

## Interstitial Diffusion of Gold and Silver in Indium\*

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The diffusivities  $D$  of silver in the  $c$  and  $a$  directions of indium and gold in randomly oriented single crystals of indium have been measured by a radioactive-tracer technique. They are described by:  $D_{Ag/In}^a = 5.2 \times 10^{-1} \exp(-12\,800/RT)$ ,  $D_{Ag/In}^c = 1.1 \times 10^{-1} \exp(-11\,500/RT)$ , and  $D_{Au/In} = 9 \times 10^{-3} \exp(-6700/RT)$ . The rates of diffusion of silver and gold in indium are thus several orders of magnitude greater than the self-diffusion rate of indium. These results indicate that gold and silver are dissolved at least partly in the interstitial state, in agreement with a theory which predicts that  $d$ - $d$  correlation forces should cause dissolved noble metals to favor interstitial sites in indium.

### INTRODUCTION

THE occurrence of interstitial solutes, such as the metalloids (carbon, nitrogen, and boron) in many of the polyvalent transition metals, was explained by Hagg<sup>1</sup> in the 1930's in terms of a pure size effect. He showed that a solute atom would fit into the interstices of a solvent matrix if the ratio of the diameter of the solute atom to that of the solvent was less than the diameter ratio corresponding to the largest sphere that will fit interstitially into a close-packed lattice of hard spheres. According to this criterion, no system constituted entirely by metals with the exception of the alkalis should have any interstitial components. This conclusion is in agreement with the general experience that metallic alloys are substitutional solutions.

However, recent experimental evidence<sup>2-5</sup> shows that the noble metals (Cu, Ag, and Au) dissolve at least partly if not wholly interstitially in lead and tin in contradiction of Hagg's rule for interstitial formation as shown in Fig. 1. To explain this surprising interstitial character, a theory<sup>6,7</sup> was developed that, in addition to explaining the interstitial dissolution of the noble metals in lead and tin, predicted that the noble metals should dissolve interstitially in indium and thallium. In the following discussion, we will briefly review this theory and then apply it specifically to the dissolution of silver and gold in indium.

It is expected that the substitutional dissolution of a monovalent metal such as silver in a trivalent solvent such as indium will be small since the heat of solution of the silver in indium will be roughly equal to the formation energy of a vacancy in indium.<sup>8</sup> There is no *a priori*

reason to believe that there should be any appreciable solubility in the interstitial state.

To understand the unexpected interstitial behavior of the noble metals in lead, tin, thallium, and indium, we must first examine the binding force present in the pure noble metals. Calculations of the cohesive energy of the pure noble metals have suggested that in addition to the electrostatic cohesion of the  $s$  valence electrons, part of the cohesive energy must arise from van der Waal's interactions between the  $d$  electron shells of neighboring ionic cores.<sup>9</sup>

Because of the existence of such correlation forces in the pure noble metals, it is probable that van der Waal's forces between ion cores in general will arise whenever ion cores isoelectronic with those of the pure noble metals are separated by distances typical of the pure-noble-metal ion-ion separations. In the metallic state, the ion cores of lead, tin, thallium, and indium have the same electronic subgroups as the ion cores of one of the noble metals. Because the solvent ion cores are identical to the ion cores of one of the noble metals, the van der Waal's forces present in the pure noble metals should also exist between these solvent and solute ion cores.

The frequency characteristic of the van der Waal's interaction<sup>10</sup> is such that there is little reduction or

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<sup>1</sup> G. Hagg, *Z. Physik Chem.* **6B**, 221 (1929); **7B**, 339 (1930); **8B**, 445 (1930).

<sup>2</sup> B. F. Dyson, T. R. Anthony, and D. Turnbull, *Bull. Am. Phys. Soc.* **10**, 1094 (1965); *J. Appl. Phys.* **37**, 2370 (1966).

<sup>3</sup> G. V. Kidson, *Phil. Mag.* **13**, 247 (1966).

<sup>4</sup> B. Dyson, *Bull. Am. Phys. Soc.* **11**, 184 (1966); *J. Appl. Phys.* **37**, 2375 (1966).

<sup>5</sup> T. R. Anthony, B. F. Dyson, and D. Turnbull, *J. Appl. Phys.* **37**, 2925 (1966).

<sup>6</sup> T. R. Anthony, *Bull. Am. Phys. Soc.* **11**, 216 (1966).

<sup>7</sup> T. R. Anthony and D. Turnbull, *Appl. Phys. Letters* **8**, 120 (1966).

<sup>8</sup> T. R. Anthony and D. Turnbull (to be published).

Alloy Size Ratio Rules

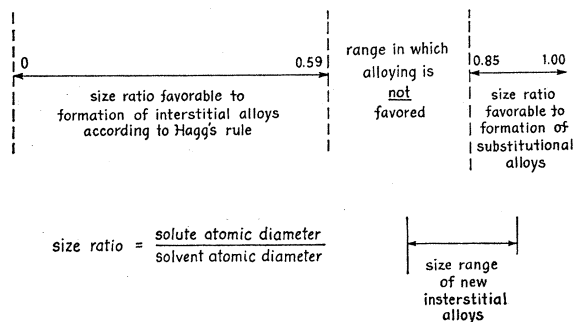


FIG. 1. Alloy size-ratio rules.

<sup>9</sup> N. F. Mott, *Rept. Progr. Phys.* **25**, 218 (1962); J. Friedel, *Proc. Phys. Soc. (London)* **65B**, 769 (1952).

<sup>10</sup> H. Ehrenreich and H. R. Phillip, *Phys. Rev.* **128**, 1622 (1962).

screening of these intercore forces by the conduction-electron gas. Calculations indicate that these correlation or van der Waal's forces are very large when the noble-metal solute is in the interstitial position and are negligibly small if the noble-metal solute atom occupies a substitutional site. The existence of these large attractive forces with the interstitial noble-metal solute and their absence with a substitutional noble-metal solute causes the noble-metal atoms to favor the interstitial sites in these solvents.

The principal theoretical explanation of the absence of interstitial components in most alloys is the large repulsive energy that arises on interstitial formation. However, except in the case of actual overlap of the ion cores, there is only a limited screened Coulombic repulsion between ion cores isoelectronic with those of the noble metals. If one considers ion-core size instead of atomic size, then the interstitial octahedral sites in lead, tin, thallium, and indium are large enough to allow the occupancy of ion cores of silver, gold, and copper without any ion-core overlap. In addition, because of the high valence of these solvents, there is a large amount of screening by the valence electrons. Thus the high repulsive forces that have ruled out interstitial formation in other metallic systems are absent here and in contrast have been replaced by attractive van der Waal's force.

Previous experiments<sup>2-4</sup> in lead and tin have shown that the interstitial solubility of the noble metals in these solvents leads to a high solute diffusion coefficient that is two to three orders of magnitude greater than the solvent self-diffusion coefficient at the melting point. Thus in the family of solvents in which the noble metals dissolve interstitially, a large solute diffusion coefficient is a strong indication of appreciable interstitial solubility. Consequently, we have measured the diffusion coefficients of gold and silver in indium to determine whether or not an interstitial mechanism is indicated.

## EXPERIMENTAL PROCEDURE

### 1. Specimen Procedure

Single-crystal and polycrystalline specimens in cylindrical form ( $\frac{1}{2}$ -in. diam. and 5-in. long) were prepared from indium of 99.99% purity obtained from the Indium Corporation of America. The cylinders were sectioned into  $\frac{1}{8}$ -in. lengths using a Servomet spark machine with a tantalum wire cutter. After sectioning, each specimen was cleaned in 4*N* HCl and mounted on aluminum  $\frac{1}{2}$ -in.-diam. slugs with epoxy resin in order that they might be held rigidly during microtoming. The indium is too soft to be gripped directly. The specimens were then mounted in a horizontal microtome and the free ends of the specimens were planed flat. Afterwards, the specimens were annealed for 12 h at 140°C and furnace cooled.

### 2. Silver

Radioactive Ag<sup>110m</sup> (specific activity 1 Ci/g) was chemically deposited from a neutral AgNO<sub>3</sub> solution onto the microtomed surface of the indium which had been freshly cleaned with 4*N* HCl and washed in distilled water. The chemical deposition lasted for four minutes after which the solution was blotted dry with absorbent cotton.

The samples were exposed to the atmosphere during the diffusion anneals. Since the oxide film on indium, like that on aluminum, is highly protective, there was no visible change in the appearance of the samples during the diffusion periods, which ranged from three hours to five days. These diffusion heat treatments were made in furnaces whose temperatures were stabilized to within  $\pm\frac{1}{2}$ °C by a J. P. West controller. The temperature was measured by a thermocouple which was inserted into a small hole in the base of the indium sample and was checked against a standardized Pt-(Pt-Rh) couple. The heating curve was recorded in order to obtain corrected diffusion times for the shorter experiments. At the conclusion of the diffusion anneals, the samples were quenched in a blast of high-pressure air and the diameters of the cylindrical specimens were reduced on a lathe by  $3\sqrt{(D^2)}$  to eliminate surface-diffusion effects. The sample was then placed in the microtome and the active face was made parallel to the plane of motion of the microtome blade by means of a mechanical dial gauge which could be read to 1  $\mu$ . An optically flat glass disk was interposed between the specimen surface and the arm of the dial gauge in these operations to prevent any damage of the indium surface.

The specimen was then sliced into 15- $\mu$  sections which were collected into groups of three for weighing and counting. The samples were counted in a well-type single-channel  $\gamma$ -ray spectrometer and weighed on a Mettler semi-micro balance. Slice thickness was calculated from the final specimen diameter and the weight of each section, using a density of 7.28 g/cm<sup>3</sup> for indium. The times of the diffusion treatments were such that the concentration of the diffusing silver fell an order of magnitude in the sectioned portion of each specimen.

As in previous experiments with lead,<sup>2</sup> there was a trapping of a small amount of the isotope at the active surface of the indium by an oxide film. This trapping gave rise to high activity for the first section. However, because the trapped isotope was unable to move during the duration of the experiment, the distribution of the solute in the rest of the sample was Gaussian.

### 3. Gold

The same experimental techniques that were used in the silver experiments were utilized in the gold-diffusion studies with the exception of the solution used for the chemical deposition. In the case of the Au<sup>198</sup> (specific activity 1 Ci/g) a 4*N* HCl solution of AuCl<sub>3</sub> seems to

TABLE I. Diffusivities of gold, silver, and indium in indium.

Element	$D_0^c$	$D_0^a$ (cm <sup>2</sup> /sec)	$Q^c$	$Q^a$ (kcal/mole)
In	2.7	3.7	18.7±0.3	18.7±0.3
Ag	1.1×10 <sup>-1</sup>	5.2×10 <sup>-1</sup>	11.5±0.3	12.8±0.3
Au		9×10 <sup>-3</sup>		6.7±0.9

minimize the formation of an oxide film at the surface, allowing most of the deposited isotope to diffuse into the specimens. Other solutions that were tried led to a partial trapping of the deposited isotope at the surface and a non-Gaussian behavior in the decrease of isotope concentration with distance.<sup>2</sup>

### RESULTS

The solute concentration for both the gold and the silver obeyed a Gaussian distribution. Diffusion coefficients were determined from the slope of a plot of the logarithm of tracer concentration versus the square of the penetration. In Fig. 2 the logarithm of the diffusivities of gold and silver are plotted against the reciprocal of the absolute temperature. The diffusivity of silver was measured for both the *c* and *a* directions in indium, while the diffusivity of gold was measured only in randomly oriented single crystals. In Table I the activation energies  $Q$  and the pre-exponential factors  $D_0$  that resulted from a least-squares analysis of the data are presented along with the self-diffusion data for pure indium.<sup>11</sup>

Indium possess a slightly distorted face-centered-cubic lattice which is a face-centered-tetragonal structure with a *c/a* ratio of 1.07. For self-diffusion, which is most probably by a vacancy mechanism, the diffusional anisotropy is small with the *a* axis being the fastest direction. For silver, the anisotropy is reversed, with the *c* direction being the fastest. No attempt was made to measure the exact anisotropy for the tracer diffusion of gold. However, from the available data, it appears that the diffusivity difference between the *c* and *a* axis of the indium is greater for gold than for silver.

If the noble metals were diffusing by a vacancy, exchange, or interstitialcy mechanism, an enhancement of the indium self-diffusion constant would result from the mixing action of the rapidly moving noble-metal solute.<sup>12</sup> However, in a solution of indium saturated with gold, Powell and Braun found no increase in the diffusion constant of indium.<sup>13</sup> Rapid diffusion by "dislocation short circuiting" was also ruled out as a possible mechanism because of the shape of the tracer penetration curve<sup>14</sup> and the relatively large number of solute atoms per atomic plane in comparison to the dislocation density. Moreover, there is a striking similarity of the

<sup>11</sup> J. E. Dickey, *Acta Met.* 7, 350 (1959).

<sup>12</sup> R. E. Hoffman, D. Turnbull, and E. W. Hart, *Acta Met.* 3, 417 (1955).

<sup>13</sup> G. W. Powell and J. D. Braun, *Trans. AIME* 230, 694 (1964).

<sup>14</sup> R. W. Balluffi, *Acta Met.* 11, 1109 (1963).

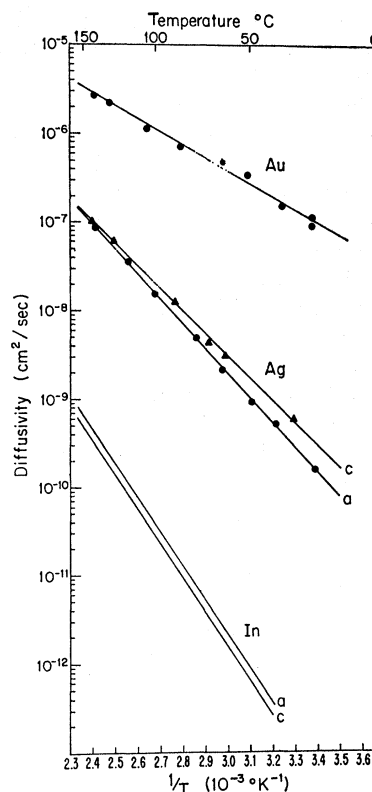


FIG. 2. Diffusivities of gold, silver, and indium in indium.

In-Au and In-Ag systems with other gold and silver interstitial systems.<sup>2-4</sup> Therefore we conclude that both silver and gold diffuse interstitially in indium, in agreement with theoretical predictions.<sup>15</sup>

### DISCUSSION

Because gold and silver have almost identical atomic diameters and hence should cause equal amounts of strain energy in the interstitial positions, their dissolution behavior is of some interest. As shown by Kambe, the discrepancy between the electrostatic cohesion<sup>16</sup> arising from interactions between the *s* valence electrons and positive-ion cores and the experimental cohesive energy is greatest for gold and smallest for silver in the pure noble metals, indicating that van der Waal's forces are highest between gold ion cores and smallest between silver ion cores. It is expected that this unequal interaction will be carried over into indium so that, for equal amounts of dissolved gold and silver, a higher percentage of gold will be found in the interstitial state. In support of this view, the diffusion evidence in the following manner suggests that the interstitial position is more favored by the gold than the silver solute atoms.

Since gold and silver have almost identical atomic

<sup>15</sup> We have also measured the diffusivities of gold and silver in thallium and have found strong indications of interstitial solute diffusion in these systems. Anthony, Dyson, and Turnbull (to be published).

<sup>16</sup> K. Kambe, *Phys. Rev.* 99, 419 (1955).

diameters, it is expected that the activation energy necessary to dilate the indium lattice to allow the solute atoms to diffuse from one interstitial site to another will be the same for both atoms. However, in apparent contradiction of this simple picture, the experimental diffusion activation energies are 7 kcal/mole for gold and 12 kcal/mole for silver. One model which may explain this anomaly is that silver solute atoms are distributed between substitutional and interstitial sites in indium whereas gold dissolves largely interstitially. Thus the additional 5 kcal/mole necessary for the silver diffusion would represent the energy that is required to activate silver from a substitutional to an interstitial site before silver interstitial diffusion could occur. In contrast, gold being dissolved entirely interstitially would need only 7 kcal/mole of activation energy for diffusion, the work required by both the equally sized

gold and silver atoms to jump from one interstitial site in the indium lattice to another. Hence, on the basis of this tentative model, gold would dissolve and diffuse wholly interstitially while the diffusion of silver in indium would be best described by the dissociative mechanism proposed by Frank and Turnbull.<sup>17</sup>

As a final comment, it should be mentioned that theoretical considerations and diffusion results for other systems indicate that copper should also dissolve interstitially in indium and that it should diffuse faster than both gold and silver.

#### ACKNOWLEDGMENT

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<sup>17</sup> F. C. Frank and D. Turnbull, *Phys. Rev.* **104**, 617 (1955).

## Theory of the Galvanomagnetic Properties of Magnesium and Zinc

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A theory of the galvanomagnetic properties of magnesium and zinc is developed. It is restricted to magnetic fields parallel to the hexad axis and takes into account the effects of magnetic breakdown. The transverse magnetoresistance shows the expected transition from electron-hole compensation at low fields to a noncompensated state at high fields, i.e., a transition from quadratic behavior to saturation. The Hall resistance shows the corresponding behavior. In addition, all transverse components of both conductivity and resistivity tensors show strong oscillations of the de Haas-van Alphen type due to coherent effects in the tunneling probability through small pieces of the Fermi surface. Theoretical curves are shown for various components of the galvanomagnetic tensors and compared with experimental measurements. Most parameters involved in the comparison are provided, or at least checked, by other experiments; only the breakdown field strength  $H_0$  is unknown. It is found that a single  $H_0$  suffices for Zn, but that for Mg,  $H_0$  varies along the hexad axis. With this limited degree of adjustability, good agreement may be obtained between theory and experiment, though minor discrepancies remain unexplained.

### 1. INTRODUCTION

THE hexagonal-close-packed (hcp) metals Zn,<sup>1-3</sup> Mg,<sup>4-6</sup> and Be<sup>7</sup> show remarkable galvanomag-

netic properties which depart drastically from those usually found in metals. As is well known<sup>8</sup> the transverse magnetoresistance commonly exhibits, for single-

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<sup>1</sup> R. W. Stark, *Phys. Rev. Letters* **9**, 482 (1962); *Phys. Rev.* **135**, A1698 (1964).

<sup>2</sup> N. E. Alekseevskii and Yu. P. Gaidukov, *Zh. Eksperim. i Teor. Fiz.* **43**, 2094 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 1481 (1963)].

<sup>3</sup> W. A. Reed and G. F. Brennert, *Phys. Rev.* **130**, 565 (1963).

<sup>4</sup> R. W. Stark, T. G. Eck, and W. L. Gordon, *Phys. Rev.* **133**, A443 (1964).

<sup>5</sup> R. W. Stark, in *Proceedings of the IXth International Conference on Low Temperature Physics, Columbus, Ohio 1964* (Plenum Press, Inc., New York, 1965), p. 712.

<sup>6</sup> R. W. Stark (private communication).

<sup>7</sup> W. A. Reed, *Bull. Am. Phys. Soc.* **9**, 633 (1964), and private communication.

<sup>8</sup> For complete reviews of the general theory and experimental situation of the galvanomagnetic effects in metals see for instance R. G. Chambers, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1962), p. 100; E. Fawcett, *Advan. Phys.* **13**, 139 (1964) and the many references quoted there.