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Point Defects in Metals*

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I. INTRODUCTION

Let us attempt to summarize what is presently known about point defects in metals. We shall emphasize pure metals since even now little is known about point defect impurity interactions. We also attempt to describe areas where further information is needed.

In metals Huntington and Seitz(1) and Huntington(2) made early theoretical calculations concerning the properties of lattice vacancies and interstitial copper atoms in the copper lattice which were approximately correct. These calculations were important historically since they provided guidance for the experimental determinations of E_F^V, the energy required to form a lattice vacancy; E_M^V the activation energy required for vacancy migration, and for E_F^I, the energy required to form an interstitial, and E_M^I, the activation energy required for interstitial migration.

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DISCLAIMER

II. BASIC INFORMATION PRESENTLY AVAILABLE

A. Diffusion Data

In most metals self diffusion occurs by the migration of lattice vacancies. The activation energy for self diffusion Q is then$^{(3)}$

$$Q = E_F^V + E_M^V \tag{1}$$

The determination of the vacancy formation energy can be done by measuring the lattice parameter and specimen length versus temperature (the Simmons-Balluffi$^{(4)}$ equilibrium method). If vacancies and divacancies are the only defects present in appreciable concentrations then:

$$C_V + 2C_{2V} = 3\left(\frac{\Delta L}{L} - \frac{\Delta a}{a}\right) \tag{2}$$

where C_V is the atomic fraction of vacancies present and C_{2V} is the fraction of atoms that are divacancies. $\Delta L/L$ is the fractional length change in going from low temperature where C_V is negligible to T. $\Delta a/a$ is the fractional change in lattice parameter in going from low temperature to T. Usually $C_{2V} << C_V$.

E_F^V can also be measured by measuring the extra resistivity $\Delta\rho_{Qu}$ quenched in upon rapid cooling from T. One expects

$$\Delta\rho_{Qu} = \rho_V C_V(T) = \rho_V\, e^{\frac{S_F^V}{k}}\, e^{-\frac{E_F^V}{kT}} \tag{3}$$

Here $C_V(T)$ is the vacancy concentration present in thermal equilibrium at T. $\rho_V/100$ is the electrical resistivity increase introduced by the addition of 1% vacancies to the pure metal. S_F^V is the entropy increase of the metal when a lattice vacancy is formed. It is difficult in quenching to be certain that negligible annealing occurs during the quench.

Migration energies can be determined from the decay of the quenched in resistivity during annealing.(5)

Divacancy migration and binding energies have not been measured in very many metals, but the few values available for fcc metals are reasonably large (see Table I). Nothing is known about trivacancies etc. Eventually voids or dislocation loops result from coagulation. It is known that the presence of impurities such as H, He encourage voids over the competing dislocation loops.(6)

Table I gives the presently available data for vacancies and divacancies in fcc metals. In Table I it is assumed that self diffusion occurs by a vacancy mechanism. This has been established for Cu, Ag, Au, Pb, and for Pt.

Data for body centered metals is given in Table II. It is more difficult to obtain data of high quality for body centered cubic metals. Moreover for transition metals theoretical calculations are complicated by the presence of unfilled d bands. The anomalous diffusion data of titanium and zirconium could result from the presence of impurities.

Lattice parameter and length measurements have been made for Li and Na giving vacancy type defects (since $\Delta L/L \geq \Delta a/a$ for all temperatures). In lithium the resulting E_M^V obtained by using the measured Q and the measured E_F^V seems reasonable, but the small value obtained in this way for E_M^V in sodium appears strange. It is possible that although lattice vacancies are the most prevalent defect in equilibrium at high temperature self diffusion occurs by the migration of another defect (say, by interstitialcy migration).

In vanadium two different mechanisms compete, possibly lattice vacancies at low temperature and divacancies at high temperature.

Table I

Properties of Vacancies and Divacancies in Face Centered Cubic Metals

Metal	Q(eV)	E_F^V(eV)	E_M^V(eV)	ΔV_F (at vol)	ρ_V (ohm cm)	B_{2V}(eV)	E_M^{2V}(eV)
Mg*	1.44	.89 ± .06					
Al	1.247	0.75 ± .07	.60 ± .05	0.62	3.0×10^{-4}	.17 ± .05	.50 ± .04
Ni	2.95		1.40 ± .02				.85 ± .05
Cu	2.05	1.17 ± .10	.85 ± .15		1.6×10^{-4}		
Rh							
Pd	2.76						
Ag	1.91	1.10 ± .04	.83 ± .05		1.7×10^{-4}	.38 ± .05	.57 ± .06
Ir							
Pt	2.96	1.51 ± .04	1.38 ± .05	0.70	5.8×10^{-4}	.40 ± .10	1.10 ± .03
Au	1.81	0.94 ± .02	.88 ± .04	0.54	1.5×10^{-4}	.40 ± .05	.69 ± .03
Pb	1.05	0.52 ± .10	.53 ± .1				

*Mg is close packed hexagonal

Most Q data from Y. Adda and J. Philibert, LaDiffusion Dans Les Solides, Presses Universitaires De France, Vol. II (1966)

E_F^V data from Y. Quere, Defauts Ponctuels Dans Les Metaux, Masson and Cie (1967).

Divacancy data: Al M. Doyama and J. Koehler, Phys. Rev. 134, A522 (1964); Ag M. Doyama and J. Koehler, Phys. Rev. 127, 21 (1962); Pt, J. J. Jackson in Lattice Defects in Quenched Metals, ed. by Cotterill, Doyama, Jackson and Meshii, p. 467 Acad. Press (1967); Au, C. G. Wang, D. N. Seidman and R. W. Balluffi, Phys. Rev. 169, 553 (1968).

Formation Volume data from R. P. Huebner in Lattice Defects in Quenched Metals, ed. Cotterill, Doyama, Jackson, Meshii, p. 569, Acad. Press (1965).

Table II

Properties of Defects in Body Centered Cubic Metals

Metal	Q(eV)	E_F^V(eV)	E_M^V(eV)	ΔV_F (at vol)	ρ_V (ohm cm)	f ΔK
Li	$.54 \pm .02$	$.34 \pm .04$	.20			
Na	$.445 \pm .015$	$.42 \pm .03$	.04	.52		.36
K	.423					
Ti	ANOM-CURVED					
V	T<1360C 3.192 T>1360C 4.080					
Cr	3.194					
αFe	$2.57 \pm .09$	$1.52 \pm .1$	1.05		10×10^{-4}	.45
Zr	ANOM-CURVED					
Nb	4.16					
Mo	3.99					
Ta	4.28					
W	$5.55 \pm .4$	$3.30 \pm .1$	$2.25 \pm .4$		2.5×10^{-4}	

Q data from N. L. Peterson, article in Solid State Physics, Vol. 22. ed. by Seitz, Turnbull, Ehrenreich Acad. Press (1968).

E_F^V; Li, R. Feder, Phys. Rev. B2, 828 (1970).

E_M^V; Fe, W. Glaeser and H. Wever, Julich Conference on Vacancies and Interstitials in Metals, preprints p. 733 (1968).

E_F^V; W, H. Schultz, p. 761 in Lattice Defects in Quenched Metals, ed. Cotterill, Doyama, Jackson, Meshii, Acad. Press (1965).

f is the correlation factor for diffusion. In the vacancy mechanism if the tracer atom exchanges places with the vacancy then the next jump of the tracer is likely to be the reverse jump. ΔK is the fraction of the translational kinetic energy of the jumping atom at the saddle point.

f ΔK is obtained from measurements of the isotope effect.

Clearly additional data and further theoretical calculations are needed for the body centered metals.

B. Irradiation Data

Low temperature irradiation introduces Frenkel pairs provided enough energy is given in a collision to a lattice atom. The energy required to displace a lattice atom E_d can be measured by using electrons of energy about 0.5 MeV. Actually the displacement energy required is a function of the direction of the initial impact. Thus far directional measurements have only been made for tantalum(7) (bcc) where E_d varies by a factor of 3.5 with direction. Low values $E_d \simeq 35$ eV exist for impact in the <111> and in the <110> directions. Calculations by Gibson, Goland, Milgram and Vineyard(8) suggest that E_d varies by a factor of 3.5 in copper with lowest E_d obtained for impact in the <100> direction. Values obtained on polycrystals are given in Table III.

Huntington(2) found that self interstitials in copper have a large formation energy but a small activation energy for migration. This prediction is in agreement with experiment. Palmer, Magnuson and Koehler(9) first observed close interstitial vacancy pair recombination peaks in experiments observing resistivity annealing on irradiated copper and silver. Corbett, Smith and Walker(10) observed 1_E, an annealing peak which occurs at a lower temperature as the defect concentration produced by irradiation increases. This peak is associated with long range interstital migration. Nilan and Granato(11) measured the energy released during the annealing of deuteron irradiated copper. They saw the 1_B, 1_C, 1_D close pair peaks and also 1_E. Their measured $\Delta E/\Delta\rho$, where ΔE was the energy released over the entire stage I annealing (25°K to 60°K) was 6.4 cal/gm per microohm cm

Table III

Properties of Irradiated Metals

Metal	E_d (eV)	T_{1A}	T_{1B}	T_{1C}	T_{1D} (K)	E_M^I (eV)	E_F^I (eV)	E_{III} (eV)	E_M^V (eV)	ρ_{FP} (ohm cm)
Mg	10 eV		5.5	6.5	11					
Aℓ	19		17	29	33	0.11 eV		.62 ± .04	.60 ± .04	
Ni	24		27	42	56	0.15 eV				
Cu	22 eV	17	27	32	39	0.12 eV	4.4 eV	.69	.88	2.5×10^{-4}
Pd										
Ag	28		15	19	27			.57 to .73	.82 ± .05	
Pt	36	11	16	20	23	0.063 eV				
Au	35 eV	ANNEALS AT 2 K						.86 ± .02	.88 ± .02	
αFe	24	53	56	87	101,108	.33 eV	3.3 eV			
Nb				42	63					
Mo	37	15	22	27	40,45					
Ta					9					
W	>37	8.2	11	17.5	30,65			1.25 eV	1.93 ± .3 eV	

Data from Vacancies and Interstitials in Metals, ed. Seeger, Schumacher, Schilling, Diehl; North Holland 1970.

Also from Electron Radiation Damage in Semiconductors and Metals, Solid State Physics, Supp. 7, J. W. Corbett, Acad. Press, 1966.

± 15%. If 1% Frenkel pairs give a resistivity increase of 2.5 microohm cm in copper this corresponds to an energy release of 4.4 eV when one Frenkel pair is annihilated. This agrees with Huntingtons(2) theoretical calculation.

Shimomura(12) has shown that after stage I annealing in silver and in gold interstitial clusters are present. The clusters are probably extra planes of atoms parallel to the (111) planes. Since there are more such clusters in less pure specimens the clusters are probably nucleated at impurities. Annealing through stage III reduces the average size of the cluster.

The following questions still remain concerning irradiated specimens. Why does gold have an interstitial mobile at 2°K? Platinum behaves normally. At present good data is not available for lead.

What is the close pair annealing structure for body centered cubic crystals? Present data looks similar to fcc data. Only 1_D differs being split into two peaks in body centered cubic crystals.

In aluminum, platinum, and gold the activation energy measurements show that lattice vacancy migration is responsible for Stage III. In copper and silver $E_{III} < E_M^V$; why? Do similar discrepancies exist for body centered cubic crystals? The data for tungsten suggests that at least one bcc material shows the same discrepancy.

C. Recent Developments

Recently position annihilation measurements have been made on specimens containing vacancies.(13) A comparison of the annihilation rate with and without vacancies is used to determine the vacancy concentration. The technique has been applied to Li, Na, Cu, Aℓ, Pb. It is as yet too early to tell how useful the technique will be.

Several methods of determining the atomic configuration near a point defect are under development. Thus for changes in anomalous X-ray transmission(14) and measurements of the diffuse X-ray scattering(15) near various Bragg reflections have been used. The next decade will surely bring additional research in this area.

Finally the practical problems associated with high temperature reactor operation have stimulated considerable high temperature research and some new phenomena have been observed. The most important is the generation and growth of voids during high temperature irradiation.(16)

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