

Diffusion of Ruthenium in Single Crystals of Silver*

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The diffusion coefficient of ruthenium in monocrystalline silver has been measured over the temperature range 793°C to 945°C, using Ru¹⁰³ and Ru¹⁰⁶ tracers, and a sectioning technique. The results may be expressed by an Arrhenius relation as $D = (180 \pm 70) \exp[-(65\,800 \pm 1000)/RT]$ cm²/sec. The present result is consistent with earlier theoretical models, unlike the results obtained by Mackliet for Fe in Cu.

THE rate of diffusion of Ru¹⁰³ and Ru¹⁰⁶ into single crystals of pure silver has been determined over a temperature range 793°C to 945°C, using precision sectioning techniques.

Large single crystals were prepared from Handy and Harmon 99.99% pure silver in a vacuum furnace. Cylindrical diffusion samples were prepared from these by methods described previously.¹ An extremely thin layer of ruthenium isotope, obtained from the Oak Ridge National Laboratory, was electroplated onto the specimens. Electroplated specimens were then sealed off in evacuated vycor capsules and placed in electronically controlled diffusion furnaces for times ranging from two days at the highest temperature to seven months at the lowest. An attempt was made to measure the diffusion coefficient at 725°C after an anneal of one year. However, the results were inconclusive and apparently much lower than could be expected on the basis of the other data. During the diffusion anneals, the temperatures were continuously recorded. Due to the long times involved, total temperature variations amounted to several degrees, but it was possible to determine the average temperature to within $\pm 1^\circ\text{C}$.

After diffusion, the samples were sectioned in a precision lathe and the activity in each slice determined by standard beta-counting techniques. In the two cases where Ru¹⁰³ was used as a tracer, each slice was dissolved in dilute nitric acid and counted with an immersion beta counter. Where Ru¹⁰⁶ was used as a tracer, the cuttings were counted directly, using a thin end-window Geiger tube.

Data analysis was complicated by the fact that all the plots of $\log(\text{specific concentration})$ vs (penetration depth)² showed a sharp drop near the surface before leveling out into the straight line from which the diffusion coefficient is determined. This surface effect is presumably caused by the buildup of impermeable intermetallic phases or by an extremely low solubility limit for ruthenium in silver. The effect was considerably reduced, although not completely eliminated, by using extremely small amounts of tracer, of the order of a few percent of one atomic layer in some cases.

Because of this extremely limited amount of tracer which could be used and the small values of the diffusion coefficient, the relative precision of this experiment is considerably below that obtained previously with more soluble impurity tracers.

The experimental results, together with estimated limits of error, are given in Table I. The temperature variation of the diffusion coefficient is shown in Fig. 1. Within the limits of error, the diffusivity is seen to vary exponentially with temperature according to the usual Arrhenius relation, $D = D_0 \exp(-Q/RT)$, with an activation energy, $Q = 65.8 \pm 1$ kcal/mole, and a frequency factor $D_0 = 180 \pm 70$ cm²/sec.

It is of interest to compare the present result with theoretical predictions based on consideration of the screening of an impurity atom in a metal,² and with the

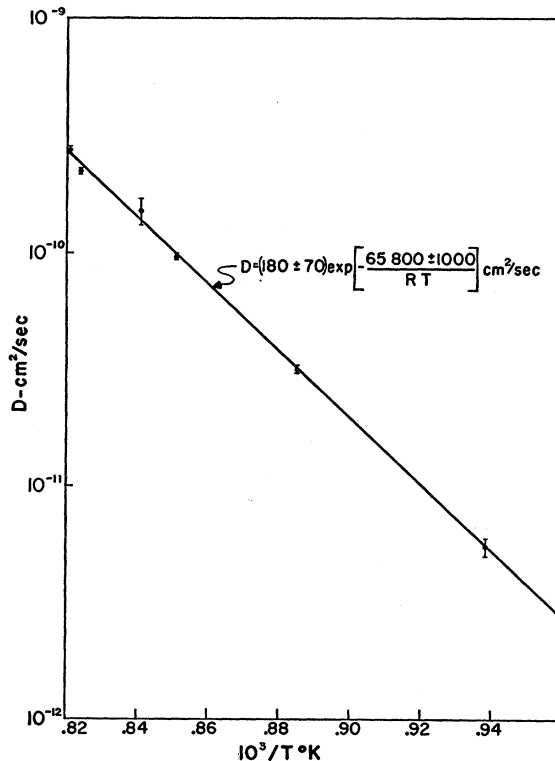


FIG. 1. Diffusion of ruthenium into silver.

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¹ Slifkin, Lazarus, and Tomizuka, *J. Appl. Phys.* **23**, 1032 (1952).

² D. Lazarus, *Phys. Rev.* **93**, 973 (1954).

experimental results of Mackliet³ who studied tracer diffusion in the analogous system, iron in copper. Mackliet found that while iron diffused in copper with a somewhat higher activation energy than that measured for self-diffusion, the quantitative agreement with theory was extremely poor, and, in fact, the activation energy for iron diffusion was lower than that for the less electropositive impurities, cobalt and nickel. In the present case, the result is in excellent qualitative and quantitative agreement with the screening model, particularly as amplified by the more recent calculations of Blatt⁴ and Alfred and March.⁵

The present result is also qualitatively consistent with the well known rate-theoretic analysis of Wert and Zener,^{6,7} although the quantitative agreement is poor. Substituting values of $\beta=0.45$ and $\lambda=0.55$ (which give good results for diffusion of electronegative impurities in silver) into their equation $D_0 = a^2\nu \exp(\lambda\beta Q/RT_m)$,

³ C. A. Mackliet, Phys. Rev. **109**, 1964 (1958).

⁴ F. J. Blatt, Phys. Rev. **99**, 600 (1955).

⁵ L. C. R. Alfred and N. H. March, Phys. Rev. **103**, 877 (1956); Phil. Mag. **2**, 985 (1957).

⁶ C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

⁷ C. Zener, J. Appl. Phys. **22**, 372 (1951).

TABLE I. Diffusion of ruthenium in silver.

| Temperature (°C) | Tracer | Diffusion coefficient (cm ² /sec) |
|------------------|-------------------|--|
| 945.5 | Ru ¹⁰⁸ | $(2.74 \pm 0.08) \times 10^{-10}$ |
| 941.7 | Ru ¹⁰⁶ | $(2.21 \pm 0.07) \times 10^{-10}$ |
| 916 | Ru ¹⁰⁶ | $(1.5 \pm 0.2) \times 10^{-10}$ |
| 900.2 | Ru ¹⁰⁸ | $(9.6 \pm 0.3) \times 10^{-11}$ |
| 856.2 | Ru ¹⁰⁶ | $(3.17 \pm 0.12) \times 10^{-11}$ |
| 792.8 | Ru ¹⁰⁶ | $(5.5 \pm 0.5) \times 10^{-12}$ |

and appropriate values for the lattice parameter a , the Debye frequency ν , and the melting temperature T_m , one calculates a value for the frequency factor $D_0=5.9$, considerably less than the measured value.

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Application of the Morse Potential Function to Cubic Metals

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The Morse parameters were calculated using experimental values for the energy of vaporization, the lattice constant, and the compressibility. The equation of state and the elastic constants which were computed using the Morse parameters, agreed with experiment for both face-centered and body-centered cubic metals. All stability conditions were also satisfied for both the face-centered and the body-centered metals. This shows that the Morse function can be applied validly to problems involving any type of deformation of the cubic metals.

INTRODUCTION

BECAUSE of the widespread use of central pairwise potential functions in the description of the solid state, a thorough study of the types of problems to which this function may be applied is quite desirable. The purpose of this paper is to investigate the applicability of a special type of pairwise potential function, the Morse function, to the description of the properties of cubic metals.

After discussing the conditions which any potential function must satisfy if it is to describe reality, various crystal properties are expressed in terms of the Morse function. These include the cohesive energy, the lattice constant, the compressibility, the equation of state, and the elastic constants. Calculations are then done to determine the Morse function parameters, which are in turn used to compute the equations of state and the

elastic constants for six face-centered and nine body-centered cubic metals.

PROCEDURE

A. General Properties of Potential Functions in Crystals

If $\varphi(r)$ is the energy of interaction of two atoms a distance r apart, then, in order that $\varphi(r)$ represent the interatomic potential of two atoms in a stable crystal, it must satisfy the following conditions:

- (1) The force $-\partial\varphi/\partial r$ must be attractive at large r and repulsive at small r ; therefore, $\varphi(r)$ must have a minimum at some point $r=r_0$.
- (2) The magnitude of φ must decrease more rapidly with r than r^{-3} .
- (3) All elastic constants are positive.