ELSEVIER
Journal of Alloys and Compounds 253–254 (1997) 401–405
Journal of ALLOYS AND COMPOUNDS

Correlation of mass dependence between heat of transport and effective charge of hydrogen isotopes in V, Nb and Ta

M. Sugisaki*, K. Hashizume, K. Fujii

Department of Nuclear Engineering, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka, Post No. 812-81, Japan

---

Abstract

The experimental data of heat of transport Q^* and effective charge Z^* of protium, deuterium and tritium in vanadium, niobium and tantalum recently measured by the present authors are summarized for comparison. The data of Q^* show a definite mass and element dependence whereas those of Z^* do not show such a trend. Simple correlation of mass and element dependence between Q^* and Z^* is not found out by direct comparison of these data. Similarities of the atomistic origins between Q^* and Z^* are discussed, in particular the screening effect due to electrons is discussed by correlating the atomistic interpretation of the mass and element dependence of Q^* with the interpretation of the direct charge.

Keywords: Thermomigration; Electromigration; Hydrogen isotopes; Group V metals; Mass effect

---

1. Introduction

Thermomigration and electromigration have been challenging and controversial subjects for a long time, and many theoretical and experimental investigations have been carried out. In particular, the hydrogen–metal system has been investigated by many researchers because hydrogen is the simplest atom and a large mass effect can be expected by using isotopes. However, the experimental data have been very confusing in some cases, because the experiments have been carried out by different investigators for different isotopes, in different temperature and concentration regions. Therefore, a systematic experimental study to examine the isotope, temperature and concentration dependence of the heat of transport, Q^*, characterizing the thermomigration and the effective charge, Z^*, characterizing the electromigration may be required.

Challenged by the controversial studies, we have recently measured the mass dependence of Q^* and Z^* of hydrogen isotopes in V, Nb and Ta in the alpha-phase and established that an appreciable mass dependence exists in both Q^* and Z^* [1–10]. In these papers, atomistic origins of the mass and element dependence of Q^* and Z^* have been discussed, but their correlation has not been discussed even though their atomistic origins may be related to the identical interaction between hydrogen isotopes and the host metal lattice or electrons. Actually, some investigators have discussed the correlation between Q^* and Z^* [11–15].

In the present paper, we shall summarize our recent data of Q^* and Z^* and discuss the correlation of the mass and element dependence between Q^* and Z^*, in particular the screening effect will be discussed by correlating the atomistic interpretation of Q^* to that of Z^*.

2. Experimental data

2.1. Heat of transport

The data of heat of transport Q^* of hydrogen isotopes in vanadium, niobium and tantalum measured by the present authors [1–5] are summarized in Fig. 1, in which the data of protium and deuterium in vanadium are cited from Peterson and Smith [16]. These authors also reported the data of protium and deuterium in niobium and tantalum, though those data are not cited to avoid redundancy because they are almost identical with our data. Common features of these data are; (i) the sign is always positive; (ii) the magnitude of Q^* increases in the order of vanadium, niobium and tantalum for each isotope, $Q^*(\mathrm{Ta})>Q^*(\mathrm{Nb})>Q^*(\mathrm{V})$; and (iii) the magnitude of Q^*

---

*Corresponding author.

0925-8388/97/$17.00
PII S0925-8388(96)02907-6

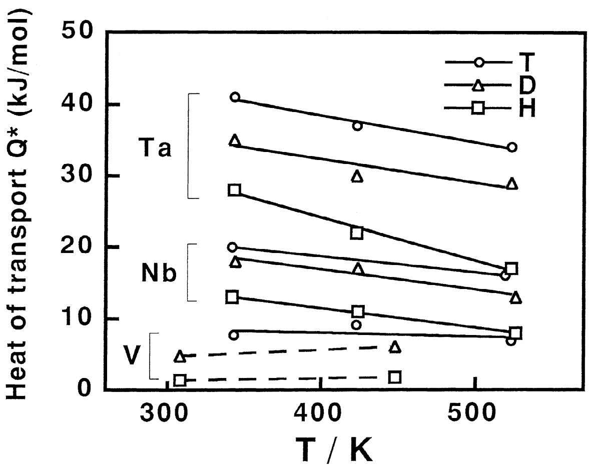

Fig. 1. Summary of the experimental data of Q^* for hydrogen isotopes in V, Nb and Ta. The average atomic ratio of hydrogen to metal is 0.005.

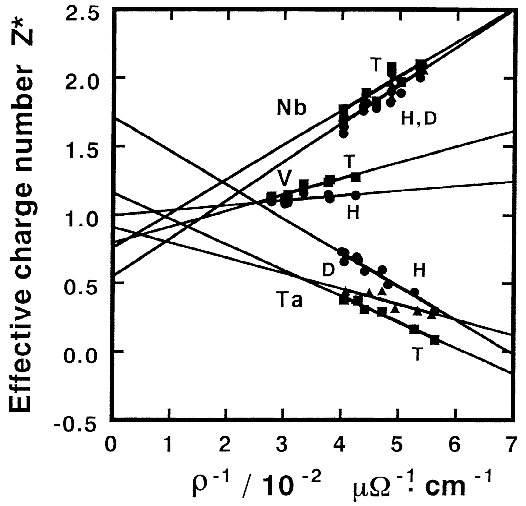

Fig. 3. Plots of effective charge against inverse of resistivity.

increases in the order of protium, deuterium and tritium in each metal, $Q^*_T > Q^*_D > Q^*_H$.

2.2. Effective charge

The experimental data of the effective charge of hydrogen isotopes in vanadium, niobium and tantalum measured by the present authors [6–9] are summarized in Fig. 2. The effective charge Z^* is usually decomposed into contributions of direct charge Z_d and wind charge Z_w, and the temperature dependence of the effective charge is attributed to the wind charge. Since the wind valence is usually considered to be inversely proportional to the electric resistivity $\rho(T)$ of the specimen, the temperature dependence of the effective charge is expressed by the equation

$$Z^* = Z_d + Z_w = Z_d + K/\rho(T) \qquad (1)$$

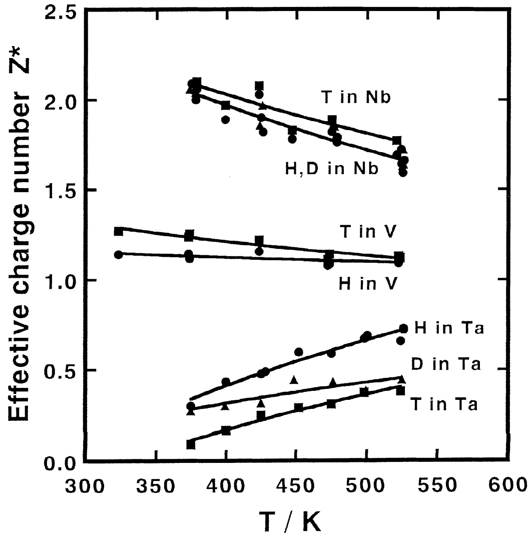

Fig. 2. Summary of the experimental data of Z^* for hydrogen isotopes in V, Nb and Ta. The average atomic ratio of hydrogen to metal is 0.005.

where K is a constant [17]. By using this relation, Z_d can be determined from the intercept of Z^* vs. $1/\rho(T)$ plots on the assumption that Z_d is not dependent on temperature. Such plots of the present data are shown in Fig. 3. As is seen in this figure, the effective charge Z^* linearly varies with $1/\rho(T)$. Then, the present data satisfy Eq. (1) in the resistivity region of the present experiment. The obtained values of Z_d and K are summarized in Table 1. The characteristic features of these results are as follows: (i) The values of direct charge Z_d are not necessarily near unity, e.g. it is appreciably smaller than unity in the case of Nb; (ii) The simple mass dependence can be observed for Z_d and K in the cases of V and Nb but such a simple trend cannot be seen in the case of Ta; (iii) The sign of K is negative in the case of Ta even though the sign of the Hall coefficient is positive.

3. Discussion

3.1. Correlation of mass dependence between Q^* and Z^*

As has been reviewed in the previous section, the experimental data of Q^* show a definite mass and element dependence whereas those of Z^* do not show such a definite trend. So, simple correlation of the mass and element dependence cannot be observed between Q^* and Z^* by their direct comparison. Since the mass and element dependence of Q^* has been successfully interpreted in our previous paper [5], we shall discuss what type of correlation can be predicted from such an interpretation.

Next, we shall briefly review the outline of our previous interpretation of Q^*. The mass and element dependence of the heat of transport Q^* is interpreted with a biased-jump diffusion model which has been first proposed by Weeks and Shuler [18]. According to this model, the heat of

Table 1
The values of Z_d and K of hydrogen isotopes in V, Nb and Ta

Metal	V		Nb			Ta		
Isotope	H	T	H	D	T	H	D	T
Z_d	1.0±0.2	0.8±0.1	0.5±0.1	0.6±0.1	0.8±0.2	1.7±0.1	0.9±0.2	1.2±0.1
K (μΩ·cm)	4±3	11±2	28±3	27±3	25±3	−24±2	−11±3	−19±2

transport Q^* is related to the activation energy of diffusion ΔH_m by the following equation,

$$Q^* = \Delta H_m + \delta \qquad (2)$$

where δ represents the so-called bias effect.

The present data of Q^* are compared in Fig. 4 with those of ΔH_m measured by Zh Qi et al. [19] via the Gorsky effect. As is seen in this figure, the mass and element dependence of Q^* corresponds well to that of ΔH_m. The values of the bias effect δ defined as the difference between the values of Q^* and ΔH_m are summarized in Fig. 5. The bias effect shows a temperature dependence because the activation energy of diffusion does not have a temperature dependence whereas the heat of transport has a temperature dependence. These results show following characteristics: (i) The bias effect shows also a definite mass and element dependence; (ii) The bias effect decreases with an increase in temperature irrespective of the sign of the bias effect.

These results of the bias effect are interpreted in terms of the lattice distortion energy and the electronic polarization energy surrounding hydrogen isotopes. The bias effect is decomposed into two terms,

$$\delta = \delta_L + \delta_E$$

where δ_L represents a contribution due to the lattice distortion which is defined as negative, and δ_E stands for the contribution from the electronic polarization, which is defined as positive. Therefore the bias effect takes a negative or positive sign depending upon whether $\delta_L > \delta_E$ or $\delta_L < \delta_E$. Thus, the bias effect summarized in Fig. 5 can be explained as follows: In the case of niobium and tantalum, the electronic bias effect predominates over the lattice bias effect, so the total bias effect becomes positive. However, the total bias effect takes a negative sign in the case of vanadium, since the lattice bias effect predominates over the electronic bias effect.

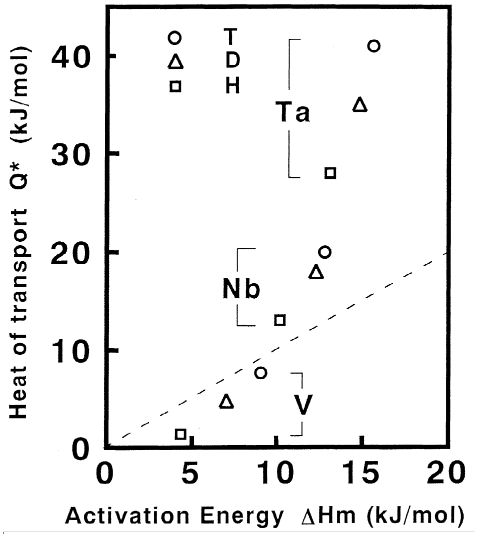

Fig. 4. Comparison of the heat of transport Q^* with the activation energy of diffusion ΔH_m. The broken line represents the relation $Q^* = \Delta H_m$.

According to recent theories [20,21], hydrogen isotopes dissolved in metals are embedded in a self-trapped state by distorting their surrounding host lattice and the self-trapped state is strongly dependent upon the mass of hydrogen isotopes. The lattice distortion energy calculated by the present authors [5] for protium, deuterium and tritium in vanadium, niobium and tantalum using the method similar to that of Sugimoto and Fukai [20] shows a definite mass dependence such that it decreases with increase in the mass of hydrogen isotopes in each metal.

Therefore, if we relate this lattice distortion energy to the lattice bias effect δ_L, we can explain the trend of the mass dependence of δ_L even though the quantitative relation between them is unknown. Then, the mass dependence of the lattice bias effect δ_L must show the following trend

$$|\delta_L(\mathrm{H})| > |\delta_L(\mathrm{D})| > |\delta_L(\mathrm{T})|$$

in each metal. Since the contribution of δ_L to Q^* is defined as negative, this relation leads to the mass dependence of the total bias effect such that

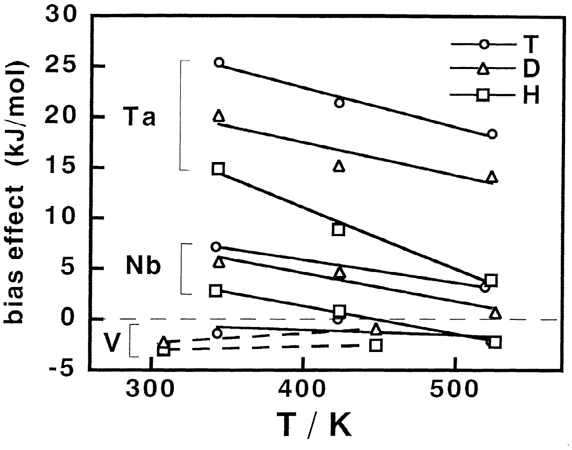

Fig. 5. Temperature dependence of the bias effect δ.

$$\delta(\mathrm{T}) > \delta(\mathrm{D}) > \delta(\mathrm{H})$$

This relation certainly holds good for the present data in Fig. 5.

On the other hand, the contribution of δ_E can be explained with a ''screened proton model'', which was proposed by Ebisuzaki and O'Keeffe [22] for explanation of the enthalpy of solution of hydrogen in metals. According to this model, a positive charge of hydrogen isotopes is more or less screened by electrons of host metals. Then, the present positive bias effect can be ascribed to the screening effect even though the quantitative evaluation of δ_E is not tractable at the present time. Since the relation such that $\delta_\mathrm{E}(\mathrm{Ta}) > \delta_\mathrm{E}(\mathrm{Nb}) > \delta_\mathrm{E}(\mathrm{V})$ must be satisfied to explain the present element dependence of the bias effect, the screening effect must show the same element dependence.

This result is suggestive for the interpretation of the direct charge. As has been discussed by many investigators, the interpretation of the direct charge has been a controversial subject for a long time [23]. Some investigators have asserted that a positive charge of hydrogen isotopes dissolved in metals is completely screened by electrons, i.e. the direct charge should be zero. On the other hand, some investigators have insisted that the direct charge of hydrogen isotopes should be unity. Recently, a model asserting that the screening is dependent upon the sample resistivity, a so-called ''sample-resistivity-dependent effective valence'' model, has been proposed by Lodder [24]. Thus, the screening effect is very controversial problem even at the present time. Therefore, if the concept of ''screening effect'' used for the interpretation of Q^* is identical with the ''screening effect'' used for the interpretation of Z_d, the element dependence of the direct charge must satisfy the following relation:

$$Z_\mathrm{d}(\mathrm{V}) > Z_\mathrm{d}(\mathrm{Nb}) > Z_\mathrm{d}(\mathrm{Ta}).$$

This relation, however, is not in satisfactory agreement with the present experimental results, because the case of Ta does not satisfy this relation.

Therefore, we cannot conclude that the screening effect leads to a correlation between Q^* and Z^*. However, it should be pointed out here that the case of Ta seems unusual from other points of view, because the experimental result of Z_d of protium in Ta is larger than unity, which seems unreasonable from the physical interpretation of the screening effect of the bare charge of the proton. This result may be related to the validity of Eq. (1) in a high temperature region. The detailed discussion of this problem is given in our other papers [7,9].

Next, we shall discuss the mass effect of the screening effect. As has been discussed above, the extent of the lattice distortion increases with decreasing mass of hydrogen isotopes. Since the lattice distortion is considered to be unfavourable to the screening effect, the mass dependence of the screening effect must be such that $Z_\mathrm{d}(\mathrm{H}) > Z_\mathrm{d}(\mathrm{D}) > Z_\mathrm{d}(\mathrm{T})$. This relation, however, does not hold well in the present data. In any case, we can conclude from both the above discussion and the experimental data of the direct charge that the positive charge of hydrogen isotopes may be more or less screened by electrons.

In addition, we have to refer to the theoretical work carried out by van Ek and Lodder [25] who calculated the mass and element dependence of the wind charge of hydrogen isotopes in V, Nb and Ta. Their calculated results are basically in agreement with the present data, though the mass dependence of the present data is not necessarily predicted. From the theoretical point of view, the mass effect can be considered to originate from the zero point motion of hydrogen isotopes. Then, if a certain physical quantity P has a mass dependence, it may be natural to consider that the trend of mass effect must be such that $P(\mathrm{H}) > P(\mathrm{D}) > P(\mathrm{T})$ or $P(\mathrm{H}) < P(\mathrm{D}) < P(\mathrm{T})$. From such consideration, the present data of Ta seem strange. Considering this, the analytical method for decomposing the effective charge into the direct and wind charges should be reconsidered.

Finally, we shall refer to the empirical relation reported by some investigators [10–13] that the sign of Q^* and Z^* is usually reverse. This relation is surely observed in some cases. The present data, however, do not satisfy this relation. As has been discussed above, the sign of Q^* is determined by the relation of magnitude between the activation energy of diffusion ΔH_m and the bias effect δ, and the sign of Z^* is also determined by the relation of magnitude between the direct charge Z_d and the wind charge Z_w. Therefore, it may be unreasonable to expect that a definite relation of the magnitude exists among these quantities. Consequently, this empirical relation should be considered to be a product of a period when experimental data were scarce.

As has been discussed above, the experimental data of the mass effect are the important criteria to judge the validity of the theoretical interpretation of thermomigration and electromigration of hydrogen isotopes. In particular, data of tritium are very important to ascertain the mass effect. Then, the accumulation of the experimental data of tritium in addition to those of protium and deuterium may be required.

4. Conclusions

(1) The experimental data of heat of transport Q^* and effective charge Z^* of protium, deuterium and tritium in vanadium, niobium and tantalum recently measured by the present authors have been summarized for comparison.

(2) Simple correlation of mass and element dependence between Q^* and Z^* has not been found out by direct comparison of these data, because the data of Q^* shows a

definite mass and element dependence whereas those of Z^* do not show such a trend.

(3) Similarities of the atomistic origins between Q^* and Z^* have been discussed, in particular the screening effect due to electrons has been discussed by correlating the atomistic interpretation of the mass and element dependence of Q^* with the interpretation of direct charge. The definite correlation of the screening effect has not been confirmed by the present data.

References

[1] M. Sugisaki, K. Idemitsu, S. Mukai and H. Furuya, *J. Nucl. Mater., 102* (1982) 1493.

[2] M. Sugisaki, S. Mukai, K. Idemitsu and H. Furuya, *J. Nucl. Mater., 115* (1983) 91.

[3] M. Sugisaki, H. Furuya and S. Mukai, *J. Less-Common Met., 107* (1985) 79.

[4] M. Sugisaki, H. Furuya and T. Narai, *Z. Phys. Chem. NF, 145* (1985) 251.

[5] M. Sugisaki, T. Ichigi, K. Hashizume and H. Furuya, *J. Less-Common Met., 161* (1990) 213.

[6] K. Hashizume, Y. Kawabata, K. Matsumoto, N. Tsutsumi and M. Sugisaki, *Defect Diffus. Forum, 95-98* (1993) 329.

[7] K. Hashizume, Y. Kawabata, K. Fujii and M. Sugisaki, *J. Alloys Comp., 215* (1994) 71.

[8] K. Hashizume, K. Fujii and M. Sugisaki, *Fusion Technol., 28* (1995) 1179.

[9] K. Hashizume, K. Fujii and M. Sugisaki, to be published in Defect Diffus. Forum.

[10] K. Fujii, K. Hashizume and M. Sugisaki, Publication of the data of vanadium is in preparation for submission to J. Alloy and Comp.

[11] R. Kirchheim and E. Fromm, *Acta. Meta., 22* (1974) 1543.

[12] J.G. Shaw and W.A. Oates, *Met. Trans., 2* (1971) 2127.

[13] O.D. Gonzalez and R.A. Oriani, *Trans. TMS-AIME, 233* (1965) 1878.

[14] J. Mathuni, O.N. Carlson, E. Fromm and R. Kirchheim, *Met. Trans., 7A* (1976) 977.

[15] A.M. Stoneham and C.P. Flynn, *J. Phys. F: Metal Phys., 3* (1973) 505.

[16] D.T. Peterson and M.F. Smith, *Metall. Trans., 13A* (1982) 821.

[17] A.H. Verbruggen, R. Griessen and D.G. de Groot, *J. Phys. F, 16* (1986) 557.

[18] J.D. Weeks and K.E. Shuler, *J. Chem. Phys., 56* (1972) 1883.

[19] Zh Qi, J. Völkl, R. Lässer and H. Wenzl, *J. Phys.F, Metal Phys., 13* (1983) 2053.

[20] H. Sugimoto and Fukai, *Phys. Rev. B, 22* (1980) 670.

[21] M.J. Puska and R.M. Nieminen, *Phys. Rev. B, 29* (1984) 5382.

[22] Y. Ebisuzaki and M. O'Keeffe, *Prog. Solid State Chem., 4* (1967) 187.

[23] A.H. Verbruggen, *IBM J. Res. Develop, 32* (1988) 93.

[24] A. Lodder, *Physica A, 158* (1989) 723, and *J. Phys. Cond. Matt., 3* (1991) 399.

[25] J. van Ek and A. Lodder, *J. Phys.;Cond. Matt., 3* (1991) 7331.