

## Electromigration of hydrogen in B, Nb and Ta: a new description of the measured sample-resistivity-dependent effective valence

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 399

(<http://iopscience.iop.org/0953-8984/3/4/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:04

Please note that [terms and conditions apply](#).

## Electromigration of hydrogen in V, Nb and Ta: a new description of the measured sample-resistivity-dependent effective valence

A Lodder

Faculteit Natuurkunde en Sterrenkunde, Vrije Universiteit, De Boelelaan 1081,  
1081 HV Amsterdam, The Netherlands

Received 2 July 1990

**Abstract.** Resistivity-dependent expressions for the direct force valency  $Z_d$  are presented, starting from a recently proposed new theory for the driving force in electromigration. Using these expressions a good description is found for the measured effective valency of hydrogen in the transition metals V, Nb and Ta. Fits based on a constant  $Z_d$  which are at present available led to the values 1.1, 0.44 and 1.23 for  $Z_d$  in the three hosts in question. These values are not understood yet. According to the new expressions,  $Z_d$  ranges between the bare-charge value of unity and the completely screened value of zero, which are limiting values obtained in the high- and low-resistivity limits, respectively. While the available experimental data are not able to discriminate between the description with a constant  $Z_d$  and the new one with a resistivity-dependent  $Z_d$ , the latter can be considered as much more satisfactory. Regarding a long-standing controversy concerning the magnitude of the direct valency, it is concluded that the new theory in fact reconciles the two extremes involved.

### 1. Introduction

Electromigration is diffusion with a preferential direction, induced by an applied electric field  $E$ . For example, an interstitial, such as hydrogen in a metal, moves either to the anode or to the cathode, depending on the balance of forces. Since the early ballistic-model contributions by Fiks (1959) and Huntington and Grone (1961), the total force on a migrating impurity is written commonly as

$$F = F_d + F_w = (Z_d + Z_w)eE = Z^*eE. \quad (1)$$

The measured quantity is the effective valency  $Z^*$ . The wind valency  $Z_w$  is generally (Sorbelli *et al* 1982, Verbruggen 1988) accepted to be inversely proportional to the sample resistivity  $\rho$ :

$$Z_w = K/\rho. \quad (2)$$

Until recently, two contradictory opinions were defended with respect to the direct force valency  $Z_d$  for an interstitial (see Verbruggen (1988) for a recent review). Some researchers (see, e.g., Sham 1975, Das and Peierls 1975) find negligible corrections to

valency  $Z_i$  of the migrating impurity. Others (Turban *et al* 1976) find a complete cancellation of the direct force, so that

$$Z_d = 0. \quad (4)$$

This controversy started with the first derivation of the result (4) by Bosvieux and Friedel (1962). Rimbey and Sorbello (1980) tried to improve upon existing theories by a derivation designed for strong migrating-impurity potentials, but, unfortunately, their contribution was not conclusive. They found a partial cancellation of the direct force, but for the remaining finite term, made more explicitly by Sorbello (1985), a physical interpretation is lacking (Verbruggen 1988).

Challenged by this theoretical uncertainty, apparently manifesting a conceptual problem, Verbruggen and Griessen (1985) measured  $Z^*$  as a function of  $\rho$ . By extrapolating to large  $\rho$ -values (and thus small  $Z_w$ -values), using equation (1) with equation (2), they hoped to decide this controversy. For hydrogen in V, Nb and Ta the analysis of their results led to the values  $1.11 \pm 0.1$ ,  $0.44 \pm 0.1$  and  $1.23 \pm 0.1$ , respectively, for  $Z_d$ . It is clear that, although the value for Nb could imply considerable screening, the results cannot be understood from a theory predicting complete screening (equation (4)). A new question arises, however, because it is hard to understand a direct force valence which is larger than the bare-ion valency, as it is found, particularly for Ta, in a significant way (Verbruggen *et al* 1986).

Recently Lodder (1989a, b, 1990a, b) formulated a new theory for the driving force. Brouwer and Griessen (1989) mentioned the two limits for  $Z^*$  according to this theory. In the large- $\tau$  limit, complete screening, expressed by equation (4), is found,  $\tau$  being the transport relaxation time of the system while, in the small- $\tau$  limit, the full bare-charge valency could result, expressed by equation (3). This behaviour would imply a resistivity-dependent  $Z_d$ . It has not been investigated yet with which other system quantity the value of  $\tau$  has to be compared in deciding whether it is large or small. Further the new theory has not been used yet to describe the intriguing experimental results mentioned above. These two points form the subject of the present paper.

In section 2, resistivity-dependent expressions for  $Z_d$  are presented which are based on the new theory. In section 3 these expressions are used to describe the measured results. Conclusions are given in section 4.

Atomic units are used throughout, in which  $\hbar = 2m = 1$ ,  $m$  being the electron mass. Only resistivities are expressed in micro-ohm centimetres ( $\mu\Omega$  cm).

## 2. Resistivity-dependent expressions for $Z_d$

For clarity it is necessary to review briefly the recently obtained results. For details the reader is referred to Lodder (1989a, b). The linear-response expression for  $F$  is (Lodder 1989b)

$$F = Z_i e E + ie \sum_{\nu=1}^3 E_{\nu} \int_0^{\infty} dt \exp(-at) \text{Tr}\{n(\hbar)[r_{\nu}, f_1(t)]\} \quad (5)$$

in which  $n(\hbar)$  is the Fermi-Dirac distribution function

$$n(\hbar) = \{\exp[\beta(\hbar - \varepsilon_F)] + 1\}^{-1} \quad (6)$$

containing  $\beta^{-1} \equiv k_B T$ , the Fermi energy  $\varepsilon_F$  of the system and the one-electron Hamiltonian  $\hbar$ . The time dependence of the force operator

$$f_1 = -\nabla_1 v \quad (7)$$

for the impurity at the position  $R_1$  represents the Heisenberg picture, and  $v$  is the electron-impurity interaction potential. The time-dependent exponential with the infinitesimally positive number  $a$  represents the adiabatic switching on of the electric field, as usual in linear-response expressions. It may be useful to stress that equation (5) is completely equivalent (Lodder 1989a) to the various expressions used in the literature, e.g. by Rimbey and Sorbello (1980).

It has been shown (Lodder 1989b, 1990a) that, for an impurity in jellium, the second term of equation (5), after the replacement of  $n(h)$  by  $n(h_0)$ , precisely reduces to the usual wind force, i.e. the corresponding wind valency  $Z_w$  can be written in the form (2). In this respect the new theory confirms all previous theoretical results. The resulting expression for the direct force, for low impurity concentrations, is

$$F_d = Z_i e E - e \sum_{\nu=1}^3 E_\nu \text{Tr} \left( [n(h_1) - n(h_0), r_\nu] \frac{1}{\hbar_1 + i/\tau} f_1 \right) \quad (8)$$

in which  $\tau$  is the transport relaxation time of the system,  $\hbar$  is a Liouville or commutator-generating operator with the property  $\hbar A = [h, A]$  and the Hamiltonian  $h_1$  contains, in addition to the Hamiltonian  $h_0$  of the unperturbed system, a jellium, the potential of the migrating impurity only. The starting point for the resistivity-dependent expressions for  $Z_d$  follows from equation (8) after elaborating the trace operator in terms of the eigenstates of  $h_1$  with eigenvalues denoted by  $\varepsilon_h$ :

$$F_d = Z_i e E + e \sum_{\nu \hbar \hbar'} E_\nu [n(h_1) - n(h_0)]_{\hbar \hbar'} \frac{\varepsilon_{\hbar' \hbar}}{\varepsilon_{\hbar' \hbar} + i/\tau} \nabla_{\hbar' \hbar}. \quad (9)$$

In this expression,  $\varepsilon_{\hbar' \hbar} = \varepsilon_{\hbar'} - \varepsilon_{\hbar}$  and the subscripts  $h$  and  $h'$  label the states. For  $\tau \rightarrow \infty$  the imaginary part of equation (9) has been shown to be identically zero, while the principal-value part of the second term reduces exactly to  $-Z_i e E$ , implying a complete cancellation of the direct force in this limit.

In the first presentations of the new theory the result for this limit has received much emphasis, mainly because it was at variance with a kind of consensus in the field amongst a group of investigators (Landauer 1989) and it formed an independent support of the controversial theoretical result (4). It has not been investigated yet what this limit actually means, as the systems of interest are all relatively good conductors and the experimental data exclude complete screening (Verbruggen *et al* 1986). It is not excluded *a priori* that the small- $\tau$  limit of equation (9) is of interest, although for truly low-conductivity systems this expression is not claimed to be exact. Therefore we now discuss the small- $\tau$  limit.

First we show that the imaginary part of the second term vanishes, not in the trivial sense because  $\tau \rightarrow 0$  but owing to an approximation which is valid for small  $\tau$ . In that limit the energy difference  $\varepsilon_{\hbar' \hbar}$  in the denominator is negligible compared with  $1/\tau$ . The limiting form for the imaginary part obtained in that way is easily shown to be equal to the resolvent form occurring in equation (8) after omission of the operator  $h_1$  in it. The remaining trace is identically zero, irrespective of the magnitude of the factor  $\tau$ , because  $r_\nu$  and  $f_1$  commute. Assuming that this property of the imaginary part in the two limits contains information about the intermediate- $\tau$  region we further discuss equation (9) containing only the real part

$$\text{Re}[\varepsilon_{\hbar' \hbar}/(\varepsilon_{\hbar' \hbar} + i/\tau)] = 1/[1 + (\varepsilon_{\hbar' \hbar} \tau)^{-2}] \quad (10)$$

as a factor. It is known to be impossible in practice to give a reliable evaluation of the

remaining expression by calculating the matrix elements and summing over all states. In order to make progress we choose quite a different approach and try a replacement of the factor (10) by an average to be denoted by

$$1/[1 + (\varepsilon\tau)^{-2}] \equiv 1/[1 + (\rho/b)^2] \quad (11)$$

or by the simulation of an average over an energy interval

$$\frac{1}{2\varepsilon_c} \int_{-\varepsilon_c}^{+\varepsilon_c} \frac{d\varepsilon}{1 + (\varepsilon\tau)^{-2}} = 1 - \frac{1}{\varepsilon_c\tau} \tan^{-1}(\varepsilon_c\tau) \equiv 1 - \frac{\rho}{b_c} \tan^{-1}\left(\frac{b_c}{\rho}\right). \quad (12)$$

The parameters  $b$  and  $b_c$  are related to the parameters  $\varepsilon$  and  $\varepsilon_c$  and are defined through the well known relation (Ziman 1972)

$$\rho^{-1} = \frac{e^2\tau}{4\pi^3} \int_{FS} \frac{dS_k}{v_k} v_k \times v_k \quad (13)$$

between the resistivity  $\rho$  and the transport relaxation time, containing an integral over the Fermi surface to be evaluated for the actual hosts (Van Ek and Lodder 1990). Although such an approach can by no means be claimed to be exact, in the literature it is well known, and it retains an important feature of equation (9) for the direct force, namely its  $\tau$  or resistivity dependence. Replacement (11) in equation (9) leads to

$$Z_d = Z_i/[1 + (b/\rho)^2] = Z_i/(1 + \varepsilon^2\tau^2) \quad (14)$$

while replacement (12) gives

$$Z_d = Z_i(\rho/b_c) \tan^{-1}(b_c/\rho) = (Z_i/\varepsilon_c\tau) \tan^{-1}(\varepsilon_c\tau). \quad (15)$$

For completeness we mention the form

$$Z_d = Z_i/(1 + a/\rho) \equiv Z_i/(1 + \varepsilon_a\tau) \quad (16)$$

given by Brouwer and Griessen (1989), which was written in an early stage of trying to arrive at a useful expression for  $Z_d$  starting from the new theory. It is clear from the steps given above that equation (16) is less well founded than equations (14) and (15).

A common property of equations (14)–(16) is that  $Z_d$  approaches the bare-impurity valency  $Z_i$  in the higher-resistivity region while it approaches zero in the low-resistivity region. Further it may be helpful to realize that the  $\rho$ -dependent  $Z_d$  functions are linearly independent of the  $Z_w$  function (2). By fitting  $Z^*$  to measuring points a parameter corresponding to  $Z_d$  will remain available in addition to the wind valency parameter  $K$ .

### 3. Description of experimental data

The measured resistivity-dependent effective valency  $Z^*$  for hydrogen in the three transition-metal hosts V, Nb and Ta is to be described by the commonly accepted expression

$$Z^* = Z_d + K/\rho \quad (17)$$

which follows from equation (1), with (2) for the wind valency. In addition to a constant  $Z_d$ , in which case  $Z_d$  itself is a fitting parameter, the resistivity-dependent equations (14)–(16) are now available. The bare valency  $Z_i$  in these new expressions is taken to be the hydrogen value equal to unity. The fitting parameter in these expressions is expected

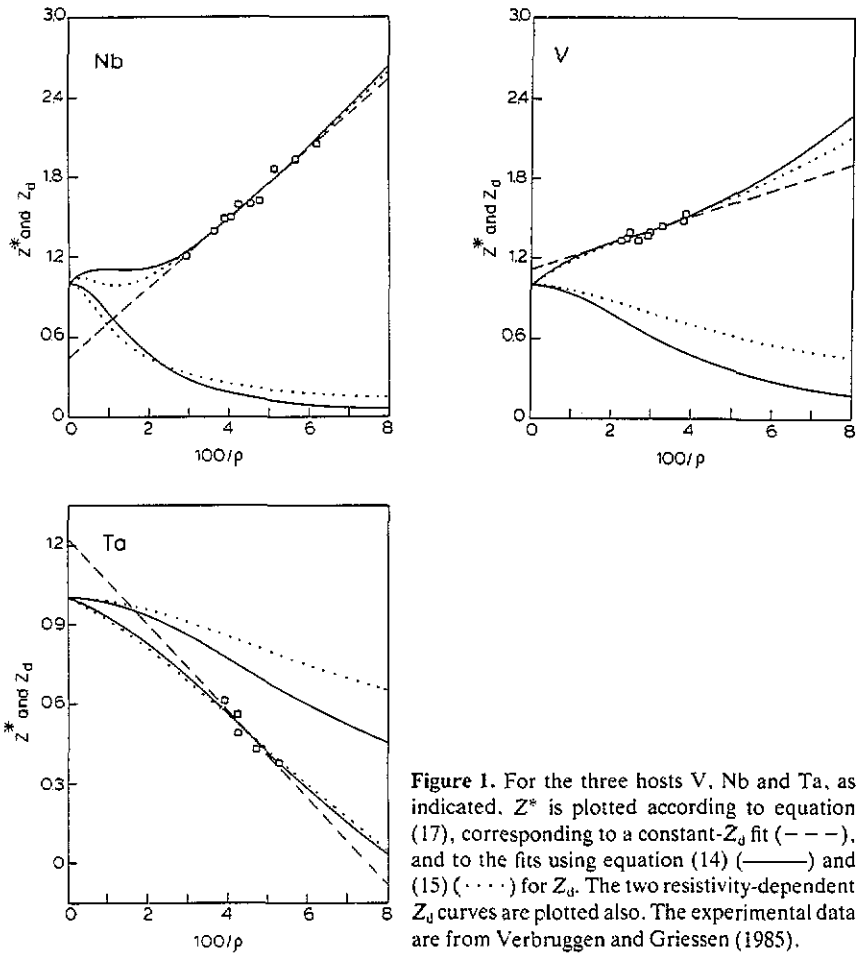


Figure 1. For the three hosts V, Nb and Ta, as indicated.  $Z^*$  is plotted according to equation (17), corresponding to a constant- $Z_d$  fit (---), and to the fits using equation (14) (—) and (15) (····) for  $Z_d$ . The two resistivity-dependent  $Z_d$  curves are plotted also. The experimental data are from Verbruggen and Griessen (1985).

to reveal the meaning of the indications small and large used in the discussion of the two limits of the new theoretical expression (9).

In figure 1, for the three hosts, curves for  $Z^*$  are shown as a function of  $1/\rho$ , corresponding to a constant  $Z_d$  and the resistivity-dependent equations (14) and (15), together with the experimental points. In addition the two corresponding  $Z_d$  curves are displayed. In table 1 the fitting parameters and the root mean square deviation

$$\Delta = \left( \sum_{j=1}^N \frac{Z_{th,j}^* - Z_{exp,j}^*}{N} \right)^{1/2} \quad (18)$$

for each fit are given, where  $N$  is the number of measuring points being 12, 10 and 5 for V, Nb and Ta, respectively. The resistivity-dependent measuring points were fitted to the  $\rho$ -dependent expressions. The energy parameters  $\varepsilon$  and  $\varepsilon_c$  (and  $\varepsilon_u$  for Nb) were obtained from the parameters  $b$ ,  $b_c$  and  $a$  using equation (13), in which the Fermi surface integral was evaluated for the actual hosts (Van Ek 1990) described within a muffin-tin model (Van Ek and Lodder 1990a).

The constant- $Z_d$  fit reproduces the linear behaviour and the parameters published by Verbruggen *et al* (1986), as it should. It is remarkable to see how well the new

**Table 1.** The fitting parameters according to equation (17), including the root mean square deviation (18), for the three hosts investigated, corresponding to a constant- $Z_d$  fit (first three rows) and to fits using the resistivity-dependent equations (14), (15) and (16) (fourth to seventh rows, eighth to eleventh rows and twelfth to fifteenth rows, respectively).

	V(H)	Nb(H)	Ta(H)
$Z_d$	1.11	0.44	1.22
$K$ ( $\mu\Omega$ cm)	9.9	26	-16
$\Delta$	0.031	0.037	0.029
$b$ ( $\mu\Omega$ cm)	26	53	14
$K$ ( $\mu\Omega$ cm)	26	32	-5.3
$\varepsilon$ (Ryd)	0.018	0.069	0.027
$\Delta$	0.030	0.041	0.031
$b_c$ ( $\mu\Omega$ cm)	33	140	19
$K$ ( $\mu\Omega$ cm)	21	31	-7.5
$\varepsilon_c$ (Ryd)	0.023	0.182	0.037
$\Delta$	0.032	0.039	0.033
$a$ ( $\mu\Omega$ cm)	0	68	0
$K$ ( $\mu\Omega$ cm)	13.8	30	-11.3
$\varepsilon_a$ (Ryd)	0	0.088	0
$\Delta$	0.037	0.038	0.038

expressions (14) and (15) describe the experimental data. For all three hosts the deviations  $\Delta$  are very small and as small as the value for the constant- $Z_d$  fit. So the data are by no means able to discriminate between the different fits. It may be interesting to mention that equation (16) did not result in a physically useful least-squares fit for V and Ta. The lowest  $\Delta$ , obtained for  $a = 0$ , in fact implies a constant  $Z_d$  equal to  $Z_i$  which is unity as mentioned above, while the corresponding energy parameter  $\varepsilon_a$  takes the meaningless value of zero. The intriguing feature of the new expressions for  $Z_d$ , their  $\rho$  dependence, is completely lost. It is clear that in this degenerate situation a constant- $Z_d$  fit is bound to give a lower value for  $\Delta$  and therefore works better. This can be seen from figure 2, in which for Ta the linear  $Z^*$  is drawn corresponding to the constant- $Z_d$  fit and the curves for  $Z^*$  and  $Z_d$  are shown corresponding to a small value of the parameter  $a$ . For Nb the curves are given according to the successful fit. On comparison of figures 1 and 2 the difference between the  $Z_d$  curves according to (14) or (15) and (16) is most striking in origin.  $Z_d$  according to equations (14) and (15) approaches the origin parabolically, while (16) gives a linear approach. For Nb the body of the  $Z_d$  curve according to (16) lies on the left of the experimental points. We conclude that owing to this fortuity for Nb a successful fit could be obtained also for this expression, although it is expected to have a more restricted reliability compared with equations (14) and (15).

It is seen from figure 1 that the curves corresponding to equations (14) and (15) are not very different. They all approach the value of unity for larger resistivities, as they should. For V the curves in the large-wind-valency region diverge somewhat, so that experiments for higher-conductivity samples could discriminate between them. The direct force valency  $Z_d$  according to equation (14) for the sample with the highest conductivity, at the experimental point most to the right in the figures, is 0.50 for V, 0.08 for Nb and 0.66 for Ta. The corresponding values according to equation (15) are 0.71, 0.17 and 0.78 (dotted curve). According to the present description the experimental data apparently imply an almost-screened direct force in the higher-conductivity samples

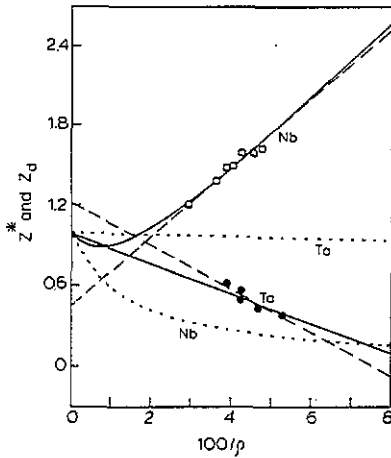


Figure 2. Experimental data and fits (—) for  $Z^*$  according to equation (16) for  $Z_d$  are shown for Nb and Ta:  $\cdots$ , corresponding  $Z_d$  curves;  $---$ , for comparison the constant- $Z_d$  fits as in figure 1.

Table 2. The ranges of the dimensionless parameters  $\epsilon\tau$  and  $\epsilon_c\tau$ , which have to be much larger than unity for complete screening of the direct force, the lengths  $\lambda$  and  $\lambda_c$ , the ranges of the mean free path  $\Lambda$  and the average Fermi velocities in the three systems investigated.

	V(H)	Nb(H)	Ta(H)
$\epsilon\tau$	0.58–1.00	1.5–3.3	0.53–0.72
$\epsilon_c\tau$	0.74–1.27	4.1–8.7	0.74–1.00
$\lambda$	26	15	57
$\lambda_c$	21	6	41
$\Lambda$	15–26	23–48	30–41
$v_F$	0.47	1.01	1.50

of Nb, while in V and Ta the direct force is at most partially screened. It is clear from figure 1 that this is not simply a sample resistivity effect. The  $Z_d$ -values for Nb at the highest conductivity values in the V and Ta samples are at most 0.27 and 0.22 respectively. One has to conclude that electronic structure effects are quite large, a conclusion which could have been drawn already from the constant- $Z_d$  fit results. Such effects are inherently missing in the jellium-based equations (14) and (15) and are explicitly neglected in choosing the value of unity for the bare-ion valency  $Z_i$ . We shall return to this point in the concluding section.

As for the fitting parameters, we notice the smallness of the energy parameters  $\epsilon$  and  $\epsilon_c$  (and  $\epsilon_a$  for Nb) compared with the Fermi energy, which is of the order 0.7 Ryd for these systems. On the other hand these energies are still much larger than the thermal energies of the samples, measuring the thermal broadening of the Fermi surface, and which are of the order of 2.5 mRyd. At this stage the physical meaning of these parameters is not clear. The complete screening limit mentioned in section 2 is obtained for  $\tau \rightarrow \infty$  but, in view of equations (9) and (14), one really needs  $\epsilon\tau \gg 1$ . In table 2 the ranges of  $\epsilon\tau$  and  $\epsilon_c\tau$  are given for the three systems, which are reasonably good metallic conductors with resistivities in the range 16–44  $\mu\Omega$  cm. Only in Nb are values appreciably



larger than unity found; this reflects the small  $Z_d$ -value of 0.44 according to the constant- $Z_d$  fit and which led to the very small  $Z_d$ -values according to equations (14) and (15) mentioned above. One apparently would need much lower resistivities to find complete screening. A good conductor such as copper could be an interesting candidate, because it has a pure-sample resistivity of  $1.6 \mu\Omega \text{ cm}$  at room temperature. Unfortunately, such a good conductor also has a large wind valency, since for copper the effective valency is measured to lie between  $-15$  and  $-20$  (Sidorenko *et al* 1970). These considerations indicate that the experimental conditions for the measurement of a well screened direct valency are very unfavourable.

For a further understanding of our analysis and the drift of the new theory we present the energy parameters in another way. Since  $\epsilon\tau$  is dimensionless,  $1/\epsilon$  has the dimension of time. It may be useful to recall that the quantities are expressed in atomic units. We want to compare the lengths  $\lambda = v_F/\epsilon$  and  $\lambda_c = v_F/\epsilon_c$  with the mean free path  $\Lambda = v_F\tau$ . The values for  $v_F$  are obtained from an average over the Fermi surface of the actual host (Van Ek 1990), being a quotient of two integrals similar to the integral occurring in equation (13). These quantities are given in table 2 also. The reason is that, on the one hand, in the controversy screening is an important issue, which invites us to implicate the screening length in the discussion and that, on the other hand, in the new theory the transport relaxation time enters explicitly, which implies that the mean free path plays a role. It is seen that for V and Ta the mean free path lengths are mostly smaller than the lengths  $\lambda$  and  $\lambda_c$ , while for Nb they are larger. The fitting parameter lengths  $\lambda$  and  $\lambda_c$  are larger than the screening length, which is of the order of the interatomic spacing, being about 6 for the three systems. A conclusion that comparison of the mean free path with the screening length forms the key in deciding whether electronic screening of an impurity reduces the direct force on the ion or not is not excluded by the data investigated, but it would require further support and presumably also some refinement. Regarding the results it is more a conjecture than a conclusion at the present stage. Nevertheless, a conjecture of this type is very attractive and no longer without theoretical grounds. In electromigration, dynamic screening is distinguished from static screening, although the full static screening of an impurity in a metal, due to the severe requirement of charge neutrality described correctly by the Friedel sum rule, is also the result of the dynamics of the electrons. The concept of dynamic screening in electromigration points to the question of how far the force on the bare ion is counterbalanced by the force on the screening electrons. The new theory leads quite naturally to the idea that in a jellium this depends on the mobility of the electrons. The more mobile the electrons are, the better is the dynamic screening of the direct force.

It is clear that more research is required for a better understanding of the physics involved, from both theoretical and experimental viewpoints. Theoretically it would be important to develop methods which make it possible to elaborate the theory, in particular equations (8) and (9) and their equivalents for a real host, without tentative averaging procedures. Experimental data for other systems and for samples with lower hydrogen concentrations and larger resistivity ranges would be welcome.

#### 4. Conclusions

The experimental data for the effective valency  $Z^*$  in V(H), Nb(H) and Ta(H) are described using resistivity-dependent expressions for the direct force valency  $Z_d$ . The new expressions represent the data as well as the previously used constant  $Z_d$ , but from

a theoretical point of view the new description is much more satisfactory. The resistivity dependence enters in a natural way through the transport relaxation time dependence made explicitly in the new theory. This new theory is shown to reconcile the two extremes in the controversy, namely derivations which end up with a complete screening of the direct force and other derivations which find small to negligible corrections to a full direct force on the bare charge of the migrating ion.

A tentative conclusion is mentioned—that a key in deciding whether (dynamic) screening of the direct force dominates or is small may lie in the comparison of the (static) screening length and the mean free path in a system. It is admitted that this conjecture may need some refinement in future research.

The differences for the different hosts are not explained in the present description. This is a separate challenge and was not the aim of this study. Equations (14) and (15) are written, starting from a theory for an impurity in a jellium. Although all assertions in the literature with respect to an interstitial are based on impurity-in-jellium theories, a real metallic background (in particular in transition metals) has much more structure than a jellium. Therefore it is in fact rather surprising that a good fit could be obtained for all three hosts. It is not excluded that part of the screening of the proton is taken care of by a rather localized narrow state, the characteristics of which are closer to a bound state than to a scattering state. In that case a bare proton charge  $Z_1$  would not occur in the theory and particularly not in equations (14) and (15). In these expressions one would expect a reduced value compared with unity, which could be different for the different hosts. Electronic structure calculations for interstitial alloys could reveal such differences. Unfortunately, such calculations have already been only in a preliminary stage for several years (Ellialtioglu *et al* 1985). It may be interesting to mention that the marked difference in slope for the effective valency, as is seen in figure 1, is also an electronic structure effect. Preliminary *ab initio* results for the wind valency  $Z_w$  (Van Ek and Lodder 1991) indeed show a positive  $K$ -value for Nb and a negative value for Ta.

### Acknowledgments

The author wishes to thank Dr A H Verbruggen for providing him with the original table of measuring points and J Van Ek for useful comments.

### References

- Bosvieux C and Friedel J 1962 *J. Phys. Chem. Solids* **23** 123
- Brouwer R C and Griessen R 1989 *Phys. Rev. Lett.* **62** 1760
- Das A K and Peierls R 1975 *J. Phys. C: Solid State Phys.* **8** 3348
- Ellialtioglu S, Akai H, Zeller R and Dederichs P H 1985 *Proc. 15th Int. Symp. on the Electronic Structures of Metals and Alloys* vol 15, ed P Ziesche (Dresden: Technische Universitat) p 99
- Fiks V B 1959 *Sov. Phys.—Solid State* **1** 14
- Huntington H B and Grone A R 1961 *J. Phys. Chem. Solids* **20** 76
- Landauer R 1989 *Solid State Commun.* **72** 867
- Lodder A 1989a *Solid State Commun.* **71** 259
- 1989b *Physica A* **158** 723
- 1990a *J. Phys. Chem. Solids* **51** 19
- 1990b *Solid State Commun.* **73** 611
- Rimbey P R and Sorbello R S 1980 *Phys. Rev. B* **21** 2150
- Sham L J 1975 *Phys. Rev. B* **12** 3142
- Sidorenko V M, Kripyakevich R I and Kachmar B F 1970 *Fiz. Khim. Mekhan. Mater.* **6** 187 (Engl. Transl. 1970 *Sov. Mater. Sci.* **6** 139)

- Sorbello R S 1985 *Phys. Rev. B* **31** 798
- Sorbello R S, Lodder A and Hoving S J 1982 *Phys. Rev. B* **25** 6178
- Turban L, Nozières P and Gerl M 1976 *J. Physique* **37** 159
- Van Ek J 1990 private communication
- Van Ek J and Lodder A 1990 *Solid State Commun.* **73** 373
- 1991 submitted
- Verbruggen A H 1988 *IBM J. Res. Dev.* **32** 93
- Verbruggen A H and Griessen R 1985 *Phys. Rev. B* **32** 1426
- Verbruggen A H, Griessen R and de Groot D G 1986 *J. Phys. F: Met. Phys.* **16** 557
- Ziman J M 1972 *Principles of the Theory of Solids* (Cambridge: Cambridge University Press) p 216