# ASPECTS OF THE MELTING OF METALLIC ELEMENTS

*A. K. Galwey*[* **]

Department of Chemistry, Rhodes Grahamstown 6140, South Africa

Melting is a most familiar phenomenon: closely similar patterns of solid/liquid transformation occur on heating innumerable and diverse crystalline substances. While some behavioural trends have been characterized, no melting theory of general applicability has yet found widespread acceptance. The present comparative survey is concerned with the melting of metallic elements, to determine quantitatively the enthalpy and density changes that accompany these solid/liquid transitions. The relationship of melting with other physicochemical processes is considered. Metals were selected as apparently the simplest systems for this analysis, many crystal structures involve the close packing of (at least approximately) spherical atoms. Appropriate physical data are available for a large number of different elements, some 70 are considered here, representing a wide range of melting points, $T_m$. Aspects of the kinetics and mechanisms of melting are discussed.

These data comparisons show that melting enthalpies for metals are relatively small. The averages found represent only about 26% of the energy required to heat these solids from 0 K to completion of melting at $T_m$ and only about 5% of the volatilization enthalpy. The density changes on fusion are also relatively small, on average –4.7%. To account for these observations, a representational model of fusion has been formulated. It is suggested that, on melting, the bonding and local structural dispositions between neighbouring atoms in the liquid and in the solid condensed phases undergo changes that are only limited in extent. Thus, the regular ordered structures, characteristic of crystalline phases, are extensively maintained in the melt at $T_m$. Melting is ascribed to destabilization of the crystal through excess vibrational energy, resulting in replacement of the overall extended and constant rigid structure of the solid by a dynamic equilibrium between small, locally regular domains in the liquid. Each such structurally ordered domain is a region of one or other of the alternative possible, crystal-type structures of comparable stability. In the liquid, constant transfer of the components between these regular arrays, stabilised by the enthalpy of fusion, within the compact assemblage of domains accounts for the fluidity of the liquid, its inability to withstand a shearing force and the absence of long-range order. Melting is, therefore, identified with relaxation, at $T_m$, of the constraint that only a single lattice form is present (as in a crystal) and the liquid is composed of all the structures that are sufficiently stable to participate in the constant flux of interconverting domains. This model of melting may have wider applicability. The small modifications both of enthalpy and of density on fusion make the formulation of a quantitative model, capable of predicting $T_m$, difficult because minor or secondary controls may be significant in determining the temperature of this physical phase change and the structural changes that occur.

*Keywords: crystal stability, fusion, melting, metal properties, phase change*

## Introduction

The melting point, $T_m$, of a pure solid is an inherent and characteristic property. This phase change, which occurs at a precise and reproducible temperature ($T_m$), is invariably endothermic and is almost always readily reversible. On fusion there is loss of long-range crystal order and rigidity, through the thermally discontinuous onset of fluidity, in a transition that is completed without perceptible temperature variation. Melting is classified as a physical change because the crystal/liquid constituents undergo no chemical modification within or as a consequence of the phase transition: there is only a discontinuous (large) increase in the ease of their relative displacement movements. Closely comparable, even identical, melting behaviour is found for innumerable and diverse solid types, in which the co-

herence and rigidity of the original crystal results from intercomponent interactions through van der Waals, hydrogen, ionic, covalent, metallic bonding and sundry combinations of these. There are, however, important exceptions to this generalization, including glasses (for which 'softening' occurs over a significant temperature interval) and liquid crystals (where there is 'stepwise' diminution of order on heating).

Although fusion is a widespread and familiar phenomenon, no generally acceptable theoretical model of melting is currently available that is capable of relating $T_m$ values to the physical and chemical properties and/or the ordered structures of the components that constitute the solid. This is a notable gap in available theory, despite the many attempts that have been made to formulate an explanation. Recognizing these shortcomings, the present review comparatively examines

*     andrew@galwey.freeserve.co.uk
**    Contact address: 5, Regents Woods, Malone Road, Belfast BT9 5RW, Northern Ireland, UK

the significance of the magnitudes of selected characteristic physical changes at $T_m$ (enthalpy, density) for the metallic elements. The trends found are comparatively (and critically) considered as a basis for the formulation of a descriptive theoretical representation of melting. The metallic elements were chosen because the necessary physical data are available for a set of about 70 different but comparable solids, each composed closely packed arrays of approximately spherical atoms. These were identified as the most extensive, and (possibly) the structurally simplest set of crystals for which reliable, quantitative physical data are available. Furthermore, fusion temperatures extended over a particularly wide range of $T_m$ values.

This account of metal melting is presented in a wide perspective that includes considerations of the following aspects. The discontinuous increase in disorder at $T_m$ is regarded as only a single, though important, step in the inevitable progressive 'thermal destruction of order' that every substance undergoes, sooner or later, during an unrestricted increase of temperature. The roles of interatomic bondings in the original solid, subsequently modified by the accommodation of thermal energy on melting, are examined. This introduces consideration of the significance of chemical controls, bonding relationships between neighbouring components of the solid and their possible changes, into theory that has more usually emphasised the physical nature of fusion phenomena. The survey also includes a comparative analysis of some characteristic features of melting and of limitations in the theories available. The possible modifications of structural order between components, an essential feature of the crystal/liquid transformation at $T_m$, are discussed. The potential value of a quantum/band theory energy representation, in accounting for the precise, invariable $T_m$ for the phase change, is also mentioned.

## Objectives of this survey

An authoritative and comprehensive review of melting was given by Ubbelohde [1]. The phenomenological characteristics of fusion are familiar and are described and discussed in Discussion, below. The present comparative survey reports a consideration of the possible theoretical significances of the extents of the physical changes that occur on melting of the metals, including some of the 'quasi-metallic' elements. Atoms in crystals of this group of about seventy elements can, to a first (imprecise) approximation, be represented as spheres packed in dense structures, typically showing high coordination numbers and symmetrical lattices. The changes of physical parameters that occur at $T_m$ are examined quantitatively in an attempt to characterize the differences between the physical and/or chemi-

cal interactions that occur between the atoms within the solid and the liquid condensed phases, and the possible stereochemical consequences. It is believed that the trends identified for these relatively simple solids may have wider applicability in the search for a general theory of melting, which remains elusive. At present, no simple model appears to be satisfactory, generally acceptable or widely applicable. The physical changes at $T_m$ are discussed in the context of the conditions believed to exist at, and in the immediate vicinity of, the liquid/solid contact during melting/solidification. From the physical evidence, inferences concerning melt structures close to the $T_m$ are used to identify controls and to formulate a mechanism of fusion. It is hoped that these conclusions will generally contribute towards an advancement of melting theory.

The quantitative physical measurements used for these comparative analyses have been obtained from data listed in authoritative and reliable 'Handbooks of Physics and Chemistry'. The most important sources were [2, 3] and a very few values were taken from other editions of the same works. These and other references are specified to confirm the reliability of the data used here. Accuracies of the individual values are not always known, these may vary between the different elements. There are a few gaps in the coverage but the data used are regarded as generally reliable.

*Term definitions*

It is convenient to consider the enthalpy of melting with reference to the sequential and distinguishable energy-absorbing processes that occur on heating a solid and the subsequent volatilization of the melt at the boiling point, $T_b$. These include: heating from 0 K to the Debye temperature, further heating to $T_m$, the enthalpy of fusion and the enthalpy of volatilization at $T_b$. The following symbols are used:

- Melting point, $T_m$; Boiling point, $T_b$; Debye temperature, $\theta_D$.
- Enthalpy of melting at $T_m$, $\Delta H_f$; Enthalpy of volatilization at $T_b$, $\Delta H_b$.
- Heat energy required to increase the temperature of solid from 0 K to $\theta_D$, $\Delta H_D$.
- Heat energy required to increase the temperature of solid from $\theta_D$ to $T_m$, $\Delta H_S$.
- Heat energy required to heat from 0 K to form melt at $T_m$, $\Delta H_M$ ($=\Delta H_D+\Delta H_S+\Delta H_f$).

Crystal lattice structures: CCP – cubic close packed, HCP – hexagonal close packed and BCC – body centred cubic.

Positions of elements in the periodic table are specified by the 'New Notation' described by Lide [2] (inside front cover): the alkali metals (and hydrogen) are in Group 1 and Group 18 is the inert gases.

## Enthalpy changes on heating the condensed phases

### *The solid*

#### Heating from 0 K to the Debye temperature, $\theta_D$

68 values of $\theta_D$ (at 298 K) were obtained from [4]. The energy required to raise the temperature of the solid from 0 K to $\theta_D$, $\Delta H_D$, was obtained by numerical integration of the increase of heat capacity, $C_v$, from zero to the (theoretically) constant value ($3R$) above $\theta_D$, using information from [5]. Most values of $\Delta H_D$ were between 2 to 7 kJ mol$^{-1}$ and no trend of variation with $T_m$, or other relationship, was found. For example, listed $\theta_D$ (298 K [4]) values for Fe and Co were 373 and 386 K ($T_m$, 1811 and 1768 K) whereas for Ho, Er and Lu $\theta_D$ values were much lower at 161, 163 and 116 K, respectively, while $T_m$ magnitudes were comparable (1747, 1802 and 1935 K). Again, for the alkali metals these parameters varied considerably: $\theta_D$ for Li (448 K) was just less than $T_m$ (453 K), whereas for Cs there was a much more significant difference, 258 K, between $\theta_D$ (43 K) and $T_m$ (301 K).

#### Heating from $\theta_D$ to $T_m$

Above $\theta_D$ the molar specific heat of a solid is constant, $C_v = 3R$ [5], consequently a plot of $\Delta H_S$ *vs.* ($T_m - \theta_D$) is expected to be linear. Values of $\Delta H_S$ for 68 metals were obtained by numerical integration, with extrapolation where necessary, from listed $C_v/T$ data [4], with some additional values from [6]. Enthalpies of crystallographic transformations [4, 6] (generally small) were included in $\Delta H_S$. $T_m$ values from [7] and $\theta_D$ values from [4] are used in Fig. 1, from which the linear relationship (with some scatter of data) between $\Delta H_S$ and ($T_m - \theta_D$) generally confirms expectation. The slope of the line shown, 32.2 J K$^{-1}$ mol$^{-1}$, is slightly greater than the theoretical value, $3R = 24.94$ J K$^{-1}$ mol$^{-1}$ [5]. The single 'outlier' is Ge. A number of points, including Co, Cr, Mn, Mo, Sm, U and some others, are appreciably above the mean trend, some by 10 kJ mol$^{-1}$, or more. No explanation for this scatter is suggested, however, because no correlation could be found between the apparent deviations and either the chemical properties of the elements concerned or the crystal structure at $T_m$. The overall trend was, however, in general accordance with theory.

[Plots of ($\Delta H_D + \Delta H_S$) and of $\Delta H_M$ (to heat solid 0 K to $T_m$ and to melt at $T_m$) *vs.* $T_m$ and *vs.* ($T_m - \theta_D$) were closely similar to Fig. 1, including comparable scatter.]

#### Enthalpy of fusion at $T_m$, $\Delta H_f$

68 values of $\Delta H_f$ [7] are plotted *vs.* $T_m$ on Fig. 2: metals are distinguished by crystal structures at $T_m$, as given in [8], as follows.
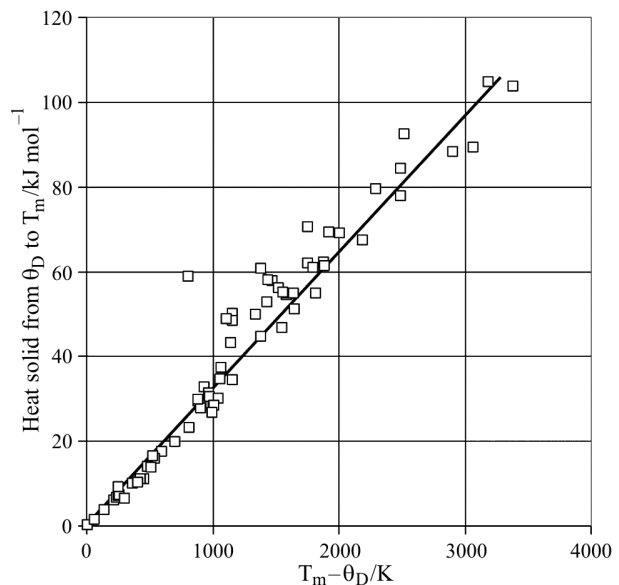


**Fig. 1** Plot of energy required to heat the solid from 0 K to $T_m$ *vs.* ($T_m - \theta_D$). The mean slope is slightly greater than expectation for the (theoretically constant, $C_v = 3R$) heat capacity of the solid [5]

- CCP and HCP. Ten metals (Ag, Al, Au, Cu, Ir, Ni, Pb, Pd, Pt, Rh) were CCP (□ on Fig. 2), another eleven (Cd, Er, Ho, Lu, Mg, Os, Re, Ru, Tc, Tm, Zn) were HCP (■) for which no changes of structure with temperature are listed [8]. Indium is close to CCP and Co changed HCP to CCP (and is included as □). $\Delta H_f$ values increase with $T_m$ and the rate is greater for $T_m$ values above about 1800 K: these trends appear in Fig. 2 as two straight lines.
- BCC. Eleven metals (Ba, Cs, Cr, Eu, K, Mo, Nb, Rb, Ta, V, W) crystallized in the BCC form only, undergoing no structural change with temperature. Below their respective $T_m$ values, ten more (Be, Gd, Hf, Li, Na, Sc, Ti, Tl, Y, Zr) changed first to HCP, later to BCC, and a further three (Dy, Sm, Tb) showed a lower temperature form prior to HCP followed by the transition to BCC. Four metals (Ca, Ce, Sr, Th) changed CCP to BCC and another four (Fe, La, Mn, Yb) showed an additional low temperature form before changing to CCP and later to BCC. Finally Nd, Pm, Pr and U transformed to BCC below $T_m$. The 36 elements mentioned adopted the BCC structure prior to fusion: the trend of $\Delta H_f$ with $T_m$ is shown in Fig. 2 (○). Values are again represented by two straight lines, with the greater slope above about 1800 K. For comparable $T_m$ values, melting enthalpies for the BCC metals are consistently lower than for crystals having the more closely packed lattices, CCP or HCP.
- Other. Nine elements (As, Bi, Ga, Ge, Hg, Sb, Se, Si, Te: all of which show some metallic properties) crystallised with structures different from those
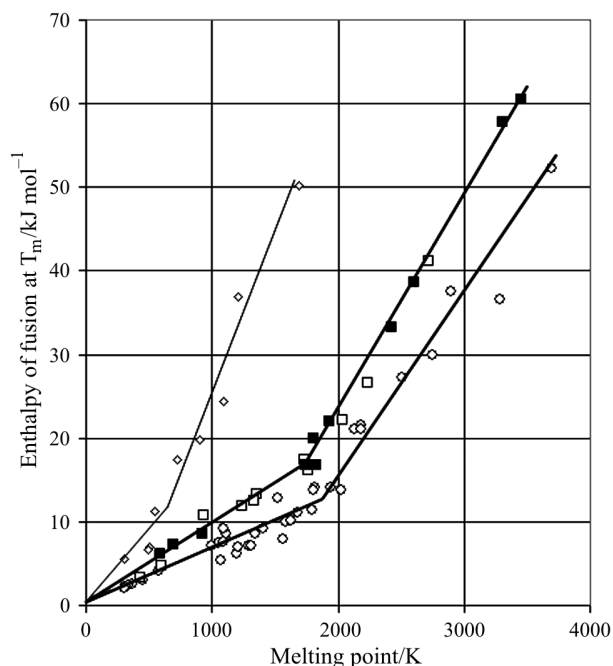
**Fig. 2** Plot of $\Delta H_f$ vs. $T_m$ for 68 metals. Two linear relationships were found for each of three groups of metals, distinguished by the crystal structure at $T_m$:
○ – BCC, the same relationship for both
□ – CCP and ■ – HCP and ◇ – 'others'

mentioned above. Most were close to two straight lines on Fig. 2 (◇); $\Delta H_f$ values were relatively much greater than those of the more closely packed elements of comparable $T_m$. The two possible exceptions, Se and Sn, were only slightly below this mean trend.

- Pressure. Some effects of pressure on structure are mentioned in [8]: a pressure increase tends to form the most closely packed structures. Transformation to CCP is noted for Cs, La, Nd and Pm with a pressure rise, or to HCP for Al, Ba, Fe and Pb.

*Comment*

A majority (43) of these 68 metallic elements crystallize in a closest packing form (i.e., CCP or HCP) though, on heating, 21 of these transform to BCC, making this the most usual structure in the immediate approach to the $T_m$. Most metals adopt one, or more, of these three packing arrangements, except for the quasi-metals of periodic table Groups 14 (Si, Ge), 15 (As, Sb, Bi) and 16 (Se, Te), classified as 'Other' in Fig. 2. For these a contribution from covalent bonding diminishes atomic packing density, directed bonds may be stronger and $\Delta H_f$ values are relatively high, Fig. 2 (compared with $T_m$). The feature of Fig. 2 identified as having greatest significance is the relatively low $\Delta H_f$ magnitudes for the BCC salts. The tendency of

metals to adopt the BCC structure at elevated temperature is ascribed to enhanced stability of this form when thermal energy is increased. The greater vibrational energy presumably tends to minimize the consequences of the spacing difference between the 8 nearest neighbours and those 6 that are 15% more distant [9]. Thus the effective coordination number of the constituent atoms is increased above 8 (towards 14) but the stabilization energy of the crystal, compared with that of the liquid with which it is in equilibrium at $T_m$, is diminished as shown by the relatively lower magnitudes of $\Delta H_f$. The phase transitions, CCP or HCP to BCC can, therefore, be regarded as a precursor step to fusion, a 'loosening' of the lattice order, tending to increase coordination numbers through accommodation of additional thermal (vibrational) energy.

Figure 1 is in (general) accordance with theory ($C_v=3R$) [5], $\Delta H_S$ is directly proportional to ($T_m-\theta_D$). While data show appreciable scatter, no trends were identified with metal structures or other properties of the elements concerned. At $T_m$ there were variations of $\Delta H_f$ with crystal structure, Fig. 2, attributable to a relative diminution of the energy change associated with the solid/liquid transition from BCC to melt. A plot of $\Delta H_M$ vs. $T_m$ was similar to Fig. 1, in showing a good linear relationship, with marginally less scatter, but with the three 'outliers', Be, Ge and Si.

*The liquid*

Relationship between $T_m$ and $T_b$

There was a general tendency for high $T_m$ value metals also to be less volatile, the plot of $T_b$ vs. $T_m$ for 67 elements showed considerable scatter (arsenic was omitted because it sublimed). The overall mean ($T_f/T_b$) was 0.489, most magnitudes were between 0.3 to 0.7: with low values for Ce – 0.289, Li – 0.28, Ga – 0.183, Sn – 0.175 and high values for Cr, Yb – both 0.74 and Tm – 0.81. For two-thirds of these elements $T_b$ is approximately $2 \times T_m$. No significant trends were discerned within groups of chemically related metals or for crystals having a similar structure. The alkali and the alkaline earth metals each formed clusters on a plot of $T_b$ vs. $T_m$ but values for the lanthanides were more dispersed. Plots of ($T_b-T_m$) vs. $T_m$ and ($T_m-\theta_D$) also showed considerable scatter within which no trends were recognised.

A plot of the enthalpies, $\Delta H_b$ vs. $\Delta H_f$, showed scatter; the ratios ($\Delta H_b/\Delta H_f$) for (30/67) metals were in the range 15–25, but no trend of systematic variation with either $T_m$ or $T_b$ could be recognized. There was a weak correlation between $\Delta H_b$ and $\Delta H_M$: (44/67) ratios ($\Delta H_b/\Delta H_M$) were between 3.0–6.0, with a few values greater than 10 (Ga, In, Sn, Li), but no trend of systematic variation with either $T_m$ or $T_b$. $\Delta H_b$

generally increased with $T_m$, though there were some exceptions: Ga, In, Sn gave relatively large enthalpy values, those of Cr and Mn were lower and lanthanides tended to be scattered about the mean trend. Overall, only very weak correlations were indicated between melting and volatilisation processes.

Volatilization enthalpy and $T_b$

The plot of $\Delta H_b$ [6] *vs*. $T_b$ [7], Fig. 3, shows similarities with the plot of $\Delta H_f$ *vs*. $T_m$ (Fig. 2). Again there are linear relationships within two ranges, though here the differences associated with crystal structures are absent for the melts, and data for the (67) metals are distributed (with some scatter), about a single line showing two linear ranges. $\Delta H_b$ values for Ba, Th, U, and some lanthanides (Gd, Nd, Pm and Tb), were below those for the main trend. The variations of volatilization enthalpy at 298 K [10] with $T_b$ were closely similar, except that the relatively large values for As, Sb, Se and Te were appreciably above the mean trend.

*Comment*

The enthalpy relationships identified above and regarded as having significant interest and possible theoretical value are summarised as follows. The energy required to heat the solid from $\theta_D$ to $T_m$, $\Delta H_S$, is directly proportional to $T_m$, Fig. 1. This is a measure of crystal stability and is also in accordance with the theoretical expectation that $C_v$ (=$3R$) is constant [5]. $\Delta H_f$ is linearly related to $T_m$ in two temperature intervals and different constants of proportionality are found for different crystal structures, Fig. 2. Similarly, $\Delta H_b$ is directly proportional to $T_b$ in two linear intervals but structural distinctions are absent from the melts, Fig. 3. These are the dominant trends: the data show appreciable scatter, attributable to secondary influences including differences for the 'less metallic' elements of Groups 13–16. An important conclusion is that, despite the obvious and apparently profound changes in physical properties at $T_m$, melting involves a relatively small enthalpy uptake. The average $\Delta H_f$ value for 67 metals, 16.6 kJ mol$^{-1}$, is significantly less than the (average) energy required to heat these solids from 0 K to $T_m$, ($\Delta H_D+\Delta H_S$)=41.8 kJ mol$^{-1}$ (only 40%), and very small compared with their mean volatilization enthalpy, $\Delta H_b$=325 kJ mol$^{-1}$ (only 5.1%). Omitting the ('less metallic') elements of Groups 15–17, the mean ratio $\Delta H_f/(\Delta H_D+\Delta H_S)$ was 0.315: values ranged from 0.155 (Ce) to 0.608 (Os) and the mean ratio ($\Delta H_f/\Delta H_b$) was 0.046, between 0.014 (Ce) and 0.086 (Re).

## Density changes on metal melting

Changes of density on metal fusion were determined to identify characteristic trends present and any informa-
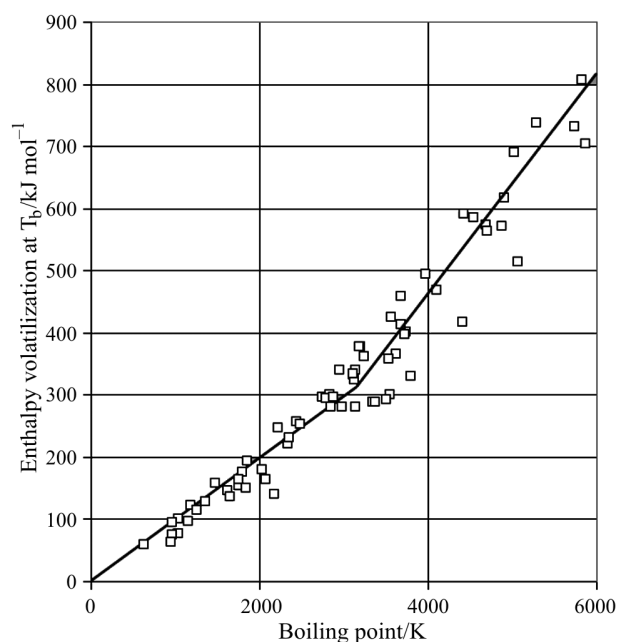


**Fig. 3** Plot of $\Delta H_b$ *vs*. $T_b$. Two linear trends, with some scatter, were found for the 67 metals considered. Note similarity with Fig. 2 but here the molten metals were not distinguished by structures

tion that may be capable of yielding insights into probable/possible melt structures. The density of each liquid element at its $T_m$, $\rho_L$, was obtained from [11]. The density of each metallic solid, also at $T_m$, $\rho_S$, was calculated from the lattice spacing listed [8] for the highest temperature crystal form and corrected for the temperature difference by the coefficient of linear expansion [7]. For several elements a large temperature interval introduced some uncertainty into $\rho_S$ values. Lattice spacings for some of the lanthanides (Pm, Sc, Sm, Tb, Y) were reported in brackets [8], indicative of lower reliability, and data for (Dy, Gd, Ho, La, Nd, Pr, Yb) were recorded to three significant figures only. Accordingly, the lanthanides (together with Sc and Y) are considered as a separate group here.

*Overall mean density changes*

Invariably the solid was the relatively denser phase and all density changes on fusion are reported as $\Delta\rho$%=100(1−$\rho_L$/$\rho_S$): mean error limits reported below (as ±) are root mean square deviations. The mean, overall calculated $\Delta\rho$% value was 4.7±2.6% for 52 metallic elements listed in [8] as having the BCC or the closest packed, CCP or HCP, structures in the highest temperature range (assumed to extend to $T_m$). Magnitudes of $\Delta\rho$% values for the metals distinguished in sets having common structure are shown on Fig. 4. No systematic variations of $\Delta\rho$% with $T_m$ were found.

*Density changes on melting of metallic elements of the same structure*

- CCP. Values varied appreciably within this set of eleven elements, with Ag, Al, Au, Co, Cu, Ni and Pd being close to the mean $\Delta\rho=7.1\pm2.4\%$. Values for Pb and Pt (3.2, 3.5%) and Rh and Ir (9.6, 11.7%) were relatively small and large, respectively.
- HCP. Seven metals crystallised in this form with average $\Delta\rho\%=5.4\pm1.7\%$: Cd, Ga, Mg, Os, Re and Zn were close to the mean but Ru was significantly larger, 9.3%.
- BCC. The average $\Delta\rho\%$ for fusion of the 22 elements, BCC at $T_m$ [8], was $4.7\pm1.8\%$. Values for the Group 1 metals were relatively small, from 1.9% (Li) to 4.3% (Rb). Magnitudes for Cr, Zr, Hf and Be (10.7, 8.5, 7.1 and 6.2%, respectively) were large and all the others (Ba, Ca, Fe, Mn, Mo, Nb, Sr, Ta, Ti, Tl, U, V and W) were closer to the average.
- Lanthanides. Most of the elements of this group, including Sc and Y, crystallise in the BCC form at $T_m$, excepting Er, Ho, Tm and Lu which are HCP. The lanthanides are listed separately because of the apparently lower accuracy of the data [8]. From the available information, it is estimated that $\Delta\rho=2.0\pm1.6\%$, values ranging from 0.1 (Y) to 5.4 (Yb) and no systematic trends of variation were discerned.

*Trends in density changes on melting*

The density diminutions on melting of the metallic elements are all relatively small. The plot of $\Delta\rho\%$ *vs.* $T_m$ for 52 metals, Fig. 4, shows no systematic changes with $T_m$ or with crystal structure: most values are small, many being $\Delta\rho=4\pm2\%$. The overall mean (4.7±2.6%) is the same as that (4.7±1.8%) for those (22) of BCC structure and the slightly higher mean for the (7) HCP metals (5.4±1.7%) apparently results from the single relatively large value for Ru. The mean value for the (11) CCP metals (7.1±2.4%) appears to be slightly larger than the average, a possible reason is mentioned in entalphy changes at $T_m$. Values for the lanthanides are more difficult to appraise due to data shortcomings, some magnitudes are relatively small but others are comparable with those for metals with similar structures. Support for the overall reliability of these results is provided by the similarities of values within several groups of chemically related metals, including Groups 1, 2 and 11.

The average density change (4.7%) at $T_m$ may alternatively be represented as an (average) rise of only 1.67% in the linear spacing of atoms (or unit cell edge) on the phase change solid to liquid. Nevertheless, the physical consequences associated with this relatively small expansion are considerable: loss of rigidity in the liquid and also loss of extended order, as shown by the diffuse X-ray diffraction patterns
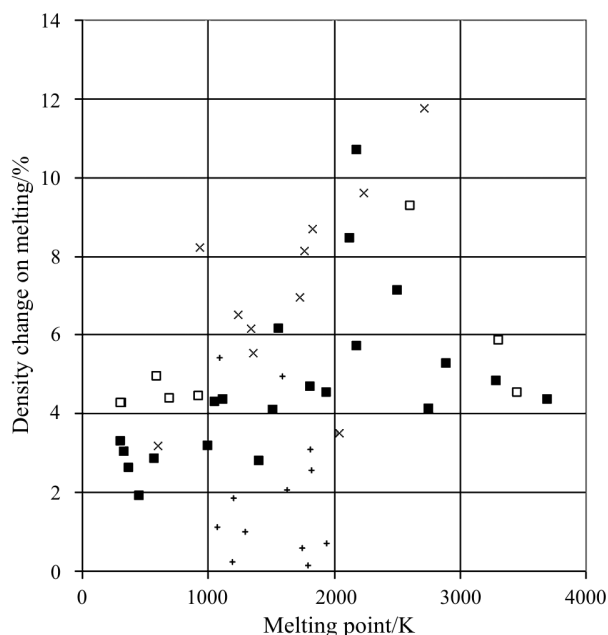


**Fig. 4** Plot of $\Delta\rho\%$, density diminution on melting, *vs.* $T_m$ for 52 metallic elements that crystallise in the $\times$ – CCP, $\square$ – HCP and ■ – BCC forms at $T_m$: the lanthanide metals have been distinguished – +. Further explanation is in the text

characteristic of the melts. In contrast with the precursor solid, above $T_m$ the melt is mobile, fluid and unable to withstand any shearing force.

## Structures and crystallographic transformatons of the metallic elements

The metals listed in [8] are most usually characterised by close packed structures: CCP, HCP and/or BCC arrays of approximately spherical ions. Of the 54 metals in Groups 1–12 (including the lanthanides), 33 record no structural transformation between 0 K and $T_m$. The others undergo crystallographic changes, attributable to variations of the relatively most stable lattice with temperature and pressure. Overall there are very wide variations in crystal stabilities as shown by $T_m$ values which rise from Hg, Cs and Ga (234, 301 and 303 K) to Os, Re and W (3306, 3459 and 3695 K).

Eight elements in Groups 9–11 are exclusively CCP (and exceptionally Co undergoes the HCP to CCP transformation at 695 K): $T_m$ values range widely from 1234 to 2719 K. Six of the metals in the adjoining Groups, 7, 8 and 12, are exclusively HCP and $T_m$ values for these vary widely from the lowest for Cd (594 K) and Zn (692 K) to the highest for Os (3306 K). There are the low temperature forms of Mn ($\alpha$ and $\beta$, Group 7) and of Fe (BCC, Group 8) which, on heating, transform first to CCP and subsequently

to BCC, below the $T_m$. Finally, and exceptionally, Hg melts at the lowest $T_m$ (234 K) for any metal. Both forms of stable closest packing of atoms are, therefore, associated with the 'middle' of the periodic table (Groups 7–12) and there are a few other additional examples, including Mg (HCP, Group 2), Ho, Er, Tm and Lu (HCP, Group 3) also Al and Pb (CCP, Groups 13 and 14).

The elements of Groups 1–6, together with Tl, but excluding Mg, Ho, Er, Tm and Lu, either crystallise in the BCC form only or transform to this structure below $T_m$. Values of $T_m$ for the BCC metals vary from the readily fusible alkali metals (from Cs – 301 K) to the most infusible metals (W – 3695 K, Ta – 3290 K). No simple pattern could be discerned in the stable phase forms of the lanthanides, which apparently varied with numbers of $4f$ electrons. The lowest values of $T_m$ increased (1071–1191 K) in the sequence: Ce, Eu, Yb and La (containing 1, 6, 13 and 0–$4f$ electrons, respectively) and these (except Eu, which is always BCC) transformed to the BCC structure before fusion. In the series of 7 elements from Pr to Dy (containing 2 to 9–$4f$ electrons, but excluding Eu with 6) values of $T_m$ progressively increased from 1204 to 1685 K, and all transformed from other structures to BCC at 200 K (or less) below the $T_m$. The remaining elements, Ho, Er, Tu and Lu (containing 10–12 and 14 $4f$ electrons) maintained the HCP structure to the relatively highest $T_m$ values for metals of this Group (1747 to 1936 K).

## Melting points, boiling points and physical properties

The possibility that there are relationships between $T_m$ and/or $T_b$ values for these metals and the physical properties of the component atoms was explored to determine whether these exerted dominant, or recognisable, controls on fusion or volatility: secondary effects were more difficult to identify and to characterise.

- Ionization potentials of metal atoms. No trends of correlation were found and no simple or obvious relationship was recognised between the ionization potentials (IP) [12] and $T_m$ or $T_b$. Although 1st and 2nd IP values for Be (9.322, 18.21 eV) and Zn (9.394, 17.96 eV), both divalent metals, are comparable, $T_m$ (1560, 693 K) and $T_b$ (2744, 1180 K) values are significantly different. Again, $T_m$ values for Fe (1811 K) and Tm (1818 K) are close, whereas the 1st–3rd IP values represent large energy differences (Fe – 7.90, 16.18, 30.65 and Tm – 6.18, 12.05, 23.68 eV). The overall pattern of IP values within the elements of Groups 4–12 did not relate simply to the magnitudes of $T_m$. 1st–3rd IPs for the lanthanides showed a general tendency to increase between La to Lu, the anomalous values were found at Gd and Lu, whereas Ce, Eu and Yb showed the low melting points. (Similarly, there was no simple or obvious relationship between $T_m$ or $T_b$ and electron affinity [13].)

- Polarizabilities of atoms. The electric dipole polarizabilities of atoms [14] for the Group 1–3 metals were all greater than $20 \cdot 10^{-24}$ cm$^3$, except for the elements: Al, Be, Mg and Sc. Values for all the other metals were below this value and no trends of variation with $T_m$ or $T_b$ were found. A similar comparison, based on the more limited data available for the cations [15], again revealed no identifiable correlations.

- Metallic properties. Neither the electrical resistivity at 300 K [16] nor the electron work function of the metal [17] showed any trend of correlation with either $T_m$ or $T_b$. The coefficient of expansion (298 K) [7] generally decreased with increase both of $T_m$ [18] and of $T_b$.

- Lanthanides. The Group 3 metals appear to be potentially suitable for the recognition of trends because listed [7] values of $T_m$ (1071–1936 K) and of $T_b$ (1469–3793 K) vary widely. A linear relationship was found between $\Delta H_M$ and $T_m$ (as in Figs 1 and 2), the highest values were for the HCP (only) metals (Er, Ho, Lu and Tm) together with Sc and Y (both BCC). Similarly, $\Delta H_b$ values increased with $T_b$ (as in Fig. 3), though with some scatter. While relatively low $T_b$ values were associated with almost empty (Ce), half-filled (Eu) and filled (Yb) $4f$ electron shells, this pattern did not correlate with any identifiable features for the IPs of the lanthanide atoms [12]. Ce, Eu and Yb also showed relatively low $T_b$ values and there were somewhat smaller diminutions for Sm and Tm. Other $T_b$ values (between 3370–3793 K) did not vary systematically but $T_m$ values increased with atomic number (1193–1936 K). No simple explanation for the significant variations of $T_m$ and $T_b$ values for the lanthanides was found.

- Molecular bonding in metals. The possibility that the strength of bonding in the metal ($M$) crystal or liquid was comparable with that in the gaseous diatomic molecule ($M_2$) was investigated through plots of $D°(M–M)$ vs. $T_m$ and $T_b$ (48 values of $D°(M–M)$ were obtained from [19]). Both plots showed considerable scatter from which no significant trends were recognised: data for Group 15 and 16 elements showed relatively high bond energies for elements having low $T_m$ and $T_b$ values. A trend of increase of $\Delta H_b$ with $D°(M–M)$ is shown in Fig. 5, from which the elements in Groups 1, 15 and 16 have been omitted. The enthalpies of vola-
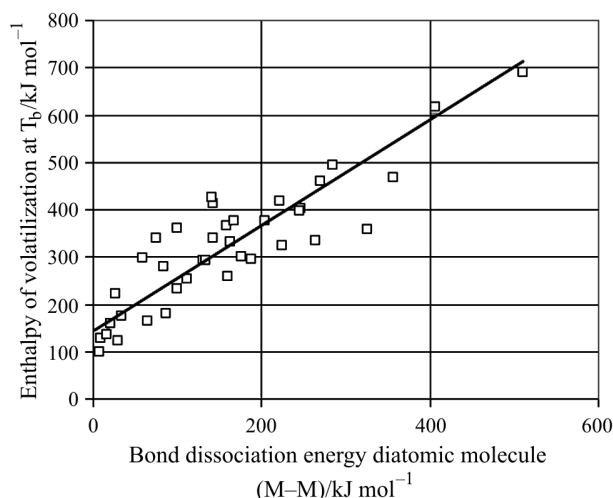
**Fig. 5** Plot enthalpy of volatilization *vs.* enthalpy of dissociation of diatomic molecule, $M_2$, $D°(M–M)$: an approximate trend is discerned. 38 metals, for which the data were available [19], are included but values for the elements of Groups 1, 15 and 16, which did not conform to the trend, have been omitted

tilization are in the vicinity of the line representing ($M–M$ bond dissociation enthalpy +150 kJ mol$^{-1}$). This is consistent with evaporation control through a surface step involving rupture of a metal-metal bond having strength similar to that characteristic of the diatomic ($M_2$) molecule, associated with an atomic product desorption step.

- Ionic structures of metals. The possibility that the stability of metallic crystals is based on ionic interactions ($M^+M^-$) was investigated for several metals, but no encouraging results were obtained. For example, if sodium metal consisted of a BCC array of Na$^+$ and Na$^-$ ions, the total lattice energy can be estimated, through the Born-Haber cycle, to be about 333 kJ mol$^{-1}$. This is significantly less than the value obtained from the Madelung calculation [20], about 560 kJ mol$^{-1}$.

## Discussion

*The melting process: kinetics and mechanisms*

Fusion/crystallization is a first order phase transformation because [21] energy is transferred under isothermal conditions, accompanied by discontinuities of energy and of volume, quantitatively discussed above for metals. Melting is invariably endothermic, usually reversible, and proceeds readily in either direction depending on whether energy is supplied or withdrawn at the melt/solid contact. Above $T_m$ the regular long-range structure of the rigid crystal is replaced by less extended order in the liquid. In contrast

with most chemical reactions, crystallization/melting is completed without perceptible temperature variation at the characteristic $T_m$. The relationship of fusion to other physicochemical processes is discussed.

- Solid superheating and melt supercooling. Crystal superheating is exceptional, though a few instances have been described [22], and the extent is usually small. Supercooling occurs for many melts, in the absence of the solid phase at which component ordering results in crystal growth, accompanied by energy loss ($-\Delta H_f$). A 'seed crystal' may be necessary to initiate solid formation and nucleation of the crystal phase in the melt is a difficult step for many substances. The solid provides a template or foundation for extension of the long-range order of the crystal and (equally importantly) enables the excess enthalpy ($\Delta H_f$) to be dispersed, warming the cooler solid and/or the supercooled liquid towards $T_m$.

- Melting/crystallization kinetics: the interface. The solid/liquid contact boundary in a melting/crystallization system may be regarded as analogous to the interface of solid state chemistry [23]. This is a contact zone within which the constraints on change may be locally relaxed, reactivity is enhanced and thus the transformation is facilitated. Melting involves chemically identical components of both liquid and solid so that the solid is invariably 'wetted' by the liquid, ensuring maintained and effective interfacial contact between the phases. In contrast with chemical reactions, there is no variation in 'reactant' (or 'product') concentration as the change proceeds because no modification of the (space-filling) components is involved (except for the minor density difference). Similarly, in the pure liquid or solid there is no diffusion limitation on the rate of change that results from the availability of 'reactant' at the wetted interface. Consequently, the rate of melting (or crystallization) is determined by local temperature differences: the rate at which energy is supplied to (or removed from) melt/solid contacts at $T_m$. These conditions (an effective interface, constant concentration, no diffusion limitation) differ from the kinetic controls applicable to most chemical rate processes where rates change with reactant concentrations and may be subject to diffusion controls on the frequency of those encounters which lead to product formation. Specific kinetic characteristics apply in reactions of solids [23].

The facile reversibility of melting/solidification is evidence that any activation step involved offers only a negligible barrier to the rate of phase change. This contrasts with most chemical reactions, which are rate determined by activated bond redistribution controls so that rates are temperature dependent. Fusion and solidification, however, occur at the invariant temperature, $T_m$, that is a characteristic of each

solid. The rate dependence of this phase change on temperature is, however, discontinuous. Immediately below $T_m$ a crystal remains unchanged indefinitely but, following the smallest rise above this temperature, melting proceeds at a perceptible rate. Consequently, a conventionally calculated activation energy for melting, $E$, is expected to be very large, even approaching infinity, depending on the magnitude of the small temperature difference from $T_m$ that is considered. Such rate data do not fit the Arrhenius equation, there is no evidence of a significant energy barrier, representing an activation step, for changes in component dispositions and mobilities at $T_m$. An apparently large $E$ value cannot be reconciled with a reversible, facile melting process so that conventional kinetic theory is not applicable [24].

Nucleation, the initiation of melting, is (almost) invariably facile, as demonstrated by the inability of (almost all [22]) solids to superheat. It is believed that components of the surface layers of solids, subjected to asymmetric forces, are 'loosened' and become more mobile in the approach to $T_m$. This is the effective prenucleation change that is the precursor to fusion, thus ensuring virtually immediate formation of the liquid phase at $T_m$. The (local) relative ease of change at an established interface contrasts with the relative difficulty (in many solid state chemical reactions) of initiation by formation of the smallest particle of product phase, nucleation [23, 25].

- Crystallization kinetics. The principles set out in the previous paragraph for melting apply (suitably amended) to the reverse process, with the exception of supercooling. In the absence of product phase, the melt may (though for many solids does not) cool significantly below $T_m$ before a mechanism for the local removal of excess energy of the liquid ($\Delta H_f$) is associated with nucleation of the solid. Again the kinetics of crystal growth are controlled by the (relatively rapid) diffusion of heat and rate measurements are generally impracticable.
- A mechanism of melting. The above characteristics of melting are explained by a model in which the energy barrier (activation step, represented by $E$) to the structure/order change at the solid/liquid interface is inconsequential compared with the thermal energy available. Facile addition/loss of atoms (or of molecules) at the crystallographic sites which form the solid/liquid contact interface proceed easily at $T_m$, without appreciable opposition from bond reorganization steps that require any significant pre-investment of energy. Because crystal growth takes place at a 'wetted' contact between solid and liquid, wherein bonding is facile, the rate of change is controlled by heat diffusion. [Orientation of liquid components is unlikely to exert a significant influence on crystalliza-

tion rates of metals in which the atoms are spherical.] The movement of heat within crystals, having relatively high thermal conductivities, is more rapid than that in liquids [26] and internal temperature deviations, within solid particles, are small. Thus, in a solid–liquid mixture the rate of melting or solidification is controlled by the movement of heat in the liquid phase, to and from solid particles present and also the boundary walls (heat source/sink) of the system. Under the conditions most usually encountered, modelling of energy flow is impracticable within a heterogeneous system with ill-defined interface geometry [23] and subjected to small, probably locally variable, temperature gradients. The solid surface not only provides a template for crystal growth but also a sink, or dispersion route, for the excess energy released ($\Delta H_f$) on liquid component immobilization when accommodated into the crystal surface during solidification. Progress in understanding the factors that control melting kinetics might be achieved by measuring the minimum sizes of particles required to form effective crystallization nuclei and the dependence on the degree of supercooling.

- Lindemann theory of melting. On this model [18] fusion is ascribed to unsustainable lattice instability, that arises from excess thermal energy in the form of vibrational interactions between lattice components. The relationship identified above between $T_m$ (and $T_b$) as a fraction of the bonding energy of the condensed metal phase (solid or liquid) suggests that energy in excess of a characteristic (quantum level) vibration energy level results in loss of cohesion and long range order. When this limiting energy is exceeded, a (most readily removed) surface atom of the crystal is detached and is transferred into the fluid phase, diminishing the unsupportable 'energy excess' from the crystal by conversion to $\Delta H_f$ on liquefaction. The solid melts when a critical quantum level is exceeded: this accounts for the consistency and precise constancy of $T_m$, also the inability of crystals to superheat.

### Boiling point and melting point magnitudes for metals

As shown in Figs 2 and 3, there are correlations of $\Delta H_f$ with $T_m$ and of $\Delta H_b$ with $T_b$: the latter trend was closely similar to a plot of the enthalpy of volatilization at 298 K [10] *vs.* $T_b$. While these data show some scatter, values for all the metals considered contribute to and are close to the overall trend. It is concluded, therefore, that $T_b$ provides a measure of the intercomponent bond energy that stabilizes the liquid phase. A plot of $T_b$ *vs.* $T_m$ shows a weak correlation. The ratio of ($T_m/T_b$) for 25 transition metals from Groups 4–12 were in the range

0.55±0.12: the two values outside this interval were Cr- 0.74 and Hg- 0.37.

- Groups 1–3. There were some similarities in values of $T_m$ and of $T_b$ for the metals that constitute each of the Groups 1–3, but there were also significant exceptions. Both values for Li were relatively larger than those for the other alkali halides. In Group 2, Be showed high values of $T_m$ and $T_b$, while those for Mg were relatively less than the magnitudes for Ca, Sr and Ba. In Group 3, including the lanthanides, the pattern of $T_m$ and $T_b$ magnitudes was more complicated, including $T_m$ values for Ce, Eu and Yb that were lower than the mean trend and, similarly, $T_b$ values were relatively low for Eu, Sc, Sm, Tm and Yb.

The increasing overall mean values for the metals of Groups 1, 2 and 3 ($T_m$: 335, 1130 and 1496 K and $T_b$: 1142, 1940 and 3055 K respectively) might be ascribed to increased strength of bonding in the condensed phases. One possible reason is the progressive increase in the number of valence electrons available ($1\rightarrow3$). This can, however, be only a partial explanation because it does not account for the many exceptions to an approximate and incomplete representation. Attempted correlations with the IP values of the constituent atoms (and of the ions) [12] identified no patterns of variations to explain the above trends, including the apparent exceptions.

- Groups 4–12. The most significant trends found were the linear relationships between the enthalpies of volatilization at $T_b$ [6] and at 298 K [10]: volatility was directly related to the strength of bonding (dissociated on volatilization) within the coherent, condensed phase. For the Groups 4–12 metals, most data points on the $T_b$ *vs.* $T_m$ plots were close to the mean line: Hg was the most distant, followed by Au and Cr (below and above the mean line). Scatter was less than for the metals of Groups 1–3. The magnitude of $T_m$ may be regarded as providing an approximate measure of metallic crystal stability.

- Periodic table. No obvious or simple correlation between $T_m$ or $T_b$ values with position of the element in the periodic table was found. Overall, the highest values tended to be for metals of Groups 5–7 and generally increased in the sequence 1st, 2nd and 3rd Transition Metal Series. The largest of all $T_m$ and $T_b$ magnitudes were for W and Re, followed by their neighbours, Ta and Os, all in the 3rd Series. This may be identified with the largest numbers of potential bonding electrons (5 electrons in the half-filled/empty $5d$ electron shell in Re) and 68 electrons in the inner shells, offering screening from the nucleus. $T_m$ and $T_b$ magnitudes for the 3rd Series metals mentioned are followed, in descending sequence by Nb and Mo (again followed by their neighbours, Tc and Ru), which are the rela-

tively highest values in the (less screened) 2nd Series. Finally, it is the Group 5 metal, V, that shows the highest $T_m$ and $T_b$ magnitudes for the smaller atoms of the 1st Series, again followed by its neighbours, Ti and Cr. Values are, however, significantly below those of the 2nd and 3rd Series metals of higher atomic number, though slightly above those of the Group 3 metals. One explanation is that, in the 1st Series, (about) 3 electrons participate in metal crystal bonding, consistent with the +3 valence cations that are frequently observed for these metals: $T_m$ values are comparable with those of the Group 3 elements.

Thus, there is a qualitative association of the highest values of $T_m$ and $T_b$ with the half-filled/empty $d$ orbitals in the middle of the periodic table, Groups 5–8, which offer the greatest possibilities of electron donation/acceptance, thus the strongest bonding [27]. Lower stabilities, with some variations, are shown by the decreasing (average) number of available electrons in the electropositive elements in the sequence Groups 1–3. For Groups 10–12, progressive filling of the $d$ shells diminishes the availability of electron accepting levels, again reducing the number of electrons available to participate in bonding so that $T_m$ and $T_b$ magnitudes are generally comparable with those of metals in Groups 1–3. Crystal cohesion of the Groups 13–16 elements involves contributions from covalent bonding (e.g., diamond). This influences crystal structures and physical properties for the lower atomic number elements but the later, more metallic members of these Groups, show a greater ability to form ionic compounds and are more readily fusible.

These comparisons identify a complicated pattern of variation of metal $T_m$ and $T_b$ magnitudes with position in the periodic table [27]. The dominant trends are qualitatively consistent with variations of the maximum number of electrons and unoccupied orbitals available for bond formation between neighbouring atoms. This stability, however, significantly diminishes with decrease in atomic number, which may be ascribed to less effecive screening of the outer orbital electrons in the smaller atoms. The increases in atomic radii of the metals in the transition series 1–3 are small and all 21 elements in Groups 5–11 are within the range 125 to 146 pm [27]. $T_m$ and $T_b$ magnitudes for the 1st Transition Series are (approximately) comparable with (the relatively variable) values for Group 3, identified with (about) 3 bonding electrons. Greater condensed phase stabilities, higher $T_m$ and $T_b$ values for the metals of Groups 5–8, are then associated with effectively larger numbers of interacting electrons/orbitals. The diminishing crystal stability of metals of Groups 2 and 1, 11 and 12 (lower $T_m$ values) is similarly identified with bonding

involving only 2 or 1 electron/orbital. An extensive comparison of the $T_m$ and $T_b$ magnitudes with the (incomplete) listed values [12] of the first and subsequent atom IPs revealed no significant trends capable of accounting for the patterns of variations of properties observed. While the fusabilities (at least, approximately) and volatilities of these metals correlate with condensed phase stabilities ($\Delta H_b$), the atomic/electronic interactions determining these properties have not been characterized quantitatively.

Some support for the view that fusibility is determined by the electropositive character (electronic donor properties) of the metal is indicated by the tendency for values of $T_m$ to increase with the standard reduction potentials [28]. Group 1 (alkali) metals melted readily (301–453 K) with EMF values between –2.71 and –3.04 V and values rose progressively to tungsten (3695 K and $W^{3+}$ at 0.1 V). A similar trend was shown by graphs of $T_b$ *vs.* EMF values, though data tended to be slightly more widely dispersed. No correlation, however, was found in the highly scattered data points on plots of $T_m$ and of $T_b$ *vs.* EMF values for the elements of Groups 7–13.

### The value of a model melt structure at $T_m$

Laidler has emphasized [29] the value and importance of representational models in advancing theory (rejecting, for example, relationships that are 'theoretically sterile' in discussions of the significance of the Arrhenius equation in chemical kinetics). Consequently, the absence of a model for the melt structure at, and just above, the $T_m$ can be regarded a factor limiting [1] melting theory development. A suitable theoretical representation should be capable of providing insights into and understanding of the physical controls that determine properties of solid/liquid systems and the variations in ordered packing arrangements of components that occur at $T_m$. A principal motivation in undertaking the present comparative analysis was to determine the magnitudes of the energy and of the density changes that accompany fusion. Such information identifies the possible types and limiting extents of the structural differences that distinguish solid and melt. The model formulated below is intended as a contribution towards theory advancement.

### Changes of enthalpy and of density at $T_m$

It is emphasized in the following paragraphs that the magnitudes of the changes of $\Delta H_f$ and of $\Delta\rho$ on metal melting at $T_m$ are remarkably small. The values cited are averages from the 68 elements considered, the exceptions mentioned are mainly those metals from Groups 13–16 that exhibit some non-metallic charac-

teristics. It follows that the structures of and bonding in the melts must be similar to the dispositions of atoms in the metallic crystals. The spontaneous tendency to maintain order in the melt is expected from the strong propensity, shown by assemblages of atoms, ions or molecules, towards arrangement in regular close packing arrays, as demonstrated by the widespread tendency for cooled melts to crystallize. The model formulated below is based on the conclusion that the ordered dispositions of atoms in the melt can be little different from the (well-characterized) structures of the solids.

### Enthalpy changes at $T_m$

[$\Delta H_f/(\Delta H_D+\Delta H_S)$]: overall mean – 0.381. A majority of the values were between 0.17 and 0.4, a few were 0.4 to 0.6, higher values were found for As, Bi, Sb and Te (0.85–0.88) and the highest were Ga – 1.0 and Si – 1.3.

[$\Delta H_f/\Delta H_M$]: overall mean – 0.261. A majority of values were between 0.13 and 0.3, a few were 0.3 to 0.4, and, again, higher values were found for As, Bi, Sb and Te (about 0.46), with Ga – 0.50 and Si – 0.56.

[$\Delta H_f/\Delta H_b$]: overall mean – 0.0497. Almost all values were between 0.015 and 0.08, with higher ratios for Re – 0.086, Sb – 0.103, Ge – 0.11, Si – 0.14 and Te – 0.15.

[$\Delta H_f$/Enthalpy of volatilization at 298 K [10]]: overall mean – 0.0434. Most values were between 0.012 and 0.08, but higher for As – 0.081, Ge – 0.099 and Si – 0.112.

Enthalpies of fusion generally represent only about a quarter of the energy required to heat the solid from 0 K to the melt at $T_m$ and about 5% of the energy required for volatilization at $T_b$ (without including the energy required to heat solid and liquid).

### Density changes at $T_m$

The overall average density change for the fusion of 52 metallic elements (CCP, HCP, BCC structures and others) was $\Delta\rho$=4.7±2.6% (Density changes on metal melting). Such expansions represent only very small linear changes of the unit cell edges (average 1.67%). Two illustrative (BCC) examples are for sodium where the unit cell edge for the solid (4.312 Å) (apparently) rises on melting to 4.351 Å (change 0.039 Å) and, similarly, at $T_m$ the iron spacing (2.936 Å) is increased by only 0.047 Å.

### A structure for melts

Ordering within assemblages of large numbers of very small particles is the powerful spontaneous process that characterizes crystallization. The attractive bonding forces (ionic, covalent, metallic, van der Waals, hydrogen) result in the generation of extended three-dimensional, closely packed and regular arrays of atoms,

ions or molecules. For some substances only a single crystal structure is known, others are polymorphic, exhibiting two, or more, alternative arrangements of components within the unit cell. The solids formed are coherent, rigid and the extended regular arrays maintained often contain few imperfections. Above the characteristic $T_m$, long range order and rigidity are lost on liquefaction. The following representational model is proposed to account for the melting of metals and may be of potentially wider applicability to other systems in theory development.

The model formulated here reconciles the large and discontinuous difference of component mobility that distinguishes the fluid and the solid states with the relatively very small enthalpy and density changes that occur on fusion (Enthalpy changes at $T_m$ and Density changes at $T_m$). It follows that only relatively minor structural and bonding modifications are possible during melting. Furthermore, there are only a limited number of spatial arrangements capable of achieving the dense packing of the spherical metal atoms in the melts discussed here. Consequently, there must be extensive retention of the ordered structure characteristic of the crystalline solid in the dense and, therefore, densely packed liquid. The dynamic melt model described is consistent with the observed changes at $T_m$, as discussed below.

## A model for the melt

Melting can be represented by a model in which it is assumed that at, and above, $T_m$ there is relaxation of the restriction, applicable to crystals, that the components are immobilized in a single spatial (lattice) structure. The melt is then represented as an assemblage of local domains within each of which the constituents are arranged in one of two, or more, alternative structures. Each such small domain is envisaged as a local region within which components are packed in one (or other) regular array of the types that are familiar from crystals. The properties of the liquid can then be ascribed to a dynamic equilibrium maintaining the rapid and continual transfer of material to and from each of the domains. A constant flux of components between locally ordered (crystal-like) material (regliq domains) occurs across the dynamic and constantly reorganizing interfacial contacts composed of locally more irregular arrays: irregliq zones. The (thermal vibration activated) mobility of irregliq material accounts for the inability of the system to sustain a stress and thus accounts for the fluid properties of the liquid. Irregliq zones are analogous to, but much more mobile than, the 'grain boundary' material in solid-state chemistry and constitute the relatively less ordered zones that are the contact areas joining contiguous more perfect crystalline regions

(regliq domains). The rapidity and ease of movement within the relatively less ordered irregliq material, that constitute the neighbouring regliq domain boundary interfaces, can be likened to lubrication of the contact surfaces. Vibrational activation of irregliq components explains the mobility and fluidity of the liquid. A suitable descriptive label is the SET/LIQ model. 'Set' describes the crystal as a 'Single Extended Tesselation' which is replaced at $T_m$ by the 'Lattice Interconversion Quadrille' (a 'quadrille' is a structured form of dance).

An essential feature of the set/liq representation of the melt is the dynamic interconversion between the alternative structural forms that participate in the equilibria. The existence of pseudomorphs, having comparable stabilities, is well established for the many metals that undergo phase transitions on heating from 0 K to $T_m$ [8]. Enthalpies of these polymorphic changes are small (e.g., Fe – 0.90 and 0.837 kJ mol$^{-1}$ at 1184 and 1665 K, respectively and La – 2.85 kJ mol$^{-1}$ at 1141 K [6]). It is reasonable to assume that those metals known in only one form [8] may similarly be capable of adopting alternative lattices of comparable, but slightly lower, stabilities, although these do not appear as distinct crystalline phases. On the addition of the small amount of energy ($\Delta H_f$) required for melting at $T_m$, all sufficiently stable structural forms may then coexist and participate in the dynamic interconversion equilibrium of the liquid. Therefore, $\Delta H_f$ sustains (*i*) all participating structures, including crystal forms of relatively (slightly) lower stabilities, (*ii*) the less perfect (less stable) irregliq zones and (*iii*) the dynamic transfer of material across irregliq zones between contiguous regliq domains. (This model is potentially of wider applicability. Crystal lattice energy calculations for the alkali halides [20] identify stability differences for alternative structural forms that are often small and the density and enthalpy changes at $T_m$ are again consistent with the above model [30].)

The maintenance of component ordering in liquid metals is consistent with the geometric properties of the various alternative lattices that can be formed by the regular packing of spheres [31]. The significant conclusion is that the relative density changes, Table 1, between the structures possible are comparable with those (invariably diminutions) that are observed on metal melting, on average only 4.7%. It has already been pointed out (Structures and crystallographic transformations of the metallic elements) that many metals adopt the BCC structure below $T_m$: this is 8.14% less dense than the CCP and HCP forms (12 coordination). The coordination number for BCC is 8 with 6 atoms that are 15% more distant, tending towards a larger number (14) of nearest neighbours. Sim-

ple hexagonal packing (18.35% less dense than CCP and HCP) similarly is coordination number 8 with 12 atoms that are 40% more distant (total: 20 surrounding atoms). Enhanced vibration in the melt above $T_m$ will tend to increase the effective coordination number, this apparently occurs for those metals that adopt the BCC structure below $T_m$. There is also the possibility that packing changes are accompanied by some vibration imposed distortion and/or symmetry loss of the unit cell, so that the spacing distinction between the nearest and next-nearest neighbours is diminished. Thus, enhanced thermal vibration, in a less rigid structural repeating unit, can be associated with a tendency to increase coordination numbers, accompanied by a diminution in density and symmetry/long range order: these property changes are characteristic of melting.

The participation of domains composed of (perhaps slightly and unsymmetrically) distorted variants of these (Table 1) coordinated structures, in dynamic equilibrium with dominant representation by the preferred solid-stable forms, BCC, CCP and/or HCP, accounts for the magnitudes of enthalpy and density changes on melting. Furthermore, specific low temperature and high coordination structures [9], possibly close packing arrangements distorted to lower symmetry and characteristic of particular low temperature forms of metal crystals (e.g., Co, Hg, Mn and some lanthanides), may also be sufficiently stable to participate in melt equilibria. The comparatively large mean $\Delta\rho$ value for CCP metals (Trends in density changes on melting) may be ascribed to relatively greater proportions of the alternative structures, Table 1, in the melt.

The continual, rapid and facile transfer of atoms across the interdomain (irregliq) contact zones, containing locally high concentrations of imperfections, confers liquid properties on the assemblage by facilitating relative displacement movements of the contiguous regliq domains. Mobility of components between sites of comparatively low stabilities, within the less-regular arrays that form the contact between regliq domains, is promoted by thermal (vibrational) energy. Continual reforming of the irregliq material, due to the appearance, growth, shrinkage and loss of individual regliq zones within the dynamic equilibrium of order redistribution means that the compact matrix of the regliq domains is incapable of withstanding stress. An applied shear force results in the immediate relative movements of the more ordered zones through overall flow of the system, the necessary rearrangements being perceived as viscous drag. Rigidity and long range order of the crystal has been lost.

Structures and related properties of solid metals (and, indeed, of diverse other crystals) have been extensively characterized from the distribution patterns of diffracted X-rays. Similarly precise information is not obtainable for liquids, where reinforcement of scattered X-rays is ineffective due to the absence of long-range order. This is consistent with the model proposed above for the following conditions.

(*i*) When the sizes of particles, composed of regularly spaced components, are reduced in the approximate range 100 to 20 Å diffraction lines become broadened [32] to imprecise haloes.

(*ii*) Two or more regliq structures, together with the irregliq material, contribute to overall X-ray scattering. Variations of sizes and shapes of regliq particles will also diminish reinforcement of the scattered X-ray maxima.

(*iii*) Distorted high coordination number structures, within which the symmetry is diminished by enhanced vibrational energy and having varied orientations relative to the beam, contribute to the general scattering.

These effects are complementary but, if the small size of regliq domains is a dominant factor, their average diameter would appear to be 10–20 atoms or less [32].

Other models for melting

No theory of melting, having general applicability and acceptability, appears to be available. Two proposals, that undoubtedly include similarities with the set/liq model proposed here, are based on imperfection proliferation, in the form of dislocations [33] and of vacancies [34, 35]. In associating the melting process with the presence and/or generation of relatively high concentrations of crystal lattice defects [23], these theories perhaps also imply the retention of regions of crystal-type structure to which the imperfections are related. The (apparent) maintenance of order in these explanations of

**Table 1** Relative densities of alternative structures for packing spheres of equal size [31]

| Crystal structure | Coordination | Relative density | Density change from 12 coordination/% |
|---|---|---|---|
| CCP, HCP | 12 | 1.0000 | 0.00 |
| Body centred tetragonal | 10 | 0.9427 | −5.73 |
| BCC | 8 | 0.9186 | −8.14 |
| Hexangonal (simple) | 8 | 0.8165 | −18.35 |
| Cubic (simple) | 6 | 0.7070 | −29.30 |
| Diamond | 4 | 0.4593 | −54.07 |

fusion [33–35] would find extensive common ground with the models of alternative emphasis proposed here. Kuhlmann–Wilsdorf [33], predominantly concerned with metals, regarded melting as occurring at the temperature at which the free energy of the glide dislocation cores decreases below zero. Ksiazek and Gorecki [34, 35], discussing the alkali halides, identified melting with vacancy creation by enthalpy accommodated at $T_m$, $\Delta H_f$. For these ionic crystals, melting was initiated when the concentration of Schottky defects in the solid reached a critical value, 0.0017, and increased on fusion to about ($\Delta c=$) 0.15. Application of this model to metals would apparently be associated with lower concentrations of vacancies (Schottky-type) in the melt, on average $\Delta c= 0.047$, (presumably) with maintenance of the pre-melting structure in the intervacancy material. It is not clear whether this representation [34, 35] is intended to be generally applicable, e.g., also to metals.

*Summary: the set/liq melting model for metals*

Melting

Melting/solidification is a facile, readily reversible, discontinuous change in component mobility at the crystal/melt interface that occurs at the characteristic, invariant temperature, $T_m$. Melting is invariably endothermic. The occurrence and progress of this phase change is controlled by the movement of energy to or from the interface under conditions representing the critical limiting stability of the crystal structure at its boundary. Additional energy supplied to already 'loosened' crystal surface atoms, ions or molecules, readily results in the transfer of these chemically unchanged components to the liquid phase without a perceptible activation barrier at the solid/liquid contact. Solid superheating is rare but crystallization may be facilitated at an existing crystal face and (for some liquids) withdrawn energy results in the equally facile reverse process, components from the cooled liquid crystallize to augment the solid particle. The rate of the melting/crystallization process (in either direction) is determined by energy transport (convection/diffusion, conduction and/or radiation) to/from the crystal/melt interface. Chemical controls do not apply to this physical change which is limited to modifications of the ordering and of the mobilities of unaltered participating species.

The melt

The small changes of enthalpy and of density at $T_m$ are strong evidence that both bonding and structural order between neighbouring components in the melt and in the solid undergo only relatively minor changes during fusion/solidification. It is suggested, therefore, that a principal difference between the solid and the melt is that the latter is composed of (regliq) small domains (believed to be less than about 30 Å diameter) within each of which the components are ordered in one of the possible alternative (crystal-like and stable) forms. This is consistent with, indeed represents an extension of, the well-known ability of metals to adopt different structures. On this model regliq domains are envisaged as undergoing constant and rapid interconversion across (irregliq) less ordered interfaces that form the contact interfaces between the contiguous, different domains. The irregliq network, analogous to the 'grain boundaries' of solid state chemistry, is regarded as highly mobile in the liquid, participating in a constant flux of components moving from and to regliq domains. The mobility and dynamic character of the irregliq material, movements resulting from thermal vibrational energy, accounts for the fluidity of the liquid and its inability to withstand a stress. This dynamic equilibrium, structure interconversions between regliq domains of all possible arrangements that have comparable stabilities, is sustained by the excess energy supplied as the enthalpy of fusion. This model extends the theoretical concepts developed to explain crystal properties to the representation of melts. It is suggested that the common characteristics of both condensed phases are distinguished by comparatively small modifications of enthalpy and density at $T_m$. Moreover, the representation proposed may have applicability beyond the metals considered here: preliminary comparative analyses of alkali halide melting, similar to that described above, have given promising results [30].

The melting point

The precise magnitudes of $T_m$ values for the pure metals (and indeed for diverse other substances) offer a challenge to the theorist to formulate an explanation. However, it must be concluded that, up to now, no adequate or general theory of melting has been provided. The present analysis describes trends of $T_m$ with $\Delta H_f$, Fig. 2 (influenced by crystal structure), and of $T_b$ with $\Delta H_b$, Fig. 3. These relationships may be interpreted as evidence that fusion and volatilization temperatures are determined by strength of inter-component bonding in the crystalline and in the liquid condensed states. However, despite the wealth of data available for these many (apparently) relatively simple metal melting systems, no fundamental physical explanation has been found for the observed trends. This is entirely consistent with the conclusions from the above analyses. Melting represents only small change both of bonding energy ($\Delta H_f$ values are usually only about 5% of $\Delta H_b$) and of densities (again approximately 5%). Furthermore, on the set/liq melt model, $T_m$ is regarded as the transition of the single

crystal structure to the dynamic interconversion between alternative atom-packing arrangements, presumably subject to competition between the different possible bonding modes. This type of change is not readily modelled. Variations of the lattice adopted by metals, including the pseudomorphic transformations below $T_m$ [8], must depend on the detailed electronic interactions between neighbouring atoms. These are not readily or simply related to any measurable physical parameters of the atoms concerned. The dominant role of the secondary and subtle stability controls makes the explanation of $T_m$ values difficult. It is concluded that, despite the large increase of mobility at $T_m$, the structural/bonding changes on the melting of metals are not fundamental and are limited in extent. This accounts for the notable lack of success in the search for an explanation of the magnitudes of $T_m$ and offers little hope that a simple theory may yet be found. Nevertheless, the recognition of the significance of order retention in the melt may have value in understanding the properties of liquids, particularly at their lowest temperatures.

Footnote

Qualitatively and briefly, the present paper presents the case that metal melts must retain much of the characteristic bonding and the structural order that are present in the crystal. The changes of enthalpy and density at $T_m$ are simply too small to permit significant loss of lattice order in systems that possess inherent tendencies to conform to crystal-type packing arrangements. The absence of long-range order in the melt is ascribed to replacement of the rigid and constant unit cell by dynamic interconversions of polymorphic (and perhaps slighly deformable) structural components that constitute the small domains. The tendency shown by many metals to adopt the BCC structure below $T_m$ suggests that higher effective coordination numbers become stable with rise of thermal vibrational energy and this may further increase after fusion. Temporary and continually changing asymmetry in slightly distorted unit cells that constitute each regliq domain (coordinations approaching 14 or even 20, (Enthalpy changes at $T_m$)) explains the diffuse nature of diffracted X-rays due to loss of precise maintained dimensions of the unit cells in this model for the melt.

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