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Self-diffusion considerations in ω-phase of hard HCP metals

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Abstract. Hard hcp metals like Zr and Ti undergo ω-phase transformation under high pressures. Ample experimental evidence to suggest that this phase can be retained under ambient conditions of temperature and pressure is also available. The structural implications of the phase, consisting of two inequivalent lattices with different co-ordination numbers and nearest neighbour distances, impose certain restrictions on atomic migration *via* lattice vacancies. The present paper describes the configurational problems associated with vacancies, and also gives a calculation for correlation factor for self-diffusion taking into account the lattice anisotropy of the ω-structure.

Keywords. Hard hcp metals ; vacancy diffusion ; correlation factor ; omega phase; self-diffusion.

1. Introduction

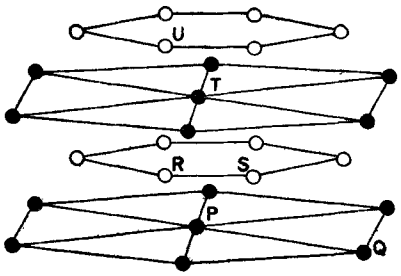
Hard hcp metals—titanium, zirconium, and hafnium belonging to group IVB of the periodic table, exhibit several common features. Firstly, these metals undergo hcp → bcc phase transformation at elevated temperatures. Secondly, both self-diffusion and those of impurities in these metals is known to be of anomalous nature. Whereas, in hcp phase these metals reveal enhanced diffusion rates, in bcc β-phase curved $\ln D$ vs $1/T$ plots are observed (Le Claire 1965; Kidson 1963; Askill and Gibbs 1965). Thirdly, under high pressures, titanium and zirconium (but not hafnium) have also been found to transform to a more open hexagonal ω-phase which can be retained in a metastable state even after removal of the pressure at the ambient temperatures (Jamieson 1963). Existence of metastable phase in several Zr and Ti base alloys including Zr-Nb and Zr-V (Hall and Roberts 1960), and Ti–V (Silcock *et al* 1955) systems, is also confirmed during quench-ageing experiments (Hickman 1969). Recently, Vohra *et al* (1979) carried out both band structure calculations and ESCA (xps) studies to examine various features relating to density of states.

Presence of ω-phase is also of some interest to diffusion problems in bcc zirconium and titanium. This is because Sanchez and De Fontaine (1975) have ascribed the diffusion anomaly in Zr and Ti to the presence of metastable ω-embryos just above the α–β phase boundary, Experimental evidence for such embryos has

been found from neutron diffraction studies (McCabe and Saas 1971; De Fontaine *et al* 1971). Though the exact diffusion mechanism in these metals is still controversial, the structural implications of this phase consisting of two inequivalent sublattices with different coordination numbers and nearest neighbour distances impose certain restrictions on the migration of lattice vacancies. The present paper discusses this situation.

2. Description of ω-phase

The ω-phase can be visualised to be arising from the collapse of alternate (111) pairs of planes of a bcc lattice (De Fontaine 1973). The unchanged (111) planes have (3–6) tessellation and form *A* sublattice (figure 1), while the collapsed planes have (6–3) tessellation and form B sublattice. The above structure though similar to hcp lattice is quite different from it because of the presence of three atoms in the unit cell at 000, 1/3 2/3 1/2, 2/3 1/3 1/2 as against two in hcp unit cell. Further the c/a ratio is less than 1. This makes the sublattice highly inequivalent and makes the local environment of an A sublattice atom completely different from that of a B sublattice atom. The A atom has two A atoms as first neighbours, twelve B atoms as second neighbours while the B atom has three B atoms as first neighbours, two B atoms as second neighbours and six A atoms as third neighbours (Jamieson 1963).



● - A Sublattice

○ - B Sublattice

$PR = a$; $RS = a' = a/\sqrt{3}$; $PT = RU = c$

$$PR = a\left[\frac{1}{3} + \frac{c^2}{4a^2}\right]^{1/2}; \quad c/a < 1$$

$$RS < PT = RU < PR < PQ$$

Figure 1. The omega lattice ●—A sublattice. ○—B sublattice.

3. Vacancy migration in ω-lattice

The vacancy formation and migration in ω-lattice become quite interesting as the vacancy formation and migration energies at A site may not be equal to those of B site. Normally vacancy migration in all metallic lattices occurs *via* the nearest

neighbour exchange with atoms. The probability for the next nearest jump is quite low and that for next to next neighbour is negligible. Thus for a vacancy on B sublattice the first two nearest sites are occupied by B atoms and diffusion will be confined to only B sublattice. B to A being next to next neighbour, jump will not occur. For a vacancy on A sublattice the nearest neighbours are two A sites to any one of which the vacancy can migrate. Since B to A tranition is discarded, the reverse would also be true—otherwise it will lead to non-equilibrium situations. Diffusion in basal plane of A sublattice is absent as otherwise it would involve vacancy jump to sites farther than the first two nearest neighbours. In other words, as far as the vacancy migration is considered the ω-lattice will have two types of vacancies each moving in its own sublattice and the problem of diffusion in ω-lattice splits into two diffusion problems, one in each of A and B sublattices. The calculation to be given below are based on the above arguments.

4. Diffusion calculations

Let N be the total number of lattice sites, then there are $N/3$ A sites and $2N/3$ B sites. Let E_{FA} and E_{FB} be the vacancy formation energies in the two sublattices which may or may not be equal. Vacancy concentrations on the two sublattices C_{VA} and C_{VB} are given by

$$C_{VA} = K_A \exp(-E_{FA}/kT), \tag{1}$$

and

$$C_{VB} = K_B \exp(-E_{FB}/kT), \tag{2}$$

where K_A and K_B are suitable constants.

According to Mullen (1961) the principal diffusivities can be written with respect to a principal set of axes as

$$D_{xx} = \langle x^2 \rangle / 2\tau, \tag{3}$$

$$D_{yy} = \langle y^2 \rangle / 2\tau, \tag{4}$$

$$D_{zz} = \langle z^2 \rangle / 2\tau, \tag{5}$$

where τ is the time interval in which n jumps take place and

$$\langle x^2 \rangle = \langle (\sum_{i=1}^{n} x_i)^2 \rangle. \tag{6}$$

Similarly for $\langle y^2 \rangle$ and $\langle z^2 \rangle$ expressions can be written.

Grouping all the n_α jumps with same $\sum_{j=1}^{\infty} \langle x_i x_{i+j} \rangle$ and $|x_i|$ values into a single set, one can write

$$D_{xx} = \frac{1}{2\tau} \sum_{\alpha=1}^{M} n_\alpha x_\alpha^2 f_{\alpha x}, \tag{7}$$

where M is the total number of sets and $f_{\alpha\alpha}$ is the correlation factor given by

$$f_{\alpha\alpha} = 1 + 2 \sum_{j=1}^{\infty} \langle x_\alpha x_{\alpha+j} \rangle / x_\alpha^2, \tag{8}$$

or $$f_{\alpha\alpha} = 1 + 2 \sum_{j=1}^{\infty} \xi_j^\alpha, \tag{9}$$

where $$\xi_j^\alpha = \langle x_\alpha x_{\alpha+j} \rangle / x_\alpha^2. \tag{10}$$

As explained earlier, since there is no mixing of vacancies of A and B sublattices, it is clear that only one vacancy jump (along Z direction with jump length equal to c) is possible for A sublattice and two vacancy jumps (one along Z direction with the same jump length c, and the other normal to it with a jump length a in the open hexagonal plane) for B sublattice.

4.1. *Diffusion coefficients for A sublattice*

Since there are no vacancy jumps in the basal plane of A sublattice which are next neighbour sites, these have been discounted, one can write

$$D_{xx}^A = D_{yy}^A = 0, \tag{11}$$

(the superscripts refer to the type of sublattice)

and $$D_{zz}^A = \frac{1}{2\tau} \frac{\rho^A \tau v_z^A}{2} f_z^A c^2, \tag{12}$$

or $$D_{zz}^A = \tfrac{1}{4} \rho^A v_z^A c^2 f_A^z, \tag{13}$$

where $n_A = \rho^A v_z^A \tau/2$ is the number of jumps contributing to diffusion along Z direction with jump length equal to c, ρ^A is the probability that a vacancy will have a tracer as its neighbour and v_z^A is the vacancy jump frequency along Z direction. As the vacancy motion along Z direction of A sublattice is uncorrelated f_z^A becomes unity and hence

$$D_{zz}^A = \tfrac{1}{4} \rho^A v_z^A c^2. \tag{14}$$

4.2. *Diffusion coefficients for B sublattice*

For diffusion in basal plane with jump length a' and jump frequency v_x^B besides ρ^B being the probability of finding a tracer near the vacancy, the diffusion coefficients can be written as

$$D_{xx}^B = \frac{1}{2\tau} \left[\frac{\tau v_x^B \rho^B}{5} a'^2 f_x^B + \frac{2\tau v_x^B \rho^B}{5} \left(\frac{a'}{2}\right)^2 f_x^B \right], \tag{15}$$

or $$D_{xx}^B = \frac{3}{20} \rho^B v_x^B a'^2 f_x^B. \tag{16}$$

For diffusion normal to basal plane with jump length c' and vacancy jump frequency v_z^B the expression for D_{zz}^B becomes

$$D_{zz}^B = \frac{1}{2\tau} \left(\frac{2\tau v_z^B}{5} c^2 f_z^B \right) \rho^B. \tag{17}$$

or $$D_{zz}^B = \tfrac{1}{5} \rho^B v_z^B c^2 f_z^B. \tag{18}$$

4.3. *Calculation of f_x^B and f_z^B as a function of v_x^B/v_z^B*

To calculate f_x^B and f_z^B the method of Mullen (1961) is used. According to this method the vacancy distribution $\bar{P}$ (a column matrix) after n jumps is related to that of the initial vacancy distribution $\bar{P}_0$ (a unit column matrix) by

$$\bar{P} = (\bar{\bar{1}} - \bar{\bar{T}})^{-1} \bar{P}_0, \tag{19}$$

where $\bar{\bar{T}}$ is the transition matrix whose elements can be written by referring to the arrangement and numbering of B sublattice sites as in figure 2.

For the present B sublattice, equation (10) becomes

$$\xi_j^\alpha = (\xi_1^\alpha)^j, \tag{20}$$

so that equation (9) can be written as

$$f_{\alpha z} = (1 + \xi_1^\alpha)/(1 - \xi_1^\alpha). \tag{21}$$

From equation (19), one can obtain $P(24)$, $P(3)$, $P(1)$ which give

$$\xi_1^z = (P(3) - P(1))\, R, \tag{22}$$

and
$$\xi_1^x = (P(24) - P(1))\, S, \tag{23}$$

where
$$R = v_z^B/(3v_x^B + 2v_z^B), \tag{24}$$

and
$$S = v_x^B/(3v_x^B + 2v_z^B), \tag{25}$$

using equations (21), (22) and (23), the expressions for f_x^B and f_z^B can be given as

$$f_x^B = (1 + \xi_1^x)/(1 - \xi_1^x), \tag{26}$$

and
$$f_z^B = (1 + \xi_1^z)/(1 - \xi_1^z). \tag{27}$$

The matrix $\bar{\bar{T}}$ was generated for different values of v_x^B/v_z^B and the respective values of f_x^B and f_z^B were calculated and are shown in figure 3.

5. Conclusion

The motion of a simple defect like vacancy becomes quite complicated in the case of ω-lattice. When only vacancy jumps as in bcc and hcp lattices are allowed,

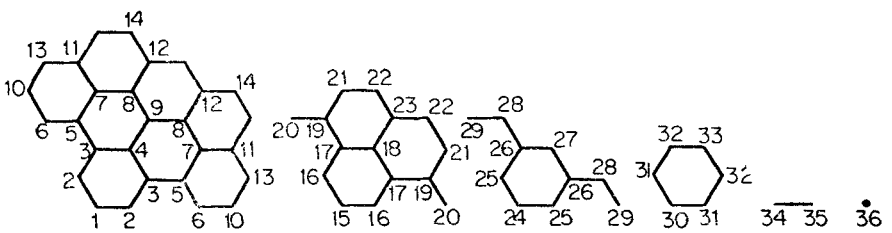


Figure 2. Lattice points numbering of six successive layers along the Z direction of B sublattice.

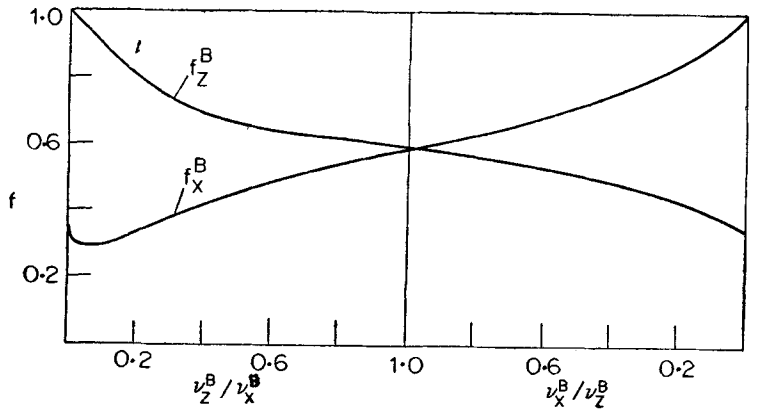


Figure 3. Correlation factors *vs.* jump frequency ratio.

the problem of vacancy motion in ω-lattice can be described by independent vacancy motion in its two sublattices.

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References

Askil J and Gibbs G B 1965 *Phys. Status Solidi* **11** 557
De Fontaine D and Buck O 1973 *Philos. Mag.* **27** 967
De Fontaine D, Paton N E and Williams J C 1971 *Acta Metall.* **19** 1153
Hall B A and Roberts J A 1960 *Acta Metall.* **8** 575
Hickman B S 1969 *J. Mater. Sci.* **4** 554
Jamieson J C 1963 *Science* **140** 72
Kidson G V 1963 *Can. J. Phys.* **41** 1563
Le Claire A D 1965 *Diffusion in Body Centred Cubic Metals* (Metal Park, Ohio : ASM Publications) p. 3
McCabe K K and Sass S L 1971 *Philos. Mag.* **23** 953
Mullen J G 1961 *Phys. Rev.* **124** 1723
Sanchez J M and De Fontaine D 1975 *Phys. Rev. Lett.* **35** 227
Silcock J M, Daview M H and Hardy H K 1955 *Symposium on the mechanism of phase transitions in metals* (London : The Institute of Metals) pp. 93
Vohra Y K, Sikka S K and Chidambaram R 1979 *J. Phys. F.* **9** 1771