

Solute Diffusion in Metals

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Use of more accurate fields around the solute atoms is shown to decrease very appreciably the discrepancy found by Blatt between the activation energies for solute diffusion in silver obtained from the theory of Lazarus and the experimental values.

RECENTLY Lazarus¹ has put forward a theory of solute diffusion in metals in which screening by the conduction electrons plays a fundamental role. In this work, the Thomas-Fermi approximation was used to obtain the potential around the solute atom, the basic equation being linearized following Mott.² It is now known, however, from the investigations of several workers³⁻⁵ that this leads to significant errors. In particular, the screening depends on the excess valence Z of the solute atom, a result which is not predicted by the first-order treatment. For this reason, Blatt⁶ has recently attempted to use more accurate screening constants than those given by this approximation. His method consisted in assuming *a priori* a form $(Z/r) \exp(-r/r_s)$ for the potential⁷ and calculating r_s as a function of Z from the condition that the total screening charge is equal to the valence difference.

However, inspection of the theory of Lazarus shows that it is the potential at a distance of approximately 5 atomic units which is important from the point of view of this theory; and while Blatt's potential will certainly give an important improvement over the first-order treatment for smaller values of r , it seems to us that a more careful investigation is called for here. This is made possible by the existence of some exact numerical solutions of the Thomas-Fermi equation for an impurity.^{4,5} From the results of the present writers for impurities in Cu, it can be shown that even at distances appreciably less than 5 atomic units the numerical solutions are accurately represented by the asymptotic form

$$V = (Z/r)\alpha \exp(-qr),$$

where $q^2 = 4k_m/\pi$, k_m is the maximum momentum of the electrons, and α is a quantity of the order of unity but

TABLE I. The quantity α as a function of valence difference for impurities in copper and silver.

	Z	1	2	3	4
Cu	α	0.77	0.67	0.60	0.55
Ag	α	0.75	0.64	(0.56)	(0.50)

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

² N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

³ J. Friedel, Advances in Phys. **3**, 44 (1954).

⁴ H. Fujiwara, J. Phys. Soc. Japan **10**, 339 (1955).

⁵ L. C. R. Alfred and N. H. March, Phil. Mag. **46**, 759 (1955).

⁶ F. J. Blatt, Phys. Rev. **99**, 600 (1955).

⁷ Atomic units are used, unless explicitly stated.

dependent on Z . We have in fact written the potential in this way in order to exhibit immediately the connection with the first-order treatment. In this first-order treatment the asymptotic form is used beyond its proper range of validity, and from the boundary condition at the origin the constant α must then be taken as unity. However, from the exact solutions of the present writers the results found for Cu are as shown in the first row of Table I. Thus, in the region of interest, in the theory of solute diffusion, the screening depends on Z through α , rather than through q as in Blatt's work. It seems clear that the potential thus obtained is preferable to that assumed by either Lazarus or Blatt, although it is perhaps open to question whether the treatment of the whole problem by Lazarus, based on the first order approximation, is not more consistent internally. However, in view of Blatt's findings, it is of interest to examine the results obtained by taking the best available theoretical potential.

For Ag, Fujiwara⁴ gives values of α for $Z=1$ and 2, and these are shown in the second row of Table I.⁸ It is easy to show from the results for Cu that $(1-\alpha)/Z^{1/2}$ is practically constant over the range of Z covered in Table I, and this is also true for $Z=1$ and 2 for Ag. Thus it is possible to estimate values of α for $Z=3$ and 4 for Ag with some certainty, and we have entered the values we shall adopt for the purposes of the present discussion in Table I. We are then in a position to obtain revised values of the activation energy H for solute diffusion from the formulas of Lazarus.

However, before presenting these values, it is worth noting that the results for negative values of Z seem also to be of interest in view of Blatt's remarks. No very satisfactory solution of the Thomas-Fermi equation seems to have been calculated in this case for any

TABLE II. Values of r_c and α for Cu and Ag for negative values of Z .

	Z	-1	-2	-3
Cu	r_c	1.41	2.04	2.49
	α	1.40	1.85	2.34
Ag	r_c	1.66	2.38	2.90
	α	1.49	2.04	2.65

⁸ Fujiwara also gives a value for $Z=1$ for Cu; this agrees with that recorded in Table I.

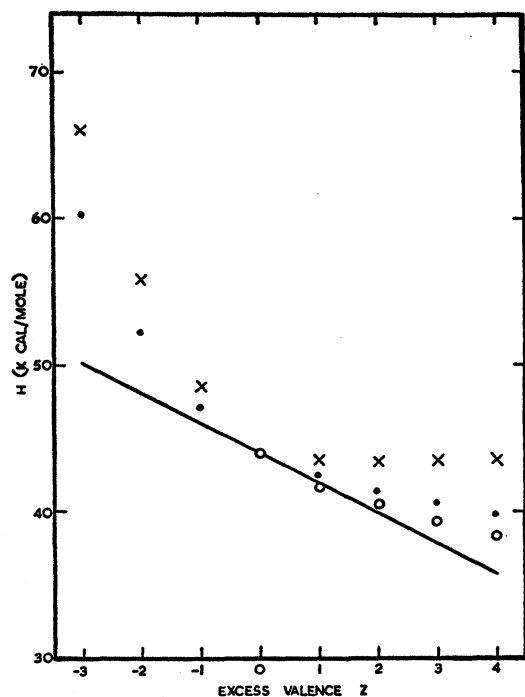


FIG. 1. Calculated and experimental activation energies for solute diffusion in silver. — Result of Lazarus, taking $q=1.70$ Å⁻¹; X results of Blatt; ● present calculations; ○ experimental results (taken from Blatt, Fig. 1).

metal, and we shall therefore describe briefly some results that we have obtained which should be more accurate than those found previously. We note, first of all, that in the Thomas-Fermi method electrons are not allowed in regions of negative kinetic energy, and hence in this approximation there is a sphere, of radius r_c say, around the negative point charge, in which there are no electrons. Then, if E_m is the Fermi energy, we have

$$-V(r_c) = E_m$$

as the equation determining r_c . We can now easily ob-

tain the potential inside this sphere; it is

$$V = -\frac{Z}{r} + \beta - \frac{2^{5/2} E_m^{3/2}}{9\pi} r^2, \quad r \leq r_c.$$

Outside the sphere, we assume that we can use the asymptotic solution, and hence we have

$$V = (Z/r)\alpha \exp(-qr), \quad r > r_c.$$

We determine the unknown constants β and α by requiring that the potential and its first derivative shall be continuous at r_c . We then find the following equations from which we can calculate r_c and α :

$$\begin{aligned} -E_m \left(q + \frac{1}{r_c} \right) &= \frac{Z}{r_c^2} + \frac{4}{9\pi} (2E_m)^{3/2} r_c, \\ -Z\alpha \exp(-qr_c) &= r_c E_m. \end{aligned}$$

These are easily solved, and we show in Table II the values thus obtained for Cu and Ag. We have a check on the method for Cu and $Z=-1$, since we have had occasion to obtain an exact numerical solution for this case in another connection; the value obtained for α was 1.5, in reasonable agreement with the result predicted by the simple argument given above.

Repeating the calculations of Lazarus and Blatt for the activation energy H , we then obtain the results displayed in Fig. 1. It will be seen that the discrepancy between theory and experiment which Blatt found is very appreciably reduced, and that the variation of H with Z predicted by the theory is of a similar form to that found experimentally. Perhaps, in view of the obvious approximations involved in the theory of Lazarus, it is not very reasonable to expect much better agreement than that obtained here.

For negative Z , our results support Blatt's conclusions entirely and we are inclined to believe that the exact values of α would lead to a curve lying above ours. Experiments to test the theory for negative Z will be of obvious interest.