degenerate band. The obtained results for the selection rules governing all transitions are summarized in Table I. All transitions will be possible between all four ladders of Landau energy levels for $k_H \neq 0$. These are the quantum-mechanical analogs of the classical result derived by Zeiger, Lax, and Dexter.[11]

We have seen that if the energy surface is taken to be spherical, that is, if γ_2 and γ_3 are taken to be equal, $\nu = 0$. Thus we have concluded that cyclotron resonance lines observed in the longitudinal geometry are all harmonics caused from the warped energy surface which depend explicitly on $\gamma_3 - \gamma_2$. Further, it has been remarked that the k_H effect plays an essential role in causing transverse harmonics for $\mathbf{H}_0 \| [111]$ and longitudinal transitions for three directions of the magnetic field, namely, [001], [111], and [110] directions.

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Self-Diffusion in Silver-Gold Solid Solutions*

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The diffusion of silver and gold tracers in silver-gold in crystals of 0, 8, 17, 35, 50, 66, 83, 94 and 100 at. % gold has been measured. It is shown that the limiting error in such measurements is due to temperature uncertainty rather than to the sectioning process. The activation energies obtained do not vary in proportion to the melting point or heat of fusion, and the deviations cannot be rectified in terms of lattice parameter arguments. The activation energies in the pure metals are better accounted for by the theory of Turnbull and Hoffman than by that of Swalin. The suggestion that the vacancy migration energy should vary as $(c_{11}-c_{12})$ is not confirmed. From the change in frequency factor with composition it is deduced that the activation entropy of migration of a vacancy decreases linearly with composition by $1.5R$ from pure silver to pure gold. The dependence of diffusion coefficient on gold content is compared with the theories of Hoffman, Turnbull, and Hart, of Reiss, of Manning, and of Lidiard, and impurity correlation factors of reasonable magnitudes are obtained. Particularly difficult to treat, however, is the decrease in diffusion coefficients resulting from additions of the rapid diffuser silver to the slow diffuser gold. An experiment to measure the effects of vacancy flux directly is proposed.

A LARGE part of present-day theory of atomic diffusion in crystals[1] is still sufficiently approximate and uncertain that the guidance and validation provided by simple and thorough experiments are welcome. In particular, much can be learned about interactions between vacancies and impurity atoms by the study of self-diffusion in binary alloys as a function of composition. There have been several such investigations in recent years, dealing with various alpha phase solutions in silver,[2] the gold-nickel system,[3] transition metal solutions,[4] and the lead-thallium system.[5] All of these alloys present various complexities—limited single-phase miscibility, thermodynamic or electronic complications, or difficulties in experimental procedure. The silver-gold system, on the other hand, appears much more amenable to theoretical interpretation. Both ions are monovalent, of essentially equal radii, and form a single face-centered cubic solid solution over the entire range of composition, with a phase diagram showing no major thermodynamic complexities.[6] From an experimental point of view, the near coincidence of the solidus and liquidus curves assures the ready production of single crystals of rather uni-

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TABLE I. Diffusion coefficients for silver tracer.

At. % gold	Diffusion temperature (°C)	Diffusion coefficient (cm^2/sec)
8.6	654.3	1.64×10^{-11}
8.6	710.2	5.52×10^{-11}
8.0	780.2	2.67×10^{-10}
7.8	858.5	1.17×10^{-9}
8.8	907.3	2.67×10^{-9}
8.0	945.2	4.77×10^{-9}
17.6	634.8	8.71×10^{-12}
17.1	653.3	1.40×10^{-11}
17.6	681.5	2.88×10^{-11}
18.1	725.2	7.33×10^{-11}
18.5	728.3	7.41×10^{-11}
17.7	782.2	2.46×10^{-10}
17.1	826.5	5.74×10^{-10}
17.2	884.5	1.57×10^{-9}
15.6	952.0	4.79×10^{-9}
35.6	634.8	8.18×10^{-12}
35.7	682.3	2.66×10^{-11}
36.3	725.2	6.81×10^{-11}
35.1	728.3	6.91×10^{-11}
36.8	782.2	2.16×10^{-10}
36.4	826.5	5.01×10^{-10}
36.9	884.5	1.37×10^{-9}
34.6	956.4	4.42×10^{-9}
51.1	634.8	8.56×10^{-12}
50.5	681.5	2.75×10^{-11}
51.5	725.2	6.75×10^{-11}
51.1	728.3	6.95×10^{-11}
51.3	782.2	2.23×10^{-10}
50.6	826.5	4.93×10^{-10}
50.9	884.5	1.29×10^{-9}
50.6	972.2	5.12×10^{-9}
66.9	654.3	1.65×10^{-11}
67.4	710.2	5.83×10^{-11}
65.9	780.2	2.39×10^{-10}
67.1	858.5	9.10×10^{-10}
66.0	907.3	2.02×10^{-9}
66.6	971.1	5.08×10^{-9}
82.4	650.1	1.95×10^{-11}
82.4	718.5	8.31×10^{-11}
80.8	776.5	2.47×10^{-10}
82.4	835.0	6.88×10^{-10}
82.4	904.7	2.07×10^{-9}
82.8	939.4	3.64×10^{-9}
85.1	975.2	5.92×10^{-9}
82.8	1010.9	9.72×10^{-9}
94.8	662.9	3.10×10^{-11}
94.4	718.0	9.57×10^{-11}
94.8	768.5	2.48×10^{-10}
94.4	822.8	6.83×10^{-10}
94.4	865.1	1.33×10^{-9}
95.0	910.4	2.67×10^{-9}
94.9	961.4	5.38×10^{-9}
100.0	699.3	6.55×10^{-11}
100.0	764.9	2.65×10^{-10}
100.0	819.9	6.01×10^{-10}
100.0	884.8	1.82×10^{-9}
100.0	940.9	4.12×10^{-9}
100.0	1007.4	1.05×10^{-8}

form composition. The availability of high specific activity Ag^{110} and Au^{198}, both of which have sufficiently long half-lives, makes possible accurate radiotracer experiments. And finally, the melting temperatures of these alloys are low enough to permit the use of base metal furnaces and Vycor glass encapsulating tubes for the diffusion specimens. In view of the theoretical simplicity of the silver-gold system and the promise of high experimental accuracy which it offers, we have made a detailed study of the self-diffusion of both components over the entire composition range.

I. EXPERIMENTAL

Coefficients of self-diffusion were measured by the radiotracer-sectioning method,[7] whereby a thin layer of tracer is allowed to diffuse in from one end of a cylindrical specimen and its distribution subsequently determined by sectioning the specimen on a precision lathe. Alloy specimens were prepared by mixing molten 99.99% silver and gold in a rotating furnace, solidifying, and growing in the form of single crystals. These operations were conducted in a vacuum of at least as good as 5×10^{-5} mm of Hg. The ingot was inverted between the mixing and the crystal growing operations in order to minimize effects of segregation of gold during solidification. A few specimens had several grains in the cross section; these were used only for measurements at the highest temperatures, where grain boundary diffusion effects are negligible.

After polishing, etching, and annealing, one end of each specimen was coated with a thin (less than about 50 Å) layer of either Ag^{110} or Au^{198}. The Ag^{110} was electroplated from a cyanide solution but the Au^{198} was deposited by chemical replacement, with no applied voltage. Chemical replacement minimizes deposition of radioactive impurities, which could constitute an appreciable fraction of the radioactivity present after substantial decay of the short-lived Au^{198}.

Each crystal was sealed in an evacuated Vycor capsule with the active face resting on a flat quartz disk, and placed in a furnace controlled to ±0.5°C. Temperatures above 850°C were determined by an NBS-calibrated Pt/Pt-Rh thermocouple; lower temperatures were read from chromel-alumel couples which had been calibrated against the noble metal couple. Warmup corrections were applied in computing the time of the diffusion anneal.

After the anneal, specimens were sectioned and assayed, using standard weighing and counting techniques. Each diffusion coefficient was determined from the slope of the straight line resulting from the plot of the logarithm of tracer concentration versus the square of the penetration depth. In several cases, a tailing off from the straight line was observed at the very deepest penetrations; this is presumably due to dislocation effects such as seen earlier under more extreme conditions.[8] The composition of each specimen was determined by measurement of its density—a rapid and reliable method in alloys such as this.

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[7] C. T. Tomizuka, in *Methods in Experimental Physics,* edited by K. Lark-Horovitz and V. A. Johnson (Academic Press Inc., New York, 1959), Vol. 6.

[8] G. P. Williams and L. Slifkin, Phys. Rev. Letters **1**, 243 (1958).

II. RESULTS

General

Diffusion of silver was measured in pure gold and in solutions of nominal composition 8, 17, 35, 50, 66, 83, and 94 at.% gold. Diffusion of gold was measured in pure silver and in these same solid solutions. 105 successful determinations were made; these are given in Tables I and II. For all specimens of a given nominal composition, the data accurately obeyed the Arrhenius equation, $D=D_0\exp(-Q/RT)$, where D_0, the frequency factor, and Q, the activation energy, are independent of temperature. The frequency factors and activation energies thus determined are given in Tables III and IV. In computing the values of these parameters from the experimental data, no corrections were made for variations in composition among the specimens of a given nominal composition. The dependence of D upon percent gold is so weak that any such corrections were small compared to the experimental error in D of approximately ±3%.

It was possible to identify the limiting source of error in these measurements as due to uncertainty in the temperature. Specimens were often diffused in groups of three, each one of different composition. When all the data for each composition were plotted according to the Arrhenius equation, it was found that the deviations from their respective plots of the three specimens diffused together were invariably the same. This demonstrates that errors in sectioning, weighing, and counting were negligible as compared to those of temperature determination. The temperature errors probably arise from the fact that the primary means of thermal communication is by radiation, and that the specimen "sees" a different distribution of side and end wall of the furnace cavity than does the thermocouple, which is shielded from one end by its ceramic tube. This effect, together with errors in calibration and reading of the thermocouple, could give rise to temperature errors of the order of 2 or 3 deg, producing an error in D of 4 to 6%.

One might seek to increase the accuracy of determination of D_0 and Q by extending the measurements to arbitrarily low temperatures. It was found, however, that the scatter of the data for those diffusion coefficients less than about 4×10^{-11} cm²/sec was not random. These points were never lower than the extrapolation of the data from higher temperatures, and were often higher. For 18 determinations at such low values of D, the average deviation above the extrapolation of the high-temperature data was 3.6%. This effect is probably the result of dislocation contribution to diffusion, as discussed by Hart,[9] Tomizuka,[10] and Mortlock.[11] Its existence also suggests that the only avenue for increased accuracy by this technique for diffusion study would be the construction of more elaborate diffusion furnaces which would permit closer temperature determination.

TABLE II. Diffusion coefficients for gold tracer.

At. % gold	Diffusion temperature (°C)	Diffusion coefficient (cm²/sec)
0.0	718.0	1.97×10^{-11}
0.0	768.5	6.05×10^{-11}
0.0	820.8	1.88×10^{-10}
0.0	862.4	4.42×10^{-10}
0.0	890.9	7.16×10^{-10}
0.0	924.6	1.34×10^{-9}
8.4	717.6	1.78×10^{-11}
8.8	771.5	6.31×10^{-11}
8.7	829.8	2.02×10^{-10}
8.4	882.3	5.52×10^{-10}
7.5	940.0	1.60×10^{-9}
16.6	717.6	1.86×10^{-11}
17.6	771.5	6.28×10^{-11}
17.7	829.8	1.94×10^{-10}
17.8	882.3	5.22×10^{-10}
14.8	902.2	7.76×10^{-10}
15.6	954.2	1.85×10^{-9}
35.5	717.6	1.88×10^{-11}
35.9	771.5	5.93×10^{-11}
35.3	835.0	2.07×10^{-10}
33.9	882.3	4.99×10^{-10}
34.1	938.3	1.36×10^{-9}
34.6	976.1	2.60×10^{-9}
50.3	715.0	2.10×10^{-11}
50.0	769.4	6.75×10^{-11}
51.8	820.8	1.80×10^{-10}
50.4	867.3	4.24×10^{-10}
50.0	924.6	1.12×10^{-9}
49.8	1001.4	3.70×10^{-9}
66.9	715.0	2.60×10^{-11}
67.0	769.4	7.99×10^{-11}
66.2	820.8	2.17×10^{-10}
66.4	867.3	5.05×10^{-10}
66.0	924.6	1.27×10^{-9}
64.8	1001.4	4.05×10^{-9}
83.8	711.7	3.66×10^{-11}
83.8	769.4	1.11×10^{-10}
82.4	815.9	2.64×10^{-10}
83.4	867.3	6.22×10^{-10}
82.6	940.0	2.01×10^{-9}
82.2	1001.4	4.72×10^{-9}
94.4	718.0	5.37×10^{-11}
94.4	768.5	1.40×10^{-10}
94.4	822.8	3.93×10^{-10}
93.2	877.5	9.33×10^{-10}
94.4	940.0	2.43×10^{-9}
94.3	1009.6	6.29×10^{-9}

The frequency factors and activation energies given in Tables III and IV were calculated with this limitation in mind; i.e., diffusion coefficients less than 4×10^{-11} cm²/sec were not considered in determining the best fits to the Arrhenius equation. For completeness, data on self-diffusion in the pure metals are also included in the tables. The results on self-diffusion in silver by Tomizuka and Sonder[12] are slightly different from the

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[9] E. W. Hart, Acta Met. **5**, 597 (1957).

[10] C. T. Tomizuka, Acta Met. **6**, 660 (1958).

[11] A. J. Mortlock, Acta Met. **8**, 132 (1960); A. J. Mortlock, A. H. Rowe, and A. D. LeClaire, Phil. Mag. **5**, 803 (1960); see also C. A. Mackliet, Phys. Rev. **109**, 1964 (1958).

[12] C. T. Tomizuka and E. Sonder, Phys. Rev. **103**, 1182 (1956).

TABLE III. Activation energy Q and frequency factor D_0 for diffusion of silver tracer.

System	Q (kcal/mole)	D_0 (cm^2/sec)
Ag in pure Ag[a]	44.47	0.49
Ag in 8 at.% Au-Ag	44.79	0.52
Ag in 17 at.% Au-Ag	44.05	0.32
Ag in 35 at.% Au-Ag	43.54	0.23
Ag in 50 at.% Au-Ag	43.11	0.19
Ag in 66 at.% Au-Ag	41.73	0.11
Ag in 83 at.% Au-Ag	41.02	0.09
Ag in 94 at.% Au-Ag	40.26	0.072
Ag in pure Gold	40.20	0.072

[a] C. T. Tomizuka and E. Sonder, Phys. Rev. **103**, 1182 (1956); Q and D_0 recalculated, omitting their lowest temperature data.

values originally published by these authors; we have recalculated D_0 and Q from their data, ignoring the very low temperature data (which are also slightly high). Of the two measurements of self-diffusion in gold,[13,14] that of Makin, Rowe, and LeClaire are consistent with our data. We have not included data on the silver-gold system of Johnson[15] or of Mead and Birchenall[16] because of the somewhat larger scatter of these determinations. Also omitted from the tables are the measurements of diffusion of gold in silver by Jaumot and Sawatzky,[17] whose diffusion coefficients agree with ours at the highest temperatures but become increasingly larger than ours at lower temperatures. It is possible that these workers inadvertently electroplated a long-lived radioactive impurity along with their Au^{198}, the effect of which would be greater at lower temperatures where the annealing times must be longer.

The individual activation energies are estimated to be accurate to approximately 250 cal/mole and the frequency factors to approximately 10%. If the data are plotted as D_0 and Q vs composition, however, as in the figures discussed below, the smoothed-out values should have a somewhat higher accuracy.

The Activation Energies

The activation energies for diffusion of Ag* and Au* are plotted in Fig. 1 as a function of composition. The data obtained in this work fit smoothly onto the self-diffusion values of Tomizuka and Sonder and of Makin, Rowe, and LeClaire for the pure metals. It is curious that although gold diffuses with a higher activation energy than silver, the activation energies for both tracers decrease with increasing gold content. Moreover, as the activation energies decrease with increasing percent gold, the melting point of the alloy increases. This is in contrast to expectations from such correlations as that of van Liempt,[18] which suggests that the activation energy for diffusion is proportional to the melting point.

There have been other reports of alloys in which self-diffusion activation energies and melting points vary oppositely: chromium in titanium-chromium solutions (Mortlock and Tomlin),[4] silver in silver-magnesium (Hagel and Westbrook),[19] and lead and thallium in lead-thallium (Resing and Nachtrieb).[5] Mortlock and Tomlin interpreted this in terms of a breakdown of vacancy-chromium association with increasing chromium content. Hagel and Westbrook attributed the effect in both their work and that of Mortlock and Tomlin to an increase in activation energy resulting from a decrease in lattice parameter. Resing and Nachtrieb discuss the effect in terms of deviations from Vegard's law. None of these explanations, however, is adequate for silver-gold: There is no reason to expect appreciable vacancy-solute association in this alloy; the lattice parameter is constant to 0.15% over the entire composition range; and the deviations from Vegard's law are both small and in the wrong direction. In fact, these results are in sharp contrast to the "law of corresponding states,"[5] which demands that the activation energy vary proportionally to the melting temperature in a binary alloy, while the frequency factor remain constant. Moreover, the data also do not corroborate the suggestion that the activation energy vary in proportion to the latent heat of melting,[20] since the heat of melting is greater for gold than for silver, but the tracer activation energies decrease with increasing proportion of gold.

Several theories have been suggested to account for the differences between self-diffusion activation energies and those of impurity atoms at infinite dilution. Of these, that of Lazarus[21,22] is not applicable here,

TABLE IV. Activation energy Q and frequency factor D_0 for diffusion of gold tracer.

System	Q (kcal/mole)	D_0 (cm^2/sec)
Au in pure Ag	48.28	0.85
Au in 8 at.% Au-Ag	48.30	0.82
Au in 17 at.% Au-Ag	47.30	0.48
Au in 35 at.% Au-Ag	46.67	0.35
Au in 50 at.% Au-Ag	45.28	0.21
Au in 66 at.% Au-Ag	44.51	0.17
Au in 83 at.% Au-Ag	43.05	0.12
Au in 94 at.% Au-Ag	42.08	0.09
Au in pure Au[a]	41.7	0.09
Au in pure Au[b]	39.4	0.31

[a] S. M. Makin, A. H. Rowe, and A. D. LeClaire, Proc. Phys. Soc. (London) **B70**, 545 (1957).
[b] B. Okkerse, Phys. Rev. **103**, 1246 (1956).

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[13] S. M. Makin, A. H. Rowe, and A. D. LeClaire, Proc. Phys. Soc. (London) **B70**, 545 (1957).

[14] B. Okkerse, Phys. Rev. **103**, 1246 (1956).

[15] W. A. Johnson, Trans. AIME **147**, 331 (1942).

[16] H. Mead and C. E. Birchenall, Trans. AIME **209**, 874 (1957).

[17] F. E. Jaumot and A. Sawatzky, J. Appl. Phys. **27**, 1186 (1956).

[18] J. van Liempt, Z. Physik **96**, 534 (1936).

[19] W. C. Hagel and J. H. Westbrook, Trans. AIME **221**, 951 (1961).

[20] N. Nachtrieb and G. Handler, Acta Met. **2**, 797 (1954).

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

[22] A. D. LeClaire, Phil. Mag. **7**, 141 (1962).

since it is concerned only with the effects of variations in the valence of the diffusing atoms. One may, however, compare the present results on diffusion of gold tracer in pure silver and of silver tracer in pure gold with the predictions of two other theoretical models: the strictly mechanical theory of Swalin[23] and the thermodynamic, quasi-chemical correlation of Turnbull and Hoffman.[24]

The Theory of Swalin

Swalin treats the metal ions as deformable spheres, and attributes the activation energy of migration to the elastic work done in forcing the jumping atom past its neighbors (which are also deformable). This theory ignores the electrostatic interactions involved when the solute atom has a valence different from that of the solvent, and is based entirely on concepts of size, compressibility, and macroscopic elasticity. The theory has been developed in detail for diffusion of solutes in silver. Since gold has the same valence as silver and on this model differs only in being much less compressible, the diffusion of gold into pure silver should provide a critical test of the validity of the theory. Swalin calculates the difference between activation energies for solute and for self-diffusion and predicts that for gold into silver this difference should be 0.5 kcal/mole. Experimentally, from Fig. 1, the difference is found to be 4.0 kcal/mole. The theory is thus qualitatively correct, but quantitatively is in error by a factor of 8.

The Theory of Turnbull and Hoffman

Turnbull and Hoffman, on the other hand, calculate this difference in activation energies in terms of thermodynamic parameters. They obtain, for face-centered cubic metals, the relation

$$Q_B - Q_A \approx (Q_A/4)[(\Delta U_{AB} - U_A + U_B)/U_A],$$

where Q_B and Q_A are the activation energies for diffusion of the solute B and of the solvent A in pure A, ΔU_{AB} is the partial molar energy of solution of B in A, and U_A and U_B are the binding energies of the pure metals. Inserting numerical values into this equation, we find that gold should diffuse into silver with an activation energy 3.0 kcal/mole higher than that for silver self-diffusion and that silver should diffuse into gold with an activation energy 1.2 kcal/mole less than that for gold self-diffusion. The experimental results for these differences are 4.0 and 2.0 kcal/mole, respectively. The agreement is thus not only qualitative, but even semiquantitative.

The Formation and Migration Energies

There is, however, an inconsistency between the detailed statements of the theory of Turnbull and Hoffman and the experimental observations. The equation for $Q_B - Q_A$ is obtained from separate relations for the vacancy formation energy E_f and the migration activation energy E_m. These relations show that the sign of $(E_m{}^B - E_m{}^A)$ is the same as that of $(E_f{}^B - E_f{}^A)$, where $E_f{}^B$ is the formation energy of a vacancy adjacent to a B atom in otherwise pure A metal. The following argument shows that this condition is not likely to be true in the silver-gold system. The formation energies of vacancies in the pure metals are 25.4 kcal/mole (1.10 eV) for silver[25] and 22.4 kcal/mole (0.97 eV) for gold.[26] It is quite improbable that gold atoms repel vacancies in otherwise pure silver, so that the greater activation energy for gold tracer must be attributed to an increase in the migration energy—we thus conclude that the above prediction is not born out.

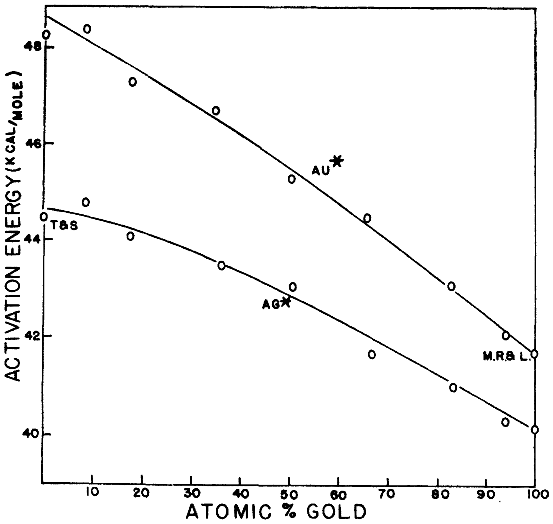

FIG. 1. Activation energies for the diffusion of silver and gold tracers in silver-gold solid solutions.

Whatever the signs of the interactions of vacancies with solute atoms in the silver-gold system, the magnitudes of these binding energies are expected to be small. We may then estimate the migration energies of the tracers in both metals by subtracting from the diffusion activation energies those for vacancy formation in pure silver and pure gold. The following values are obtained for the migration energies (in kcal/mole): 19.2 (Ag* in Ag), 17.8 (Ag* in Au), 23.2 (Au* in Ag), and 19.3 (Au* in Au), a decrease across the composition range of 7% for silver tracer and 17% for gold tracer. It has been proposed[21] that the migration energy can be estimated by $\frac{1}{2}(c_{11} - c_{12})$, and the results on self-diffusion in silver-zinc by Lazarus and Tomizuka[27]

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[23] R. A. Swalin, Acta Met. **5**, 443 (1957).

[24] D. Turnbull and R. E. Hoffman, Acta Met. **7**, 407 (1959).

[25] M. Doyama and J. S. Koehler, Phys. Rev. **127**, 21 (1962); L. J. Cuddy and E. S. Machlin, Phil. Mag. **7**, 745 (1962).

[26] R. O. Simmons and R. W. Balluffi, Phys. Rev. **125**, 862 (1962); W. DeSorbo, *ibid.* **117**, 444 (1960); J. E. Bauerle and J. S. Koehler, *ibid.* **107**, 1493 (1957); J. Takamura, Acta Met. **9**, 547 (1961).

[27] D. Lazarus and C. T. Tomizuka, Phys. Rev. **103**, 1155 (1956).

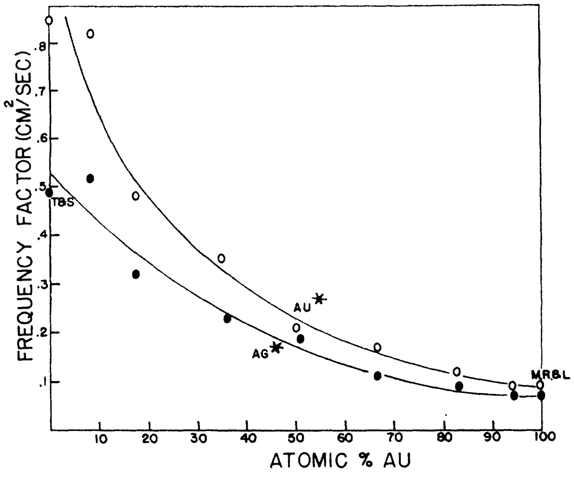

FIG. 2. Frequency factors for the diffusion of silver and gold tracers in silver-gold solid solutions.

were interpreted in this manner. In the present alloy system, $(c_{11}-c_{12})$ is almost identical ($\sim 1\%$) for pure gold and pure silver and is about 15% higher than this at 50% gold.[28] Thus, the migration energies for each tracer do not follow $(c_{11}-c_{12})$ and it is suggested that the agreement in the silver-zinc experiment was fortuitous.

The Frequency Factors and Activation Entropies

Figure 2 displays the frequency factor D_0 for each tracer as a function of composition. As in the case of the activation energies, the present data join smoothly with those of Tomizuka and Sonder and of Makin, Rowe, and LeClaire. For both tracers, D_0 decreases by roughly a factor of 8 from pure silver to pure gold.

Now, the frequency factor may be represented by[29]

$$D_0 = fa^2\nu e^{S/R},$$

where f is the correlation factor, a is the lattice parameter, ν is a vibration frequency, and S is the entropy of activation per mole. Since the product $fa^2\nu$ cannot vary by more than a few tens of percent over the range of composition, the eightfold decrease in D_0 must be primarily a result of a drop in S. A quasi-chemical approach suggests that the change in activation entropy would be linear with composition. We, therefore, plot, in Fig. 3, the logarithm of D_0 as a function of composition and find that two approximately straight parallel lines result. It may, therefore, be concluded that the activation entropy for each tracer decreases linearly with increasing gold fraction by a total of $2R$ ($e^2 \approx 8$) from pure silver to pure gold.

The activation entropy, in turn, consists of two terms: the entropy of vacancy formation and the activation entropy for migration. Simmons and Balluffi[26] have measured the formation entropy in gold to be $1.0R$ per mole; moreover, comparison of their results on silver[30] with those of Doyama and Koehler[25] gives the formation entropy in silver to be $1.5R$. Combining this difference of $0.5R$ with the total decrease in S of $2.0R$, we conclude that the entropy of vacancy migration decreases linearly by $1.5R$ from pure silver to pure gold.

Qualitatively, the direction of this change may be understood in terms of the relaxations that take place during the jump of a vacancy. In the activated state, the neighboring atoms relax into two half-vacancies instead of a single complete vacancy. Since gold is a "harder" atom than silver, less entropy is to be gained by the additional means of relaxation. There is also a tightening of the lattice in the "gate" through which the jumping atom must pass. This negative contribution to the activation entropy is of larger magnitude in the case of a harder atom. Both effects thus lead to a decrease in activation entropy with increasing proportion of gold. Although a quantitative calculation of activation entropies is quite difficult,[31] it might be possible to compute the *change* in entropy in an alloy as simple as this one, to compare with these experimental results.

Referring again to Fig. 3, at any given composition the ratio $D_0(\mathrm{Au}^*)/D_0(\mathrm{Ag}^*)$ is approximately 1.4. By an examination of how the various factors in the expression for D_0 depend on which tracer is diffusing, we can say something about the difference between the migration entropies for Au* and Ag* in a given solid solution. The correlation factor for gold tracer diffusing in a given alloy is larger than that for silver tracer in the same alloy because gold is the slower diffuser. Deferring until a later section a more detailed consideration, the ratio $f(\mathrm{Au}^*)/f(\mathrm{Ag}^*)$ is approximately

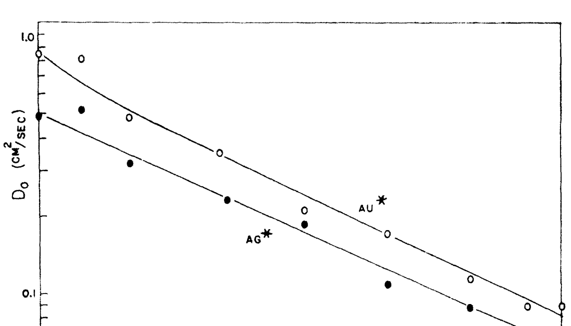

FIG. 3. The data of Fig. 2 plotted semilogarithmically.

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[28] See tabulations in H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7.

[29] A. D. LeClaire, in *Progress in Metal Physics*, edited by B. Chalmers and R. King (Butterworths Scientific Publications, Ltd., London, 1953), Vol. 4.

[30] R. O. Simmons and R. W. Balluffi, Phys. Rev. **119**, 600 (1960).

[31] H. B. Huntington, G. A. Shirn, and E. S. Wajda, Phys. Rev. **99**, 1085 (1955).

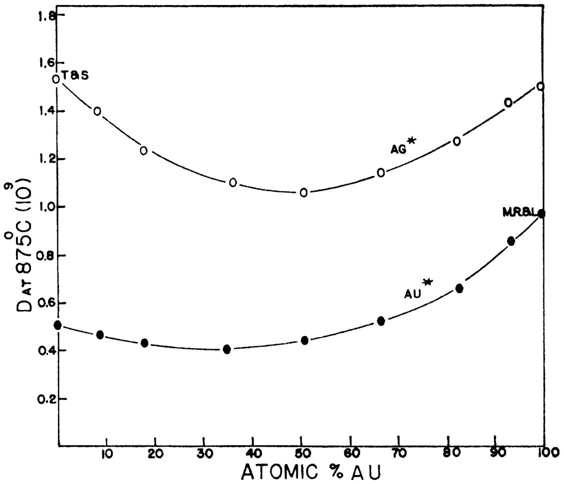

FIG. 4. Diffusion coefficients of silver and gold tracers at 875°C in silver-gold solid solutions.

1.18. The ratio $\nu(\text{Au}^*)/\nu(\text{Ag}^*)$ in a given composition may be crudely estimated from the masses and compressibilities of the atoms. In a study of the diffusion of Fe^{55} and Fe^{59} in copper and silver, Mullen[32] found that the isotope effect, defined as the ratio $(1-D_{59}/D_{55})/(1-[m_{55}/m_{59}]^{1/2})$, was only about $\frac{2}{3}$ instead of the value of unity suggested by kinetic theory. This discrepancy is due to correlation effects and to the fact that the neighboring atoms as well as the jumping atom must be activated. Applying Mullen's value of $\frac{2}{3}$ to silver-gold, the mass effect contributes a factor of 0.83 to the ratio $D_0(\text{Au}^*)/D_0(\text{Ag}^*)$. Another property affecting ν will be the effective force constant for the vibration of the tracer atom against its neighbors. We roughly estimate the ratio of effective force constants for the two tracers by the square root of the ratio of bulk moduli of gold and silver. This contributes a factor 1.29 to the ratio of the frequency factors. Multiplying these three factors together, a value 1.26 is obtained for $D_0(\text{Au}^*)/D_0(\text{Ag}^*)$. This is rather close to the experimental result of 1.4 and suggests that in a given medium the entropies of migration for the two tracers are almost equal.

The Composition Dependence of D

It is of interest to examine the variation with composition of the diffusion coefficients at a fixed temperature. The data for a temperature of 875°C are shown in Fig. 4. The curves for both tracers show minima; addition of either silver or gold as a solute to the other produces a decrease in the diffusion coefficients of both constituents. Several theoretical treatments of the effect of small additions of impurity on the solvent diffusion coefficient have been presented, and these may be compared with the experimental results at the two extremes of composition in Fig. 4.

The Theory of Hoffman, Turnbull, and Hart

Hoffman, Turnbull, and Hart[1,33] have considered the solute atom to be surrounded by a region in which all atoms have higher jump frequencies. The rapid motion of the solute through the crystal thus "catalyzes" solvent diffusion. The detailed results[33] are only valid for the case in which $D_i/D_s \gg 1$ (where subscripts i and s refer to the impurity and solvent, respectively, and both coefficients are measured in sufficiently dilute solutions that solute-solute interactions may be neglected). For diffusion in silver $D_i/D_s=0.33$, while for diffusion in gold this ratio equals 1.55; hence, the equations of Hoffman *et al.* may not be applied here. Qualitatively, however, the model predicts that addition of a faster diffusing impurity must increase the diffusion coefficient of the solvent, and in the past this has been found to be true in general.[34] The addition of the rapid diffuser silver, on the other hand, to slow diffusing gold is seen actually to decrease the diffusion coefficients. The discrepancy between this observation and theoretical expectation is probably due to the fact that addition of silver has nonlocal consequences, such as an over-all decrease in vacancy concentration.

The Theory of Reiss

This problem has also been treated by Reiss,[35] who considers separately the case in which addition of the impurity decreases solvent diffusion. It is convenient to define a parameter b by the relation $D_s(c)=D_s(0)\times(1+bc)$, where c is the concentration of the added impurity, and only the limiting region of very small c is considered. The parameter b is then negative at both extremes of Fig. 4. Reiss assumes in this case that the solvent-vacancy exchange frequency is not perturbed by the presence of a neighboring impurity atom and that the main effect of the impurity on solvent diffusion is through a decrease in the concentration of vacancies in the crystal. He, thereby, obtains equations from which b can be evaluated in terms of D_i/D_s. Applying these to the present data on the effect of gold on self-diffusion of silver, where $D_i/D_s=0.33$, one obtains $b=-1.0\ (\pm 0.2)$, in excellent agreement with the experimental value from Fig. 4 of 1.1. In spite of this agreement, however, it is disturbing that whereas the theory attributes a negative value of b to an increase in the vacancy formation energy, the curves of Fig. 1 and 2 associate the effect at the silver-rich end with a decrease in frequency factor.

If we seek to apply Reiss' theory to the gold-rich extreme, we meet an inconsistency. In the theory, the ratio D_i/D_s appears in an expression for the ratio of the vacancy concentration at the impurity to that in

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[32] J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

[33] E. W. Hart, R. E. Hoffman, and D. Turnbull, Acta Met. **5**, 74 (1957).

[34] See reference 1, pp. 101 and 106.

[35] H. Reiss, Phys. Rev. **113**, 1445 (1959).

the pure lattice. If D_i/D_s is greater than 0.55, this implies that the vacancy concentration is greater in the vicinity of the impurity atom than elsewhere. For the case of silver impurity added to gold, D_i/D_s is almost three times larger than this limit. Thus, although the theory would attribute the negative value of b to a decrease in vacancy concentration, substitution into the detailed equations lead to the opposite conclusion.

The Theories of Manning and of Lidiard

Diffusion in binary systems has also been discussed by Manning[36] from the point of view of correlation effects. For very dilute solutions, his expression for the correlation factor of the impurity is

$$f_i=(w_1+2.58k)/w_2+w_1+2.58k),$$

where w_1 is the frequency with which a vacancy adjacent to an impurity atom exchanges with any one of the solvent atoms that are also neighbors of the impurity, w_2 is the jump frequency of the impurity atom into an adjacent vacancy, and k is the frequency with which a vacancy adjacent to an impurity atom exchanges with a solvent atom which is not a neighbor of the impurity. In the less exact calculation of Lidiard and LeClaire[37] a similar equation for f_i was obtained, but with the factor 3.5 replacing the 2.58 of Manning's equation. If we assume that in pure silver or pure gold the presence of a trace of the other constituent does not affect the solvent jump frequency (i.e., that $w_1=k=w_0$, the solvent jump frequency in regions far from the impurity atom) and if we further assume that there is no interaction energy between vacancy and impurity atom, then $D_i/D_s=f_iw_2/f_0w_0$ (where f_0 is the correlation factor for the pure metal) and $f_i=3.58\,w_0/(w_2+3.58\,w_0)$. From the experimental values of D_i/D_s and the value 0.78 for f_0,[38] one may use these two relations to obtain the correlation factors for gold tracer in silver and for silver tracer in gold. For gold tracer in silver we obtain 0.92; this is larger than the 0.78 for self-diffusion because gold is a slow jumper relative to silver. For silver tracer in gold, we obtain 0.66; this is smaller than the correlation factor for self-diffusion because silver is a fast jumper relative to the gold matrix.

We may also compute these correlation factors with fewer assumptions by using the results of Lidiard,[39] who obtains the relation

$$f_i=1-4f_0(D_i/D_s)/(b+18),$$

where b is the parameter defined earlier in describing the effect of impurity additions on the self-diffusion coefficient. With this equation, and using the Lidiard-LeClaire value of f_0 (9/11) for consistency, we obtain the correlation factor for gold tracer in silver as 0.94 and for silver tracer in gold as 0.68. These results are in agreement with those obtained from Manning's equation, and are shown in Table V.

TABLE V. Correlation factors in pure silver and gold.

Solvent crystal	f_0	f_i (Manning)	f_i (Lidiard)
Silver	0.78	0.92	0.94
Gold	0.78	0.66	0.68

Quenching Experiments

The data of Fig. 4 may also be of value in interpreting experiments on the quenching-in of excess vacancies in gold to which small quantities of silver have been added. Cattaneo and Germagnoli[40] conclude from their observations that in such a solution, the vacancy is bound to the silver impurity atoms with an energy of 0.3 eV. Kloske and Kauffman,[41] on the other hand, determine this energy to be about 0.05 eV; it may even be zero or negative, within their experimental uncertainty. Since silver tracer diffuses faster than gold tracer in pure gold and yet addition of silver metal to gold decreases the diffusion coefficients, it appears very unlikely that the vacancy concentration in gold is increased upon adding silver. The present experiment thus suggests that in contrast to the conclusion of Cattaneo and Germagnoli, vacancies in gold are not preferentially bound to silver impurity atoms.

Vacancy Flux Effects

Finally, the presence of the minima in the curves of Fig. 4 suggests the feasibility of an experiment to measure the effect of a vacancy flux on the mean displacement of tracers. Suppose two specimens of compositions symmetric about the minimum in the Au* curve were welded together with a thin layer of radioactive gold at the interface. In the absence of vacancy flux effects, the tracer would diffuse symmetrically out from the interface. The presence of the gradient in chemical composition, however, coupled with the difference in diffusivities of silver and gold, will produce a Kirkendall effect. The resulting net flow of vacancies is expected to shift the center of mass of the tracer atoms in the opposite direction. A similar experiment has been performed on the silver-cadmium system by Manning,[42] but there the dominant effect was the strong and monotonic dependence of diffusion coefficients on composition. In a later paper[43] Manning gives a quantitative theory for the vacancy flux effect. He

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[37] A. B. Lidiard, Phil. Mag. **46**, 1218 (1955); A. D. LeClaire and A. B. Lidiard, *ibid.* **1**, 518 (1956).

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[42] J. R. Manning, Phys. Rev. **116**, 69 (1959).

[43] J. R. Manning, Phys. Rev. **124**, 470 (1961).

concludes that the velocity of the center of mass of tracer is given by

$$dx/dt=D(2B/\lambda+\partial \log D/\partial x-\partial \log\gamma/\partial x),$$

where B is a factor that measures the vacancy flux, λ is the jump distance, and γ is the activity coefficient of the diffusing specie. Since the second and third terms on the right are small in the proposed experiment, there would appear to be an excellent chance of directly measuring the quantity B. Such experiments are now in progress.

III. CONCLUSIONS

The main conclusions reached from this experiment are as follows. Firstly, uncertainties in temperature measurement, rather than sectioning errors, limit the accuracy of determination. Secondly, the migration entropy of a vacancy decreases linearly with composition by 1.5 R from pure silver to pure gold, and in any given composition both tracers have almost identical entropies of activation. Thirdly, although we do not yet have a diffusion theory which can provide a comprehensive description of a system as simple as silver-gold, several discussions are compatible with substantial portions of the experimental observations. In particular, the treatments of Lidiard and of Manning can be applied to the data to obtain detailed information concerning individual jump frequencies and correlation factors.

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Crystal Structure Variations in Alpha Uranium at Low Temperatures*

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The unusual temperature dependence of the elastic moduli and other physical properties of alpha uranium near 43°K which have been previously reported are found to be correlated with changes in atomic position and with cell dimensions. The atom position parameter, y, decreases to a minimum at 43°K and then rapidly rises on further cooling, as shown both by x-ray and neutron data. The a_0 and b_0 cell dimensions decrease to a minimum at 43°K and then rapidly increase, giving a large negative linear expansion coefficient in the range 43–18°K; the c_0 dimension contracts on cooling to 43°K and decreases even more rapidly below this temperature thus giving a higher positive linear expansion coefficient in the 43–18°K range. Neutron diffraction experiments disclose the existence of additional reflections at the lower temperatures which are presumably due to a magnetic moment arrangement.

INTRODUCTION

THE cusps in the curves for the elastic moduli of α uranium near 43°K,[1] and the unusual temperature dependence of various physical properties in the low-temperature region have emphasized the need for precise crystal-structure data for it down to liquid-helium temperatures. Accordingly, determinations have been made of the atom position parameter, unit cell dimensions, and expansion coefficients throughout the low-temperature range with a precision x-ray diffractometer and cryostat unit using single crystals of high purity. The atom position parameter was also determined in an independent series of experiments using neutron diffraction. Single crystals were used in these studies to avoid the effects of elastic strains that arise from the differential thermal contraction of adjoining regions of different orientation in any measurements made on polycrystalline or twinned material, and perhaps to some extent even on crystals containing lineage structure. The use of single crystals is also desirable because of the high precision in lattice constants and the high diffracted intensities that can be obtained with them when modern techniques are employed.

MATERIALS AND METHODS

The single-crystal samples used in both the x-ray and neutron investigations were rectangular blocks 1 to 3 mm on a side, furnished by Lloyd, which had been previously prepared for thermal expansion studies.[2]

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