## Melting, thermal expansion, and the Lindemann rule for elemental substances

A. V. Granato,<sup>1</sup> D. M. Joncich,<sup>1</sup> and V. A. Khonik<sup>2,a)</sup>

<sup>1</sup>Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801, USA <sup>2</sup>Department of General Physics, Voronezh State Pedagogical University, 86 Lenin St., Voronezh 394043, Russia

(Received 7 July 2010; accepted 9 October 2010; published online 29 October 2010)

An interpretation of a long-standing problem—the Lindemann melting rule—has been suggested within the framework of the interstitialcy theory. Melting is considered to be due to the rapid generation of thermodynamically equilibrium defects—dumbbell interstitials, which drastically decrease the shear modulus at the melting point. An analytical expression for the relationship between the thermal expansion coefficient and melting temperature coinciding with the Lindemann melting rule has been derived. The obtained results agree with available data on elemental substances. A correlation between the melting temperature and shear modulus has been discovered and explained within the framework of the same approach. © 2010 American Institute of Physics. [doi:10.1063/1.3507897]

In 1910 Lindemann published his famous work<sup>1</sup> in which he presented a model of melting. He suggested that since the amplitude of atomic vibrations increases with temperature, at some point it becomes large enough so that the atoms start to invade the space of their nearest neighbors initiating thus the melting process. In other words, melting occurs when the root-mean-square vibration amplitude  $\sqrt{\langle u^2 \rangle}$  becomes equal to a certain fraction of the interatomic distance *a*, i.e.,

$$\sqrt{\langle u^2 \rangle} = aC,\tag{1}$$

where *C* is an unspecified Lindemann constant. Equation (1) was commonly accepted later as the "Lindemann melting criterion." A development of this idea led Lindemann to the expression for the melting temperature  $T_m$ , which in the modern notation can be rewritten as

$$T_m = \text{const} \times \Theta^2 m \Omega^{2/3},\tag{2}$$

where  $\Theta$  is the Debye temperature, *m* the atomic mass, and  $\Omega$  the volume per atom. Equation (1) is approximately equivalent to

$$\alpha T_m = C, \tag{3}$$

where  $\alpha$  is the linear thermal expansion coefficient, which is assumed to be temperature-independent. Numerous experimental studies in the past century on different substances showed that relationship (3) is indeed approximately valid.<sup>2,3</sup> This relationship is usually referred to as the "Lindemann melting rule" while the Lindemann criterion (1) is currently considered to be one of the basic melting criteria<sup>4</sup> being often used in theoretical and computational studies (e.g., Refs. 5–7).

Another distinct melting model was suggested by Born,<sup>8</sup> who argued that a "rigidity catastrophe"—melting—is caused by a vanishing shear modulus due to the mechanical instability of the whole crystal. This idea found some support in computer modeling.<sup>6,9</sup> Frenkel in his seminal work<sup>10</sup> sug-

gested that melting requires *thermally accessible* intrinsic defects. The only such defects in crystals are vacancies and interstitials. Vacancies can be excluded from consideration since their formation entropy is far insufficient to explain the observed latent heat of melting.<sup>11</sup> Since vacancies and interstitials are the only thermally accessible intrinsic defects known from solid-state physics, interstitials should be the source of melting. In fact, their close relationship to melting was confirmed by extensive computer simulations.<sup>9,12,13</sup> However in general, to date there is a long-standing uncertainty about the correct criterion of melting and its microscopic mechanism.<sup>4</sup>

Figure 1 gives our own compilation of  $\alpha(T_m^{-1})$ -data for 62 elemental substances. In accordance with the Lindemann rule (3), this data set can be linearly approximated while the average slope  $C_{\exp} = d\alpha/d(T_m^{-1}) = 0.0254$  (separation of the



FIG. 1. (Color online) Linear thermal expansion coefficient  $\alpha$  of 60 metals plus Si and Ge as a function of the inverse melting temperature  $T_m$ . Thermal expansion data are taken from Ref. 15. For highly anisotropic hexagonal (trigonal) crystals,  $\alpha$  is accepted to be  $(\alpha_{\parallel} + \alpha_{\perp})/2$ , where  $\alpha_{\parallel}$  is the linear thermal expansion coefficient in the direction of sixth-(third-) order axis while  $\alpha_{\perp}$  gives thermal expansion in the perpendicular direction. In all cases,  $\alpha$ 's were taken for temperatures  $T > \Theta$  by 50–100 K.

<sup>&</sup>lt;sup>a)</sup>Electronic mail: khonik@vspu.ac.ru.

data into different structural classes (fcc, hcp, etc.) should lead to better linearization;<sup>14</sup> this is, however, out of our scope). In terms of the Lindemann criterion (1) this means that, on the average, an increase in the vibration amplitude by only  $\approx 2.5\%$  of the interatomic distance leads to melting. In our opinion, it is unclear and fairly strange why such a small increase in the vibration amplitude could cause melting. The same incomprehension was recently pointed out by de Podesta.<sup>3</sup> Moreover, it can be stated that current literature lacks any general indications that a critical vibration amplitude could indeed exist. However, independent of whether the Lindemann melting criterion is physically correct or not, the linear correlation  $\alpha(T_m^{-1})$  shown in Fig. 1 [i.e., the Lindemann rule (3) does exist and, therefore, must be explained. With the exception of the Lindemann criterion and its recent derivation<sup>14</sup> using the entropy difference between the liquid and solid phases, any other explanations of this correlation are unknown to us.

In the following, we accept that melting occurs not because of an increase in the vibration amplitude up to a certain critical limit but due to rapid generation of specific thermodynamically equilibrium defects-dumbbell interstitials (two atoms sharing the same lattice place), called also interstitialcies. It is not widely known that the ground state of interstitials in crystals represents a dumbbell (split) configuration =interstitialcy (e.g., Ref. 9). These defects have been reliably documented in various crystalline structures by different experimental, theoretical, and computational studies.<sup>9,16–18</sup> The reason why interstitialcies can cause melting originates from their large compliance to the external shear stress that leads to big anelastic deformation (in addition to the homogeneous ideal elasticity) and, therefore, sharp reduction in the shear modulus G. A thermoactivated increase in the interstitialcy concentration  $c_I$  becomes extremely rapid just below  $T_m$  (because of a decrease in the formation enthalpy with  $c_1$  so that, for instance, for Cu the equilibrium concentration  $c_I$  changes from  $\sim 10^{-5}$  just below  $T_m$  (Ref. 13) to a few percent just above  $T_m$  (Ref. 11) providing a catastrophic decay of the shear modulus to a small (but nonzero) quantity. A nonvanishing G in the liquid state was documented by molecular dynamics simulations.<sup>6,12</sup>

These features were determined by Granato in the Interstitialcy theory of condensed matter (ITCM).<sup>11</sup> By supposing that melting occurs when the Gibbs free energy  $\Gamma(c_I)$  of the solid equals to that of the liquid and the derivatives of  $\Gamma$  with respect to  $c_I$  are zero in both solid and liquid states, he derived a relationship exactly equivalent to Eq. (2). Thus, melting within the framework ITCM is viewed as a thermodynamic phenomenon being achieved through heterogeneous nucleation of the liquid phase in the presence of defectsinterstitialcies. Their large vibration entropy provides the required latent heat of melting.

Later, the ITCM was shown to quantitatively explain a number of basic thermodynamic and kinetic properties of (supercooled) liquids and glasses<sup>18–23</sup> (for a review, see Refs. 20 and 22). The purpose of the present Letter is to show that the ITCM also explains the Lindemann rule (3) and Lindemann-like behaviors found recently in metallic glasses. This theory also interprets a correlation between  $T_m$  and G presented below in this letter.

According to the ITCM, melting is controlled by the interstitialcy formation enthalpy, which increases with the

melting temperature. The formation enthalpy of an isolated interstitialcy was found to be  $^{11}$ 

$$H_f = \alpha_g G \Omega \approx \beta k_B T_m, \tag{4}$$

where  $\alpha_g \approx 1$  is a parameter accounting for the relative contribution of the shear modulus *G* (assumed to be known at T=0 K) to the formation enthalpy,  $k_B$  the Boltzmann's constant,  $\Omega$  the volume per atom, and  $\beta$  a substance-dependent constant. A fit for copper gives  $\beta=33.7$ .<sup>11</sup> To introduce the thermal expansion coefficient  $\alpha$ , one can use the Grüneisen law, which establishes a relationship between  $\alpha$  and the heat capacity per atom  $C_v$ ,

$$C_{\nu} = 3\alpha B\Omega/\gamma, \tag{5}$$

where  $\gamma$  is the Grüneisen constant and *B* the bulk modulus. Substituting  $\Omega$  from Eq. (4) into Eq. (5) and accepting the Dulong–Petit law,  $C_v=3k_B$ , one obtains

$$\alpha = \frac{\gamma G}{\beta B} \frac{1}{T_m}.$$
(6)

To calculate G/B here, the Poisson's ratio,  $\nu = (3B - 2G)/2(3B+G)$ , can be used. Then,  $G/B=3(1-2\nu)/2(\nu + 1)$  and, using Eq. (6), one finds

$$\alpha = \frac{3\gamma(1-2\nu)}{2\beta(\nu+1)}\frac{1}{T_m}.$$
(7)

Equation (7) analytically coincides with the Lindemann rule (3) with the Lindemann constant  $C=3\gamma(1-2\nu)/2\beta(\nu$ +1). For copper, the latter equation with  $\nu=0.35$  and  $\gamma$ =3.0 (Ref. 24) gives C=0.0297, reasonably close (within less than 30%) to its experimental value  $C_{\exp}=\alpha \times T_m$ =0.0235. Since the coefficient  $\beta$  in Eq. (4) is in general substance-dependent, one should expect some deviations from the linear relationship  $\alpha(T_m^{-1})$  given by Eq. (7). The same expectation originates from the fact that several metals undergo allotropic phase transitions at  $\Theta < T < T_m$ , which change their G,  $\beta$ ,  $\gamma$ , and  $\nu$ .

Thus, the ITCM provides an interpretation of the Lindemann rule as a result of interstitialcy-driven shear instability with no relation to any critical vibration amplitude. It is to be emphasized that the above consideration is based on the expression (4), which can be tested independently since it linearly relates  $T_m$  with the product  $G\Omega$ . The corresponding slope is  $dT_m/d(G\Omega)=1/\beta k_B$ . Then for Cu, this slope is predicted to be 344 K/eV, within a 11%-precision equal to its experimental value  $T_m/G\Omega=386$  K/eV. With G=48 GPa,  $\Omega=m_{\mu}/\rho N_A=1.26\times 10^{-29}$  m<sup>3</sup> ( $m_{\mu}$ ,  $\rho$ , and  $N_A$  are the molar mass, density, and Avogadro number, respectively) one calculates  $T_m$  for Cu to be 1303 K, coinciding within a 4%-accuracy with its equilibrium value  $T_m=1358$  K.

The melting temperatures of 62 chemical elements as a function of  $G\Omega$  are shown in Fig. 2. It is seen that there is indeed a clear increase in  $T_m$  with  $G\Omega$ , which can be fitted linearly. We are unaware of any earlier publications reporting this correlation. The averaged slope on this plot  $dT_m/d(G\Omega)=228$  K/eV. A clear explainable trend of  $T_m$ -increase with  $G\Omega$  in Fig. 2 suggests that the abscissas of the data points actually represent approximate formation en-thalpies of isolated interstitialcies in the corresponding substances.



FIG. 2. (Color online) Melting temperatures  $T_m$  of 62 chemical elements as a function of  $G\Omega$ . According to Eq. (4), a linear fit is performed over the whole data set. Shear moduli are taken from Ref. 24 for room temperature.

It is to be noted also that there are a few publications on metallic glasses reporting Lindemann-like correlations [i.e., similar to Eqs. (2) and (3)] with the glass transition temperature  $T_g$  instead of  $T_m$ .<sup>25–28</sup> The interpretation of this correlation within the present approach is fairly straightforward. It was long ago suggested by Turnbull<sup>29</sup> that the reduced glass transition temperature  $T_{rg} = T_g/T_l$  ( $T_l$  is the liquidus temperature) is a good indicator of the glass-forming ability (GFA) of an alloy and the higher  $T_{rg}$  is the higher GFA is expected. Ar present,  $T_{rg}$  is considered to be one of the most successful among other criteria for glass formation.<sup>31</sup> For metallic glasses, usually  $0.5 \le T_{rg} \le 0.6$  (Ref. 31). Since the glass compositions are usually close to eutectics, their  $T_l$ 's are close to the solidus temperatures  $T_s$ 's. Therefore,  $T_g$  represents a certain fraction of  $T_l$  or  $T_s$ . Such a correlation was indeed directly shown by Lu *et al.*<sup>27</sup> In this case, Lindemann-like relationships with  $T_g$  instead of  $T_m$  must indeed exist.

In conclusion, assuming melting to be a result of interstitialcy-induced lattice shear instability, we derived a simple analytical expression (7), which coincides with the Lindemann melting rule (3). This expression agrees with available data on elemental substances. Melting is controlled by the interstitialcy formation enthalpy, which is approximately equal to the product of the shear modulus G by the volume per atom  $\Omega$ . This leads to a correlation between the melting temperature and  $G\Omega$ , which is indeed observed. The fact that the glass transition temperature represents a certain

fraction of the melting temperature explains Lindemann-like relationships found in metallic glasses.

One of the authors (A.V.G.) would like to thank Dr. W. Williams for bringing a closely related topic to his attention.

- <sup>1</sup>F. A. Lindemann, Phys. Z. **11**, 609 (1910).
- <sup>2</sup>A. R. Ubbelohde, *Melting and Crystal Structure* (Clarendon, Oxford, 1965).
- <sup>3</sup>M. de Podesta, *Understanding the Properties of Matter* (Taylor & Francis, London, New York, 2002).
- <sup>4</sup>R. W. Cahn, Nature (London) **413**, 582 (2001).
- <sup>5</sup>J. J. Gilvarry, Phys. Rev. 102, 308 (1956).
- <sup>6</sup>Z. H. Jin, P. Gumbsch, K. Lu, and E. Ma, Phys. Rev. Lett. **87**, 055703 (2001).
- <sup>7</sup>S. V. Lepeshkin, M. V. Magnitskaya, and E. G. Maksimov, JETP Lett. **89**, 586 (2009).
- <sup>8</sup>M. Born, J. Chem. Phys. 7, 591 (1939).
- <sup>9</sup>A. Kanigel, J. Adler, and E. Polturak, Int. J. Mod. Phys. C 12, 727 (2001).
- <sup>10</sup>J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1946).
- <sup>11</sup>A. V. Granato, Phys. Rev. Lett. **68**, 974 (1992).
- <sup>12</sup>M. Forsblom and G. Grimvall, Nature Mater. 4, 388 (2005).
- <sup>13</sup>K. Nordlund and R. S. Averback, Phys. Rev. Lett. 80, 4201 (1998).
- <sup>14</sup>A. C. Lawson, Philos. Mag. 89, 1757 (2009).
- <sup>15</sup>Physical Quantities, edited by I. S. Grigoriev and E. Z. Meilikhov (Energoatomizdat, Moscow, 1991) (in Russian).
- <sup>16</sup>J. Holder, A. V. Granato, and L. E. Rehn, Phys. Rev. Lett. **32**, 1054 (1974).
- <sup>17</sup>P. H. Dederichs, C. Lehmann, H. R. Schober, A. Scholz, and R. Zeller. J. Nucl. Mater. **69–70**, 176 (1978).
- <sup>18</sup>K. Nordlund, Y. Ashkenazy, R. S. Averback, and A. V. Granato, Europhys. Lett. **71**, 625 (2005).
- <sup>19</sup>A. V. Granato, J. Non-Cryst. Solids (in press). doi:10.1016/ j.jnoncrysol.2010.08.012
   <sup>20</sup>A. V. Granato, J. Non-Cryst. Solids 352, 4821 (2006); 307–310, 376
- <sup>20</sup>A. V. Granato, J. Non-Cryst. Solids **352**, 4821 (2006); **307–310**, 376 (2002).
- <sup>(2002).</sup> <sup>21</sup>A. V. Granato and V. A. Khonik, Phys. Rev. Lett. **93**, 155502 (2004).
- <sup>22</sup>S. V. Khonik, A. V. Granato, D. M. Joncich, A. Pompe, and V. A. Khonik, Phys. Rev. Lett. **100**, 065501 (2008).
- <sup>23</sup>A. N. Vasiliev, T. N. Voloshok, A. V. Granato, D. M. Joncich, Y. P. Mitrofanov, and V. A. Khonik, Phys. Rev. B 80, 172102 (2009).
- <sup>24</sup>M. A. Schtremel, *Strength of Alloys: Part I* (MISIS, Moscow, 1999) (in Russian).
- <sup>25</sup>W. H. Wang, P. Wen, D. Q. Zhao, M. X. Pan, and R. J. Wang, J. Mater. Res. 18, 2747 (2003).
- <sup>26</sup>H. Kato, H.-S. Chen, and A. Inoue, Scr. Mater. 58, 1106 (2008).
- <sup>27</sup>Z. Lu and J. Li, Appl. Phys. Lett. **94**, 061913 (2009).
- <sup>28</sup>Z. Lu, J. Li, H. Shao, H. Gleiter, and X. Ni, Appl. Phys. Lett. **94**, 091907 (2009).
- <sup>29</sup>D. Turnbull, Contemp. Phys. **10**, 473 (1969).
- <sup>30</sup>C. Suryanarayama, I. Seki, and A. Inoue, J. Non-Cryst. Solids 355, 355 (2009).
- <sup>31</sup>Z. P. Lu and C. T. Liu, Acta Mater. **50**, 3501 (2002).