Reprinted from
Philosophical Magazine, Vol. 25, No. 1, p. 45, January 1972

On Vacancy Condensation and the Origin of Dislocations in Growth from the Melt

By G. F. Bolling and D. Fainstein†
Process Research Department, Scientific Research Staff,
Ford Motor Company, Dearborn, Michigan, U.S.A.

[Received 19 April 1971 and in final form 23 July 1971]

Abstract

The formation of dislocations from condensed vacancies has been re-examined. Conditions for transformation of vacancy clusters into dislocation loops are analysed, taking into account an entropy contribution of atoms in the dislocation core. New evidence in the literature for a vacancy concentration beyond that of equilibrium at the advancing solid–liquid interface is used to calculate an excess vacancy concentration trapped in the solid as a function of freezing velocity. This excess leads to an estimation of the nucleation frequency of loops and supports the condensation mechanism as the source for dislocations. The critical stage for dislocation formation in growing crystals is also shown to depend upon the temperature distribution in the solid. Results of this analysis are applied to the formation of dislocations in a general f.c.c. metal, and specifically in lead, aluminium and copper, for which experimental information is available. Striation formation is discussed for these metals ; it is concluded that the original mechanism proposed by Teghtsoonian and Chalmers (1951) and extended by Frank (1956) cannot be discarded.

§ 1. Introduction

In most examinations of vacancy condensation it has been assumed that any excess concentration arises solely through temperature change; for melt-grown crystals the initial vacancy concentration is then assumed to be the equilibrium value at the melting-point. Considerations by Schoeck and Tiller (1960), proceeding from this assumption, showed that it was improbable for dislocation arrays (striations) to form in melt-grown crystals through the vacancy condensation mechanism. Webb (1962) departed from the assumption and considered the trapping of vacancies for crystal growth in general. For growth from the melt, in one instance he assumed a diffuse interface, and suggested that growth-trapped defects due to a vacancy excess at the solid–liquid interface might still be a contributing factor in the formation and evolution of a mosaic substructure.

Most recently, Rastogi and Mukherjee (1970) have shown that high purity lead quenched from the melt has a vacancy concentration greater than that of equilibrium at the melting point. Such a result had been

---

† On leave from the Departamento de Metalurgia, Comision Nacional de Energia Atomica, Buenos Aires, Argentina.

obtained for aluminium by Thomas and Willens (1964), but as discussed by Rastogi and Mukherjee (1970) there was argument about these experiments, and although the original work was subsequently supported (Thomas and Willens 1966) it remained in some controversy. Now it seems that both investigations were correctly interpreted and they prompt a re-examination of the formation of dislocation loops from condensed vacancies. The work by Rastogi and Mukherjee (1970) is especially valuable since it provides data for lead; Sekerka, Bolling and Tiller (1960) had investigated dislocation array formation in high purity lead, in order to test some of the assertions made theoretically by Schoeck and Tiller (1960), and a plausible argument is available for the minimum excess vacancy concentration required at the melting point.

In the present appraisal, only dislocations formed by vacancy condensation will be considered, for it seems that the original suggestions (Teghtsoonian and Chalmers 1951, Frank 1956) can be correct and do provide an acceptable mechanism for forming sufficient dislocations to explain all the experimental observations. This finding does not preclude subsequent examinations of other means for dislocation production, such as those suggested by Jackson (1962 b) and Jaffrey and Chadwick (1968), but they may be unnecessary.

Our procedure will be to examine the magnitudes and forms for precipitation of vacancies in § 2, regardless of how an excess arises, and then to consider the reasons and possible magnitudes for a vacancy excess created at the melting point during freezing, in §§ 3.1 to 3.3. In § 4 the nucleation of dislocations is examined, first in the abstract and then as affected by vacancies trapped during freezing; a 'general f.c.c. metal' is taken for these first calculations since a critical result may be illustrated without relying upon one metal or upon particular observations. Section 5 provides a description of solid–liquid interface width for the general f.c.c. metal and particularly for lead, copper and aluminium. The goal of discussing dislocation array formation is reached in § 6 where the critical example of lead is chosen; calculations are also given for aluminium and copper where pertinent information exists, and for the general f.c.c. metal. Finally, the discussion of § 7 is centred upon a clarification of the critical assumptions we use throughout the analysis.

§ 2. PRECIPITATION OF VACANCIES

2.1

In a material with an excess vacancy concentration there will be clusters of vacancies (see Jackson 1962 a). It is not known what shapes these clusters will take; however, at high temperatures, the change from some particular cluster shape to any other shape of lower free energy should occur very rapidly. For these high temperatures (i.e. low supersaturations) it can also be shown that the critical size for a stable cluster in the form of a spherical void or a void of some other regular shape would contain a great number of vacancies. Simple void formation is then improbable and smaller irregular clusters are of concern in this range of supersaturation.

The formation of a dislocation loop from an unknown cluster of vacancies will occur as long as the excess free energy due to the dislocation is less than that for the cluster, each having eliminated the same number of vacancies. Two real cases can be differentiated for any given small supersaturation: *either* the size of the dislocation loop is large enough when it is formed from vacancies so that it may grow freely by climb and reduce the free energy of the system; *or* it is sub-critical when it is formed from vacancies and can only grow in the manner of a dislocation embryo, being ill-defined as a dislocation loop because it is so small. If the former case were true, the nucleation of dislocation loops would be a complex combination of vacancy cluster probability and cluster transformation. It will be shown that the latter case of small loops seems reasonable and therefore that the nucleation of dislocation loops can be treated in a simple fashion.

2.2

First, the energy of a dislocation loop must be considered. For a circular form this was given by Franz and Kroener (1955), and may be written as

$$E_d = \tfrac{1}{2}\,\frac{G}{(1-\nu)}\,b'^2 r\left[\ln\frac{r}{b}+Z\right]+\pi r^2\gamma, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where b' is the appropriate Burgers vector, b the interatomic distance, r the loop radius, ν the Poisson ratio, G the appropriate shear modulus, and γ is the energy of the stacking fault enclosed by the loop. As shown by Schoeck and Tiller (1960) Z is a constant number ($Z \approx 2$) which takes into account the strain energy in the core of the dislocation. There is however a contribution to the entropy of a crystal from the atoms in the dislocation core as pointed out by Cottrell (1953). This can be written as αk per atom plane of the dislocation; Cottrell shows that $\alpha \lesssim 3$. For dislocations of appreciable length, this entropy term will develop only a negligible contribution to the free energy of a crystal compared to the strain energy term, but for small loops it becomes considerable. Therefore the free energy of a circular loop is written as

$$F_d = \tfrac{1}{2}\,\frac{G}{(1-\nu)}\,b'^2 r\left[\ln\frac{r}{b}+Z\right]+\pi r^2\gamma-2\pi\frac{r}{b}\,\alpha kT. \quad . \quad . \quad . \quad (2)$$

The value of α will be slightly dependent upon loop size, but will be taken as $\alpha = 3$ in calculation for a circular dislocation loop with Burgers vector $\tfrac{1}{3}[111]$ in the f.c.c. structure. The circular loop is not a restriction; an equivalent equation could be derived for any polygon using the formulae set out by Yoffe (1960) for planar loops with straight sides.

2.3

Now the condition for transformation of a vacancy cluster can be examined. A dislocation loop would eliminate ($\pi r^2/b^2$) vacancies and the cluster to be considered must contain the same number. The radius of a spherical cluster would be $r_v = (\frac{3}{4}r^2b)^{1/3}$, and would transform to a dislocation loop when†

$$\tfrac{1}{3}\frac{G}{(1-\nu)}b^2r\left[\ln\frac{r}{b}+Z\right]+\pi r^2\gamma-2\pi\frac{r}{b}\alpha kT \leqslant 4\pi(\tfrac{3}{4}r^2b)^{2/3}\gamma_c. \quad . \quad . \quad (3)$$

Here γ_c is the specific surface free energy of the cluster, assumed to be isotropic or otherwise a sphere would not form. An equivalent expression would be derived for an octahedron or other form if the appropriate surface free energies were used.

An evaluation of eqn. (3) for the conditions of interest (using the numbers to be given in § 4.2 and a reasonable value for γ_c) shows that loops would form at sizes small enough that the notion of a dislocation is suspect; (i.e. $r/b \sim 2$). The results are not surprising and may be compared to those of Schoeck and Tiller (1960) who examined the collapse of vacancy discs. It is therefore concluded that the cluster of lowest free energy resembles a dislocation loop. This is consistent with the results expected if the constraints due to long-range forces in metals could be accurately handled for small clusters; for example, as shown by Nabarro (1940) the elastic strain around precipitate particles is least for discs.

It has not yet been established whether the size at which a cluster transformation occurs is one at which the dislocation is either growing or embryonic as discussed in § 2.1. Even though condition (3) is fulfilled at such small sizes that it seems the dislocation loop cannot be more than embryonic, further support is needed and will be given *a posteriori* in § 4.3.

§ 3. EXCESS VACANCIES DURING FREEZING

3.1

A rigorous mathematical treatment of the excess vacancies trapped during freezing requires a better knowledge about the nature of the interface than is yet available. Even on the basis of existing models, it appears difficult to take into account the presence of any vacancy-type defects developing across the interface. Thus, only a simple analysis may be performed in which no interface models or growth mechanisms will be assumed, except for the implicit choice of a diffuse interface following Cahn (1960) or Temkin (1964).

If there is to be any degree of local order in the liquid, at least in the liquid immediately adjacent to the interface, so as to make the description

---

† The Burgers vector for a faulted dislocation in the f.c.c. structure (eqn. (2)) has been replaced by b, using $b'^2 = \frac{2}{3}b^2$.

of a vacancy meaningful, then at equilibrium the vacancy concentration at the interface will vary from its characteristic value in the solid up to some value characterizing this immediate liquid. We take the latter value to be the liquid free volume, but by-pass the problem of describing vacancies in the liquid.

In Appendix I we use the concept of a diffuse interface to derive the trapped vacancy concentration at the melting temperature[†]. This is a first approximation made up to be a lower bound for the vacancy concentration. It is calculated for the case of no sinks other than the liquid. Set in another form (from eqn. (A 6) it is exactly that derived by Webb (1962)

$$C_q = C_{\mathrm{E}} + \frac{C_{\mathrm{L}} - C_{\mathrm{E}}}{1 + \dfrac{D}{Vd}}, \qquad (4)$$

where C_{E} is the equilibrium concentration in the solid, C_{L} the 'concentration' of free volume in the liquid at equilibrium, D the diffusion coefficient of vacancies in the solid, V the growth velocity, and d the interface width discussed in § 5.

If a non-diffuse interface were assumed (its width limited to b, say), then an abrupt change in the vacancy concentration function should occur at the interface. Since $C_q \ll C_{\mathrm{L}}$, an accumulation of 'vacancies', or some form of excess free volume, would arise in the liquid closely adjacent to the interface for any reasonable growth velocity. This alternative is provided for in the Appendix, but not expanded at all. It is suggested here in the text that a fictitious interface of effective width d' must be adopted in this extreme. Within d' the excess in the liquid layer would be accommodated, and so forth; but this would lead to a form just like eqn. (4) using an unknown d' rather than an unknown d. Since we shall eventually develop values of d based on Temkin's model (1964), the alternative of a non-diffuse interface is discarded.

3.2

The equilibrium concentration of vacancies in a solid, at any temperature, is given by

$$C = \beta \exp - (E_{\mathrm{v}}/kT), \qquad (5)$$

where E_{v} is the energy for vacancy formation and $\beta = \exp(S_{\mathrm{v}}/k)$, S_{v} being the self-entropy of a vacancy.

It will prove convenient to define a parameter q which specifies the concentration C_q, by an expression similar to that of eqn. (5)

$$C_q = \beta \exp - (E_{\mathrm{v}}/qkT_{\mathrm{M}}). \qquad (6)$$

[†] The variation of C_q with distance from the interface due to the thermal gradients along the solid is negligible.

At the melting temperature we obtain

$$\frac{C_q}{C_E}=\exp\left[\left(1-\frac{1}{q}\right)\frac{E_V}{kT_M}\right], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

so that

$$q=\left[1-\frac{kT_M}{E_V}\ln\frac{C_q}{C_E}\right]^{-1}$$

$$=\left[1-\frac{kT_M}{E_V}\ln\left(\frac{\Delta C}{C_E}+1\right)\right]^{-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

3.3

Rastogi and Mukherjee (1970) and Thomas and Willens (1964) have shown how much smaller C_q is than the change in volume on freezing (C_L) and have discussed why it affects properties only to a minor degree. Both investigations also show that the value of C_q increases as the quenching temperature increases. Jackson (1965) used this observation as one basis for doubting the interpretation of Thomas and Willens (1964); but later Thomas and Willens (1966) stated the common experience that their splat cooling brought about faster solidification when higher initial temperatures were used for the melts, perhaps because of better thermal contacts with substrates, thinner splats, etc. The increase of C_q with quenching temperature is large for lead and can be compared with the difference in the thermal expansion of the liquid and the solid at the melting temperature (Wilson 1965). Simple calculations, where the vacancy volume is chosen as one-half that of an atom, show that a major fraction of the expansion difference can be accounted for by the 'vacancies' in the liquid in the temperature range investigated by Rastogi and Mukherjee (1970). This seems reasonable since the atomic binding forces in lead should differ very little from solid to liquid in the range up to 150°c above the melting temperature.

§ 4. NUCLEATION OF DISLOCATIONS

4.1

In the absence of non-uniform fluxes the chemical potential of a vacancy may be approximated by

$$\mu_V=kT\ln\frac{C_q}{C}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where C is the equilibrium concentration of vacancies in the solid at temperature T. Hence the free energy increase of the crystal upon the formation of a dislocation loop is obtained from eqn. (2) and a loop/disc of $\pi r^2/b^2$ vacancies as

$$\Delta F=\frac{1}{3}\frac{G}{(1-\nu)}b^2r\left[\ln\frac{r}{b}+Z\right]+\pi r^2\gamma-2\pi\frac{r}{b}\alpha kT-\pi\frac{r^2}{b^2}\mu_V. \quad . \quad . \quad (10)$$

From this, the critical loop size at which the loop will grow may be calculated from the condition $\partial\Delta F/\partial r = 0$, yielding the maximum free energy increase ΔF^*:

$$\frac{\partial\Delta F}{\partial r} = \frac{G}{3(1-\nu)} b^2 \left[\ln\frac{r}{b} + Z + 1\right] + 2\pi r\gamma - \frac{2\pi\alpha kT}{b} - \frac{2\pi r}{b^2}\mu_{\mathrm{v}} = 0. \qquad (11)$$

r^*/b is calculated from eqn. (11). Or substituting for μ_{v} in eqn. (10):

$$\Delta F^* = \frac{Gb^3}{6(1-\nu)}\frac{r^*}{b}\left[\ln\frac{r^*}{b} + Z - 1\right] - \alpha\pi kT\frac{r^*}{b} \quad . \quad . \quad . \quad . \quad (12)$$

4.2

If it is now assumed that the embryonic dislocation loop forms the critical nucleus for dislocation growth, a simple nucleation rate equation may be written following Turnbull and Fisher (1949).

$$I = K_{\mathrm{r}} \exp - \left(\frac{\Delta F^* + E_{\mathrm{m}}}{kT}\right); \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

here I is the nucleation rate per unit volume and E_{m} may be considered as the energy for vacancy transfer in the matrix. The rate constant K_{r} can be constructed for the dislocation loop by analogy with a disc-shaped precipitate; however, it is sufficient to specify it here within only a few orders of magnitude. Accordingly, $K_{\mathrm{r}} \simeq nkT/h \simeq 10^{30}\,\mathrm{sec}^{-1}\,\mathrm{cm}^{-3}$; n is the number of vacancies per cm^3 at the temperatures considered, near the melting point. Similarly for our purposes, the rate I need be specified within only a few orders of magnitude. Then, noting that for most metals near their melting points $E_{\mathrm{m}}/kT \sim 10$, the condition for nucleation of dislocation loops may be taken from (12) and (13) as

$$\frac{r^*}{b}\left\{\frac{1}{6(1-\nu)}\frac{Gb^3}{kT}\left[\ln\frac{r^*}{b} + Z - 1\right] - \pi\alpha\right\} = \ln\frac{K_{\mathrm{r}}}{I} - 10. \quad . \quad . \quad (14)$$

From this equation the loop size which may nucleate at a reasonable frequency at any temperature is given under the restriction of eqn. (11). The chemical potential of a vacancy can be written, from eqns. (7) and (9) as

$$\begin{aligned}\mu_{\mathrm{v}} &= -\frac{E_{\mathrm{v}}}{k}\left(\frac{1}{qT_{\mathrm{m}}} - \frac{1}{T}\right)kT \\ &= \frac{E_{\mathrm{v}}}{q}\left\{\frac{\Delta T}{T_{\mathrm{m}}} + (q-1)\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)\end{aligned}$$

where $\Delta T = T_{\mathrm{m}} - T$.

Since $q \geqslant 1$, equation (11) may then be written as

$$q - 1 \geqslant \frac{b}{r^*}\left\{\frac{1}{6\pi(1-\nu)}\frac{Gb^3}{E_{\mathrm{v}}}\left[\ln\frac{r^*}{b} + Z + 1\right] - \frac{\alpha kT}{E_{\mathrm{v}}}\right\} + \frac{\gamma b^2}{E_{\mathrm{v}}} - \frac{\Delta T}{T_{\mathrm{m}}}. \qquad (16)$$

Therefore a complete solution of the problem of dislocation formation in growing crystals depends upon the temperature distribution in the solid

Table 1 (*a*)

Metal	T_m [°K]	b [Å]	$\gamma^{(a)}$ [erg/cm²]	$G \times 10^{-23(b)}$ [ev/cm³]	Gb^3 [ev]	Gb^3/kT_m	$\frac{\gamma}{Gb} \times 10^3$	E_v [ev]	Gb^3/E_v
Pb	600	3·49	25	1·94	0·85	16·4	22·9	0·63[c]	1·35
Al	933	2·86	150	9·14	2·14	26·3	35·8	0·76[d]	2·82
Ag	1233	2·88	22	8·21	1·96	18·4	5·8	1·09[e]	1·80
Au	1336	2·88	50	9·26	2·22	19·2	11·7	0·94[f]	2·36
Cu	1356	2·55	55	12·2	2·04	17·4	11·0	1·17[g]	1·74
Ni	1728	2·49	225	27·3	4·21	28·2	24·2	1·4[h]	3·01
Pt	2042	2·77	75	11·0	2·33	13·2	15·9	1·2[i]	1·94

(*a*) Gallagher (1970). These values are taken at room temperature and may be smaller near T_m.
(*b*) Köster (1948).
(*c*) Rastogi and Mukherjee (1970).
(*d*) Simmons and Balluffi (1960 a).
(*e*) Simmons and Balluffi (1960 b).
(*f*) Simmons and Balluffi (1962).
(*g*) Budin, Denayron, Lucasson and Lucasson (1963).
(*h*) Nakamura (1961).
(*i*) Piercy (1960).

Table 1 (*b*)

Metal	C_E [Mole fraction]	$C_L^{(d)}$ [Mole fraction]	D† [cm^2/sec]	$\frac{r^*}{b}$	$\frac{L^{(h)}}{T_m}$ [kcal/mol deg]	η	$\frac{d}{b}$
Pb	$1\cdot3\times10^{-4(a)}$	0·035	$10^{-5(e)}$	10	1·98	0·67	8·6
Cu	$2\times10^{-4(b)}$	0·042	$2\cdot3\times10^{-5(f)}$	9	2·28	0·76	5·5
Al	$6\times10^{-4(c)}$	0·060	$1\cdot6\times10^{-5(g)}$	6	2·68	0·90	3·7
‘ f.c.c. ’	10^{-4}	0·050	10^{-5}	8	2·20	0·74	6·2

(*a*) Rastogi and Mukherjee (1970).
(*b*) Simmons and Balluffi (1963).
(*c*) Thomas and Willens (1964).
(*d*) Smithells (1967).
(*e*) See Appendix II.
(*f*) Kuper, Letaw, Slifkin, Sonder and Tomizuka (1955).
(*g*) Stoebe and Dawson (1970).
(*h*) Wilson (1965).

† References (*e*), (*f*), (*g*) report values of the bulk diffusion coefficients D_b. The values given in the table are $D = D_b/C_E$.

through the term $\Delta T/T_{\mathrm{m}}$. It is apparent, in the absence of other sinks, that the condition of eqn. (16) may be fulfilled at some ΔT for any metal. However, in order to determine a $q \geqslant 1$ as well, it is best to examine the most restrictive conditions available.

Table 1 (*a*) shows that for most metals $Gb^3/kT \leqslant 20$ and considering that $E_{\mathrm{m}}/kT_{\mathrm{m}} \leqslant 10$ a high nucleation frequency is obtained for $r^*/b \sim 8$. Taking extremes $\gamma/Gb \leqslant 0{\cdot}023$†, $kT_{\mathrm{m}}/E_{\mathrm{v}} \geqslant 0{\cdot}082$ and $Gb^3/E_{\mathrm{v}} \leqslant 2{\cdot}5$, then $q-1 \geqslant 0{\cdot}14-\Delta T/T_{\mathrm{m}}$ (from eqn. (16)) and with $C_{\mathrm{L}} \sim 0{\cdot}05$, $C_{\mathrm{E}} \sim 10^{-4}$, $D \sim 10^{-5}\,\mathrm{cm}^2/\mathrm{sec}$, $d \sim 2 \times 10^{-7}$ cm (see Appendix II) and $V \sim 10^{-2}$ cm/sec, the excess concentration is $\Delta C \sim 0{\cdot}1 \times 10^{-4}$ which corresponds to a value $q = 1{\cdot}01$. So, at $\Delta T = 0{\cdot}13T_{\mathrm{m}}$, the excess is sufficient to nucleate dislocation rings of radius $8b$.

4.3

The preceding estimate applies to the question of dislocation nucleation *per se*. It was assumed that the embryonic dislocation loop served as a critical nucleus for dislocation formation. Inspection of eqn. (16) for a value of $r^*/b \sim 2$ with $\Delta T \sim 0{\cdot}13T_{\mathrm{m}}$ would necessitate values of $q \sim 1{\cdot}18$ with correspondingly increased concentration excess of vacancies at the melting point. *But* such an excess, attainable with higher growth velocities ($\sim 0{\cdot}6$ cm/sec), would allow loops of bigger radius to nucleate without any supercooling (i.e. immediately behind the interface) and eqns. (14) and (16) to be satisfied. These larger loops would grow and eliminate the excess vacancies, thus prohibiting the otherwise attainable $q \sim 1{\cdot}18$. Therefore, it is seen that sufficient conditions are given for favouring reasonable size dislocation loop nucleation, instead of small suspect ones.

§ 5. THE INTERFACE WIDTH

This section is a digression which must be made in order to evaluate d. A brief sketch of the diffuse interface analysis performed by Temkin (1964) is presented in Appendix II. The interface widths which may be obtained for lead, copper, aluminium, etc., are large enough for us to justify the formation of all types of dislocations and then arrays. Temkin's model is, however, not applicable to the f.c.c. metals that we limit ourselves to treat quantitatively; but as stated in the Appendix we can use his reasoning to find a scaling parameter. We chose lead as a reference metal to provide this parameter since there are experiments at the two extremes, quenching and slow unidirectional growth. The chosen 'interface width' is $d/b \sim 9$. We do not suppose that lead actually will display such a 'thick' interface, but we do suspect that it is an acceptable width for vacancy distribution. Arguments to support such acceptance follow those presented already in § 3.1.

Another justification for this procedure depends critically upon the function used to describe interface widths in a theory for diffuse interfaces.

---

† Aluminium will be treated separately.

The 'width' $d/b \sim 9$, is largely a distributional number. If Temkin's paper and calculations are taken critically at face value, then the transition from all liquid to all solid does require such an extent. However, a width less than half this value suffices (for metals in the Temkin range, $d/b \sim 2$ to 10) to account for 90% of the solid–liquid transition. Width, as a concept, has a magnitude that depends strongly on the use to which it will be put. Here, for vacancies the larger value seems better.

A comparison with experimental data for Pb (Rastogi and Mukherjee 1970) can be made at this point. If d is taken as shown in Appendix II (Temkin 1964), a value is found for Pb of $d \sim 3 \times 10^{-7}$ cm. Then a freezing rate of $\geqslant 0{\cdot}5$ cm/sec can be calculated (Burden and Jones 1970) for the experimental arrangement described by Rastogi and Mukherjee†. A proper value of $10^{-5}\,\mathrm{cm^2\,sec^{-1}}$ for D, and the value of $C_{\mathrm{L}} = 0{\cdot}035$, give

$$\frac{C_q - C_{\mathrm{E}}}{C_{\mathrm{E}}} \equiv \frac{\Delta C}{C_{\mathrm{E}}} \sim 4.$$

This is just the value derived from Rastogi and Mukherjee's experiments.

§ 6. Examples of Dislocation Formation

6.1. *Separate Loops*

We shall now rely upon tables 2 (*a*) and (*b*) showing calculated and experimental results for three metals. It is most convenient to begin with the real experimental results shown in table 2 (*a*) and then proceed to the hypothetical cases in 2 (*b*); both of these use the data of tables 1 (*a*) and (*b*).

For lead, calculations from eqn. (16) show in table 2 (*a*) the satisfactory agreement between theory and experiment obtained with the Temkin interface width. That is, for the slow growth rate of 2 (*a*), i, the calculated undercooling is within the allowed range; and for the quench rate of 2 (*a*), ii, even less than no undercooling seems necessary—we have chosen too severe a set of conditions. For copper the calculations are reasonable but not critical. For aluminium we find a reasonable but proportionately larger undercooling necessary in order to explain the experiments of Thomas and Willens (1964).

As we proceed to table 2 (*b*), and the conditions for lead are relaxed, we find that no undercooling is necessary for loop nucleation assuming $q > 1{\cdot}07$ giving $\Delta C > 1{\cdot}15 C_{\mathrm{E}}$, a degree which can be obtained at velocities $V \geqslant 0{\cdot}14$ cm/sec. Dislocation loops of $r^*/b \leqslant 10$ nucleate in these cases immediately behind the interface; and the higher the supersaturation, the more easily these loops should expand under the strong stresses produced by the excess vacancies (Hirth and Lothe 1968). These conditions are certainly fulfilled in the experiments performed by Rastogi and Mukherjee (1970).

---

† The lower limit is most reasonable because it is just at the value of fastest cooling and freezing rates obtained by Cline and Livingston (1969) for metals of the same conductivity, forced to freeze as fast as possible without going to the extreme of splat cooling.

Table 2 (*a*). Comparisons with experimental results

Pb

i: Unidirectional growth (Sekerka, Bolling and Tiller, 1960)

Data: $\Delta T = 32°\text{c} >$ ———————————— ↓
$V = 3 \times 10^{-2}$ cm/sec
allowable

Calculated for this V: $C_q/C_E = 1{\cdot}025$; $q = 1{\cdot}018$; $\Delta T_{\text{min}} = 30°\text{c}$

ii: Quenching experiment (Rastogi and Mukherjee 1970)

Data: $\dfrac{C_q}{C_E} = 5$; $V = 0{\cdot}5$ cm/sec (estimated)

Calculated: $q_{\text{min}} = 1{\cdot}15$; $\Delta T_{\text{min}} = -48°\text{c}$ (i.e. $T > T_{\text{m}}$: allowable)

Cu

i: Unidirectional growth (Young and Savage 1964)

(Few dislocations at $V = 7 \times 10^{-4}$ cm/sec, furnace at 1180°c.
More dislocations for furnace at 1125°c; and for special conditions.
We deduce agreement and $C_q/C_E \sim 1{\cdot}00$. Thus, for the one instance we take:)

Data: $\Delta T \sim 0 \ll$ ———————————— ↓
$V = 7 \times 10^{-4}$

Calculated for this V: $C_q/C_E = 1{\cdot}001$, $q \simeq 1$; $\Delta T_{\text{min}} = 108°\text{c}$
(i.e. no appreciable dislocations)

Al

ii: Quenching experiment (Thomas and Willens 1964)

Data: $\dfrac{C_q}{C_E} = 1{\cdot}69$; $V = 1$ cm/sec (estimated)

Calculated: $q_{\text{min}} = 1{\cdot}06$; $\Delta T_{\text{min}} = 160°\text{c}$ (i.e. $T < T_{\text{m}}$: possible)

Table 2 (*b*). Intercomparison for quenching, $\Delta T = 0$ assumed

Metal	q	C_q/C_E	V [cm/sec]	I loops/sec cm^3
Pb	1·07†	2·15	0·14	4×10^2
Cu	1·08†	2·1	0·90	$1{\cdot}2 \times 10^3$
Al	1·10†	2·36	3·54	$< 10^{-8}$
Al	1·23	5·8	7·4	4×10^2
‘ f.c.c. ’	1·14	4·5	0·35	10^5

† The values $q = 1{\cdot}07$, 1·08 result from nucleation frequencies in accord with average experimental conditions. For Al, a large stacking-fault energy forces the value $q \geqslant 1{\cdot}10$. This and the consequent ring size, $r \sim 10^3 b$ imply that better values of q should come from the nucleation of perfect loops.

For aluminium the results are ambiguous; yet Thomas and Willens (1964) showed (except for the highest quenching temperature investigated, above 1200°C) perfect and imperfect dislocation loops as well as "small spherical black spots which could be small loops or vacancy clusters". Our calculation for $r^*/b < 10$ indicates that nucleation of faulted loops is more favourable, becoming equal to that for unfaulted loops near $r^*/b \sim 10$. Thomas and Willens (1964) report an excess $\Delta C/C_E = 0{\cdot}69$ in this case, thus allowing either loop nucleation at $\Delta T \sim 160$°C with $r^*/b \sim 6$, as calculated for imperfect loops (table 2 *a*)[†]; or no supercooling necessary for $\Delta C/C_E \geqslant 4{\cdot}8$ which can be obtained under growth velocities $\geqslant 7{\cdot}4$ cm/sec (table 2 *b*). Thomas and Willens (1964) show the existence of a high density of dislocations making sub-boundaries for splats quenched above 1200°C which should agree with their reported faster growth for quenches from higher temperatures (viz. ~ 10 cm/sec).

Lead and aluminium present two distinguishable cases, the first with small values both for Gb^3 and γ, the second with large values for these quantities. Copper comes out as an intermediate case displaying a large Gb^3 value but a relatively small γ. Finally, it is worth while repeating that table 1 (*b*) shows the values of the interface widths, *d*, calculated using a consistent set of parameters for the three metals. The trend in *d* that should be expected according to the Temkin analysis[‡] (1964) for interface extension was deduced for lead and aluminium. The value of *d* for copper then was obtained by interpolation, and used to calculate *V* with $\Delta T = 0$ (table 2 *b*). Other f.c.c. metals could have been used as well.

6.2. *Striation Formation*

The particular lead crystals produced by Sekerka *et al.* (1960) under a high ambient temperature at low growth velocities present the critical borderline case for our arguments, as appears immediately from the results in table 2 (*a*) (see also Atwater and Chalmers, 1957).

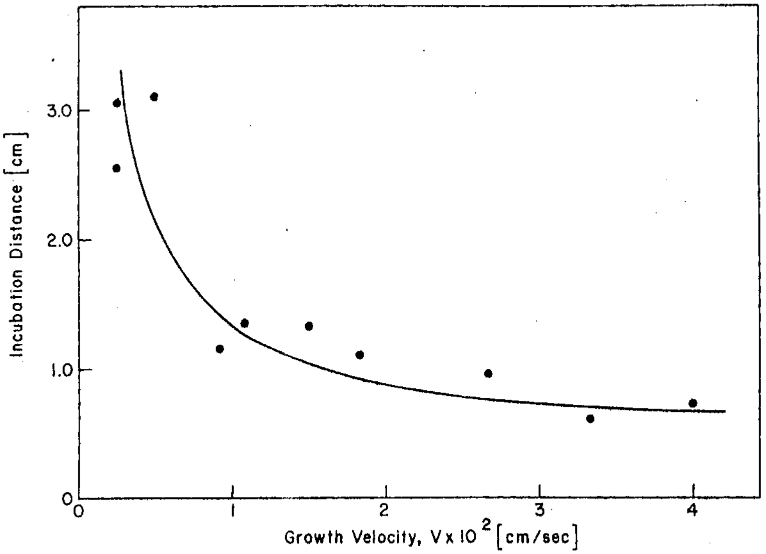
The observations of Teghtsoonian and Chalmers (1951, 1952), however, set forth a more detailed examination of velocity effects in tin. Their results are replotted here in a convenient manner and will be used first. The amount of crystal grown before striations were observed is plotted in fig. 1 as an incubation distance which is a function of the growth velocity. It can be seen that above 8×10^{-3} cm/sec (5 mm/min) the incubation distance is roughly constant; extrapolating the results to slower rates of growth would indicate that striation-free crystals can be grown by

---

[†] Their subsequent expansion as a consequence of the high stresses present could facilitate a Shockley partial if possible in part of these imperfect dislocation loops, and would transform them into perfect loops with a decrease in free-energy. This high supercooling for Al corresponding to this level of super saturation would favour (because of the more sluggish diffusion of vacancies) the nucleation of many loops and limited loop expansion, rather than the development of larger dislocations forming as a consequence of loops climbing.

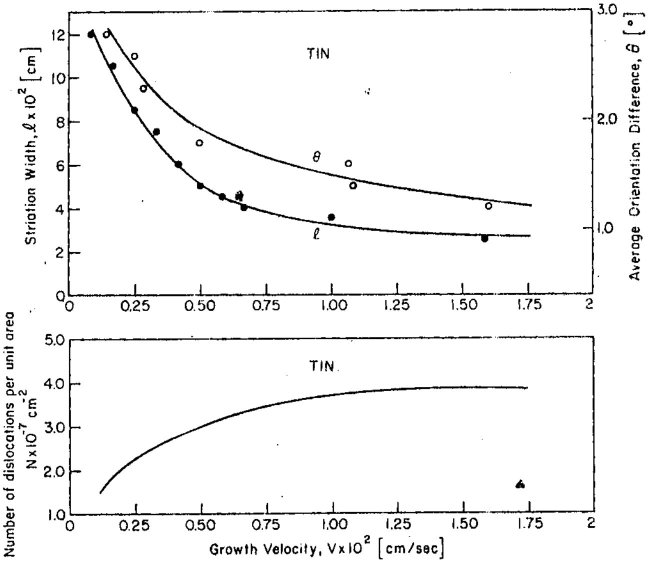
[‡] The parameter γ used by Temkin in his analysis has been identified here as η.

Fig. 1



Incubation distance for the macromosaic substructure (striations) as a function of growth velocity for tin (derived from data by Teghtsoonian and Chalmers 1952).

Fig. 2



(*a*) Striation width and average angular misorientation between striations as a function of growth velocity in tin (derived from data by Teghtsoonian and Chalmers (1951 and 1952)). (*b*) Dislocation density in striation boundaries as a function of growth velocity in tin.

manipulating the growth rate alone. In fig. 2 (*a*) both the distance between striations and their angular misorientation are plotted against growth velocity. When smoothed-curve values of these functions are used the total dislocation concentration per cm^2 involved in the striation boundaries can be plotted as a function of growth velocity as in fig. 2 (*b*). (This was done by assuming uniform tilt boundary arrays of angle θ, separated a distance l.) Depending upon the smooth curves plotted in 2 (*a*), or the constants used, this curve may vary slightly but will always exhibit a concentration $\sim 10^7/\mathrm{cm}^2$, rapidly diminishing at low velocities and approaching a steady state at high velocities.

These results are consistent with the proposed mechanism for obtaining excess vacancies at the melting point. Below velocities $\sim 3\times10^{-3}$ cm/sec (1·8 mm/min) the incubation distance increases rapidly and the dislocation density decreases; at high velocities a steady state is approached. However, even though the details of striation formation cannot be investigated except in a qualitative manner some additional points must be proved. The reader is referred to the original arguments of Teghtsoonian and Chalmers (1951), the more detailed development by Frank (1956) and the objections of Schoeck and Tiller (1960).

6.3. *The Climb Problem*

The description by Frank (1956) is still plausible except for the part of the argument by Schoeck and Tiller (1960) stating that, even if vacancies collapse to form dislocations, their forward velocity of growth in the direction of the interface will fall below the crystal growth rate before the region of surface image forces is reached. This is true for equilibrium vacancy concentrations, but must be modified in the presence of C_q vacancies. Following Schoeck and Tiller the steady-state climb velocity of dislocations, v_0, may be set as

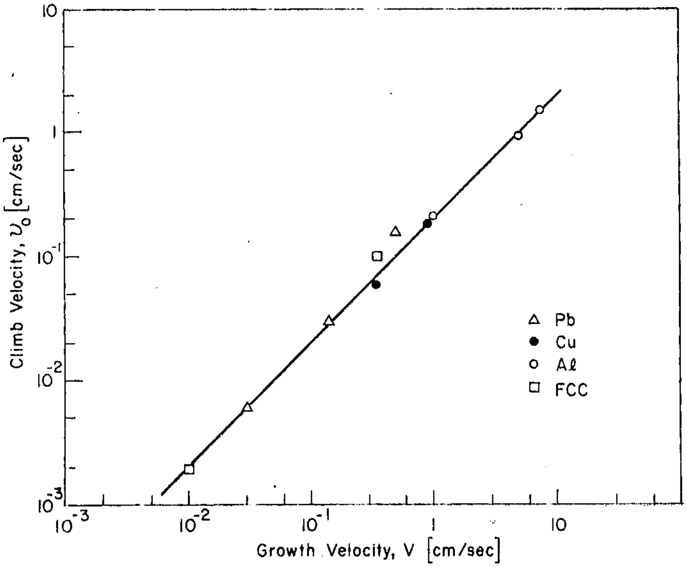
$$\frac{v_0 r}{2D_{\mathrm{v}}}\ln\left(\frac{2D_{\mathrm{v}}}{v_0 r}\right)=\pi\frac{r}{b}\Delta C. \qquad (17)$$

A calculation of the v_0 values for the three specified metals gives fig. 3† (this holds for many metals) and shows that the steady-state values are all less than the growth velocities no matter what the choice of V. We do however have the experiments for lead (Sekerka *et al.* 1960) at hand, along with the criteria developed here for the same metal from the work by Rastogi and Mukherjee (1970). Considering $V=3\times10^{-2}$ cm/sec as a safe

---

† Figure 3 was obtained first for the condition $\Delta T=0{\cdot}053\,T_{\mathrm{M}}$, the only critical value for controlled crystal growth, as used in the experiments of Sekerka *et al.* (1960). Values for V and the related v_0 were then calculated for aluminium, copper and the general f.c.c. metal at the same condition to obtain comparable results. The other points are for all the metals with $\Delta T=0$ (table 2 *b*) and for the two quenching experiments (table 2 *a*).

Fig. 3



Growth velocity is larger (by a constant factor) than the steady state climb velocity calculated for dislocation loops, using (*a*) the 'average f.c.c. metal' ($\Delta T_{\mathrm{min}}=0$; $\Delta T_{\mathrm{min}}=0{\cdot}053T_{\mathrm{m}}$), (*b*) Pb ($\Delta T_{\mathrm{min}}=0$; $\Delta T=32°\mathrm{c}$ (S, B & T); $\Delta T=0$ (R & M)), (*c*) Al ($\Delta T_{\mathrm{min}}=0$; $\Delta T_{\mathrm{min}}=0{\cdot}053T_{\mathrm{m}}$; $\Delta T_{\mathrm{min}}=160°\mathrm{c}$ (T & W)), (*d*) Cu ($\Delta T_{\mathrm{min}}=0$; $\Delta T_{\mathrm{min}}=0{\cdot}053T_{\mathrm{m}}$).

velocity for which striations would be stable in view of figs. 1 and 2 (even though they are for tin, not lead), and in view of the velocities since that time used for lead by one of the present authors in experiments like those of Sekerka *et al.* (1960), the criterion of climbing insufficiency seems suspect. That is, striations containing $\rho \sim 10^7\,\mathrm{cm}^{-2}$ dislocations do form in very pure lead at $V=3\times10^{-2}\,\mathrm{cm/sec}$ in the experiments of Sekerka *et al.*, when there is no seeming reason for their systematic formation.

Since eqn. (17) has been derived for steady-state dislocation loop climbing, it should not apply to the initial stage of loop expansion through climbing. (Here the existing forces are larger and should be sufficient to allow climbing to occur up to the region of surface image forces.) This we believe to be a fallacy in the application of Schoeck and Tiller's climb test when the differences in rate of climbing and crystal growth are small. The values of v_0 calculated from eqn. (17) are consistently smaller than V by a factor of 1/5 as shown in fig. 3. The correlation is too strong for coincidence to serve as an explanation; however, we cannot presently develop a proper solution for the non-steady-state climb problem.

§ 7. Remarks

The calculations presented here have depended upon disclosing a number of small points differing finally from those already existing in the literature. We have paid special attention to the entropy contribution of atoms in the dislocation core to the *free energy* of a dislocation loop. We have relied upon the experiments of Thomas and Willens (1964) and Rastogi and Mukherjee (1970), which show that an excess concentration of vacancies may be trapped in the solid by rapid freezing. We have adopted the viewpoint of Temkin (1964) that a solid–liquid interface must be treated as a diffuse entity, whether or not this be purely statistical artifice or completely proper interface description (see Bolling 1969). This adoption was then extended to the degree of calculation, for we have introduced Temkin's magnitudes to obtain the interface widths of this paper. In fact, it is just the results of using Temkin's calculations which allow us to note the important overall inconsistency between growth velocities and dislocation climb velocities as calculated by Schoeck and Tiller.

None of our calculations has been critically chosen to obtain the best justification of sets of numbers, and we may therefore feel confident about the plausibility of generating dislocations by vacancy condensation during growth from the melt. It is another matter to assume that dislocations naturally interact to produce striations. However, we are not satisfied by alternative mechanisms for the production of dislocations and striations suggested since Schoeck and Tiller (1960) seemed to eliminate the sequence starting with vacancies. For example, when Jaffrey and Chadwick (1968) presented some new observations on the appearance of striations they reviewed some of the field and paid special attention to the possible effects of foreign particles in producing dislocations. While the model they consider is acceptable, the interpretation of information in this field seems open to argument and does not seem clear enough for a balance in favour of any mechanism. Following the results we present, we recommend that the elegant mechanism of Teghtsoonian and Chalmers (1951) extended by Frank (1956) be reconsidered. For so many other simple reasons (such as the question of why striation boundaries are predominantly alternating tilt arrays: their climb preserves the arrays and eliminates vacancies) it has always been difficult to discard the mechanism now again suggested possible.

APPENDIX I

In order to calculate the trapped concentration of vacancies, we assume the existence of a diffuse solid–liquid interface. Such a gradual transition allows us to describe the interface as constituted partly by 'solid' and partly by 'liquid' atoms, and enables us to conceive of both free volume† and vacancies in the transition zone. Whatever the discrete form of vacancies, the concentration must decrease continuously from its value in the solid to zero in the liquid. The case for free volume is not so clear. Free volume must be zero in the solid; but, through the interface free

---

† Here we mean that quantity sometimes called 'excess free volume' in distinguishing liquids from solids. We retain the shorter name for a reason which follows.

volume is created as a result of the difference in density between liquid and solid. This might allow a local increase in the amount of free volume, above the bulk value to be achieved in the far-away liquid. Linear convective motion should nevertheless occur in the melt allowing it eventually to act as a sink for any of the 'extra' free volume created at the interface by the solidification (Chambré 1956). This flow depends on the growth velocity, so that the sink is more effective the higher the growth velocity.

In steady-state growth, the convective velocity must be constant, and thus the divergence of free volume at any plane across the interface plus the divergence of vacancies, must equal the vacancy excess divided by the mean free life of a vacancy in that plane. That is, for c_L as the liquid free volume, c_q as the vacancy concentration trapped in the solid, c_E as the equilibrium vacancy concentration, and V as the growth velcoity:

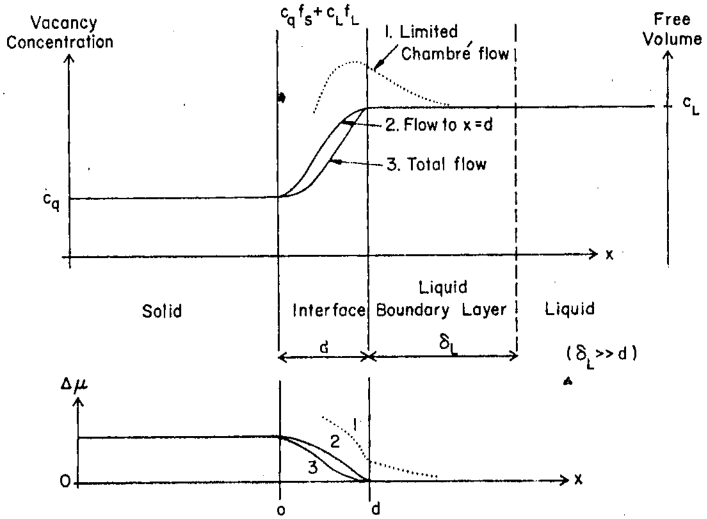
$$\operatorname{div}\,[(c_L+\Delta c_L(x))f_L(x)V]+\operatorname{div}\,[c_q(V,x)f_S(x)V] = \frac{c_q(V,x)-c_E(x)}{\tau(x)}f_S(x), \quad . \quad . \quad (A\ 1)$$

where f_S and f_L are the fractions of 'solid' and 'liquid' volumes respectively and all quantities are expressed per unit volume. τ is the mean time of escape within the boundary layer of a vacancy to be described for the plane considered. The integral of eqn. (A 1) can be expressed for the interface region extending from zero through d (as shown in fig. 4) as

$$[c_L+\Delta c_L(d)]V-c_qV=(c_q-c_E)\int_0^d \frac{f_S(x)}{\tau(x)}\,dx, \quad . \quad . \quad . \quad (A\ 2)$$

since $f_S(0)=f_L(d)=1$ and $f_S(d)=f_L(0)=0$.

Fig. 4



(*a*) Schematics of $c_q f_S + c_L f_L$ across the solid, the liquid and the solid–liquid interface. (*b*) Schematics of the chemical potential across the system.

Equation (A 2) has been obtained from the limit that the trapped vacancy concentration c_q is always less than $c_q(V,x)$. If we then assume that Δc_L, which is the excess free volume created at each plane and which of course depends upon the coordinate, has a value $\Delta c_L = 0$, independent of growth velocity, we also have a limiting assumption. In this instance a lower bound is obtained for $(c_q - c_E)$. The situation corresponds to a total Chambré inflow through the interface wherever there may be any 'liquid'. The assumption is clearly an outer bound no matter what the detail of the diffuse interface description, as shown in fig. 4.

We then proceed by taking the function $f_S(x)$ to vary linearly:

$$f_S(x) = 1 - \frac{x}{d}. \qquad \text{(A 3)}$$

And we can obtain an upper bound for the vacancy lifetime through a random walk approximation of the form†,

$$\tau = \frac{\langle l^2 \rangle_x}{D}, \qquad \text{(A 4)}$$

where D is the vacancy diffusion coefficient and $\langle l^2 \rangle_x$ must be such that its maximum value at $x = 0$ should be at least d^2, and its minimum value at $x = d$ should be zero, and so forth. Simple considerations, avoiding the fact that a vacancy can be annihilated at a plane inside the interface, combined with our desire to use an integrable function, lead to a form such as

$$\langle l^2 \rangle_x = d(d-x)/\lambda; \quad \lambda \leqslant 1.$$

(An alternative form $\langle l^2 \rangle_x = (d-x)^2$ is less critical than the one chosen, and is moreover non-integrable within useful limits.) The fact that the interface is moving at velocity V implies that $\tau = [d(d-x)/\lambda D]F(Vd/D)$; but for equilibrium we can derive a minimum value of $F(Vd/D) = F(0) = 1$. Use of both these extremes allows us to maintain our bound for the quantity $(c_q - c_E)$ when we write

$$\tau \geqslant d(d-x)/\lambda D. \qquad \text{(A 5)}$$

Integration of eqn. (A 2) then yields

$$(c_L - c_q)V \leqslant \frac{D}{d}(c_q - c_E). \qquad \text{(A 6)}$$

The lower limit here is identical to the expression obtained by Webb (1962), using a far more explicit development.

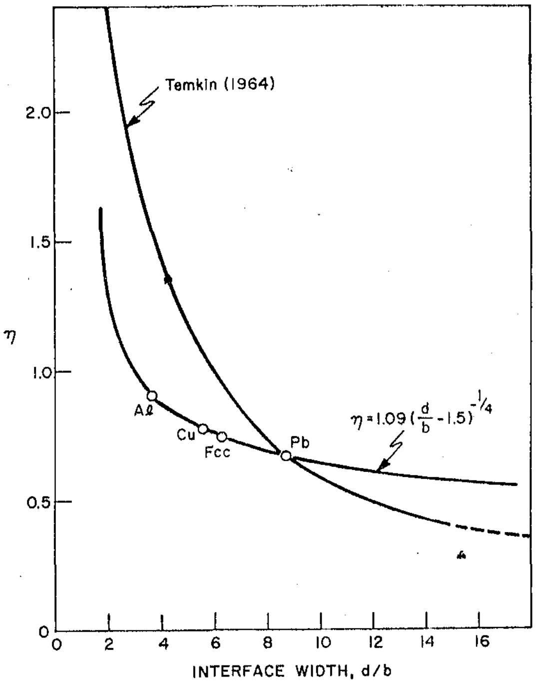
---

† Here it is assumed that recombination with interstitials is negligible.

APPENDIX II

Temkin (1964) studied the distribution of atoms within a solid–liquid interface by using a statistical thermodynamics. His model consists of a simple cubic lattice, limited by the elementary considerations of nearest neighbour atoms and equal solid and liquid densities. Even so, his analysis constructed in terms of the 'solid' fraction, f_S, in planes parallel to the interface with eminently proper boundary conditions, leads to an infinite set of simultaneous equations in terms of two parameters. The first of these, $\beta = \Delta\mu_{LS}/kT$, can be taken as zero at $T = T_m$ since $\Delta\mu_{LS}$ is the difference in chemical potential between the liquid and the solid and is negligible for growth rates of interest. The second parameter is $\eta = 4w/kT$, where w is the difference between a 'solid atom–liquid atom' bond energy and the mean energy of the solid–solid and liquid–liquid atom bonds. w can be related to the latent heat of fusion, and since for $T = T_m$ the solutions of the equations depend only upon the parameter η, a measure of the interface width may be obtained. Temkin presented the results of numerical computer calculations for four different values of η, leading to the curve shown in fig. 5.

Fig. 5



Plot of η versus the interface width from Appendix II following Temkin's analysis.

The metals, lead, aluminium and copper are not immediately adapted to fit Temkin's description. However, they are all face-centred cubic, and it should be at least plausible that some monotonic scaling is possible and that the solid–liquid interface width must be higher in Temkin's model than for any real f.c.c. metal. We therefore chose to position the metal lead at Temkin's value as shown in the figure, at the same time constructing a reasonable scale of distances so that aluminium gives us a value for fitting. (Although the latent heat of fusion was used for this positioning just as in Temkin's model it is only a rationalization, but alternative choices or procedures seem unjustified.) The same procedure applied without change to copper and the average f.c.c. metal gives good values that provide an overall consistency as discussed in § 6 of the text. Temkin's interface model, as we have used it, can then be regarded as a scaling guide or procedure with one adjustable parameter.

The choice of lead as a reference metal is based upon the fact that more information is available for lead about crystal growth and vacancies. However, there is a diversity among the values available for the self-diffusion coefficeint for lead at its melting point, a number needed in the text. We have chosen the highest value $\sim 10^{-5}\,\mathrm{cm}^2/\mathrm{sec}$ in accord with Oberdorfer and Grass (1970). Other values that may be derived from Miller (1969), Resing and Nachtrieb (1961), Nachtrieb and Handler (1955), Okkerse (1954) or Von Hevesy, Seith and Keil (1932) can give slightly lower values for D at 327°c. With adjusted parameters, these not only satisfy the matching of experimental results we try in the text, but can provide us with seemingly better interface widths (i.e. smaller values). Nevertheless, we understand the concept of interface width, as stated in § 5 of the text, in a way that does not suffer from the use of higher values. Therefore, the value chosen for lead is the most recent value, as for the other metals, and a more severely critical one.

ACKNOWLEDGMENTS

The authors are grateful for the constructive criticism offered by many of their colleagues, particularly Dr. A. D. Brailsford.

REFERENCES

ATWATER, H. A., and CHALMERS, B., 1957, *Can. J. Phys.*, **35**, 208.

BOLLING, G. F., 1969, *Can. Metall. Q.*, **8**, 183.

BUDIN, C., DENAYRON, F., LUCASSON, A., and LUCASSON, P. G., 1963, *C. r. hebd. Séanc. Acad. Sci. Paris*, **256**, 1518.

BURDEN, M. H., and JONES, H., 1970, *J. Inst. Metals*, **98**, 249.

CAHN, J., 1960, *Acta metall.*, **8**, 554.

CHAMBRÉ, P. L., 1956, *Q. Jl Mech. appl. Math.*, **9**, Pt. 2, 224.

CLINE, H. E., and LIVINGSTON, J. D., 1969, *Trans. metall. Soc. A.I.M.E.*, **245**, 1987.

COTTRELL, A. H., 1953, *Dislocations and Plastic Flow in Crystals* (Oxford University Press), p. 40.

Frank, F. C., 1956, *Deformation and Flow of Solids*, Madrid Conference (Springer-Verlag).

Franz, H., and Kroener, E., 1955, *Z. Metallk.*, **46,** 639.

Gallagher, P. C. J., 1970, *Met. Trans.*, **1,** 2429.

Hirth, J. P., and Lothe, J., 1968, *Theory of Dislocations* (McGraw-Hill).

Jackson, K. A., 1962 a, *Phil. Mag.*, **7,** 1117; 1962 b, *Ibid.*, **7,** 1615; 1965, *Acta metall.*, **13,** 1081.

Jaffrey, D., and Chadwick, G. A., 1968, *Phil. Mag.*, **18,** 573.

Köster, W., 1948, *Z. Metallk.*, **39,** 145.

Kuper, A., Letaw, H., Slifkin, L., Sonder, E., and Tomizuka, C. T., 1955, *Phys. Rev.*, **98,** 1870.

Miller, J. W., 1969, *Phys. Rev.*, **181,** 1095.

Nabarro, F. R. N., 1940, *Proc. phys. Soc.*, **52,** 90.

Nachtrieb, N. H., and Handler, G. S., 1955, *J. chem. Phys.*, **23,** 1569.

Nakamura, Y., 1961, *J. phys. Soc. Japan*, **16,** 2167.

Oberdorfer, N., and Grass, F., 1970, *Z. Metallk.*, **61,** 458.

Okkerse, B., 1954, *Acta metall.*, **2,** 551.

Piercy, C. R., 1960, *Phil. Mag.*, **5,** 201.

Rastogi, P. K., and Mukherjee, K., 1970, *Met. Trans.*, **1,** 2115.

Resing, H. A., and Nachtrieb, N. H., 1961, *J. Phys. Chem. Solids*, **21,** 40.

Schoeck, G., and Tiller, W. A., 1960, *Phil. Mag.*, **5,** 43.

Sekerka, R. F., Bolling, G. F., and Tiller, W. A., 1960, *Can. J. Phys.*, **38,** 883.

Simmons, R. O., and Balluffi, W., 1960 a, *Phys. Rev.*, **117,** 52; 1960 b, *Ibid.*, **119,** 600; 1962, *Ibid.*, **125,** 862; 1963, *Ibid.*, **129,** 1533.

Smithells, C. J., 1967, *Metals Reference Book*, Fourth edition (London: Butterworths).

Stoebe, T. G., and Dawson, H. I., 1970, Presented at the Spring Meeting of the Metallurgical Soc. of A.I.M.E. in Las Vegas, U.S.A.

Teghtsoonian, E., and Chalmers, B., 1951, *Can. J. Phys.*, **29,** 370; 1952, *Ibid.*, **30,** 388.

Temkin, D. E., 1964, *Crystallization Proceesss*, edited by N. N. Sirota, F. K. Gorski and V. M. Varikash (translated by Consultants Bureau, New York, 1966), p. 15.

Thomas, G., and Willens, R. H., 1964, *Acta metall.*, **12,** 191; 1966, *Ibid.*, **14,** 1385.

Turnbull, D., and Fisher, J. C., 1949, *J. chem. Phys.*, **17,** 71.

Von Hevesy, G., Seith, W., and Keil, A., 1932, *Z. Phys.*, **79,** 197.

Webb, W. W., 1962, *J. appl. Phys.*, **33,** 1961.

Wilson, J. R., 1965, *Metall. Rev.*, **10,** 381.

Yoffe, E. H., 1960, *Phil. Mag.*, **5,** 161.

Young, F. W., and Savage, J. R., 1964, *J. appl. Phys.*, **35,** 1917.