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Diffusion of Iron, Cobalt, and Nickel in Single Crystals of Pure Copper*†

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The rates of diffusion of radioactive tracers of Fe, Co, and Ni in single crystals of pure copper have been measured as a function of temperature from about 700 to 1075°C. The results, obtained by the tracer-sectioning technique, are as follows:

$$D_{\mathrm{Fe}\to\mathrm{Cu}}=1.4\exp(-51\,800/RT);\quad D_{\mathrm{Co}\to\mathrm{Cu}}=1.93\exp(-54\,100/RT);\quad D_{\mathrm{Ni}\to\mathrm{Cu}}=2.7\exp(-56\,500/RT);$$

all in units of cm^2/sec. An exploratory measurement for a Mn tracer in copper was made at 1069°C with the result $D=1.49\times10^{-8}$ cm^2/sec.

The results of several current theoretical calculations are compared with the present data: Wert and Zener's correlation of D_0 and Q is supported by the present work; the basic qualitative prediction of Lazarus' screening theory is borne out by the present results, although the extent of the detailed agreement is not clear at this time. The experimental data yielded unexpectedly large diffusion coefficients at low temperatures in some cases and several possible causes are considered. Finally, a new experimental method is described for determining diffusion coefficients with tracers emitting only very low-energy particles.

INTRODUCTION

RECENT theoretical work on tracer diffusion in metals includes Lazarus' screening theory[1–3] (relating tracer-impurity diffusion to self-diffusion) and the thermodynamic correlation of D_0 and Q by Wert and Zener.[4,5] The screening theory met good agreement with the limited amount of accurate, relevant data then available, although subsequent theoretical work by Blatt[2] seemed to reduce the extent of the agreement. However, the relatively recent calculations of Alfred and March[3] are in complete qualitative agreement with Lazarus' work, although there are marked quantitative differences.

An important feature of Lazarus' treatment was the prediction that, contrary to general opinion at the time, tracers of increasing electropositivity would diffuse progressively more slowly than a matrix tracer—and with progressively larger activation energies. Subsequent fragmentary data[6] for a Ru tracer in the silver lattice seemed to support this conclusion and a more extended investigation seemed called for. The present determination of the temperature dependence of the rates of diffusion of tracers of Fe, Co, and Ni in single crystals of pure copper was carried out in order to establish the nature of electropositive-tracer diffusion for a convenient lattice and tracers.

EXPERIMENTAL PROCEDURE

Specimen preparation was similar to that used previously by other workers at this laboratory.[7–9] Single crystals were grown by vacuum melting 99.998$^+$% pure copper (obtained from the American Smelting and Refining Company) in high-purity graphite crucibles and by then slowly cooling through the melting point. The resultant ingots were etched to check monocrystallinity and were cut into cylinders about a centimeter long; the diameter was about 1.9 cm. The newly exposed surfaces were flattened and the worked layer removed by alternate application of etching and of polishing on successively finer grades of emery paper. After an etch in FeCl$_3$, the specimens were annealed under vacuum for 3 or 4 days at about 25°C below the melting point. A final etch revealed a filamentary substructure in all cases, but only a few of the specimens showed any evidence of polycrystallinity and they were discarded. Specimens were then electroplated with tracers of Fe^{59}, Co^{60}, Ni^{63}, or, in one case, Mn^{54}, using radioisotopes obtained from the Oak Ridge National Laboratory. The usual industrial baths[10] produced excellent results for Ni and barely usable results for Co. A special solution[11] was required for Fe; attempts to electroplate Mn were mostly unsuccessful. The thickness of the plated layer was estimated as about 3×10^{-4} mil (75 A) for Ni and less than a tenth as much for the other tracers. Specimens were sealed in evacuated Vycor or quartz capsules—a quartz flat was usually placed against each face to help reduce evaporation of the radioisotope from the surface—and then placed in electronically controlled

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

[2] F. Blatt, Phys. Rev. **99**, 600 (1955).

[3] L. C. R. Alfred and N. H. March, Phys. Rev. **103**, 877 (1956).

[4] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[5] C. Zener, J. Appl. Phys. **22**, 372 (1951).

[6] C. T. Tomizuka and C. A. Mackliet (unpublished data).

[7] Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. **23**, 1032, (1952); **23**, 1405 (1952).

[8] Sonder, Slifkin, and Tomizuka, Phys. Rev. **93**, 970 (1954).

[9] C. T. Tomizuka and L. Slifkin, Phys. Rev. **96**, 610 (1954).

[10] W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming* (McGraw-Hill Book Company, Inc., New York, 1949), third edition.

[11] R. E. Peterson, Anal. Chem. **24**, 1850 (1952).

furnaces for diffusion. Temperatures ranged from about 700 to 1075°C and the corresponding diffusion times from about 40 days to 4 hours. The over-all excursion of the furnace temperature was about 1°C at the higher temperatures, $1\frac{1}{2}$°C in most other cases, and 3 to 5°C in several extreme cases at the lowest temperatures. A calibrated platinum—platinum-rhodium thermocouple was used throughout the work and frequent measurements of the temperature were made.

Diffused specimens were quenched, mounted in a precision lathe, reduced in diameter to preclude edge effects, and sectioned.[12] From 9 to 18 cuts were taken on each face and total penetrations ranged from about $3\frac{1}{2}$ to 20 mils. The slices were analyzed by means of several different methods.[12] The Mn point and the Fe-719.2°C and Co-701.4°C points were analyzed by gamma counting the dry chips with a typical scintillation counter utilizing a NaI crystal and a photomultiplier tube. Co-1077.5°C (face I) and Ni-979.8°C (face I) were analyzed by beta counting the dry chips with a sensitive end-window Geiger-counter tube. All other Fe and Co specimens were solution beta-counted with a thin-walled glass immersion Geiger counter. Accurately reproducible geometry was maintained in all cases.

TABLE I. Impurity diffusion in copper.

Tracer	Temperature (°C)	Diffusion coefficient (cm²/sec)
Mn^{54}	1069.2	1.49×10^{-8}
Fe^{59}	1073.7	5.65×10^{-9}
	973.9	1.11×10^{-9}
	895.0[a]	2.85×10^{-10}
	895.0[b]	2.87×10^{-10}
	830.5	7.80×10^{-11}
	779.5	2.67×10^{-11}
	719.2[a]	6.55×10^{-12}
	719.2[b]	6.88×10^{-12}
Co^{60}	1077.5[a]	3.43×10^{-9}
	1077.5[b]	3.56×10^{-9}
	983.3	7.64×10^{-10}
	904.4	1.77×10^{-10}
	843.8	5.09×10^{-11}
	792.7	1.65×10^{-11}
	744.5	5.31×10^{-12}
	701.4	1.76×10^{-12}
Ni^{63}	1075.8	1.98×10^{-9}
	979.8[c]	3.57×10^{-10}
	979.8[c]	···
	900.0	7.87×10^{-11}
	847.2	2.61×10^{-11}
	791.5	6.82×10^{-12}
	742.6[a]	1.84×10^{-12}
	742.6[b]	1.94×10^{-12}

[a] One face of a given specimen.
[b] The other face of the same specimen.
[c] See Fig. 5.

TABLE II. Temperature dependence of the diffusion coefficients.

Tracer	Points	D_0 (cm²/sec)	Q (kcal/mole)
Fe^{59}	first 4	1.4±20%	51.8±0.9%
Fe^{59}	last 2	0.13···	46.7···
Co^{60}	first 4	1.93±3%	54.1±0.14%
Co^{60}	last 3	0.39±0.2%	50.6±0.01%
Ni^{63}	all 6	2.7±13%	56.5±0.5%

Diffusion coefficients were calculated in the usual manner from the Gaussian penetration plots. Slice thicknesses and penetration distances were determined from the slice masses by means of a mass-distance ratio calculated in turn from the diameter and density of the specimen. Variation of the specimen temperature during both the warmup and diffusion periods was taken into account by means of a simple relation[13] which follows easily from the Gaussian character of the penetration profile and the $\exp(-Q/RT)$ dependence of the diffusion coefficient. The actual calculations of specific activity, square of penetration, least-squares slope, and diffusion coefficient and its error were all carried out on the University of Illinois electronic digital computer (Illiac). It should be mentioned that in a number of cases not all observed points were used in the calculation of the diffusion coefficients. The tendency for curvature of the initial portion of some penetration plots—especially noticeable for Mn and Fe tracers—was apparently connected with the condition of the surface during diffusion. Several control experiments indicated that such curvature did not materially affect the slope of the remainder of the plot and the points involved were therefore ignored in the least-squares calculation. Similarly, a slight curvature of the final portions of several plots was believed to be of no essential significance and the points involved were also ignored. Finally, a small correction (ranging from $-\frac{1}{2}$ to -2%) was applied to the diffusion coefficients in order to take account of the fact that it is not correct to attribute the average specific activity of a slice to the geometrical midpoint. Tables computed by Schoen[14] were used for this purpose. The temperatures and the fully-corrected diffusion coefficients were used to calculate D_0 and Q and their errors, again by means of a least-squares calculation on the Illiac.

RESULTS

Measurements were made of the rates of diffusion of the radioactive tracers Fe^{59}, Co^{60}, and Ni^{63} in single crystals of pure copper. One exploratory measurement for a Mn^{54} tracer was also made. The diffusion coefficients and corresponding temperatures are given in Table I; the values of D_0 and Q appear in Table II. The

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[12] The nickel-plated specimens were sectioned and counted by means of a special method, the details of which are given in the appendix.

[13] It may be shown that $\Delta t_{T+\Delta T} \leftrightarrow [\Delta t_T \exp(Q\Delta T/RT^2)]$, where Δt is some interval of time and T is the nominal value of the absolute temperature. The approximation made in obtaining this formula is completely adequate for the range of Q's, T's, and ΔT's encountered in the present investigation.

[14] A. H. Schoen (private communication).

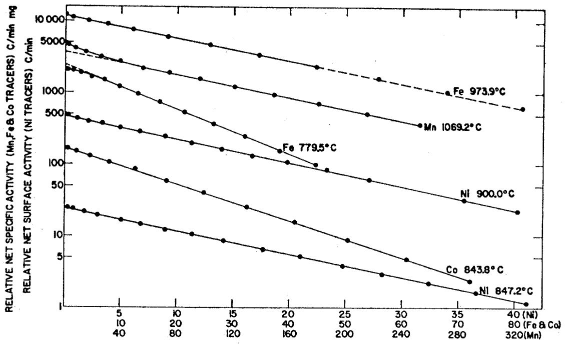

FIG. 1. Typical penetration plots.

penetration plots shown in Fig. 1 were chosen to give a fair indication of the quality of the data. The final ln$D$ *vs* $1/T$ plots are shown in Fig. 2. Because of the nonlinearity of the latter plots for Fe and Co tracers, calculations of D_0 and Q and their errors were made for both the initial and final portions of these curves, with the aim of showing that the differences in slope and intercept for the two portions are much greater than the statistical errors in the individual values.

In connection with a discussion to be given later concerning the unexpectedly large diffusion coefficients found at the lower temperatures in several cases, it is necessary to consider the experimental errors that might reasonably have occurred in the present work. On the one hand, the specific activity and the square of the penetration distance were each determined to within 1 or 2% in most cases; the error in the time of diffusion is less readily determined, but may be estimated as perhaps a percent. The error in the slope of a penetration plot may then be estimated as definitely less than a percent, while the diffusion coefficient might have a typical error of a percent or two.

The temperature, on the other hand, was probably determined to within 1°C in most cases, although the error may have been as large as $1\frac{1}{2}$ or 2°C in several extreme cases at low temperatures. If the exponential dependence of the diffusion coefficient upon temperature is taken into account, then the *combined* effect of all errors may be conveniently stated as follows: the points on a ln$D$ *vs* $1/T$ plot should exhibit a typical scatter-from-the-average of a few percent, except that the lowest temperature Fe and Co points might exhibit a scatter twice that large.

DISCUSSION

No very profitable comparison of the present data with that obtained by other workers can be made because most earlier work involved one or more of the following differences and/or limitations: polycrystalline specimens; finite concentrations of diffusing material; less accurate experimental techniques. The present results will, however, be used to examine several current theoretical calculations concerning some aspects of tracer diffusion in metals.

Wert and Zener's work[4] on the correlation of D_0 and Q for interstitial diffusion was extended by Zener[5] to cover the cases of self and of tracer-impurity diffusion. The final result was $D_0 = a^2\nu \exp(\Delta S/R)$ and $\Delta S = \lambda\beta Q/T_m$, where, presumably, the "entropy of activation" ΔS is positive and the constant of proportionality λ is of the order of less than or equal to unity; β is to be determined from elasticity measurements on the base material. For the present data, λ was found to equal 0.59, 0.60, and 0.44, for Fe, Co, and Ni tracers, respectively. [β was taken from Zener's paper as 0.46, ν was taken as the Debye frequency (6.6×10^{12} sec^{-1}), and D_0 and Q were taken from the first, third, and fifth lines of Table II.] It might also be noted that $\lambda = 0.47$ for a Zn tracer in copper,[15] and 0.40 for self-diffusion in copper[16]; it varies from 0.35 to 0.51 for self-diffusion[16] in Ag, Pb, and Au, and from 0.44 to 0.54 for tracer diffusion of Cd, Sn, In, and Sb in silver.[8,9] It is evident therefore that most accurate data on tracer diffusion in metals do satisfy a relation of the above type reasonably well, with $\lambda \lesssim 1$ and, therefore, $\Delta S > 0$—as predicted by Wert and Zener.

The observed relative constancy of λ may, incidentally, be used to estimate D_0 and Q for a Mn tracer in copper. Simultaneous solution of $D_0 = a^2\nu \exp(\lambda\beta Q/RT_m)$ and $D = D_0 \exp(-Q/RT)$ may be carried out

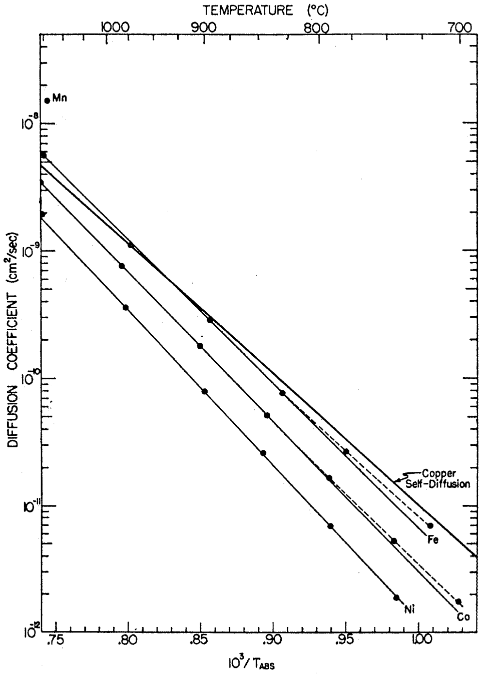

FIG. 2. Temperature dependence of the diffusion coefficients.

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[15] J. Hino, thesis, Metallurgy Department, University of Illinois (unpublished).

[16] See the compilation of B. Okkerse, Phys. Rev. **103**, 1246 (1956).

by using the single observed diffusion coefficient; the results, for as extreme a variation in λ as might be expected, are

$$D_{\mathrm{Mn}\rightarrow\mathrm{Cu}}\sim\begin{cases}0.08\exp(-41\,000/RT) & \text{for }\lambda=0.40,\\ 0.5\ \exp(-46\,000/RT) & \text{for }\lambda=0.60,\end{cases}$$

in units of $\mathrm{cm}^2/\mathrm{sec}$.

A second theoretical treatment of diffusion is Lazarus' screening theory,[1] the primary aim of which was to determine the amount by which the activation energy for diffusion of a tracer-impurity atom differs from that of a solvent atom. His procedure was to calculate the changes which the perturbing potential around an impurity atom would produce in the energies required for formation and for motion of an imperfection. (A vacancy mechanism was assumed.) Lazarus computed the required perturbing potential by solving a linearized Thomas-Fermi equation, after the manner of Mott.[17] The result of the latter procedure is a screened Coulomb field, with a screening radius, ρ, independent of the valence of the impurity atom. On the basis of these and other considerations, Lazarus obtained $Q(\text{impurity-tracer})=Q(\text{self-tracer})-\epsilon Z$, where Q is the activation energy and Z is the "excess valence." More exactly, $1+Z$ is the number of electrons given up to (or if $1+Z$ is negative, taken from) the lattice by the dissolved impurity atom. The quantity ϵ, which is a definite function of ρ in this treatment, is found to be positive for the Cu, Ag, and Au lattices, for example. For the specific case of copper, Lazarus' theory yields $Q(\text{impurity-tracer})=(47.12-3.35Z)$ kilocalories/mole. This result is shown as a solid line in Fig. 3, for a fixed screening radius of 0.55 A.[17] The experimental results of the present investigation are indicated along the axis for activation energy—but before comparing theory with experiment it is of interest to consider several more recent papers which have dealt with certain phases of Lazarus' work in more detail. Blatt,[2] on the one hand, retained the screened Coulomb form for the perturbing potential but discarded the usual Thomas-Fermi equation in favor of a more accurate approximation. He determined the screening radius by requiring that the total screening charge equal the valence difference (Friedel sum rule). Although Blatt's calculations were carried out only for the silver lattice and are therefore not of direct interest, it may be mentioned that a marked dependence of ρ upon Z was found; Q, in turn, was essentially constant for $Z>0$, and varied more strongly with Z for $Z<0$ than had been found by Lazarus. Alfred and March,[3] on the other hand, solved the exact Thomas-Fermi equation for $Z=-1$, and for $Z=+1$ to $+4$, and employed an approximate, two-part solution for $Z=-1$, -2, and -3. They found that in the region which is of importance in Lazarus' approach, the perturbing potential may be represented by the asymptotic form $(\alpha Z/r)\exp(r/\rho)$; the quantity α is of the order of magnitude of unity and varies with Z, whereas the screening radius ρ is in this case fixed for a given lattice. Upon employing the remainder of Lazarus' formalism, Alfred and March obtained the results shown by crosses in Fig. 3. It is evident that there is complete qualitative agreement with Lazarus' work, although the dependence of Q upon Z is much stronger for $Z<0$ and somewhat weaker for $Z>0$.

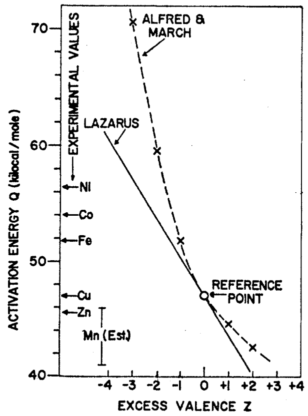

FIG. 3. Comparison of the predictions of the screening theory with the results of the present investigation. (The experimental data are presented in a manner which requires no assumptions concerning the values of Z appropriate to the various tracers.)

Upon comparing the predictions of the screening theory with the present experimental results, it is to be noted that Fe, Co, and Ni tracers all have larger activation energies than does a self-tracer—in general agreement with one of the main results of the screening theory. However, the order of increase is the opposite of what might have been expected. And the behavior of an Fe tracer in diffusing first more rapidly and then more slowly than a matrix tracer as decreasing temperatures are considered, is entirely unexpected. Zn and (probably) Mn tracers, on the other hand, have smaller activation energies than a self-tracer, a result which is reasonable for Zn but surprising for Mn.

The screening theory in its present form is therefore apparently unable to account for the detailed behavior of the electropositive tracers in copper, inasmuch as rather unusual valences would apparently have to be exhibited by the various tracers. Yet it must be noted that the predicted results are very sensitive to changes in the value of the screening radius, which is itself not well defined. Only moderate changes in ρ are "equivalent" to rather large changes in Z. For example, if the "periodic-table" values of $Z=-1$, -2, and -3 are arbitrarily assigned to tracers of Ni, Co, and Fe, respectively, and if, in addition, the screening radius is treated as an adjustable parameter, then the present experimental data would require that $\rho=0.65$, 0.55, and 0.50 A for Ni, Co, and Fe, respectively. Such a range of variation is not unreasonable: Blatt found a much larger spread in his calculations; and the experimental value[17] is hardly determined to within a factor of 2.

In conclusion, it would seem that while one of the

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[17] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

general features of the screening theory is in qualitative agreement with experiment, the extent of detailed agreement or disagreement cannot be determined until further information becomes available. Additional experimental work in the area of electropositive-tracer diffusion in pure metals would seem to be of the most immediate value. Measurements of the rate of diffusion of a matrix tracer in dilute, homogeneous alloys containing small but finite amounts of electropositive elements would also be of interest.

A prominent feature of the present experimental results is the upward curvature of the $\ln D$ *vs* $1/T$ plots for Fe and Co tracers at low temperatures. In the discussion of errors given earlier, it was concluded that the points of the $\ln D$ *vs* $1/T$ plot might exhibit a typical scatter from the average of a few percent (except for the lowest temperature Fe and Co points, in which case the typical scatter might be twice that). Since the low-temperature points in question lie consistently above the extrapolation of the high-temperature data—and by as much as 30%—it follows that experimental error is in all probability not the source of the deviation and, furthermore, that simply drawing the best straight line through all of the points for a given tracer is not justified. If it is also noted that specimens from several ingots were used for measurements with each tracer, then the possibility of bad specimens is excluded and the upward curvature may finally be taken as a significant result of the present investigation.

In the past, "anomalously" large diffusion coefficients have frequently been observed at low temperatures. Relatively recent work[18] has shown that such behavior may in fact be attributed to the presence of large-angle gain boundaries, in which the diffusion rate may be greatly increased. However, all specimens used in the present work were well-annealed, excellent single crystals. Furthermore, both theory[19] and experiment[20] indicate that the presence of grain boundaries destroys the linearity of a plot of ln(specific activity) *vs* square-of-penetration, whereas such linearity was consistently observed in the present work. The possibility of short-circuiting diffusion along undetected large-angle gain boundaries may therefore be entirely excluded.

Yet it must be noted that all specimens exhibited a distinct filamentary substructure. The filamentary regions, which could be traced from specimen to specimen along an ingot, were of the order of a few millimeters in diameter and extended in the direction of diffusion. Although no measurements of orientation were made, the work of Greninger[20] on copper single crystals and of Teghtsoonian and Chalmers[21] on tin would suggest that orientation differences were of the order of a few degrees or less and consisted of slight rotations of the various regions about the specimen (and growth) axis. Such structure would in turn produce a somewhat larger-than-random number of dislocation lines extending parallel to the direction of diffusion. Now the work of Hendrickson and Machlin[22] shows that self-diffusion in silver is more rapid along dislocations than it is in the matrix, or even in large-angle grain boundaries; a similar behavior could probably be expected for tracer-solute diffusion[23] if the dislocation density were large enough. However, the present data yielded penetration plots that were strictly characteristic of lattice diffusion; and since there is no evidence that small-angle boundaries could produce a contribution of the lattice-diffusion type, it must be concluded that the observed structure most probably produced no measurable effects and was not responsible for the observed low-temperature deviations.

A more likely explanation, brought to the author's attention by Lazarus,[24] concerns some recent work of Hart,[25] who considered the effect upon the self-diffusivity of the randomly distributed dislocations ordinarily present in a metal. Hart found that the dislocation contribution would resemble that of volume diffusion [i.e., would preserve the linearity of a ln(specific activity) *vs* square-of-penetration plot] and, in the specific case of silver, might increase the diffusion rate by roughly 5% at a temperature of 600°C. Although the present work concerns tracer-solute diffusion, a qualitatively similar behavior might well be expected. And, in fact, the effect might be especially pronounced for those tracers which fit into the lattice very poorly. This view is consistent with the present results: the lack of a deviation for a Ni tracer would be traced to the relatively high temperatures and to the complete miscibility of Ni and Cu (and consequent lack of any appreciable degree of misfit); the very noticeable deviations for Co and Fe tracers would in turn be correlated with the rather small (5% for Co, 4% for Fe) maximum solid solubilities, and therefore large degree of misfit, of these elements in copper.

An interesting alternative explanation of the observed deviation has been suggested recently by Lazarus and Okkerse.[26] They have measured the diffusion rates of Fe^{55} and Fe^{59} in silver and find that the variation with mass is roughly four times as great as the inverse-square-root dependence predicted by reaction rate

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[18] See, for example, R. E. Hoffman and D. Turnbull, J. Appl. Phys. **22**, 634 (1951); M. R. Achter and R. Smoluchowski, J. Appl. Phys. **22**, 1260 (1951); D. Turnbull and R. E. Hoffman, Acta Met. **2**, 419 (1954).

[19] J. C. Fisher, J. Appl. Phys. **22**, 74 (1951); R. T. P. Whipple, Phil. Mag. **48**, 1225 (1954).

[20] A. B. Greninger, Trans. Am. Inst. Mining Met. Engrs. **117**, 75 (1935).

[21] E. Teghtsoonian and B. Chalmers, Can. J. Phys. **29**, 370 (1951); **30**, 358 (1952).

[22] A. Hendrickson and E. S. Machlin, Trans. Am. Inst. Mining Met. Engrs. **200**, 1035 (1954).

[23] See D. Turnbull and R. E. Hoffman, reference 18, for example.

[24] D. Lazarus (private communication).

[25] Edward W. Hart, Bull. Am. Phys. Soc. Ser. II, **2**, 145 (1957), and Memo No. MA22, January 1957, Metallurgy and Ceramics Research Department, General Electric Research Laboratory (unpublished).

[26] D. Lazarus and B. Okkerse, Phys. Rev. **105**, 1677 (1957).

theory. They suggest that diffusion may, at least in some cases, partially involve quantum mechanical tunneling, which would in turn lead to unexpectedly large diffusion rates at low temperatures.

ACKNOWLEDGMENTS

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APPENDIX: SURFACE COUNTING

The comparatively very short range[27] of the electrons emitted by Ni^{63} not only makes impossible the use of solution counting techniques, but also very seriously limits the accuracy of conventional end-window counting procedures. Fortunately, however, this very limited power of penetration suggests a natural alternative method in which each slice is counted before, rather than after, it is removed from the specimen (see Fig. 4). It will be shown below that such a procedure yields accurate diffusion coefficients in a manner very similar to that usually employed.

Consider the ideal case of an infinitely thin layer of radioactive tracer diffusing into a semi-infinite solid for a time t; let C be the specific activity, X the total thickness of material removed by previous slicing, and x the distance into the specimen as measured from the the newly-exposed surface. And of those electrons originating at a depth x, let a fraction $f(x)$ emerge from the surface with sufficient energy to enter the counting tube. It is important to note that although f is a function of x and depends upon the counting geometry, it is independent of X.

It then follows that

$$\text{“the surface activity”} \equiv S(X) = \lambda \int_0^{R_m - d} C(X+x) f(x) dx, \quad (1)$$

where $S(X)$ is the total number of electrons which in unit time emerge from unit area of the surface and enter the counting tube, λ is the fraction of the tracer atoms which disintegrate in unit time, R_m is the range[27] of the most energetic electrons, and d is that thickness of specimen material[28] having the same absorbing power as the air layer and counter window combined.

If the usual Gaussian penetration $C = C_0 \exp(-X^2/4Dt)$ is assumed, and if the approximation[29] $\exp[-(x^2+2xX)/4Dt] = [1-(x^2+2xX)/4Dt]$ is made, then Eq. (1) yields

$$S(X) = \lambda \left(a_0 - \frac{a_1 X + a_2}{Dt} \right) C(X), \quad (2)$$

and, consequently,

$$\frac{d \ln S(X)}{dX^2} = -\frac{1}{4Dt} \left\{ 1 + \frac{2a_1'}{X[1-(a_1'X+a_2')/Dt]} \right\}, \quad (3)$$

where $a_n' \equiv a_n/a_0$ and

$$a_n = 2^{-n} \int_0^{R_m - d} x^n f(x) dx; \quad n = 0, 1, 2. \quad (4)$$

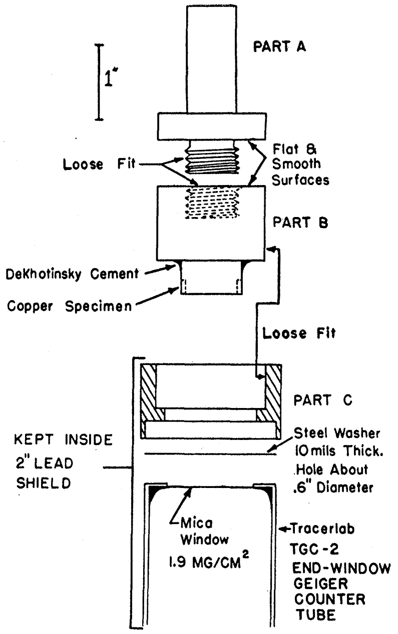

FIG. 4. Diagram of the surface-counting apparatus. The analysis of a specimen proceeds as follows. Part A is securely clamped in the lathe chuck and never loosened during subsequent operations. The specimen is cemented to Part B which in turn is carefully attached to Part A. The specimen diameter is reduced (to avoid edge effects) and one cut is taken across the face of the specimen. Part B is then removed and placed in Part C for surface-counting of the newly exposed face. The sectioning-counting procedure is then repeated as required.

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[27] For Ni^{63}, a pure beta emitter, the maximum range is roughly 0.3 mil in copper, 3 mils in water, or 5 cm in air.

[28] For currently available tubes, and with an air layer several mm thick, $d \sim 0.05$ to 0.15 mil of Cu.

[29] This approximation is clearly valid for small X because (a) $x \leq R_m - d = 0.2$ mil Cu and (b) for the present data, $4Dt \sim 3.5$ mil^2 for Ni−742.5°C and 10 to 20 mil^2 for all other specimens. For large X, only the term $xX_{\max}/2Dt$ is important and this quantity was $\sim\frac{1}{2}$ for Ni−742.5°C and from $\frac{1}{5}$ to $\frac{1}{8}$ in all other cases, so the approximation is valid for all cases except possibly the last few slices of Ni−742.5°C.

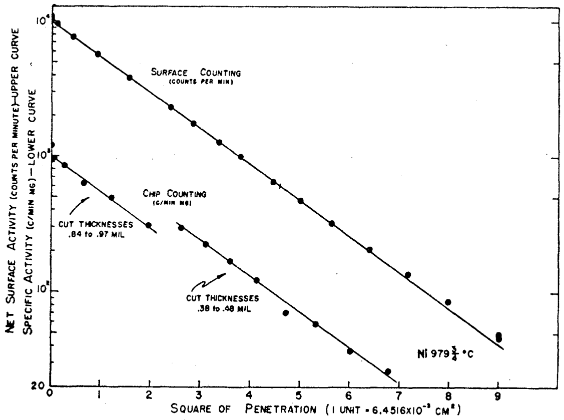

FIG. 5. Comparsion of surface counting and conventional end-window counting. *A single face* of the specimen was sectioned and surface-counted. The chips were saved and later counted separately by means of conventional methods. For ease of comparison, the lower lines were arbitrarily drawn parallel to the upper one.

The applicability of the new method clearly depends upon the values of the a's—compared not only to one another, but also to $X_{\max}$ and to (Dt). If the a's are small enough, and if the initial portion of the curve is ignored, then a $\ln S$ *vs* X^2 plot will have the *same* slope as the customary $\ln C$ *vs* X^2 plot.

Several estimates of the a's will be made. The first, although rather rough, has the advantage of requiring no new assumptions: it follows immediately from (4) that $a_2'<0.01$ and $a_1'<0.1$, simply because $x\leq 0.2$ and $0\leq f(x)\leq 1$. A more accurate estimate involves a direct calculation of $f(x)$. If $F(R)dR$ is the fraction of the electrons having a range in dR about R, then simple geometrical considerations lead to

$$f(x)=\int_{x+d}^{R_m}\tfrac{1}{2}\left(1-\frac{x+d}{R}\right)F(R)dR, \tag{5}$$

where it has been assumed that no scattering of the electrons occurs. Although such an assumption is certainly not correct for the low-energy electrons involved, it seems reasonable to conclude that insofar as scattering effects do not cancel, they will in fact decrease the contribution from lower lying levels, with the result that the method will be somewhat better than the calculations indicate.

Substitution of (5) into (4) yields

$$a_n=\frac{2^{n-1}}{(n+1)(n+2)}\int_d^{R_m}\frac{(R-d)^{n+2}}{R}F(R)dR;\qquad n=0,\,1,\,2. \tag{6}$$

Published data[30] for $F(R)$ were used to perform a direct numerical integration of (6) for $n=0$ and $n=1$. For a reasonable value[31] of $d=0.09$ mil, it was found that $140a_1'<1$. Now the form of Eqs. (6) plus the fact that $R-d\leq R_m-d\simeq 0.2$ mil, implies that $20a_2'<a_1'$ and, therefore, that $2800a_2'<1$.

Substitution of these estimates of a_1' and a_2' into Eq. (3) gives

$$\frac{d\ln S(X)}{dX^2}=\frac{-1}{4Dt}(1+1/\eta), \tag{7a}$$

where

$$\eta>70X\left(1-\frac{1+20X}{2800Dt}\right), \tag{7b}$$

and where X and $(Dt)^{\frac{1}{2}}$ are expressed in mils. Now $X_{\max}$ was about $3\frac{1}{2}$ to 4 mils for Ni-742.6°C and varied from about 5 to 9 mils for all other Ni-plated specimens; (Dt) was about 1 mil^2 for Ni-742.6°C and varied from about $2\frac{1}{2}$ to 5 mil^2 for the other specimens. It therefore follows that the term $(1+20X)/2800Dt$ is never greater than about 1/30 and Eq. (7b) may be rewritten as

$$\eta>67X_{\text{mils}},\ \text{for the present data.} \tag{7b$'$}$$

The following conclusions may therefore be drawn concerning a $\ln S$ *vs* X^2 plot for Ni^{63} diffusing into copper: (a) for $X\rightarrow 0$, the curve *may* rise, perhaps fairly sharply; (b) for larger X, the plot should be a straight line of slope $-1/4Dt$. In practice, the $\ln S$ *vs* X^2 plots were, in general, accurate straight lines; and the possible tendency for the initial portion of the curve to be concave upward was found in most cases. A very direct comparison of surface-counting with conventional techniques was carried out in one case (see Fig. 5); agreement was limited only by the poor accuracy of the conventional method.

In conclusion, it may be stated that for the present data on the rate of diffusion of a Ni^{63} tracer into the copper lattice, the surface-counting technique yields accurate diffusion coefficients in a simple and unambiguous manner.

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[30] H. W. Wilson and S. C. Curran, Phil. Mag. **40**, 634 (1949).

[31] Values of $d=0.06$ and 0.12 were also used, but a_1' was essentially the same.