

data into different structural classes (fcc, hcp, etc.) should lead to better linearization;¹⁴ 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.³ 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 derivation¹⁴ 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.^{9,16–18} 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_I) 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.^{6,12}

These features were determined by Granato in the Interstitialcy theory of condensed matter (ITCM).¹¹ 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 Γ 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 defects—interstitialcies. 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^{18–23} (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 be¹¹

$$H_f = \alpha_g G \Omega \approx \beta k_B T_m, \quad (4)$$

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, Ω the volume per atom, and β a substance-dependent constant. A fit for copper gives $\beta=33.7$.¹¹ To introduce the thermal expansion coefficient α , one can use the Grüneisen law, which establishes a relationship between α and the heat capacity per atom C_v ,

$$C_v = 3\alpha B \Omega / \gamma, \quad (5)$$

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

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

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

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

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 $C_{\text{exp}}=\alpha \times T_m=0.0235$. Since the coefficient β 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 , β , γ , and ν .

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, $\Omega=m_\mu/\rho N_A=1.26 \times 10^{-29}$ m³ (m_μ , ρ , 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 enthalpies of isolated interstitialcies in the corresponding substances.

