wrong. It may be shown [4] (also see Appendix) that the correct formula is:

$$\Delta E_C (= D_{\text{stand}}) = A^F + \sum_{i=1}^{r} I_i - Q - r\phi E$$

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where $A^F$ is the atomic binding energy in the presence of the applied field, and $\phi^R$ is the work-function of the relevant retarding surface; both the binding energy and the work-function terms are different here.

The formula for definition of an appearance energy given in ref.[1] is also incorrect. The standard appearance energy $A_{\text{stand}}$ for the above $r$-fold ion is given in terms of the standard energy deficit by:

$$A_{\text{stand}} = \Delta_{\text{stand}} + r\phi^R \tag{3}$$

$A_{\text{stand}}$ is given by the first three terms in eq.(2), and is determined solely by the emission process.

The theoretical arguments given by Tsong [1-3] are incorrect because they fail to take account of effects due to contact potentials and patch fields. It is slightly difficult to understand how the work-function error arose, since references [5,6] that are cited in [1] do give formulae in terms of the collector/retarder work-function. However, this error does occur elsewhere in the literature; so it has been thought useful to summarise in the Appendix a formal derivation of eq.(2).

In many circumstances the numerical difference between $\phi^E$ and $\phi^R$, which is nearly always less than 1 eV, is quite unimportant. However, it is not trivial in the context of energy-deficit measurement via pulsed-laser atom-probe (PLAP) techniques when a potential resolution of ±0.1 eV is being discussed. To see this, let us re-examine how appearance energy ($A^E$) theory should be applied to the atom-probe situation.

Consider a "standard" ion as defined in the Appendix that approaches the flight-tube entrance in an $r$-fold-charged state, and suppose that a voltage $\Delta_{\text{stand}}$ would be necessary to bring it to a halt just outside the entrance to the flight tube. If the actual applied voltage between the emitter and the flight-tube walls is $V$, then the ion enters the flight tube with a kinetic energy $\xi_{\text{stand}}$ given by:

$$\xi_{\text{stand}} = reV - r\phi^R \tag{4}$$

And, since $\Delta_{\text{stand}} = r\phi^R$ by definition, we obtain by use of eq.(3):

$$\xi_{\text{stand}} = reV - A_{\text{stand}} + r\phi^R \tag{5}$$

where $\phi^R$ is a local work-function associated with the flight-tube entrance.

In reality, it is clear from the work of the Berlin group [7,8] that some ions are created by processes in which the transferred electrons enter the emitter at levels below the Fermi level, and the escaping ions may also have some thermal energy. In consequence, some ions have individual voltage deficits slightly less than $A_{\text{stand}}$, and hence individual $A^E$s slightly less than $A_{\text{stand}}$. The ion energy distribution thus has an onset, on the low energy deficit side, corresponding to some $A^E$s slightly lower than $A_{\text{stand}}$, and we write this lower $A^E$ in the form: $(A_{\text{stand}} - \Delta A)$. An ion with this lower $A^E$ enters the flight tube with slightly higher kinetic energy ($K^*$) than the standard ion, where $K^*$ is given by:

$$K^* = reV - A_{\text{stand}} + \Delta A + r\phi^R \tag{6}$$

It is necessary to understand that this $\Delta A$ is not well-defined until we have specified exactly how onset is to be defined, and that in general this question cannot be epistemologically well separated from other questions, such as how the distribution is to be measured. Also, scattering effects during beam transport (for example effects due to coulombic repulsion), if any such effects exist in a particular situation, would contribute to observed values of onset appearance energy, and hence to $\Delta A$. However, it is known from the work of the Berlin group that thermal effects alone might contribute $\Delta A$ values of some tenths of an eV, even
in "ordinary" (i.e. not PLAP) field evaporation conditions, so likely values of $\Delta A$ are not negligible in the context of hypothesised potential resolution of $\pm 0.1$ eV.

There are further special difficulties with the atom-probe situation, arising from the possibility of work-function variations along the inside surface of the flight tube. Any such variations will give rise to a patch-field distribution inside the flight tube, and the kinetic energy at any point of the ion path will be determined by some kind of "effective work-function" relating to the situation of the walls in the near surroundings of the ion. The value of the "effective work-function" may vary from point to point along the ion path. In a time-of-flight atom probe the value of kinetic energy derived from the measurements is necessarily some sort of average over the flight; so, even if flight time could be precisely measured without difficulty, and a corresponding "mean kinetic energy at onset" determined, it would be necessary to know the "mean effective work-function" before this kinetic energy could be converted into a corresponding appearance energy (and thence into information about the emission process).

In practice, the value of the "mean effective work-function" would probably be determined by some form of calibration experiment using a species of presumed known onset appearance energy, possibly helium. But it would of course be necessary to ensure that there was no change in the state of the walls (due for example to the adsorption or desorption of contaminant gases during vacuum cycling) between the calibration run and the main experimental runs.

In reality, as indicated by Tsong and Kinkus [1], a main factor currently limiting the energy resolution of the PLAP is the ability to measure flight times precisely, and further technological development is to hoped for. If the current precision of kinetic energy measurement is not better than about 0.5 eV, as Tsong (private communication) suggests, then the difficulties I have described above are of limited practical significance. However, the central aim of this note is to point out that, if technological development in the precision of time measurement takes place, there are factors that may prevent a precision of $\pm 0.1$ eV in derived kinetic energy from being converted to a precision of $\pm 0.1$ eV in the measurement of onset appearance energy, and hence into hard information about the emission process.

Some further points deserve mention. The first relates to the measurements of the energy distribution half-width for Ni$^+$ ions. Fig.11 in Ref.[1] shows a PLAP measured FWHM (full width at half maximum) of approximately 5 eV. By contrast, conventional retarding-potential measurements by Ernst et al. [9] show a Ni$^+$ FWHM of about 2 eV. This seems to suggest either that the current resolution of the PLAP is not as good as is believed, or that the emission process in the PLAP differs significantly from that of conventional field evaporation. (It may be relevant that the observed half-width of emission from a liquid-metal field-ion source operating in the low-current regime is about 4.5 to 5 eV [10].) Either way, it seems that studies aimed at comparing PLAP emission FWHMs and "conventional" field-evaporation FWHMs should be undertaken.

Second, it must now be clear that it is incorrect to suppose that observed changes in "critical energy deficit" can be attributed to changes in emitter work function. The discussion in ref.[1] concerning the appearance energy $I^*(H_3^+)$ of the H$_3^+$ ion is therefore partly in error.

Third, note that the theory set out above and in the following Appendix applies strictly only to metal field evaporation. Slightly different theory applies to the field-ionization of inert gases (which are not bound to the surface prior to ionization), and to the field evaporation of semi-conductors (where there may be no accessible emitter states at the fermi level); but the same need to get the work-function and $\Delta A$ terms correct exists.

Fourth, note that a distinction has to be made between the "standard" quantities, (e.g. energy deficits) as discussed in the Appendix, that are theoretically well defined and for which good formulae can be given, and the "onset" or "peak"
quantities that are the ones usually measured. The quantities tend to differ from each other by amounts often of the order of tenths of an eV. The terminology "critical energy deficit" is often applied, somewhat indiscriminately, to all these types of energy deficit. When potential energy resolution of 0.1 eV is under discussion it is necessary to be careful in making appropriate distinctions.

In conclusion, this note should not be treated as a criticism of the technique of measuring appearance energies by PLAP: rather, it is an appeal for caution and theoretical care in the interpretation of the results of the technique, since it promises to provide interesting information about the PLAP emission process.

Appendix: The Standard Energy Deficit of field-evaporated metal ions

For simplicity, consider a notional ionization process in which an r-fold ion is created from a bound atom, in the high electric field near an emitter surface, by a charge-hopping type mechanism. Further, suppose that the bound atom is initially stationary, and that the act of ionization takes place in the relevant critical surface, so the removed electrons transfer directly to the emitter fermi level.

The initially stationary ion is accelerated away by the field. Suppose that it is then retarded, and stops in a relatively field-free region slightly outside the surface of an electrode (the "retarder") of work-function $\phi_R$. This is achieved by having the retarder negative relative to the emitter, by a voltage of magnitude $g_{\text{stand}}$. If $e$ denotes the elementary (positive) charge, the positive quantity $g_{\text{stand}}$ defined by:

$$g_{\text{stand}} = r e g_{\text{stand}}$$ (7)

is termed the standard (electrochemical) energy deficit for this field-ion emission process. The description "standard" here implies that the ion was created in the relevant critical surface, with zero kinetic energy, with all the electrons in this process and any subsequent post-ionization process going directly to the fermi level, and that the ion suffers no scattering interactions during transport from the emitter to the retarder. The description "electrochemical" and the symbol D indicate that the energy deficit is defined by reference to voltage differences, i.e. differences in electrochemical potential for the electrons in the retarder and the emitter. (Another category of energy deficit, defined by reference to differences in the energy level $E$ of ions in space, and for which the symbol $\Delta E$ is also used, is occasionally employed in the literature, but this latter category of deficit is less useful theoretically.)

In practice, some ions formed by normal field-ion emission reach the retarder for voltages differences slightly lower than $g_{\text{stand}}$. Their energy deficits are defined by formulae analogous to (2). The lowest deficit systematically measured is termed the onset energy deficit and is denoted by $g_{\text{onset}}$. The value derived experimentally for $g_{\text{onset}}$ can depend on the signal analysis method. Theoretically it is best to first consider $g_{\text{stand}}$, and then consider corrections.

Consider the following electrothermodynamic cycle, which starts with the neutral atom stationary in the critical surface:
(1) Ionize the atom by taking $r$ electrons to the emitter fermi level.
(2) Move resulting ion to a position slightly outside the retarder.
(3) Take $r$ electrons from emitter to retarder fermi level, via the "battery".
(4) Take $r$ electrons from retarder fermi-level onto the ion, hence neutralising it.
(5) Return the neutral atom to its starting point in the critical surface.

Consider the works $w$ done by a hypothetical external agent in each step. $w(1)$ is zero, because the electrons transfer direct to the fermi level. $w(2)$ is also zero, because the ion is stationary at beginning and end. For the remaining steps we have:

$$w(3) = e\phi_R - r e g_{\text{stand}}$$

$$w(4) = r e g_{\text{stand}}$$

$$w(5) = -r e g_{\text{stand}}$$

$$w_{\text{total}} = -e\phi_R$$
Because the retarder is negative relative to the emitter, the external agent does work in step (3), so \( W(3) \) is positive. In step (4), \( H_r \) denotes the sum of the first \( r \) free-space ionization energies for the atom in question. In step (5), \( U_{\text{Ret}} \) denotes the potential energy of the neutral atom when slightly outside the retarder surface, and \( U_0 \) its potential energy when in remote field-free space; our specification of the cycle conditions means that \( U_{\text{Ret}} = U_0 \). \( U_{\text{PA}} \) is the potential energy of the atom at its starting and ending point, which in the cycle just considered is in the critical surface.

The above cycle is closed, so the total work done by the external agent must be zero. Hence we obtain:

\[
d_{\text{Stand}} = H_r + (U_0 - U_{\text{PA}}) - r\phi R
\]  

The bracketed quantity is the difference between the potential energies of a evaporating entity when in a neutral state in remote field-free space and when at the top of the activation energy hump; as indicated in Fig.1, this bracket can be identified with \( \Delta F - Q \), where \( \Delta F \) is the total binding energy of the atom to the surface (including all field-dependent energy terms), and \( Q \) is the activation energy needed for a bound atom to escape. We thus obtain the standard formula:

\[
d_{\text{Stand}} = \Delta F + H_r - Q - r\phi R
\]  

The above proof is strictly valid for metal evaporation by the charge-hopping mechanism. Slight modification of the proof is necessary for the charge-draining mechanism, in which the evaporating ion may escape over the activation energy hump in an ill-defined charge state. There are more general (but less obvious) proofs in ref.[4]. These show result (10) still to be valid if \( U_{\text{PA}} \) is interpreted as the particle potential energy at the "pass" at the top of the activation-energy hump, whatever the detailed mechanism of escape.

Ref.[4] also shows that eq.(10) remains valid in form if field evaporation initially takes place into an \( n^+ \) ionic state, and this ion is subsequently post-ionized into an \( r^+ \) state. In this case \( Q \) must be interpreted as the activation energy associated with the initial escape process.

Result (10) is thus generally valid, provided that \( \Delta F \) is interpreted as the total binding energy (relative to the energy of a neutral atom in remote field-free space) of the atom in its as-bound electronic state.

Eqns (9) and (10) contain the work-function of the retarder. Experimental papers sometimes fail to give information about this. Results are better expressed solely in terms of the emission process, by using the standard field-ion appearance energy as discussed earlier. In theoretical discussion, however, it is sometimes convenient to label the various quantities involved with subscripts showing the charge states with which they are associated. With \( a \) to denote the bound state, \( n \) the state immediately after escape, and \( r \) the state on arrival at the retarder, we obtain:

\[
\Delta_{\text{Stand}}^a = d_{\text{Stand}} + r\phi R = \Delta F^a + H_r - Q_a
\]  

The idea of an appearance energy, in the above sense, was originally introduced by

Some energy relationships implicit in the above formulae are illustrated in Fig.1.

![Diagram](image_url)

**Figure 1.** A schematic diagram to illustrate some of the energy relationships inherent in the formulae derived in the Appendix. (The diagram is not to scale)

**REFERENCES**