

- acknowledgement. Also brief reference in ref. 3.
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 - 8 C. Bosvieux and J. Friedel: *J. Phys. Chem. Solids* **23** (1962) 123.
 - 9 Th. Hehenkamp: *Rev. Sci. Inst.* **33** (1962) 229.
 - 10 We are indebted to R. V. Penney for pointing out this effect and analyzing it quantitatively.
 - 11 S. Bushman, L. W. Dunbar, and H. Huthsteiner: *J. Appl. Phys.* **74** (1944) 108.
 - 12 G. V. Kidson and R. Ross: *Proceedings of the International Conferences Radioisotopes in Scientific Research, Paris* (1957).
 - 13 J. P. Jan: *Solid State Physics*, Academic Press, Inc., New York, ed. F. Seitz and D. Turnbull **5** (1957) p. 45.
 - 14 N. F. Mott and H. Jones: *The Theory of the Properties of Metals and Alloys*, Dover Publications, Inc., New York, U.S.A. (1958) p. 316.

DISCUSSION

Becker, J.: Was there any correlation between the anisotropic marker motion and the orientation of the crystals?

Huntington, H. B.: Experiments have been carried out so far only with polycrystalline specimens. We hope, however, to repeat the measurements on copper in the near future using single crystal wires.

Lidiard, A. B.: I would like to point out that the "electron wind" effect is another example where the non-vanishing of the Onsager cross-coefficient leads to a departure from the simple Einstein relation. Here the two components are, of course, ions and electrons.

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Diffusion of Thallium in Single Crystals of Copper

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The diffusion coefficient of thallium in single crystals of copper has been measured as a function of temperature over the range 785-996°C. The frequency factor and activation energy have been determined as $D=0.71 \exp(-43.3/RT)$. Comparison of these values with other existing data on diffusion shows that the diffusion of solute atoms having large atomic radii are accelerated especially for the solute atoms of large valency. This may be interpreted as the large atoms are compressed by the surrounding lattices and hence an excess ionization of the closed shell takes place.

Introduction

It has been found that the impurity atoms in monovalent noble metals may diffuse at the rates considerably different from that of self-diffusion of the solvent atoms. These results should be interpreted in terms of three types of effects, firstly the effects arising from the excess valency of impurity atoms, secondly the effects arising from the difference in size between impurity and solvent atoms and thirdly the effects arising from the correlation between the motions of impurity and solvent atoms.

The first of these effects, *i.e.* valence effects, have been considered initially by Lazarus¹⁾ in a Thomas-Fermi model of screened solute ions and later modified by Alfred and March²⁾ and by Fujiwara³⁾. Their results have revealed an excellent agreement with the impurity diffusion experiments performed for silver as a solvent, while the agreement is rather insufficient for the impurity diffusion experiments for copper as a solvent.

As for the second effects, *i.e.* size effects, there is however only little work done so far. If the difference between ionic radii of solute

and solvent atoms is taken into consideration according to the theory of screened solute atoms, the activation energy of the solute atoms having large ionic radii should be larger than that of the solute atoms having small ionic radii. The experimental data seem however to show in some cases that the diffusion is accelerated with the increasing size of the solute atoms which is accompanied by the change of the inner closed shells from 3d to 4d cores or from 4d to 5d cores while the valence of the solute atoms is fixed. This is in sharp contradiction with the theoretical expectations from the Thomas-Fermi model of screened solute atom. Such a result has been demonstrated experimentally by Hirone *et al.*⁴⁾ who have measured the diffusion rate of cadmium in single crystals of copper comparing with the diffusion data of zinc in copper and have found that the activation energy of cadmium having 4d closed shell is not larger than that of zinc having 3d closed shell.

The purpose of the present investigation is to study further how the sizes of solute and solvent atoms affect the impurity diffusion. For this purpose we have measured the diffusion rate of thallium in single crystals of copper and have compared it with the existing data on the diffusion of gallium in copper. Since gallium and thallium have 3d and 5d closed shells, respectively, with Goldschmidt's metallic radii for the coordination number twelve being Ga=1.39 Å, Tl=1.71 Å and Cu=1.28 Å, it is expected for gallium and thallium to show a considerable difference in size effects.

Experiment

Single crystals of copper were grown in graphite crucibles in a vacuum furnace with a suitable temperature gradient. Cylinder-shaped single crystals of more than 99.999% purity, 1.5 cm long in diameter and 10 cm long in length were obtained. They were then etched in dilute HNO₃ solution and were carefully cut into the form of drum shaped pieces and thus flat surfaces of less than 0.01 mm in ruggedness were obtained.

Radioactive isotope Tl²⁰⁴ with the chemical form Tl₂SO₄ were electrodeposited on the flat surfaces of the single crystals of copper in a plating bath consisting of H₂SO₄ (0.01 N, 100 cc) and Tl₂²⁰⁴SO₄ (0.01 N, 1 cc) in aqueous solution

under 10 mA electric current. The electroplating was done satisfactorily by changing the plating solution anew for each specimen. The electroplated specimens showed more than 30,000 cpm by means of GM-survey meter placed 10 cm apart from the flat surfaces of the specimens.

The electroplated specimens were sealed off in evacuated fused-quartz tubes and placed in a controlled furnace. For every diffusion anneal the temperature was held constant within $\pm 5^\circ\text{C}$ over the entire period. At the same time actual values for temperature was recorded within an accuracy of 0.5°C and corrections for this temperature variation were made using these data.

In order to eliminate effects of the surface diffusion, a thickness of about 0.5 mm was removed from the side of the annealed specimens by using a file. Sectioning was then performed on a Boley's precision lathe with a specially designed specimen holder which permitted to adjust the orientation of the specimen relative to the lathe axis within an accuracy of 0.01 mm by means of a dial gauge. Each section of about 0.02 mm thick was weighed to estimate its relative thickness and was compared with the absolute value of total thickness of removed sections obtained from the reading of the dial gauge.

Counting rate of each section was measured by means of thin micawindow GM-counter with careful precautions to place the section uniformly on a circular dish of 2.5 cm in diameter to insure the reproducibility of the counting geometry.

Results

A total of 9 diffusion runs were performed covering the temperature range from 785°C to 996°C for periods ranging from 1 to 24 hours. The results are shown in Fig. 1 where the logarithm of the concentration of radioactive thallium was plotted against the square of the penetration distance. Diffusion coefficients for each annealing specimen was determined from the gradient of these curves. The Table I gives the temperature, the time of diffusion anneal and diffusion coefficients for each specimen. The Fig. 2 represents the logarithm of diffusion coefficients against the reciprocal absolute temperature in comparison with the data on self-diffusion of copper

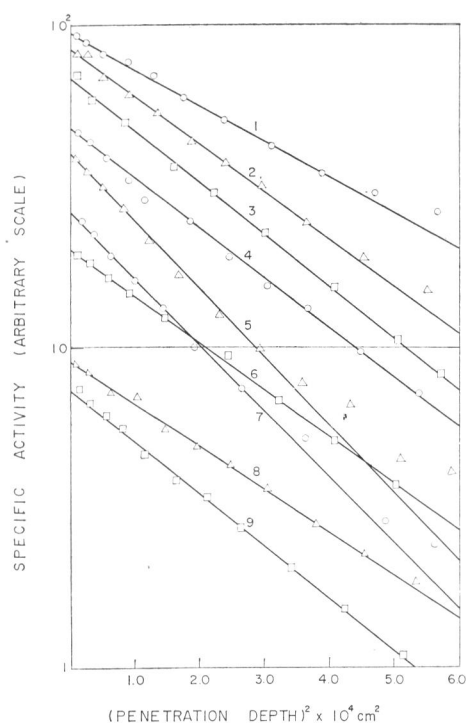


Fig. 1. Penetration curves for diffusion of thallium in single crystals of copper. See also Table I.

Table I. Diffusion data of thallium in copper.

Curve	Temperature (deg C)	Time (sec)	Diffusion Coeff (cm ² /sec)
1	996	0.34×10^4	2.82×10^{-8}
2	963	0.52×10^4	1.42×10^{-8}
3	932	0.64×10^4	1.06×10^{-8}
4	905	1.08×10^4	6.50×10^{-9}
5	880	1.31×10^4	3.74×10^{-9}
6	856	2.99×10^4	2.53×10^{-9}
7	824	3.07×10^4	1.72×10^{-9}
8	795	7.18×10^4	1.14×10^{-9}
9	785	8.62×10^4	7.77×10^{-10}

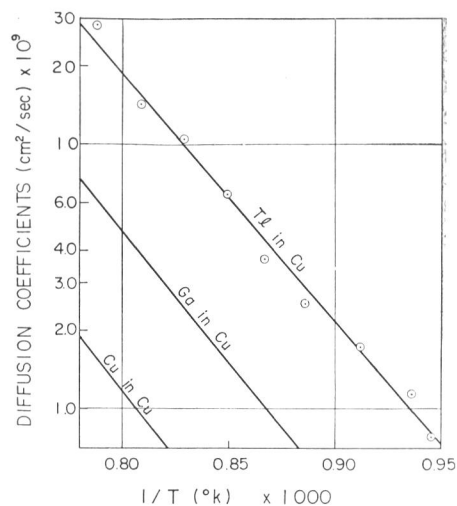


Fig. 2. Diffusion coefficients plotted as $\log D$ vs $1/T$.

and diffusion of gallium in copper.

These results are expressed by the Arrhenius⁸ equation $D = D_0 \exp(-H/RT)$, where D_0 is the frequency factor and H is the activation energy. The calculation by means of the least square method gives the values

$$D_0 = 0.71^{+0.69}_{-0.34} \text{ cm}^2/\text{sec}$$

$$H = 43.3 \pm 1.5 \text{ kcal/mol.}$$

Discussion

Since gallium and thallium have the same valence and different ionic radii, it is interesting to compare both the diffusion data of gallium in copper and thallium in copper. According to Tomizuka⁵⁾ the diffusion data of gallium in copper are

$$D_0 = 0.55 \text{ cm}^2/\text{sec}$$

$$H = 45.9 \text{ kcal/mol,}$$

indicating apparent size effects, *i.e.* the activation energy of thallium having 5d closed shell is smaller than that of gallium having 3d closed shell.

To interpret these results we might consider the situation quite different from that in simple Thomas-Fermi model of screened solute atoms. This is expected from the assumption that when the solute atoms having large atomic radii pass through a saddle point of the crystal lattices, the solute atoms are compressed by the surrounding lattices and hence an excess ionization of the closed shell takes place. This results in an increase of valence effects of

large impurity atoms effectively beyond their nominal values of valency and leads to the consequence that the larger the atomic radii of impurity atoms, the smaller is the effective activation energy of the impurity atoms.

We have summarized all the existing data on impurity diffusion of the solute atoms having the same valency and different sizes in silver and copper as solvents in Table II.

Table II. Diffusion data in copper and silver as solvents.

Solute		Cu		Ag	
Valence	Element	$D_0(\text{cm}^2/\text{sec})$	$H(\text{kcal/mol})$	$D_0(\text{cm}^2/\text{sec})$	$H(\text{kcal/mol})$
1	Cu	0.20	47.1	1.23	46.1
	Ag	0.63	46.5	0.40	44.1
	Au	0.1	44.9	0.26	45.5
2	Zn	0.34	45.6	0.54	41.7
	Cd	0.94	45.7	0.44	41.7
	Hg	0.35	44.0	0.08	38.1
3	Ga	0.55	45.9		
	In			0.41	40.6
	Tl	0.71	43.3	0.15	37.9
4	Ge			0.08	36.5
	Sn			0.25	39.3
	Pb			0.22	38.1
5	Sb	0.94	45.7	0.17	38.3

The activation energies of various solute atoms having the same valence in the same solvent are plotted as a function of inner shell of solute atoms, *i.e.* 3d, 4d or 5d in Fig. 3, where the activation energies of solute atoms having 5d closed shell are seen to be smaller than those of solute atoms having 4d closed shell.

Now we treat the diffusion data not separating them into frequency factors and activation energies but combining them as one, for instance, in a form of diffusion coefficients at 900°C. This implies a comparison of Gibbs' free energy of activation among different solute atoms with better accuracy. In Fig. 4 the diffusion coefficients at 900°C of various solute atoms are plotted as a function of valence of solute atoms. With increasing valence of solute atoms the diffusion coefficients of mercury, thallium and lead having 5d closed shell seem to approach saturation values more slowly than other solute atoms. The size effects stated as above are pronounced especially

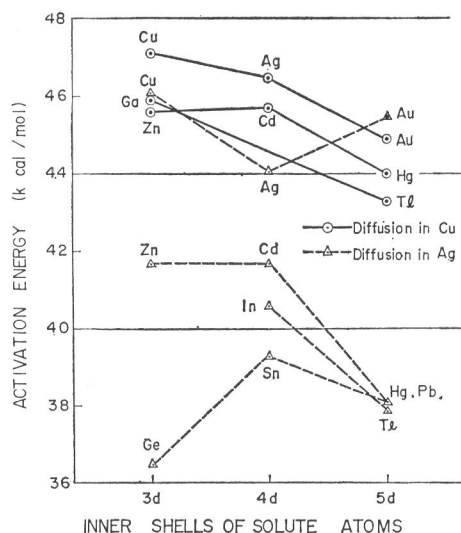


Fig. 3. Activation energies of various solute atoms in copper or silver as a function of inner shell of solute atoms.

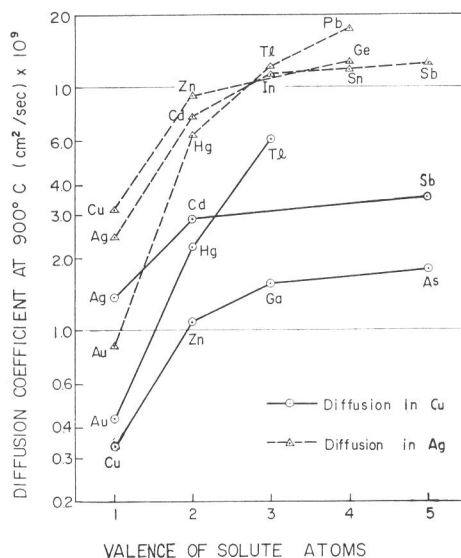


Fig. 4. Diffusion coefficients of various solute atoms at 900°C in copper or silver as a function of valence of solute atoms.

for the solute atoms of large valency, *i.e.* tri- or quadru-valent atoms having 5d shell. However the size effects of the solute atoms of small valency, *i.e.* mono- or di-valent atoms especially in silver as solvent are in an opposite sense indicating that the larger the atomic radii of solute atoms, the smaller are the diffusion coefficients at 900°C. This fact suggests that the excess ionization of the compressed solute atoms are appreciable for

the solute atoms of large valency having large atomic radii and not for those of small valency.

In comparing the diffusion data of thallium in copper with those of gallium in copper, we have calculated the following two values; one is the ratio of the difference of atomic radii between thallium and copper to that between gallium and copper using Goldschmidt's metallic radii for the coordination number twelve, another is the ratio of the diffusion coefficient of thallium in copper at 900°C to that of gallium in copper. These are

$$(r_{\text{Tl}} - r_{\text{Cu}})/(r_{\text{Ga}} - r_{\text{Cu}}) = 3.91$$

and

$$D_{\text{Tl in Cu}}/D_{\text{Ga in Cu}} = 3.93,$$

giving almost equal values.

In the same way we have chosen several pairs of diffusion data of solute A and B in a common solvent C, where the atomic radius of A is larger than that of B, and calculated the following values; ratios of difference of radii

$$(r_A - r_C)/(r_B - r_C)$$

and ratios of diffusion coefficients at 900°C

$$D_{A \text{ in } C}/D_{B \text{ in } C}.$$

In Fig. 5 the ratios of diffusion coefficients are plotted as a function of the ratios of difference of radii for several pairs of diffusion data. There seems to be a linear relationship between the ordinate and the abscissa. This fact supports the idea that the difference of atomic radii between solute and solvent atoms cause an excess ionization of closed shell of

the solute atoms. To confirm this conclusion further experimental work on diffusion of lead or bismuth having 5d shell in copper is desirable.

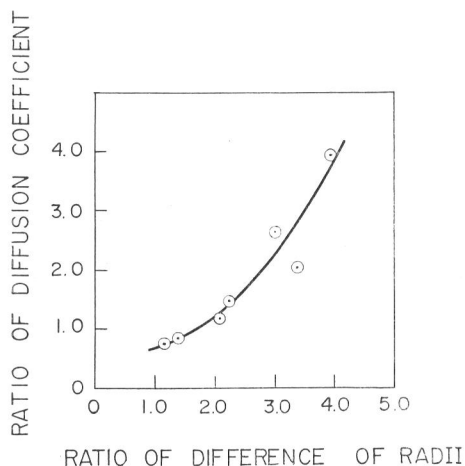


Fig. 5. Ratios of diffusion coefficients of pairs of solutes as a function of ratios of difference of solute and solvent atoms for the pairs of solutes.

References

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- 3 H. Fujiwara: J. Phys. Soc. Japan **10** (1955) 339; **13** (1958) 250, 935.
- 4 T. Hirone, N. Kunitomi, M. Sakamoto and H. Yamaki: J. Phys. Soc. Japan **13** (1958) 838.
- 5 C. T. Tomizuka: To be published.

DISCUSSION

Tomizuka, C. T.: How much importance do you seriously place on the numerical values of the various ionic radii?

Komura, S.: Besides the numerical values of Goldschmidt's metallic radii for the coordination number twelve, *i.e.* in face-centered cubic structure, we have also taken other numerical values of ionic radii, for instance Pauling radii or Goldschmidt's ionic radii. Calculations of ratios of the difference of atomic radii between solute and solvent atoms by using these numerical values have shown that the linear relationship holds best for the Goldschmidt's metallic radii.

Lazarus, D.: According to the reported data, Tl diffuses some 30 times faster than the rate of self-diffusion of copper, but with only a small difference in activation energy. In view of the expected large effects of correlation, it is difficult to see how these two observations are self-consistent.

Komura, S.: As seen in Fig. 4 the diffusion coefficients of solute atoms having 3d or 4d closed shell seem to approach saturation values quickly with increasing valency of solute atoms. This may be interpreted either by the fact that the activation energies get constant values as the valency of the solute atoms increases or by the correlation of the motion of the solute and solvent atoms.