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Self-Diffusion in Silver*

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Self-diffusion coefficients in single crystals of pure silver were determined between 630°C and 935°C. The results can be expressed by $D=0.40\exp(-44\,090/RT)$ cm^2/sec. The activation energy agrees with the value extrapolated from the results of diffusion in impure silver crystals.

INTRODUCTION

Recent work[1,2] on the effect of impurity addition on the self-diffusion of silver showed that the diffusion coefficients and the activation energy obtained by extrapolation to the case of pure silver are not in good agreement with the customarily accepted values of the coefficients and the energy which had been actually determined for pure silver.[3-5] Upon examining the experimental results for the existing data on self-diffusion, it can be seen that the scatter of points is far greater than can be expected by present standards of accuracy.[6] Repeated measurements performed at one temperature to ascertain the reproducibility of the technique also indicated that the currently accepted value for the activation energy of self-diffusion could be slightly in error.[7] For the above reasons, careful redetermination of the activation energy and the frequency factor for self-diffusion in pure single crystals of silver was repeated.

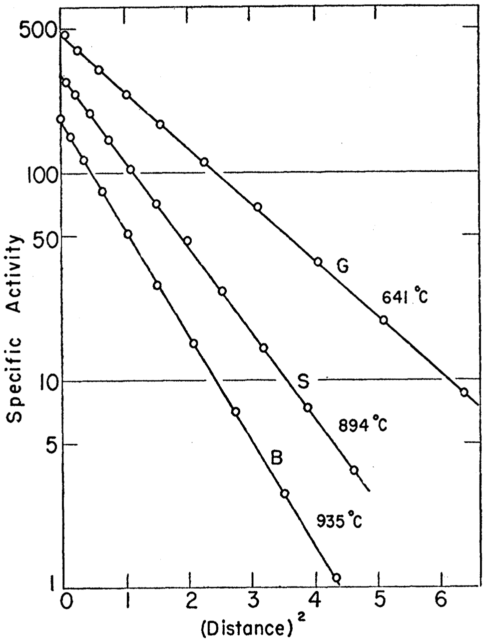

Fig. 1. Penetration curves for diffusion. Arbitrary scaling factor for distance is used for each plot. *G*: Gamma counting (solution), *S*: Scintillation counting (dry), *B*: Beta-immersion counting.

EXPERIMENTAL

Single-crystal specimens of 99.99 percent pure Handy and Harmon silver were prepared. An Ag 110 radioisotope was used as a tracer. Standard sectioning techniques were employed. Description of the detailed experimental procedures can be found elsewhere.[5,8] In most cases, one end of the specimen was analyzed by the gamma-counting method[5] by one of the authors, and the other end of the specimen was analyzed by the beta-immersion counting method[8] by the second. The average of these two values were taken. In most cases, the dis-

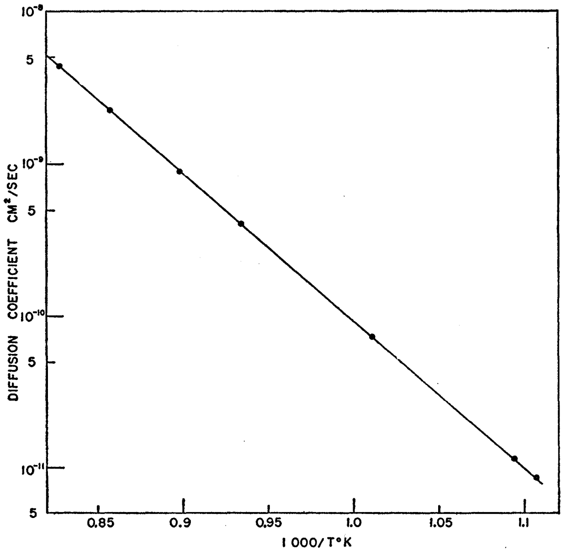

Fig. 2. Diffusion data plotted as log$D$ *versus* $1/T$.

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[1] Hoffman, Turnbull, and Hart, Acta Metallurgica **3**, 417 (1955).

[2] E. Sonder, Phys. Rev. **100**, 1662 (1955).

[3] W. A. Johnson, Trans. Am. Inst. Mining Met. Engrs. **143**, 107 (1941).

[4] R. E. Hoffman and D. Turnbull, J. Appl. Phys. **22**, 634 (1951).

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

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

[7] C. T. Tomizuka and D. Lazarus, J. Appl. Phys. **25**, 1443 (1954).

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

crepancy between the two values did not exceed one percent. Some of the specimens were analyzed by a scintillation counter. The temperature was measured either by a chromel-alumel couple which was calibrated against a NBS calibrated chromel-alumel couple or by a standardized Pt-PtRh couple.

RESULTS

A total of 7 successful diffusion runs were performed in the temperature range of 935–630°C. Typical plots of log(specific activity) *versus* (distance of penetration)^2 are shown in Fig. 1 for each method of counting. Log$D$ is plotted against $1/T$°K in Fig. 2. The numerical data are listed in Table I. The experimental data can be best expressed by

$$D=(0.395\pm0.035)\ \exp[-(44\,090\pm180)/RT]\ \mathrm{cm^2/sec}.$$

DISCUSSION OF THE RESULTS

The present value of the activation energy differs from the previously reported value of 45.5 kcal/mole by 1.4 kcal/mole which is considerably beyond the limit of the experimental error. This discrepancy is not attributable to any single systematic error. It should be noted, however, that the previous results reported by Slifkin, Lazarus, and Tomizuka[5] are the combined results of all the available data on Ag tracer diffusion at that time.[3,4] Their results alone indicate a value of 43.7 kcal/mole for the activation energy and 0.35 cm^2/sec for the frequency factor. These are in good agreement with the present results if one considers the fact that the previous points are fewer and the probable error was larger. The present value of the activation energy and those of the diffusion in silver of cadmium, indium, tin, and antimony,[6,8] which are adjacent to silver in the periodic table in this order with increasing number of valence electrons, plotted as a function of the number of valence electrons, define a fairly straight line, as shown in Fig. 3. This picture seems to agree well with the interpretation proposed by Lazarus[9] based on the model of screened impurity atoms. The Thomas-Fermi model of screening predicts a straight-line relationship between the activation energies and the excess valency. The experimental results give a value of the screening radius of 0.57 A which is in agreement with the theoretical value 0.58 A.[10] This agreement seems fortuitous in view of the fact that the calculation by Blatt[11] of the activation energies based on Friedel's theory,[12] which should be a better approximation than the Thomas-Fermi model, does not agree with the experimental results.§

TABLE I. Diffusion of Ag^{110} in silver.

Temperature (°C)	Diffusion coefficient (cm^2/sec)
630.0	8.64×10^{-12}
641.2	1.15×10^{-11}
715.9	7.32×10^{-11}
797.0	4.03×10^{-10}
840.2	8.87×10^{-10}
893.8	2.24×10^{-9}
934.9	4.41×10^{-9}

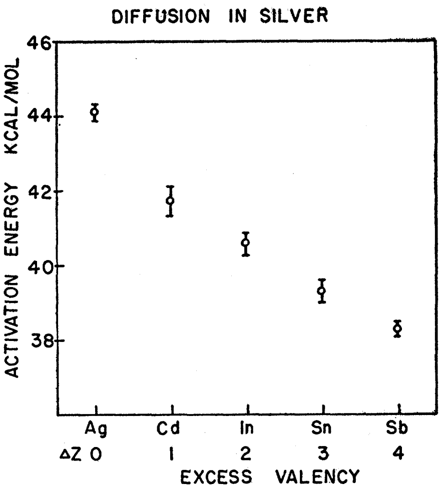

FIG. 3. Activation energy for diffusion in silver plotted as a function of atomic number.

TABLE II. Self-diffusion in Ag.

Authors	H kcal/mole	C_0 cm^2/sec	Experimental method
W. A. Johnson[a]	45.95	0.895	tracer, sectioning
Hoffman and Turnbull[b]	45.95	0.895	tracer, sectioning
Slifkin, Lazarus, and Tomizuka[c] (including J, H and T)	45.5	0.724	tracer, sectioning
S, L, and T only[c]	43.7	0.35	tracer, sectioning
Nachtrieb, Petit, and Wehrenberg[d]	43.7	0.27	tracer, sectioning
R. D. Johnson and Martin[e]	40.8	0.11	tracer, sectioning (?)
Krueger and Hersh[f]	44.9	0.835	tracer, autoradiograph
Kryukov and Zhukovitski[g]	47.4	1.8	tracer, surface counting
Finkelstein and Yamashchikova[h]	45.0	0.905	tracer, surface counting
Zhukovitski and Geodakyan[i]	45.0	0.53	tracer, surface counting
Kuczynski[j,k]	42.0	0.6	metallographic
	45.7	0.9	metallographic
This investigation	44.09	0.395	tracer, sectioning

[a] See reference 3.
[b] See reference 4.
[c] See reference 5.
[d] Nachtrieb, Petit, and Wehrenberg, J. Chem. Phys. (to be published).
[e] R. D. Johnson and A. B. Martin, Phys. Rev. **86**, 642 (1952).
[f] H. Krueger and H. N. Hersh, J. Metals 124 (1955).
[g] S. N. Kryukov and A. A. Zhukovitski, Doklady Akad. Nauk S.S.S.R. **90**, 380 (1953).
[h] B. N. Finkelstein and A. I. Yamashchikova, Doklady Akad. Nauk S.S.S.R. **98**, 781 (1954).
[i] A. A. Zhukovitski and V. A. Geodakyan, Doklady Akad. Nauk S.S.S.R. **102**, 301 (1955).
[j] G. C. Kuczynski, Trans. Am. Inst. Mining Met. Engrs. **185**, 169 (1949).
[k] G. C. Kuczynski, J. Appl. Phys. **21**, 632 (1950).

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

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

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

[12] J. Friedel, Advances in Phys. **3**, 446 (1954).

§ *Note added in proof.*—Recent calculations of screening potential by Alfred and March (L. C. R. Alfred and N. H. March, to be published in Phys. Rev.) obtained by the exact numerical solution of the Thomas-Fermi equation, reduced very appreciably the discrepancy between experiment and theory on the variation of H with Z.

The diffusion coefficients and the activation energy from the present work agree with the values extrapolated from the results on impure crystals.[1,2]

All the available results on self-diffusion in silver are listed on Table II. Most nearly consistent results are apparently obtained by use of both tracer *and* sectioning techniques.

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Radiation Damage in Diamond and Silicon Carbide[*]

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Diamond and silicon carbide were irradiated in nuclear reactors and were found to be damaged in a manner similar to that for graphite. Detailed observations were made of the dilatation and increase in energy content and their annealing. Dilatations as great as about 3.7 percent and increases in energy content as great as about 400 cal/g were observed. The dilatations and the energy content (release of stored energy) seemed to anneal in a parallel manner and could be treated kinetically as a distribution of processes in activation energy. The initial distribution for diamond showed a peak at about 1.6 ev and a plateau extending (at about $\frac{1}{4}$ the height of the peak at short irradiations and greater proportionately for long irradiations) to activation energies in excess of 3.7 ev. The initial distribution for silicon carbide showed a smaller narrow peak at about 1.6 ev and a very broad larger peak extending from about 2.2 ev to 4.3 ev with a maximum at about 3.4 ev. In many of the samples of irradiated diamond the stored energy exceeded the heat capacity in certain temperature ranges, and catastrophic stored energy release was observed on heating.

INTRODUCTION

An account of the prediction and discovery of radiation damage in nuclear reactors is given by Burton.[1] Of the substances investigated at first, large changes in physical properties were found only in graphite. (See Neubert *et al.*[2] for an account of the experimental investigations.) Accordingly it was suggested that the large changes in physical properties found in graphite were associated with its crystal structure. In order to test this, samples of diamond were irradiated. The energy content was the property chosen for investigation because it could be determined in the same manner as for graphite and because it seemed especially significant. A large increase, comparable to the increases observed in graphite, was found. Subsequently the dilatation was investigated and was also found to be large, comparable to that of graphite. Then α-silicon carbide (hexagonal) was irradiated, and it was found to exhibit a similar large dilatation and increase in energy content.

MATERIALS

Diamond

(a) For heat of combustion measurements, for some of the x-ray lattice constant measurements, and for some density determinations, there was used industrial diamond dust (white bort) 80–100 mesh. It consisted mainly of colorless cleavage fragments with occasional yellow ones and a few dark specks. It was cleaned by heating it with hydrofluoric acid for some hours. It was then washed with distilled water and dried. A sample was examined spectroscopically with the results: detected elements Cu 2, Mg 2, Na 5, Si 50 ppm; detection limits for undetected elements Ag 0.1, Al 5, As 20, B 0.1, Ba 2, Be 0.5, Bi 0.2, Ca 2, Co 2, Cr 1, Fe 1, Hg 5, K 10, Li 1, Mn 0.1, Ni 1, P 50, Pb 0.5, Sb 1, Sn 5, Sr 10, Ti 1, V 1, Zn 20, Zr 1 ppm. Except for a few grains which showed a very weak birefringence, the crystals were isotropic. Samples were heated for half an hour at various temperatures in a stream of purified nitrogen. No change was observed after heating at 300°C, 400°C, 500°C or 600°C. After heating at 700°C the crystals darkened slightly, turning a pale grey, so that they stood out in slightly higher relief against the white background of a porcelain boat.

(b) Colorless octahedra, 1 to 2 mm across (industrial diamond), were used for some density determinations.

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[*] Based on work performed under the auspices of the U. S Atomic Energy Commission.

[1] M. Burton, J. Phys. & Colloid Chem. **51**, 618 (1947).

[2] M. Burton and T. J. Neubert, J. Appl. Phys. **27**, 557 (1956); T. J. Neubert *et al.*, Argonne National Laboratory Report ANL-5472 (available from the Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C., 1956).