PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Theory of Melting

DORIS KUHLMANN-WILSDORF
School of Engineering and Applied Science, University of Virginia, Charlottesville, Vrginia

(Received 12 April 1965; revised manuscript received 6 October 1965)

A theory of melting is presented. It is based on the contention that melting occurs when the free energy of glide dislocation cores becomes negative. When this happens, dislocation cores are generated to fill the crystal to capacity. In the process the crystal absorbs a considerable amount of latent heat and loses all permanent resistance against shear forces. Equations are derived to relate the temperature of melting as well as the latent heat of fusion to known crystal properties, in addition to two parameters, α and X. These are related to the energy and dilatation of dislocation cores, respectively. Quantitative comparison of the theory with experimental data allows evaluating not α and X directly, but α/q and X/q, with q^{-1} the highest shear strain that can be supported by a defect-free crystal of the substance considered. From the geometry of dislocation cores, X/q can be calculated independently within rather narrow limits. For a wide variety of elements, including argon, typical fcc, hcp, alkali and bcc metals, silicon, and germanium, the values of X/q derived from the present theory agree very well with the values derived from core geometry. The data for α/q indicate that the latent heat of melting is nearly the same multiple of modulus of rigidity times the atomic volume, independent of crystal type. It is shown that the theory predicts a first-order transition. Suggestions are made of how the theory could be employed in investigations into properties of ideal crystals, crystal defects, liquids, and the electronic structure of atoms.

1. INTRODUCTION

THE problem of why crystals melt and how melting temperature and latent heat of fusion are determined has until now found no satisfactory solution. In the following, a theory will be proposed to account for the phenomenon of melting qualitatively and quantitatively. This theory is based on the contention that melting occurs when the free energy of dislocation cores assumes negative values. Some of the ideas presented in this paper were earlier discussed in papers by Mackenzie and Mott,[1,2] Rothstein,[3] Mizushima,[4] Ookawa,[5] and Siol.[6,6a]

2. BASIC PROPERTIES OF DISLOCATION CORES

a. Core Energy

It has been known for a considerable time that about 10% of the mechanical energy of a normal glide dislocation resides in its core, namely, that region very close to the dislocation axis which is so severely strained that Hooke's law does not apply. It is also well known that, because of the severely disturbed condition of the core, it is a center of dilatation. Consequently, the vibrational entropy of the dislocation core is not negligible.

Even through neither the mechanical energy of dislocation cores, nor the volume dilatation due to them, have as yet been evaluated accurately, there is general consensus that to a good approximation, the core energy per unit length of dislocation line U_c can be written as

$$U_c=(Gb^2\alpha)/4\pi. \qquad (1)$$

Here G is the modulus of rigidity, b is the Burgers vector of the dislocation, and α is a numerical factor, not far from 1, say, between $\frac{1}{2}$ and 4, more or less. The parameter α should almost certainly depend on crystal type, and one may expect it to rise with increasing width of the dislocation core, since the number of atoms included in the core does, of course, rise with the core radius.

In the majority of crystalline substances, anisotropy cannot be neglected. Correspondingly, G should be exchanged for a combination of the elastic constants, as, for example,

$$G=3c_{44}\frac{c_{11}-c_{12}}{4c_{44}+c_{11}-c_{12}}$$

for any dislocation on the close-packed planes in fcc crystals as proposed by Mackenzie and Mott,[1] or $[\frac{1}{2}c_{44}(c_{11}-c_{12})]^{1/2}$ for screw dislocations with $\frac{1}{2}\langle 110\rangle$, $\frac{1}{3}\langle 11\bar{2}0\rangle$ Burgers vectors respectively, on the close-packed plane of fcc and hcp crystals.[7]

In the present paper, this refinement has been neglected, partly for convenience sake, partly because the correct parameters are not easily available for the less intensely studied crystals, and partly because it is not yet clear what precise combination of elastic constants would be the most appropriate. It should be recognized, though, that the said refinement will be mandatory in detailed considerations of the theory presented here.

---

[1] J. K. Mackenzie and N. F. Mott, Proc. Phys. Soc. **63**, 411 (1950).
[2] N. F. Mott, Proc. Roy. Soc. **A215**, 1 (1952).
[3] J. Rothstein, J. Chem. Phys. **23**, 218 (1955).
[4] S. Mizushima, J. Phys. Soc. Japan **15**, 70 (1960).
[5] A. Ookawa, J. Phys. Soc. Japan **15**, 2191 (1960).
[6] M. Siol, Z. Physik **164**, 93 (1961).
[6a] *Note added in proof.* The author is indebted to Professor F. R. N. Nabarro, University of the Witwatersrand, Johannesburg, South Africa, and Professor A. Seeger, Stuttgart, Germany, for stimulating discussions and for directing her attention to the theories by Rothstein, Mizushima, and Siol.

[7] A. J. E. Foreman, Acta Met. **3**, 322 (1955).

b. Volume Dilatation in Dislocation Cores

The dilatation in the core may be estimated as follows: Consider a dislocation on the close-packed plane of a fcc or hcp crystal, with a Burgers vector equal to the nearest-neighbor distance. This is the most common, and at the same time most important dislocation in the named structures, and it is believed to be the decisive one also in the present theory. The path on which the atoms on one side of the glide plane move relative to the atoms on the other side, when a dislocation moves past, can be either of the two extremes indicated in Fig. 1(a), or, commonly, will be intermediate between these. Since the crystal is close packed, the two atomic planes facing each other across the slip plane must thereby "ride up" against each other, i.e., must slightly increase their normal distance of separation. If the lower, straight path is taken, then the greatest separation occurs in the position marked AA, which is sketched in cross section in Fig. 1(b). As seen, the distance of separation between the planes in this position is $(11/12)^{1/2}b$, with b the Burgers vector, as before, compared to the normal separation between neighboring $\{111\}$ planes of $(\frac{2}{3})^{1/2}b$. Thus the separation has increased by

$$\Delta h = [(11/12)^{1/2} - (\tfrac{2}{3})^{1/2}]b \cong 0.141b.$$

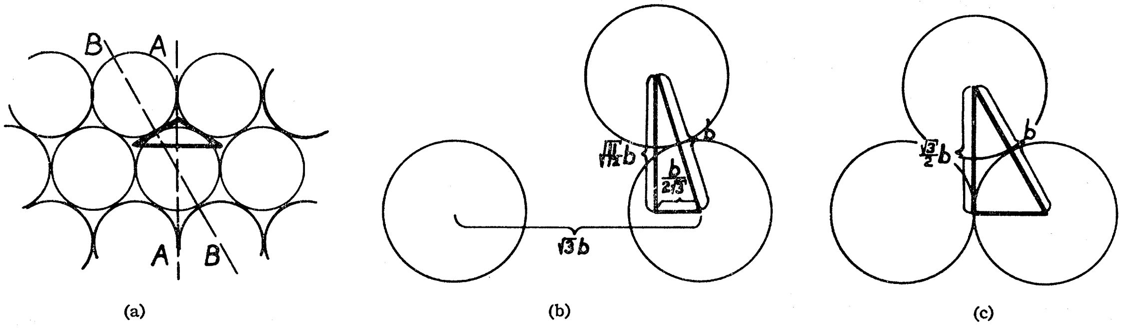
This riding-up effect becomes marked at the rim of the dislocation core, reaches its maximum at the center, and drops again to almost zero at the other rim of the core. Therefore, if the radius of the core on the slip plane is given by r_0, the volume increase due to a core segment of length b, becomes $\Delta V \cong r_0 b \Delta h$.

Previously,[8] r_0 was evaluated as $r_0 = qb/2\pi$. Here q is a numerical parameter, characteristic of any given crystal structure, fairly independent of the special substance considered. Briefly, $1/q$ is the largest shear deformation, parallel to the crystallographic slip plane, which the dislocation-free crystal could support. For the close-packed planes in fcc and hcp crystals, q is believed[9] to be not far from 30, while it is estimated at about 15 for bcc crystals, and 7 for crystals with the diamond structure. Thus, $\Delta V = 0.141(qb^3/2\pi) \cong 1.0 v_s$ is the dilatation in the core per length of b for the lower path of Fig. 1(a), introducing $v_s = b^3/\sqrt{2}$ as the space available per atom in the close-packed structures.

If, on the other hand, the atomic path goes via the stacking fault position, then maximum dilatation occurs in position BB [Fig. 1(c)]. Now $\Delta h = (\sqrt{3}/2 - \sqrt{\frac{2}{3}})b \cong 0.049b$, so that ΔV in this case becomes $\Delta V = 0.33 v_s$. Actually, this latter value will never be reached since it requires a very widely split dislocation, in which case one must consider the two partials separately. For each of these, $|b_p| = |b|/3$. Thus $\Delta V = (2/\sqrt{3}) \times 0.33 v_s = 0.38 v_s$ is the smallest value ΔV could assume in fcc and hcp metals on the basis of this consideration, and this will be found only if the stacking fault energy is quite low. In addition, some volume dilatation must occur because of non-Hookean behavior, i.e., because of the quadratic and higher terms in the stress-strain relationship. Conversely, the riding-up effect considered here may be slightly decreased through compression of the atoms.

In non-close-packed crystals, the volume dilatation presumably is smaller, mainly because q is smaller so that the cores are narrower. This decrease in ΔV must be partly counterbalanced by the greater intensity of the stresses in the cores, causing a greater contribution due to anharmonicity. Still, in first approximation, we expect $\Delta V/q$ to be roughly constant for fcc and hcp, with anharmonicity causing $\Delta V/q$ to be a little higher in diamond structures, and bcc lattices having similar values of $\Delta V/q$ as the others, probably intermediate between fcc and diamond structures.

In summary, then, and introducing the parameter



(a) (b) (c)

Fig. 1. (a) Geometry of the path taken by atoms in the core of a moving dislocation on a close-packed plane in either hcp or fcc crystals. The Burgers vector is the nearest-neighbor distance in the horizontal direction. The upper, kinked path would be taken if the stacking fault energy is very low, while the lower, straight path refers to a very high stacking fault energy. Actual atomic paths are intermediate between the two extremes drawn. (b) Vertical cross section through the atomic arrangement when a moving atom has reached the line AA marked in (a), for the case of a very high stacking fault energy. (c) As (b), but referring to line BB at very low stacking fault energies.

---

[8] Doris Kuhlmann-Wilsdorf, Phys. Rev. **120**, 773 (1960); J. Appl. Phys. **36**, 637 (1965).

[9] J. K. Mackenzie, Ph.D. thesis, Bristol, 1949 (unpublished); see A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (The Clarendon Press, Oxford, England, 1953), p. 10.

$X=\Delta V/v_s$ as the dilatation per length of b due to dislocation cores in multiples of $b^3/\sqrt{2}$, we find that X should be no less than $\cong 0.38$ in close-packed metals, rising with increasing stacking fault energy to, say, 1 or perhaps slightly more. In other crystals, X should be lower than in close-packed crystals, dropping with decreasing values of the parameter q, but such that X/q is quite slowly increasing with decreasing values of q. The value of X/q should range between ~ 0.013 and ~ 0.032 in close-packed metals, as calculated above, and should be slightly higher in bcc and diamond-type structures, in that order.

c. Vibrational Entropy of Dislocation Cores

The vibrational entropy of a crystal increases with increasing volume. According to the Grüneisen relationship, vibrational modes of original frequency ν assume the frequency ν' if the crystal volume is increased from V to V' such that $(\nu'-\nu)/\nu=-g(V'-V)/V$, where g is the Grüneisen constant. The vibrational entropy of the crystal is thereby changed by

$$\Delta S=k\sum_{j=1}^{3N}\ln(\nu'/\nu)\,,$$

to be summed over the $3N$ vibrational modes of the crystal containing N atoms. Since the frequency changes, as well as the volume changes to be considered are small, we may write

$$\ln(\nu'/\nu)=\ln[(\nu-\Delta\nu)/\nu]=-\Delta\nu/\nu$$

and

$$(V'-V)/V=\Delta V/V\,,\quad \text{i.e.,}\quad \ln(\nu'/\nu)=g(\Delta V/V)$$

and

$$\Delta S=3gNk\Delta V/V\,.$$

A crystal containing a total length of ρ_c of dislocation cores per unit volume is, as we saw, dilated such that $\Delta V/V=X\rho_c/Nb$. Here X is the same number derived in the previous section and found to lie between 0.38 and 1.0 in close-packed crystals. Thus the entropy per unit length of dislocation core is found as $S_c=3gNk\times(\Delta V/V)/\rho_c$, where $\Delta V/V=X\rho_c/Nb$, i.e.,[10]

$$S_c=3gkX/b\,. \tag{2}$$

d. Thermal Generation of Dislocation Cores

Dislocation cores must be generated spontaneously, as soon as their free energy, $F_c=U_c-TS_c$, becomes equal to or smaller than zero. Therefore a critical temperature must exist beyond which dislocation cores are generated freely, given by

$$T_c=\frac{U_c}{S_c}=\frac{Gb^3\alpha}{12\pi gkX}\,. \tag{3}$$

The result of the prolific generation of dislocation dipoles would be the absorption of a considerable amount of latent heat and the complete loss of any permanent resistance to shear stresses. Most other important crystal properties would be changed to only a moderate extent, except that diffusion would be notably enhanced since all of it would now be "pipe" diffusion.

3. CRITICAL TEMPERATURE OF DISLOCATION CORE GENERATION

In order to see whether the contemplated dislocation-core generation could or does take place, the critical temperature T_c must be calculated. To this end, the requisite data for some important elements have been collected in Table I. Not all of the quoted values are altogether reliable, and particularly the values of G (taken at the melting point) may be partly in error by up to 30%. The various parameters have been obtained from Refs. 11 to 16. Besides the quantities discussed, the molar latent heat of fusion has been listed under the symbol L_M, and also listed are the ratios L_M/T_M. According to Richard's rule, L_M/T_M usually has a value near 2, as is also evident from the values of L_M/T_M given in Table I.

In the column labeled $X/\alpha=(X/\alpha)T_c/T_M$, the calculated values of $(X/\alpha)T_c=Gb^3/12\pi gk$ [Eq. (3)] have been compared to T_M, the temperature of melting. The ratio $(X/\alpha)T_c/T_M$ is seen to lie between the extreme values of 0.21 and 1.58, with most values at about 0.5 ± 0.2. Evidently, then, if X/α had assumed these values, the critical temperature T_c would *be* the temperature of melting. Since we saw above that $0.38\lesssim X\lesssim 1$ and $\frac{1}{2}\lesssim\alpha\lesssim 4$, so that X/α should lie in this very range of values, it is a most tempting idea indeed to equate T_c with T_M. Not only that, but, by the following argument, the hypothesis that melting occurs when the free energy of dislocation cores becomes zero, can be virtually proven correct:

---

[10] The use of Eq. (2) in the further development of the present theory does not imply that the vibrational modes affected by the presence of a dislocation core are necessarily distributed. The reason is that the size of the crystal volume considered, and thus the number N in the above derivation, does not appear in the final equation. Thus the modes could well be localized, and correspondingly a rather small volume around a single core would have to be considered, but the final equation arrived at would be the same. In the present theory, moreover, no difficulties arise due to the uncertainty as to how far reaching the influence of cores on the lattice vibrations is, because the melting temperature depends on the formation of larger clusters of close-packed dipoles (see Sec. 4.a). Within these clusters, the volume expansion must be nearly uniform, and therefore, Eq. (2) must apply to a good accuracy.

[11] *Metals Handbook*, Am. Soc. Metals, Vol. 1, 1961.

[12] A. Eucken, *Grundriss der Physikalischen Chemie* (Akad. Verlags Ges., Leipzig, 1944).

[13] G. Masing, *Lehrbuch der allgemeinen Metallkunde* (Springer-Verlag, Berlin, 1950).

[14] E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 516 (1957).

[15] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936).

[16] B. R. T. Frost, Progr. Metal Phys. **5**, 96 (1954).

TABLE I. The relevant experimental parameters of 20 different elements, namely, G the modulus of rigidity, b the distance between nearest-neighbor atoms, g Grüneisen's constant, T_M the temperature of melting, L_M the molar latent heat of melting, and L_M/T_M the entropy of melting, together with calculated values of the basic parameters employed in the present theory, namely, α the extra energy possessed by unit length of the most common dislocation core in units of $Gb^2/4\pi$, and X the volume of dilatation per unit length of the same dislocation core, in units of $b^2/\sqrt{2}$. The listed values of X/α have been calculated from the hypothesis that the temperature of melting is that temperature at which the free energy of the cores of the most common dislocations vanishes. From Lindemann's relationship[a] it would follow that $g(X/\alpha)$ is nearly constant. The parameter X/q cannot only be calculated directly from the present theory, yielding the values listed, but also from geometrical considerations. The latter yield $0.013 \lesssim X/q \lesssim 0.032$ for fcc and hcp substances, and in average slightly larger values for bcc and diamond structures, in that order, as explained in Sec. 2b. (The number of significant figures retained is not meant to imply the corresponding accuracy.)

Substance	Lattice	b [Å][b]	10^{-11} G[b] [dyn/cm²]	g	T_M [°K]	$L_M\left[\frac{\text{cal}}{\text{mole}}\right]$	L_M/T_M $\left[\frac{\text{cal}}{\text{mole°K}}\right]$	X/α $=T_c(X/\alpha)/T_M$	α	X	X/q	gX/α
Ar	fcc	3.74	0.10	2.8	84	280	3.33	0.43	2.09	0.90	0.030	1.20
Al	fcc	2.93	1.90	2.17	932	2310	2.48	0.45	1.89	0.86	0.029	0.98
Cu	fcc	2.60	2.78	1.96	1356	3100	2.29	0.35	2.48	0.88	0.029	0.69
Ag	fcc	2.95	1.76	2.40	1233	2690	2.18	0.29	2.33	0.68	0.023	0.70
Au	fcc	2.94	1.69	3.03	1336	3050	2.28	0.21	2.77	0.57	0.019	0.62
Ni	fcc	2.54	4.50	1.88	1723	4240	2.46	0.44	2.23	0.98	0.033	0.83
Pb	fcc	3.54	0.45	2.73	600	1160	1.93	0.24	2.26	0.53	0.018	0.65
Pt	fcc	2.83	3.73	2.54	2045	5300	2.59	0.31	2.45	0.77	0.026	0.80
Co	fcc(hcp)	3.56	4.56	1.87	1764	3440	1.95	0.45	1.75	0.78	0.026	0.83
Mg	hcp	3.26	1.24	1.51	923	1750	1.90	0.60	1.37	0.82	0.027	0.90
Zn	hcp	2.72	2.65	2.01	692	1740	2.52	0.74	1.12	0.83	0.028	1.48
Cd	hcp	3.04	1.72	2.19	594	1380	2.32	0.72	1.12	0.80	0.027	1.56
Li	bcc	3.09	0.43	1.17	452	690	1.53	0.46	0.98	0.45	0.030	0.54
Na	bcc	3.80	0.34	1.25	370	630	1.70	0.78	0.61	0.47	0.031	0.97
K	bcc	4.72	0.13	1.34	337	570	1.69	0.58	0.75	0.44	0.029	0.78
Fe	bcc	2.53	5.0	1.60	1807	3658	2.02	0.54	0.81	0.44	0.029	0.86
Mo	bcc	2.79	7.3	1.57	2900	6700	2.31	0.67	0.76	0.51	0.034	1.05
W	bcc	2.80	9.09	1.62	3660	8100	2.21	0.65	0.73	0.47	0.032	1.05
Ge	diamond	4.09	2.96	2(?)	1231	8100	6.57	1.58	0.17	0.27	0.038	3.16
Si	diamond	3.92	3.82	2(?)	1694	12150	7.18	1.30	0.22	0.29	0.041	2.60

[a] See Ref. 17.

[b] Values at or near the melting point.

We shall postulate that the melting point is *not* equal to the critical temperature T_c at which unlimited generation of dislocation-core dipoles occurs. If this is so, and seeing that T_c involves the two parameters X and α, which depend in complicated ways on stacking fault energy, critical shear deformation, and probably still other crystal properties, we must conclude that T_c must be smaller than T_M at least in *some* cases. The result of this occurrence would be that the crystal, even though not molten, would lose all permanent resistance to shear stresses and would absorb a considerable amount of latent heat. At a higher temperature it would then melt. Such behavior is entirely unknown, and no two classes of substances exist, namely, those which lose their resistance to shear through melting and those which lose it through dislocation-core formation followed by melting. Consequently, the above postulate must be wrong and we conclude that, indeed, melting is a phase transformation occurring when the free energy of glide dislocation cores reaches zero.[16a]

In the subsequent sections, this conclusion is examined in qualitative and quantitative detail.

4. QUALITATIVE CONSIDERATIONS ON MELTING

a. Approach to Melting

The free energy of even the smallest isolated glide dislocation loops and of isolated narrow glide dislocation dipoles contains a significant contribution due to their elastic stress field. The idealization that *only* the core energy needs to be considered, which is the basis of Eq. (3), holds true only for large groups of closely spaced dipoles which, through their mobility, screen each other's stress fields. The energy of the unscreened stress field at the surfaces of close groups of dislocation cores is thus seen as the surface energy between a crystal and its melt.

At the melting point, the chemical potentials of melt and crystal phase must necessarily be the same, since at that temperature these two phases are in equilibrium. In the framework of the present theory, this requirement is fulfilled automatically, as the melt is generated from the crystalline phase by the addition of dislocation cores whose free energy vanishes at the melting point—by definition of the temperature of melting.

While it has not yet been possible to develop a satisfactory detailed treatment of the melting process, it is easily shown that it must be a first-order transition.

[16a] *Note added in proof.* Liquid crystals are seen as substances for which the relevant parameters, and thus T_c, have widely different values with respect to different directions.

Namely, the lowest energy configuration in which a section of dislocation core could arise through thermal activation within a volume element of undisturbed crystal is a glide dislocation loop of radius $R=r_0=gb/2\pi$. At the melting point, the contribution of its core to the free energy of the crystal, excepting configurational entropy, vanishes according to the present theory. The associated elastic stress field contributes a strain energy of magnitude[17]

$$[Gb^2R(2-\nu)/4(1-\nu)]\ln(8R/r_0-2) \\ =[Gb^3q(2-\nu)\ln6]/8\pi(1-\nu),$$

but virtually no vibrational entropy. Hence, the concentration of such loops (with any one combination of slip plane and Burgers vector) at the melting point is found as

$$C_L=\exp[-3qgX(2-\nu)\ln6/2\alpha(1-\nu)],$$

or, $C_L\lesssim\exp(-30)$ according to the data of Table I. Thus the concentration of dislocation cores in the crystal at its melting point is vanishingly small, precluding any significant interaction between them. Conversely, in the liquid at the melting point, the regions of order to serve as nuclei for solidification must be similarly small, since at their surface unscreened stress fields of similar energy must exist.

The fact that superheating beyond the melting point is by far less common than supercooling is consistent with the preceding consideration. Namely, slip motions by ordinary glide dislocations, particularly where they are joined at nodes, can generate interpenetrating close groups of dislocation dipoles. Hence, dislocation nodes will act as nuclei for melting. These are almost universally present in actual specimens, and only particular specimens not containing nodes (and perhaps other similarly complex crystal defects) could be expected to show superheating. Corresponding nuclei of crystal do not exist in the melt as considered in this theory and, therefore, supercooling can be accounted for.

In the present paper, configurational entropy has been disregarded throughout, except for that contribution which is due to the number of ways in which a small concentration of cores can be arranged in a crystal. The reasons for this procedure are these: The atoms within an isolated stationary core have fixed equilibrium positions with respect to the surrounding lattice, and consequently do not contribute to configurational entropy. Nor do the cores in the liquid have configurational entropy since they fill the crystal to capacity and actually have lost their identity. However, in the melt the atoms themselves greatly contribute to configurational entropy since the reference lattice has been destroyed. Therefore, as long as only the chemical potential of the solid is considered, in combination with the latent heat of melting, as is done in this theory, configurational entropy may be disregarded. This is at once a strength and a weakness of the theory. On the one hand, numerical results can be derived without involving configurational entropy which cannot readily be calculated, while at the same time the deeper understanding of the liquid state would doubtlessly require a good grasp of its configurational entropy.

It is somewhat problematical to what extent the liquid can be regarded as a solid filled with dislocation cores. Certainly no ordered structure of mutually perpendicular grids of dislocation cores is envisaged, but the cores interpenetrate to the point that single cores can no longer be distinguished. However, the state of the average atom in the melt is believed to be similar to that of an atom at the intersection point of two or more cores.

b. Alloys

The influence of alloying on the temperature of melting is partly governed by the accompanying changes in the values of G and g. However, very often a much greater influence will be exerted via the parameters α and X.

One may immediately conclude that in dilute mixed crystals α is bound to be smaller than in the pure crystal, since every type of binding between dislocation cores and substitutional as well as interstitial atoms decreases the core energy. Therefore it is not surprising that the usual effect of alloying is to decrease the melting point, i.e., to decrease the solidus temperature. Similarly, one can conclude that, in close-packed metals, the parameter X will usually be decreased through alloying. The reason lies in the tendency of alloying to decrease the stacking fault energy, and, as discussed in Sec. 2b, the parameter X is expected to be near 0.38 for close-packed metals with very small stacking fault energy, rising to about 1.0 at the highest stacking fault energies. Thus, if not overbalanced by an increase in α, the effect of alloying on X must be to raise T_M.

The above considerations thus suggest that, usually, alloying decreases T_M, but that alloying of fcc or hcp metals, particularly with substances of similar atomic radii so that Cottrell binding is slight, may raise the melting point. By scanning a considerable number of constitution diagrams of metals, the above conclusion appears to be confirmed. Namely, only the following cases were found in which dilute mixed crystals exhibit a higher melting point than the pure metal: Au+Pd, Au+Pt, Cd+Mg, Co+W, Cu+Co, Cu+Fe, Cu+Ni, Cu+Pd, Cu+Pt, Pb+Cu, Zn+Ag, Mo+W, and Zn+Cu. With the exception of Mo+W, for which the solidus line is almost straight between the two melting temperatures, suggesting an influence on T_M via G, all combinations listed concern close-packed metals, susceptible to the described effect of the lowering of the value of X to raise T_M. The case of Mo+W is not surprising either, since these two metals form a contin-

---

[17] Y. T. Chou and J. D. Eshelby, J. Mech. Phys. Solids **10**, 27 (1962).

uous range of mixed crystals, and since, according to Table I, their respective X/α values are closely alike.

Clearly, also in the other cases, the influence of G on T_M must be at least partly responsible for the positive value of dT_M/dc, but at least it is gratifying that no violations of any of the above considerations have been found. It would therefore seem feasible to study the magnitude of Cottrell interaction energies, as well as the influence of alloying on the stacking fault energy, via measured values of dT_M/dc.

c. Amorphous Substances and Organic Crystals

Materials, in which for geometrical or other reasons dislocations cannot form, do not show a definite temperature of melting. In particular, dislocations cannot be generated in amorphous substances, and correspondingly these exhibit no melting point. Conversely, we may say with better logic that in the amorphous state—as in the liquid—the density of dislocation dipoles is extremely high already. The effect of temperature on amorphous materials then consists solely in increasing the mobility of the dislocation cores in them.

Dislocations cannot be formed readily in crystals in which the smallest possible Burgers vector for glide dislocations is large, mainly because U_c is proportional to b^2. This applies to many crystals of organic substances and explains why these frequently decompose before their melting point is reached.

d. Sublimation

The argument was made above that *if* T_c and T_M were independent temperatures, then T_c should at least occasionally be smaller than T_M and therefore two classes of substances should exist: (1) substances which lose their resistance to shear because their temperature rises above T_c even while T_M is not reached, and (2) substances which melt before T_c is attained. Because of the fact that two such classes of substances do not exist, and that the anticipated behavior of a crystal when T_c is exceeded is that observed on melting, we concluded that T_M and T_c are one and the same temperature.

With respect to T_V, the temperature of vaporization as a function of pressure, however, the anticipated two classes of substances, those with $T_c<T_V$ and for which $T_c>T_V$, do indeed exist. The former are the substances exhibiting the usual transition solid ↔ liquid ↔ vapor, the latter evaporate before melting. Into this group belong many inorganic compounds, which is not surprising because of the large lattice constants and, hence, large Burgers vectors, in these.

5. QUANTITATIVE ANALYSIS

a. The Latent Heat of Fusion

Employing the model that the liquid is but a solid with such a high concentration of dislocation cores that these are in contact everywhere, the molar latent heat of fusion may be given as

$$L_M=U_c\rho_c(A/d)\,, \tag{4}$$

where ρ_c is the density of the dislocation cores in the liquid (given as line length per unit volume), A is the atomic weight, and d is the mechanical density.

In Sec. 2b above, the radius of a dislocation core in its slip plane was introduced as $r_0=qb/2\pi$. Logically, then, on any given atomistic slip plane the dislocation cores cannot be more closely spaced than a distance $2r_0$ apart. The normal distance of separation between adjacent cores will be about equal to the atomic diameter, with the core centers staggered, of course. Finally, the shears leading to the cores are acting independently on three mutually perpendicular planes, corresponding to the shear stress components τ_{xy}, τ_{yz}, and τ_{zx}. Thus we expect three times the core density that could be achieved in one dimension, and hence obtain

$$\rho_c=\frac{3}{2r_0b}=\frac{3\pi}{qb^2}\,. \tag{5}$$

Combining Eqs. (1), (4), and (5) then yields

$$L_M=\frac{3AG\alpha}{4dq}\,, \tag{6a}$$

which may be rewritten as

$$L_M=\frac{\pi NGb^3\alpha}{8pq}\,, \tag{7}$$

with N Avogadro's number and p the "volume occupancy" of the crystal, since b is generally equal to the atomic diameter, leading to $A/(Nd)=\pi b^3/6p$.

It is interesting to note that Eq. (6a) can be derived by an alternative path: In the melt, each atom partakes in three mutually perpendicular dislocation cores. It therefore posesses three times the energy of an atom in the center of a dislocation in the solid, which equals, say, twice the energy U_c divided by the number of atoms in the core. The number of atoms partaking in unit length of core may be taken as $4r_0b/v_s$, where v_s is the space available per atom in the crystal. Thus

$$\frac{L_M}{N}\simeq\frac{6U_cv_s}{4r_0b}=\frac{3G\alpha v_s}{4q}\,. \tag{6b}$$

It is $v_s=A/dN$, while the volume of each atom equals $v=(4\pi/3)(b/2)^3=\pi b^3/6$. The "volume occupancy" p is defined as space occupied by the atoms divided by space available, i.e., $p=v/v_s$, so that $v_s=v/p=\pi b^3/6p=A/dN$. Hence

$$L_M=\frac{3AG\alpha}{4qd}=\frac{\pi Gb^3\alpha N}{8pq} \tag{6c}$$

as before.

b. Richard's Law

Of considerable interest in a theory of melting must necessarily be the ratio of L_M/T_M. For many metals, this is known to be close to the gas constant R, i.e., close to 2 cal/mole °K, a relationship known as Richard's law. Combining, then, Eqs. (3) and (7), one obtains

$$\frac{L_M}{T_M}=\frac{L_M}{T_c}=\frac{3\pi^2 gX}{2pq}R=BR. \tag{8}$$

For fcc metals, for which Richard's rule is rather well obeyed, $3\pi^2\cong q$ and $g\cong 2$, so that, with $p\cong\frac{3}{4}$, one obtains $B\cong\frac{4}{3}X$. As argued in Sec. 2b above, $0.38\lesssim X\lesssim 1.0$ so that B is expected to be near unity, in agreement with Richard's law.

c. Correlation between the Entropy of Melting and Ductility

Masing (Ref. 13, p. 214) has reported that G. Tammann believed the low value of L_M/T_M in metals (as compared to organic crystals in which L_M/T_M often lies between 12 and 15) to be correlated with their greater ductility. Subsequent tests by Masing and Miething on organic crystals apparently confirmed that, indeed, a correlation between the value L_M/T_M and ductility exists, inasmuch as organic crystals with low values of L_M/T_M could be readily deformed, while those with high values of L_M/T_M were brittle up to near the melting temperature. This report, even though not detailed enough to permit a quantitative analysis, is highly interesting in connection with Eq. (8), according to which L_M/T_M is inversely proportional to q, namely, as shown in an earlier paper,[8] τ_D, the stress required to move glide dislocations, the so-called Peierls-Nabarro stress, is inversely proportional to q^2. It was given[8] as $\tau_D=G\pi/4q^2$. Hence one may write

$$\frac{L_M}{T_M}=\frac{3\pi^{3/2}gXR}{p}\left(\frac{\tau_D}{G}\right)^{1/2}. \tag{9}$$

It would be interesting to make experiments on various organic crystals—in which one may expect τ_D to govern the yield stress—in order to test Eq. (9).

d. Lindemann's Formula

Lindemann[18] has derived an empirical relationship between the temperature of melting, the Debye temperature Θ_D, the atomic weight A, and the molar volume V, of the form

$$T_M=\Theta_D^2 A V^{2/3}/C_L^2, \tag{10}$$

where C_L is a numerical constant ranging about 140 for fcc metals[15] when expressed in cgs units. One may rewrite this formula by employing the relationship[15]

$$\Theta_D=C_D A^{-1/3} d^{-1/6} K^{-1/2} f^{-1/3}, \tag{11}$$

in which d represents the density, K the compressibility, and f is a function of Poisson's ratio, such that, approximately, $f=2(KG)^{-3/2}$. The constant C_D has the value 3.6×10^{-3} in centimeter-gram-second units. With $K^{1/2}f^{1/3}$ thus equal to about $2^{1/3}G^{-1/2}$, one obtains

$$\Theta_D\cong 2^{-1/3}C_D A^{-1/3} d^{-1/6} G^{1/2}. \tag{12}$$

Inserting Eq. (12) into Eq. (10) yields

$$T_M=\frac{C_D^2 G A^{1/3} V^{2/3}}{2^{2/3}C_L^2 d^{1/3}}. \tag{13}$$

Remembering that $V=A/d$ and that $\pi b^3/6p=A/dN$, as derived in Sec. 5a above, we finally obtain

$$T_M=\frac{C_D^2 N\pi}{2^{2/3}C_L^2 6p}Gb^3\cong 2\times 10^{14}Gb^3. \tag{14}$$

This may be compared with Eq. (3), which renders

$$T_M\cong 2\times 10^{14}\frac{\alpha}{gX}Gb^3, \tag{15}$$

in good agreement with Eq. (14) since α/gX is not far from unity.

The implication that $g(X/\alpha)$ should be nearly constant for those substances for which Lindemann's formula holds, seems to be fulfilled, as seen from Table I. One should remember, though, that an approximation was made when putting $f=2/(KG)^{1/2}$, so that $\Theta_D\propto G^{1/2}$, while in reality Θ_D is also a function of Poisson's ratio.

e. Thermal Expansion at the Melting Point

For typical metals, the total thermal expansion between absolute zero temperature and the melting point amounts to about 7%. This relationship was first noted by Grüneisen in 1910. On the basis of this empirical relationship, it has often beens urmised that a critical amplitude of vibration of the atoms is required for melting, which also is the underlying idea in Lindemann's relationship. In the framework of the present theory, the Grüneisen relationship finds the following explanation:

The mechanical compressibility K, Grüneisen's constant g, the relative thermal expansion $\Delta v/v$, and the thermal energy density stored in the vibrational modes E are related as

$$\Delta v/v\cong KgE. \tag{16}$$

At high temperatures, $E=3RT/V$, where R is the gas constant and V the molar volume, as before. Experimentally, then, it is found that

$$\Delta v/v_{T_M}\cong K3gRT_M/V\cong 0.07. \tag{17}$$

Since the compressibility is connected to the modulus of rigidity as $K=3(1-2n)/2(1+n)G$, where n is

---

[18] F. A. Lindemann, Z. Physik **11**, 609 (1910).

Poisson's ratio, and since $V=A/d=\pi Nb^3/6p$, as introduced in the preceding sections, we may rewrite Eq. (17) as

$$T_M=\frac{Gb^3}{3gk}\frac{\pi(1+n)}{9p(1-2n)}\left(\frac{\Delta v}{v}\right)_{T_M}. \tag{18}$$

This is to be compared with

$$T_M=\frac{Gb^3}{3gk}\frac{\alpha}{4\pi X}, \tag{19}$$

according to Eq. (3).

For fcc metals obeying the Grüneisen relationship, $\pi(1+n)/9p(1-2n)$ has values about 3, while X/α is about 0.4, rendering $\alpha/4\pi X\cong 0.2$, so that one obtains

$$\left(\frac{\Delta v}{v}\right)_{T_M}\cong\frac{\alpha}{4\pi X}\bigg/\frac{\pi(1+n)}{9p(1-2n)}\cong 0.07,$$

in agreement with experiment. Moreover, as suggested by Eqs. (18) and (19), $(\alpha/X)/[(1+n)/p(1-2n)]$ tends to be constant. It ranges from 0.24 to 0.49 with a mean of 0.36 for the 17 metals listed in Table I, i.e., the spread is in the ratio of 1:2.0 from the lowest to the highest value found. By contrast, $(1+n)/(1-2n)$ ranges in the ratio 1:4.1, and X/α in the ratio 1:3.7. Employing the mean value of 0.36, one obtains $(\Delta v/v)_{T_M}=8.2\%$.

For the fcc metals, the scatter in the values of $(\alpha/X)/[(1+n)/p(1-2n)]$ is still smaller, ranging between 0.38 and 0.48, i.e., in the ratio 1:1.28 with the mean at 0.43. This scatter is smaller than one would have expected in view of the uncertainty in the experimental values of G and in view of the fact that anisotropy was not taken into account. The inference is that the latent heat of melting, as well as the energy in the dislocation core, might better be expressed in terms of the compressibility K, rather than the modulus of rigidity G, as done in this paper.

6. NUMERICAL RESULTS AND DISCUSSION

a. General

With the parameters listed in Table I, and employing the theoretical relationships for L_M and L_M/T_M [Eqs. (7) and (8)], the values of α and X have been calculated for a wide variety of elements as listed in Table I. The melting temperatures involved ranged between the extreme limits of 84 and 3660°K, the latent heats of fusion between 280 and 12 150 cal/mole. As may be seen, the values obtained for X, the volume dilatation due to a length b of dislocation core in units of $b^3/\sqrt{2}$, and for α, the numerical factor proportional to the energy per unit length of dislocation core, are all within the expected ranges. Perhaps the values for α in fcc metals are somewhat on the large side, but they are not unreasonable.

Most remarkable is the degree to which the derived values of X and X/q conform to the theoretical predictions set out in Sec. 2b. It should be realized that these values are subject to less uncertainty than those of α and X/α, since they do not depend on G, the least reliably determined parameter. All derived values for X in close-packed metals, given in Table I, range between 0.53 and 0.98, while in Sec. 2b it was calculated from core geometry, that $0.38\lesssim X\lesssim 1.0$, with the low values applying only if the stacking fault energy is very low—a condition not fulfilled for any pure fcc or hcp metal investigated so far. To some extent, this very close agreement must be fortuitous, since, certainly, the theoretical relationships would admit to some corrective factors of moderate magnitude. It should be emphasized, though, that throughout this investigation no attempt whatsoever has been made to make the data conform with the theory, and vice versa. The formulas presented are those which were deemed to be the most reasonable, and they have not been changed subsequent to their original derivation. Only after the theory had been developed, including the geometrical relationships pertaining to the parameter X, and including all proportionality factors, have any quantitative calculations been performed. Therefore, the fine agreement between the expected values for X, X/q, and α and those derived from experimental data on the basis of the present theory seems particularly significant.

b. The Parameters X, α, and X/α in Different Crystal Types

Basically, neither X nor α can be derived from experimental data, but only X/q and α/q. Because the latter parameters actually have even more physical significance than X and α singly, and because of the uncertainty relating to the actual values of q, this is most welcome indeed. However, we shall also discuss X and α by themselves, assuming $q=30$ for fcc and hcp, $q=15$ for bcc, and $q=7$ for diamond-type substances.

As demanded by the present theory, the parameters X and α (Table I) are grouped according to crystal types. For clarity, this aspect has been summarized and is presented in Table II. From it we see that, obviously, α changes from its highest values applicable to fcc metals, with a mean of 2.25, to a lower range of values with a mean of about 1.2 for hcp metals, to a still lower range centered about 0.78 for bcc metals, and to about 0.2 for silicon and germanium. This trend is, of course, consistent with the expectation that the dislocation energy (encompassing the energy of all atoms within a strip of $2r_0$ width) rises with rising r_0. Still, the magnitude of the change of α with lattice type—and thus with q and, through q, with r_0—is larger than had been originally anticipated. Simple elasticity theory would have α independent of r_0.[19] (We may note that $q=30$ for nominally close-packed,

---

[19] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (The Clarendon Press, Oxford, England, 1953).

Table II. Summary of the numerical results of Table I. A constant value for α/pq would indicate that the latent heat of melting, and with it the average extra energy per atom in dislocation cores, is the same multiple of Gb^3 for every substance, independent of the structure in which it crystallizes. The number of significant figures retained is not meant to imply the corresponding accuracy.

Lattice type	Value	q	T_M[°K]	L_M $\left[\frac{\text{cal}}{\text{mole}}\right]$	L_M/T_M $\left[\frac{\text{cal}}{\text{mole°K}}\right]$	X/α	α	X	X/q	α/q	α/pq
fcc (9 cases)	lowest	30	84	280	1.93	0.21	1.75	0.53	0.018	0.058	0.079
	mean	30			2.39	0.35	2.25	0.77	0.026	0.075	0.101
	highest	30	2045	5300	3.33	0.45	2.77	0.98	0.033	0.092	0.125
hcp	Mg	30	923	1750	1.90	0.60	1.37	0.82	0.027	0.046	0.071
	Zn	30	692	1740	2.52	0.74	1.12	0.83	0.028	0.037	0.057
	Cd	30	594	1380	2.32	0.72	1.12	0.80	0.027	0.037	0.051
bcc (6 cases)	lowest	15	337	570	1.53	0.46	0.61	0.44	0.029	0.041	0.060
	mean	15			1.91	0.61	0.78	0.46	0.031	0.052	0.077
	highest	15	3660	8100	2.31	0.78	0.98	0.51	0.034	0.065	0.096
diamond	Ge	7	1231	8100	6.57	1.58	0.17	0.27	0.038	0.024	0.071
	Si	7	1694	12 150	7.18	1.30	0.22	0.29	0.041	0.031	0.091

but in reality not close-packed hcp crystals, is certainly an overestimate, if $q=30$ should be correct for fcc metals.)

Similary, the X values are grouped according to crystal type. Still, as explained at the beginning of the section, the values of X and α depend on the choice of the parameter q. More significant is thus the grouping of X/α values according to crystal type, which also is apparent from the tables.

c. The Parameter α/pq

Turning to the primary parameter α/q, we note a most interesting trend, namely, as may be seen from Table II, α/q is nearly constant. This would suggest that the additional average energy per atom in a dislocation core compared to that in the undisturbed crystal and, hence, also the latent heat per atom of the liquid, is almost the same multiple of Gb^3 for every crystal type. However, if this should be so, not α/q but α/pq must be constant. This is indeed nearly the case: Dividing the respective values of α/q with those of p, namely $p=0.74$ for fcc, 0.68 for bcc, 0.34 for diamond-type lattices, 0.64 for Mg, 0.65 for Zn, and 0.74 for Cd, we obtain the values for α/pq listed in Table II. These reflect a scatter of 1:2.5 among all values of α/pq, compared to a spread of α in the range of 1:16.3 and of α/q in the range of 1:3.8. The scatter of the averages of α/pq among fcc, bcc, and diamond is still smaller, namely $\alpha/pq=0.08\pm0.02$. (In view of the considerations of Sec. 5e, the extra average energy per atom may be closer to a constant multiple of b^3/K rather than Gb^3, or it may be a combination of the two; possibly not identically the same combination in the cores and in the liquid.) That the latent heat of melting is nearly proportional to Gb^3 had earlier been noted by Mott and Mackenzie[1,2] for the case of fcc substances.[19a]

d. Comparison between X/q Derived from the Geometry of Dislocation Cores and Derived from the Present Theory

With reference to the parameter X/q—which is not dependent on G and therefore may be calculated with little experimental scatter—we note an amazing agreement between the values listed in Table I and the geometrical derivations of Sec. 2b. There it was shown that, from geometry alone, $X/q\cong\Delta V/qv_s=\Delta hb^2/2\pi v_s$ and that, in close-packed metals, $0.049b\lesssim\Delta h\lesssim0.141b$. The lower limit of $\Delta h/b$ could certainly not be reached but must be replaced by $0.049\times0.38/0.33=0.056$, as was explained. Thus we obtain, from core geometry and employing $v_s=b^3/\sqrt{2}$, $0.056\lesssim\sqrt{2}\pi X/q\lesssim0.141$ or $0.013\lesssim X/q\lesssim0.032$ for close-packed crystals. It was further stated that the lower values were correlated with low stacking fault energies, the high ones with high stacking fault energies, and that for bcc and diamond-type lattices, the values of X/q should be moderately higher, in that order, because of the higher strain energy of dislocations in these, adding to the purely geometrical effect; i.e., the lower q is, the higher X/q was expected to be.

In almost perfect agreement with the above expectations, the fcc and hcp substances in Table I show values of X/q between 0.018 and 0.033, while the bcc metals have X/q values ranging between 0.029 and

---

[19a] *Note added in proof.* The author is grateful to Dr. P. S. Rudman, Battelle Memorial Institute, Columbus, Ohio, for transmitting to her the manuscript of an unpublished theory of melting based on a model quite similar to the one employed here. The said theory demands a proportionality between Gb^3 and T_M, and it is shown by comparison with experimental values that T_M/Gb^3 is nearly constant for a considerable number of widely different elements and compounds. As seen from Eq. 14, Lindemann's relationship leads to the same proportionality, while the present theory yields $(T_M/Gb^3)(gX/\alpha)$ constant. Significantly, covalent crystals, among them germanium and silicon, with the largest values of gX/α according to Table I, show the greatest deviations from the average value of T_M/Gb^3 in Dr. Rudman's compilation, while conforming very well with the present theory, as shown.

0.034, and the diamond-type substances Ge and Si render X/q at 0.038 and 0.041, respectively.

Also the predicted correlation with stacking fault energy is apparent. Actually, the geometry of the core is not directly determined by the stacking fault energy γ but by the ratio γ/Gb, which we may name the "relative" stacking fault energy, since the width of splitting of an extended dislocation is inversely proportional to this number.[20] Gold is known to exhibit large stacking fault tetrahedra when quenched and aged, indicating the lowest relative stacking fault energy of any pure fcc metal investigated so far,[21] followed by silver which has a lesser tendency to form stacking fault tetrahedra. Copper is believed to have a higher, but still intermediate, relative stacking fault energy, while aluminum and nickel have high relative stacking fault energies. Consistent with the said sequence, the respective X/q values found are: for Au, 0.019; for Ag, 0.023; for Cu, 0.029; for Al, 0.029; and for Ni, 0.033. Little or nothing is known about the stacking fault energies of cobalt, lead, and platinum. However, cobalt must have a low or intermediate relative stacking fault energy since it transforms from fcc to hcp on cooling. The X/q values found in Table I would indicate an intermediate relative stacking fault energy for cobalt and platinum and a quite low relative stacking fault energy for lead.

It would thus seem very rewarding to recalculate X/q for all important close-packed metals, employing the most accurate known values for the various parameters involved, and to compare with known stacking fault energies. Should the described correlation between X/q and the stacking fault energy be further confirmed, then it may be used for determinations of the stacking fault energies in pure close-packed metals as well as alloys. In alloys, the stacking fault energy is usually rather small, and correspondingly X/q should have low values.

e. Remarks on the "Directionality of Bonding"

One question still to be answered is: Why should the values of α/pq not be more uniform? Should there, in fact, be any variation in α/pq, or are these variations simply due to taking incorrect values for G? Doubtlessly, the scatter in α/pq must be partly due to errors in estimating the experimental values of G at the melting point, since these are easily uncertain within 20%, and it must be partly due to the uncertainty as to which detailed combination of the elastic constants should be employed in the theory. However, the fact that the α/pq values appear to be grouped according to crystal type, suggests that beyond these extraneous causes there may be a real variation among the α/pq values with a definite physical significance: Consider the parameter q. It was first calculated by Mackenzie[9] on the basis of crystal geometry. In fact, it may be regarded as a measure of the "directionality of bonding," since as the parameter q decreases, the more directional is the bonding in the crystals. In the preceding calculations, this was allowed for by assigning the value of 30 in close-packed metals, 15 in bcc lattices, and 7 in diamond-type structures. However, the "directionality of bonding" is a property of the electronic configuration of the atoms and ions themselves. Moreover, the fact that a certain element crystallizes, say, in the bcc form, does not mean that it has identically the same proclivity for directional bonding as every other bcc metal. Instead, it means that its specific values of X, α, q, X/α, and, perhaps, stacking fault energy γ, fall into a range for which the bcc lattice has the lowest chemical potential. The apparent grouping of the values for α/pq according to crystal types may be interpreted to indicate this very state of affairs. This conclusion is further supported by the result in Table I that cobalt and iron, metals which exhibit transformations on cooling, are both borderline cases within their respective groups, as far as their values of α, and thus of α/pq are concerned, cobalt veering towards the values in the hcp group and iron towards fcc (or hcp, which cannot be distinguished). If the above consideration should be correct, then it opens up the possibility of studying the so far ill-defined "directionality of bonding" through careful measurements of the parameter α/pq.

7. CONCLUSIONS AND OUTLOOK

The theory of melting presented above is logically compelling, and is in excellent agreement with a considerable body of experimental data. The important parameters calculated, X/α and α/pq, may suffer from some systematic errors because proportionality constants in the basic equations may have been estimated incorrectly. However, at this point, it seems that the errors are small and that the conclusions drawn regarding the correlation between X and α with crystal type and stacking fault energy cannot be in error.

In a measure, the success of the theory is astounding. One may conjecture that this comes about because the state of the material in dislocation cores is more closely like a liquid than one is aware of. With respect to the volume changes accompanying melting, however, the theory is inadequate. This is already apparent from the fact that not all crystals expand on melting. The important consideration in cases in which melting causes volume contraction seems to be that the original lattice becomes mechanically instable as soon as T_c is exceeded, but that the energy possessed by the atoms

---

[20] W. T. Read, *Dislocations* (McGraw-Hill Book Company, Inc., New York, 1953), pp. 130–131.

[21] *Note added in proof.* The most recent determinations of stacking fault energies indicate that the order of gold and silver is reversed, with silver having the smallest stacking fault energy of any pure fcc metal, and gold, copper, platinum, aluminum, and nickel following in that order [see I. L. Dillamore and R. E. Smallman, Phil. Mag. **12**, 191 (1965)]. The present paper yields the values of X/q in the order of gold, silver, platinum, aluminum, copper, and nickel. However, it ought to be remembered that the present theory renders the value of the stacking fault energy *at the melting point.*

in dislocation cores is still closely like that of the atoms in the liquid. Still, the discrepancy between the actual volume change on melting and the volume expansion which would be calculated from the dislocation-core model of the liquid, is a flaw in the theory, indicating that a liquid is described incompletely by the said model, even though it may still be very useful.

The following conclusions are the most important:

(1) The temperature of melting is certainly correlated with the temperature at which the free energy of dislocation cores vanishes. Almost certainly the two are one and the same temperature.

(2) The latent heat of melting per atom is almost the same multiple of either Gb^3, or perhaps b^3/K, or a simple combination of these, for all substances considered. A slight dependence of this multiple on crystal type in the solid state apparently exists, which probably is correlated with the "directionality of bonding."

(3) The volume dilatation in dislocation cores derived from the present theory is in almost perfect quantative agreement with the values of the same quantity derived from simple considerations of core geometry, including its dependence on stacking fault energy.

The most exciting aspect of the theory presented here is the opportunity which it affords for further probing into the properties of atoms, crystal bonding, crystal defects, and, perhaps, liquids. We may look forward, now, to determining, for example, the stacking fault energy of metals from caloric data. Similarly, the Peierls Nabarro stress, which has been tantalizingly elusive, can perhaps now be determined by employing Eq. (9) as discussed, and the properties of dislocation cores will finally be better understood. Also the whole range of atomic properties, which have been described above with the term "directionality of bonding," may now become accessible to more quantitative investigation. Finally, it will most likely prove to be fruitful for the better understanding of liquids to employ the model of a crystal filled to capacity with glide dislocation cores. For example, diffusion in liquids may be better understood in terms of pipe diffusion, and vacancy concentrations in liquids might be calculated from a theory of vacancy binding in dislocation cores.[22]

8. SUMMARY

In the preceding sections, a consistent theory has been developed to show that melting occurs when the free energy of glide dislocation cores assumes negative values. It is found that, excepting the volume change, every single aspect of melting which was considered is explained satisfactorily by the proposed theory. These aspects include the magnitudes of melting temperature and of the latent heat of melting, they include an explanation for Richard's law, for Lindemann's relationship, and for Grüneisen's relationship, as well as the general trend of melting temperatures in alloys, and a little-investigated relationship which seems to exist between ductility and the entropy of melting.

Numerical calculations have been performed for 20 elements with very widely different values of melting temperature and latent heat. The parameter X representing the specific dilatation in the cores, divided by q, where q determines the width of dislocation cores, may not only be calculated from the present theory, but also on the basis of the geometry of dislocation cores. The range of values derived for X/q from the theory of melting coincides almost precisely with the range calculated from geometry. Moreover, the trend of the dependence of the experimental values of X/q on crystal type, as well as on stacking fault energy in close-paced metals, is in good accord with theoretical expectations.

The values for α/pq, reflecting the average extra energy per atom in dislocation cores as well as in the liquid, are almost constant throughout, indicating that this energy is almost the same multiple of Gb^3 for all crystal types, where G is the modulus of rigidity and b is the atomic diameter.

Throughout, the numerical calculations have been performed for pure substances, and overwhelmingly for metals. The reason for this was the better accessibility of the relevant data for metals. However, the theory is meant to apply to every crystalline substance which begins to melt at a fixed temperature, including inorganic and organic compounds and alloys. Substances in which, for one reason or the other, dislocations cannot form, are therefore expected not to have a fixed melting temperature. Many inorganic and organic crystals fall into this category because of their large Burgers vectors. These then sublimate or decompose before melting.

Perhaps the nature of liquids may now be better understood, namely, as crystals filled to capacity with dislocation cores, and it may prove possible to correlate liquid properties with those of dislocation cores, thereby leading to the better understanding of both. Similarly, through systematic studies of the derived values of X/α, X/q, and α/q, important information can presumably be gained on such diverse quantities as the stacking fault energy in close-packed metals, the magnitude of Cottrell and Suzuki-binding energies between foreign atoms and dislocation cores, the "directionality of bonding," which is a property of the electronic structure of atoms, and the frictional stress on dislocations.

Amorphous substances are understood as liquids of high viscosity, due to high frictional stresses on the dislocation cores. Thermal motion reduces it[8] as well as helps to overcome it, which explains the gradual softening of amorphous substances on heating.

It is recognized that not all data for G and g, the Grüneisen constant, as used in the tables, are entirely reliable, and errors in these may easily reach 20%,

---

[22] Doris Kuhlmann-Wilsdorf, J. Appl. Phys. 36, 637 (1965).

affecting the derived values for X/α and α/q. It is confidently expected, though, that no major changes in the results will occur through adjustments of the numerical data. The same holds true for the substitution of either the modulus of compressibility or a combination of the elastic constants for G. Such a substitution is, however, mandatory for all anisotropic crystals.

Doubtlessly, some adjustment of numerical factors employed in the theory will become necessary eventually. For example, a factor of 2 was employed to relate the energy per atom in the center of a core to the average energy of atoms in dislocation cores. Still, at the present time, knowledge of how to improve these factors is lacking. As it stands, the formulas were derived completely, including choosing the magnitude of the said numerical factors on the basis of the best logic, before the numerical calculations were made. Under these circumstances, the success of the theory and, particularly, the very good agreement between the values for X/q with those derived from core geometry must be taken as a strong indication that the numerical constants were chosen not far from their correct values. Thus, although some systematic errors must necessarily have been incorporated in the derived values for α/q and X/q, these are believed not to be severe.

ACKNOWLEDGMENTS

The continuing encouragement and scientific stimulation of my husband, Professor H. G. F. Wilsdorf, University of Virginia, Charlottesville, Virginia, has contributed immeasurably to this investigation. The financial support of the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-3108 is gratefully acknowledged, as are helpful discussions with Dr. A. L. G. Rees and Dr. J. A. Barker, C.S.I.R.O., Melbourne, Australia, and with Professor F. R. N. Nabarro, University of the Witwatersrand, Johannesburg, South Africa.

PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Low- and High-Temperature Magnetic Resonance and Relaxation of NaF:Mn^{2+}[†]

G. A. PERSYN[*] AND A. W. NOLLE
Department of Physics, The University of Texas, Austin, Texas

(Received 21 June 1965)

In single NaF crystals with 10^{18} to 10^{19} Mn^{2+} per cm^3, and in reagent-grade powder, the F^{19} NMR linewidth is studied from 300 to 1000°K, and the spin-lattice relaxation time from 2 to 1380°K (at 27 Mc/sec, with supplementary low-temperature work at 13 and 39 Mc/sec). The Mn^{2+} EPR spectrum at 9 Gc/sec, which is observed from 2 to 1000°K, with saturation-relaxation measurements below 100°K, indicates positive-ion vacancy diffusion above 250°C, and Mn^{2+} diffusion above 425°C. The NMR results yield a jump rate $\nu_{\mathrm{Na}}=8.8\times10^{16}\exp[-2\ \mathrm{eV}/kT]$ sec^{-1} in the intrinsic region, and in the extrinsic region, an energy of activation of 0.52 eV for vacancy jumps, with a frequency factor not less than 1.1×10^{13} sec^{-1}. Negative-ion diffusion with an apparent activation energy of 3.5 eV is found above 950°C. The relaxation of isolated Mn^{2+} ions changes from the direct to the Raman process near 60°K. The calculated F^{19} relaxation rate due to this Mn^{2+} relaxation is at a maximum and of the observed order of magnitude in the range 150 to 200°K. The F^{19} relaxation from 2 to 150°K is attributed to the effects of Mn^{2+} pairs or clusters and shows a change from "rapid diffusion" to "slow diffusion" near 4°K.

I. INTRODUCTION

THE temperature dependence of the nuclear spin-lattice relaxation time T_1 supplemented by information on the magnetic-field dependence of T_1 and on the nuclear-resonance linewidth, can serve to show which random disturbances are the cause of nuclear relaxation in a given solid. In this paper we describe an investigation of the F^{19} nucleus in NaF from this point of view, from 2 to 1380°K. For simple ionic crystals such as this one, the relaxation-producing disturbances at elevated temperatures are elementary ionic translations, while ordinarily those at and below room temperature are magnetic fluctuations due to paramagnetic impurities,[1] accidentally or intentionally included in the sample. In the present work, all measurements in which the presence of paramagnetic impurities is important are done with samples containing Mn^{2+} in sufficient concentration to dominate the effect of the impurities on nuclear relaxation. In addition, the paramagnetic relaxation time for isolated Mn^{2+} ions (but not for pairs or clusters, which are also present) is measured from 2 to 100°K, making it possible to show where a significant nuclear transition rate due to the isolated Mn^{2+} ions is to be expected. This particular impurity ion was chosen because it has been the subject of paramagnetic-resonance investigation in many host crystals,[2] and because it enters easily into the lattice. An incidental

---

[†] Supported by the National Science Foundation and by the U. S. Office of Naval Research.

[*] Present address: Department of Physics, St. Mary's University, San Antonio, Texas.

[1] N. Bloembergen, Physica **15**, 386 (1949).

[2] K. D. Bowers and J. Owen, Rept. Progr. Phys. **18**, 304 (1955); J. W. Orton, *ibid.* **22**, 204 (1959).