

Comments on Electrostatic Interaction Theory for Impurity Diffusion in Face-Centered Cubics in Noble Metals*

TSONG HO CHANG (張中和) and HUEI LI HUANG (黃暉理)

Department of Physics, National Taiwan University, Taipei, Taiwan

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The cancellation between the extra binding energy induced by lattice-distortion for the impurity-vacancy pair and the kinetic energy associated with the ω_4 jumps makes LeClaire's electrostatic interaction theory for impurity diffusion works in face-centered cubic noble metals. For less complete cancellation, disagreement between theory and experiment emerges.

I. INTRODUCTION

IN this investigation, we will discuss the difference between the activation energy for impurity- and self-diffusion AQ by vacancy mechanism for electropositive elements in face-centered cubic in noble metals. The AQ has been calculated by several theoretical approaches. The electrostatic theory first proposed by Lazarus⁽¹⁾ and later modified by LeClaire⁽²⁾ has shown the best agreement with experimental results, and has provided further insight into the diffusion processes. For general background and notations readers are referred to a recent review article by Petterson⁽³⁾.

Briefly stated, the electrostatic theory is based on the model that an impurity of excess point charge Ze is dissolved in a metal and screened by the conduction electrons; it is the electrostatic interaction of the vacancy with the *modified* screened Thomas-Fermi potential of the impurity@ that is used to evaluate AQ. On a cursory inspection of the theoretical calculations and experimental data, one is tempted to say that the theory gives a good account of the available data and is reasonably successful in predicting ΔQs for electropositive impurities in copper and silver. For example, data for AQ for Cd, In, Sn and Sb in Ag are, respectively, -2.57, -3.64, -4.97 and -5.95 kcal/mole, while the corresponding calculations give⁽²⁾ -2.45, -4.50, -4.65 and -5.70 kcal/mole. Other pertinent data and calculations are listed in Table II (see below).

The agreement is satisfactory, indeed. On a closer examination, however, the following details are brought to light: (1) The theory gives a satisfactory description of the variation in AQ provided that the solvent and the solute atoms occur in the same row in the periodic table. The calculated results get progressively poorer if solute atoms occur in different row from the solvent atoms. (2) Moreover, since the theory assumes the excess ionic charge Ze as a point charge located at the center of the impurity atom, it fails to distinguish among the impurity atoms occurring in the same column but in different row than that of the solvent atom in the periodic table. In this model calculation, the change in the vacancy formation energy AE as well as the change in electrostatic energy for a

* Work supported in part by National Science Council of ROC.

(1) D. Lazarus, Phys. Rev. 93, 973 (1954).

(2) A. D. LeClaire, Phil. Mag. (8) 7, 141 (1962).

(3) N. L. Petterson, "Diffusion in Metals", Solid State Physics, Vol. 22, 1968 edited by F. Seitz, D. Turnbull and H. Ehrenreich.

(4) The modified screened Thomas-Fermi potential differs from the conventional screened Thomas-Fermi potential by a factor a which can be interpreted as the sum of the higher order contributions between the point charge and its screen charges. See, for example, Umeda and Kobayashi, J. Phys. Soc. Japan 13, 148 (1958) and the references therein.

vacancy ΔH_2 from an equilibrium configuration to a saddle point configuration neighboring an impurity atom of the above types would be practically indistinguishable, were it not for the different frequency factor A_2 associated with the different impurity atoms. Here is a clear indication that different ion core size and possibly its effect on lattice distortion screening ought to be carefully weighed in a model calculation of this sort. (3) The correlation factor for impurity diffusion f_2 should reduce or approach to that for self-diffusion f_0 in pure crystal if the isolated impurity atom is replaced by a solvent atom. In this context, we have a clear choice in favor of Manning's correlation factor⁽⁵⁾ in place of LeClaire and Lidiard's⁽⁶⁾. The present investigation is based upon these observations and considerations.

II. EXTENDED ELECTROSTATIC INTERACTION

The difference in the activation energies between impurity- and self-diffusion AQ may be expressed as⁽²⁾

$$\Delta Q = Q_2 - Q_0 = \Delta E + \Delta H_2 - C \quad (1)$$

$$C = R \frac{\partial \ln f_2}{\partial (1/T)} \quad (2)$$

where the same definitions and notations are retained throughout⁽²⁾ with the exception for the correlation factor f_2 for which we adopt the expression due to Manning⁽⁵⁾ for a good reason. Manning extended the correlation factor first obtained by LeClaire and Lidiard⁽⁶⁾ to include ω_4 jumps. The expression for f_2 ^(5,7) is

$$f_2 = \frac{\omega_1 + \left(\frac{7}{2}\right)F\omega_3}{\omega_1 + \omega_2 + \left(\frac{7}{2}\right)F\omega_3} \quad (3)$$

in which

$$F = 1 - \frac{1}{7} \left[\frac{10 \left(\frac{\omega_4}{\omega_0}\right)^4 + 180.5 \left(\frac{\omega_4}{\omega_0}\right)^3 + 927 \left(\frac{\omega_4}{\omega_0}\right)^2 + 1341 \left(\frac{\omega_4}{\omega_0}\right)}{2 \left(\frac{\omega_4}{\omega_0}\right)^4 + 40.2 \left(\frac{\omega_4}{\omega_0}\right)^3 + 254 \left(\frac{\omega_4}{\omega_0}\right)^2 + 597 \left(\frac{\omega_4}{\omega_0}\right) + 436} \right] \quad (4)$$

and ω_i have their usual meaning. With Eq. (3) C now becomes

$$C = \frac{A_2}{A_0} f_0 e^{C/RT} \times [(\Delta H_2 - \Delta H_1) e^{-(\Delta H_2 + \Delta H_1)/RT} + \frac{7}{2} F (\Delta H_2 - \Delta H_3) \times e^{-(\Delta H_2 + \Delta H_3)/RT} + \frac{7}{2} R D F e^{-(\Delta H_2 + \Delta H_3)/RT}] / \left[e^{-\Delta H_1/RT} + \frac{7}{2} F e^{-\Delta H_3/RT} \right] \quad (5)$$

where DF is the differential of F with respect to $(1/T)$ and $A_2(A_0)$ is the frequency factor of the impurity (solvent) atom. It is worthwhile to note the difference that $f_2 \rightarrow f_0 = 0.78135$ which is very close to the self-diffusion correlation factor $f_0 = 0.78146$ in pure crystals⁽⁸⁾. On the other hand, LeClaire and Lidiard's f_2 reduces to $\frac{9}{11} = 0.81818$ in the limit of self-diffusion.

To extend calculation to include ω_4 jumps, hence AH_4 , for the evaluation of AQ we take note that there are three types of ω_4 jumps as there are ω_3 jumps. Correspondingly, we have three types of AH_4 . They are

$$\Delta H_4^{\text{II}} = -\frac{1}{2} \frac{Ze^2\alpha}{1.017a} e^{-1.017qa} - \frac{1}{2} \frac{Ze^2\alpha}{1.552a} e^{-1.552qa} + \frac{\alpha Ze^2}{\sqrt{2}} e^{-\sqrt{2}qa} \quad (6a)$$

(5) J. R. Manning, Phys. Rev. 128, 2169 (1962).

(6) A. D. LeClaire and A. B. Lidiard, Phil. Mag. (8) 1, 518 (1956).

(7) J. R. Manning, Phys. Rev. 136, A7158 (1964).

(8) K. Compaan and Y. Haven, Trans. Faraday Soc. 52, 786 (1956); 54, 1498 (1958).

$$\Delta H_4^{\text{II}} = -\frac{1}{2} \frac{Ze^2\alpha}{0.921a} e^{-0.921a} - \frac{1}{2} \frac{Ze^2\alpha}{1.897a} e^{-1.897qa} + \frac{\alpha Ze^2}{\sqrt{3}a} e^{-\sqrt{3}qa} \quad (6b)$$

$$\Delta H_4^{\text{IV}} = -\frac{1}{2} \frac{Ze^2\alpha}{\left(\frac{13}{16}\right)a} e^{-(13/16)qa} - \frac{1}{2} \frac{Ze^2\alpha}{\left(\frac{35}{16}\right)a} e^{-(35/16)qa} + \frac{\alpha Ze^2}{2a} e^{-2qa} \quad (6c)$$

The superscripts II, III and IV refer, respectively, to terms of vacancy jumps back to the original first nearest neighbor position from the second, third and fourth nearest neighbor positions relative to the impurity. In an actual calculation we need to take a weighted mean on these three types of AH, assuming that their corresponding ω_4 to have the same vibration frequencies. Namely, we have

$$e^{-\Delta H_4^{\text{av}}/RT} = \frac{1}{7} [2e^{-\Delta H_4^{\text{II}}/RT} + 4e^{-\Delta H_4^{\text{III}}/RT} + e^{-\Delta H_4^{\text{IV}}/RT}] \quad (7)$$

Substituting Eqs. (6-7) into Eqs. (1-5) we are ready to evaluate AQ that includes ω_4 effect. For the purpose of comparison, all the relevant input data are taken directly from the references 2 and 5 with RT set equal to 2 Kcal/mole.

III. NUMERICAL RESULTS AND DISCUSSIONS

The results of numerical calculations for ΔH_4^{av} and F are shown in Table I. Those of the experimental data, ΔQ_{exp} , LeClaire's results C_1 and ΔQ_1 and of the present calculations C_2 and AQ, (LeClaire's plus ΔH_4 -effects) are shown side by side in Table II for the sake of comparison. Surprisingly enough, with the exception of a couple of electropositive solutes, Ga and As in Cu, for which the present calculations approximate better to the experimental values, AQ, appears consistently less negative than ΔQ_1 , which in turn is less negative than ΔQ_{exp} . The results clearly suggest that carrying the calculations to higher order (including AH, terms) a la LeClaire's formulation and improving on the correlation factor would only make C more negative, hence ΔQ_2 less in agreement with the experimental data. This is highly indicative of the deficiency of the electrostatic theory, at least in its present form, to faithfully account for the available data. LeClaire's theory has been noted for its success when applied to impurity atoms Cd($Z=+1$), In($+2$), Sn($+3$) and Sb($+4$) dissolved in Ag. There is not without good reasons for it. These impurity atoms stay in the same row in the periodic table as their solvent atoms, all with the same complete shell structure, $1s$ through $4d$, having the same ion core size, the main difference among these atoms is that each atom carries a different ionic valence Z from the solvent atoms, as the model assumed.

On extrapolating the assumption, however, but for the different frequency factor A , associated with each impurity atom through the relation C shown in Eq. (5), the theory would fail to detect the difference in AQ among the impurity atoms Ge($+3$), Sn($+3$) and Pb($+3$). Furthermore, the agreement between ΔQ_{exp} and ΔQ_1 (or ΔQ_2) for solutes coming from different periods than the solvent atoms is not as satisfactory as presumed.

IV. LATTICE-DISTORTION SCREENING EFFECTS

Solute and solvent ions must differ not only in their net charge but also in the detailed form of their potential, and experimentally, of course, isovalent impurities often exhibit considerable scattering. It is well known^(9,10) that the first-order structural difference between solute and solvent ions lies mainly in their overall sizes. If V_0 is the volume occupied by a solvent ion, then the solute ion volume is $V=V_0(1+\beta)$, where β is the fractional difference between V and V_0 . The average conduction electron charge density in the host is Z_0/V_0 so that the host can provide $Z_0(1+\beta)$ electrons in the volume of the solute ion. As a result, the screening charge in the Friedel sum rule becomes

(9) F. J. Blatt, Phys. Rev. **108**, 285, 1205, (1957).

(10) D.E. Farrell, J. H. Tripp and T. J. Harding, Phys. Rev. **B1**, 4533, (1970).

$Z = Z_{\text{imp}} - Z_0(1 + \beta)^{(10,11)}$. On the other hand, one can take a different viewpoint: if lattice-distortion exists around an impurity ion, the vacancy at its nearest neighbor position would cave in (out) slightly hence attracts (repels) a large measure of the excessive screening charge $-\beta Z_0$. Under the circumstance the overall vacancy charge becomes approximately $-(1 + \beta Z_0)$ or $-(1 + \beta)$ in monovalent host metals. If the vacancy is situated at positions other than the nearest neighbor to the solute, the extra screening electron charge $-\beta Z_0$ has nowhere to go but encircling the solute whose charge is then reduced to $Z - \beta Z_0 = Z - \beta$ while that on the vacancy remains practically unaffected. Based on these *a priori* assumptions, we can evaluate the so-called size-effect, i.e., the lattice-distortion screening effects as a correction to the extended electrostatic interaction theory for impurity diffusion in noble metals. We have

$$\Delta E = -\frac{(1 + \beta)Ze^2\alpha}{a}e^{-qa} \quad (8)$$

$$\Delta H_2 = -\frac{2\left(\frac{1 + \beta}{2}\right)Ze^2\alpha}{\left(\frac{11}{16}\right)a}e^{-(11/16)qa} + \Delta E \quad (9)$$

$$\Delta H_1 = \frac{(1 + \beta)Ze^2\alpha}{1.106a}e^{-1.106qa} - \Delta E \quad (10)$$

$$\Delta H_3^{\text{I}} = \frac{-\frac{1}{2}(1 + \beta)Ze^2\alpha}{1.017a}e^{-1.017qa} - \frac{\frac{1}{2}(Z - \beta)e^2\alpha}{1.552a}e^{-1.552qa} - \Delta E \quad (11a)$$

$$\Delta H_3^{\text{II}} = \frac{-\frac{1}{2}(1 + \beta)Ze^2\alpha}{0.921a}e^{-0.921qa} - \frac{\frac{1}{2}(Z - \beta)e^2\alpha}{1.897a}e^{-1.897qa} - \Delta E \quad (11b)$$

$$\Delta H_3^{\text{IV}} = \frac{-\frac{1}{2}(1 + \beta)Ze^2\alpha}{\left(\frac{13}{16}\right)a}e^{-(13/16)qa} - \frac{\frac{1}{2}(Z - \beta)e^2\alpha}{\left(\frac{35}{16}\right)a}e^{-(35/16)qa} - \Delta E \quad (11c)$$

And similar expressions for ΔH_4 vis-a-vis Eqs. (6a-c). In the above equations β is taken from isotropic elastic continuum and is given by^(10,12)

$$\beta = \frac{1}{3}\left(\frac{1 + \nu}{1 - \nu}\right)\frac{\delta V}{V} \quad (12)$$

where $\delta V = V - V_0$ is deduced from the pure metal ion volume and ν is the Poisson's ratio. Substituting these expressions into Eqs. (5j and (1) we obtain easily the various C_s and ΔQ_s as discussed in the following section. Note that, C represents contribution to AQ from the temperature dependence of the correlation factor f_2 and is duly influenced by lattice-distortion caused by misfit impurity atoms.

V. RESULTS AND CONCLUSIONS

Complete results of the calculations are appended to Tables I and II for comparison. In Table I, $\Delta H_i^{s'}$ and F' represent the same quantities as calculated in §2 but further corrected with the lattice-distortion effects. C_4 and AQ, in Table II are the principal results of the present investigation. They are obtained via the extended electrostatic interaction compounded with the lattice-distortion effects. C_3 and AQ, are the same quantities obtainable from LeClaire's formulation coupled with the lattice-distortion effects, and are tabulated here for reference purpose only. C_1 and AQ, are as obtained by LeClaire while C_2 and ΔQ_2 are those calculated in §2.

We learn from Table I that $F > F'$, and both F and F' lie in the range of 0.5-0.7, generally.

(11) J. H. Tripp and D. E. Farrell, Phys. Rev. B7, 571 (1973).

(12) J. D. Eshelby, J. Appl. Phys. 25, 255 (1954).

Table I. Comparison between calculations and experimental data for ΔQ

	Z	C ₁	C ₂	C ₃	C ₄	ΔQ_1	ΔQ_2	ΔQ_3	ΔQ_4	ΔQ_{exp} (Kcal/mole)
in Ag										
Cd	+1	- 1.85	- 2.10	- 2.41	- 2.72	-2.45	-2.30	- 2.14	-2.43	-2.57
In	+2	- 0.62	- 0.15	- 6.22	- 6.76	-3.40	-3.00	- 4.02	-3.48	-3.64
Sn	+3	- 2.06	- 2.32	- 8.55	- 9.23	-4.65	-4.16	- 5.51	-4.83	-4.91
Sb	+4	- 3.94	- 4.34	—	—	-5.70	-5.12	—	—	-5.95
Hg	+1	- 2.68	- 3.05	- 1.05	- 1.27	-3.68	-3.55	- 4.44	-4.22	-6.17
Te	+2	- 5.15	- 5.65	- 5.34	- 5.88	-4.66	-4.29	- 5.69	-5.15	-6.3-1
Pb	+3	- 4.96	- 5.48	- 9.48	-10.22	-4.84	-4.32	- 5.98	-5.24	-6.17
Zn	+1	- 3.67	- 4.11	- 1.82	- 2.07	-2.24	-1.98	- 2.13	-1.88	-2.51
Ge	+3	- 6.22	- 6.8	- 4.0	- 4.40	-6.13	-5.69	- 6.26	-5.80	-1.77
in Cu										
Zn	+1	- 2.35	- 2.69	- 3.19	- 3.57	-3.75	-3.41	- 4.12	-3.14	-3.96
Ga	+2	- 6.36	- 6.92	-10.32	-11.09	-4.25	-3.69	- 5.14	-4.37	-3.66
AS	+4	- 9.36	-10.2	-17.65	-18.93	-8.06	-1.22	-10.00	-8.72	-7.56
Cd	+1	- 3.55	- 3.95	- 6.36	- 6.89	-2.55	-2.15	- 3.24	-2.71	-3.86
Sb	+4	-11.10	-11.97	—	—	-6.32	-5.45	—	—	-1.56
Hg	+1	- 2.4	- 2.72	- 5.40	- 5.93	- 3.1	-3.38	- 4.85	-4.32	-5.56

Note: C₁ and ΔQ_1 , C₂ and ΔQ_2 are the C, and ΔQ_3 , neglecting lattice-distortion. C₃ and ΔQ_3 , C₄ and ΔQ_4 are the C, and ΔQ_4 , taking into account of lattice-distortion. Indices 1 and 2: calculations carried upto ΔH_3 ; 3 and 4: calculations carried upto ΔH_4 .

Table II. Values for F and AH,

	Z	F	F'	β	ΔH_4^{av}	$\Delta H_4^{av'}$
in Ag						
Cd	+1	0.693	0.685	0.197	-0.516	-0.624
In	+2	0.661	0.628	0.395	-0.898	-1.286
Sn	+3	0.634	0.584	0.435	-1.219	-1.809
Sb	+4	0.609	—	—	-1.505	—
Hg	+1	0.693	0.681	0.276	-0.516	-0.670
Te	+2	0.661	0.619	0.502	-0.896	-1.395
Pb	+3	0.634	0.568	0.577	-1.219	-2.012
Zn	+1	0.693	0.697	-0.080	-0.516	-0.466
Ge	+3	0.634	0.630	0.041	-1.219	-1.265
in Cu						
Zn	+1	0.671	0.656	0.199	-0.775	-0.950
Ga	+2	0.619	0.558	0.457	-1.389	-2.125
As	+4	0.538	0.424	0.587	-2.381	-4.105
Cd	+1	0.671	0.628	0.573	-0.175	-1.285
Sb	+4	0.538	—	—	-1.389	—
Hg	+1	0.671	0.620	0.680	-0.775	-1.383

Note: F' and $\Delta H_4^{av'}$ are the quantities taking into account of lattice-distortion; ΔH_4 in Kcal/mole units.

Correspondingly, $\Delta H_4^{a'}$ is more negative than $\Delta H_4^{a''}$ as a result of the size-effects. From Eq. (4) we find that $F \rightarrow 1$ as $\omega_0 \gg \omega_4$; $F \rightarrow 0.2857$ when $\omega_0 \ll \omega_4$; and $F = 0.7357$ if $\omega_0 = \omega_4$. These numerical results amply suggest that a vacancy has a stronger tendency to jump back to (rather than away from) the nearest neighbor position of the impurity and that there exists an attractive binding energy for the impurity-vacancy pair. In other words, an impurity with a positive lattice-distortion ($\beta > 0$) will result in a stronger impurity-vacancy pair than the one with a nil or negative lattice-distortion ($\beta \leq 0$). Consequently, ΔQ_4 is more negative than ΔQ_2 , as shown in Table II. This serves to explain why electropositive impurities diffuse more readily than the electronegative impurities. From another viewpoint: In making comparison among ΔQ_s listed in Table II we note that generally ΔQ_4 is most negative, ΔQ_1 slightly less and ΔQ_2 substantially the least. This can be interpreted as resulted from the near, but not quite, cancellation of the extra binding energy provided by the lattice-distortion that has more than compensated the kinetic energy associated with the ω_4 jumps. If we accept that the present formulation for ΔQ_4 is a better and faithful representation of the interaction processes involved, it seems only natural to conclude that it is the near cancellation of the two terms that makes LeClaire's formulation for ΔQ_1 approximate well to ΔQ_{exp} , while matter-of-factly fortuitous. Roughly, ΔQ_4 does actually fare better than, or as well as, ΔQ_1 does in comparison with ΔQ_{exp} . For example, ΔQ_4 for Cd, In and Sn dissolved in Ag (Sb lacks appropriate β value to go through calculations) agree well with ΔQ_{exp} ; that for Hg, Tl and Pb shows substantial improvement over, and better period effect than, ΔQ_1 . Exceptions: ΔQ_4 for Zn and Ge dissolved in Ag and that for Ga and As dissolved in Cu are both in poorer shape. No quantitatively satisfactory explanation in this regard is available for the time being, although the detailed difference in the electronic potentials of the ion core has been suspected.

In conclusion, we want to make the following comments: It is the near cancellation between the extra binding induced by lattice-distortion for the impurity-vacancy pair and the kinetic energy associated with the ω_4 -jumps that makes LeClaire's formulation for impurity diffusion works in face-centered cubic in noble metals. For impurities where cancellation is less complete, serious disagreement between theory and experiment may emerge. Finally, in order to probe the cause behind the exceptions mentioned at the end of the last paragraph, a detailed study concerning electronic potentials of ion core is necessary.