Cluster model of melting and premelting of metals

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Using the Mitus' and Potashinskiĭ theory as the base [Soviet Physics JETP **53**, 1981; Phys. Lett. **87A**, No. 4, 179 (1982)], a cluster model of melting and premelting of metals is developed. The concentration of oriented defects, i.e., microcrystalline regions (clusters) with an irregular lattice orientation, is assumed to increase in the crystal as its temperature approaches the melting temperature T_m. The interaction between the oriented defects is described in the mean-field approximation with allowance for the entropy of the intercluster boundaries. The free energy of the system is expressed in terms of the orientation order parameter η. In the crystalline phase $\eta \approx 1$ while at the point T_m the parameter η abruptly vanishes. A melt is characterized by a completely random orientation of the crystalline clusters. The parameters of the model are estimated by comparing the calculations with the experimental data for several fcc metals. The contribution of the oriented defects to premelting effects is assessed with the specific heat as the example. Some possible mechanisms of defect formation are discussed.

The first structural theory of melting and premelting of metals was suggested by Frenkel'.[1] It assumes that the equilibrium concentration of vacancies c_v, increasing with temperature, experiences a jump from $c_v \approx 10^{-3}$–10^{-4} to $c_v \approx 10^{-1}$ at the melting point T_m. According to the theory, a melt is considered in essence as a crystal with a high concentration of vacancies. Later on, a vacancy theory of melting was developed by Lennard-Johns, Devonshire, Eyring *et al.* (see Ref. 2). It soon became clear, however, that the results of structural experimental studies give some evidence in favor of cluster rather than vacancy structure of melts. In the simplest model, the melt of a metal at the point T_m can be represented as a set of crystal clusters (10–10^2 atoms) with a chaotic mutual orientation.[3] Within the framework of this concept, the phenomenon of the premelting may include not only an increase of c_v but also the appearance in the crystal, near T_m, of microcrystal regions disoriented relative to the basic lattice. The possible role of such "collective position defects" in melting was suggested by Ubbelohde.[3] However, this idea was formulated the most clearly in the model of Mitus' and Patashinskiĭ.[4,5] The aim of the present work is to develop the model suggested in Refs. 4 and 5 in more detail and to correlate it with the available experimental data.

1. FORMULATION AND ANALYSIS OF THE MODEL

Following Refs. 4 and 5, let us suppose that near T_m the formation of microscopic regions (clusters) is possible, with their lattice substantially disoriented relative to the basic lattice of the metal. To calculate the contribution of such clusters to the free energy let us apply the cell method, similar to that which we used in Refs. 6 and 7 for the analysis of heterophase fluctuations. Let us divide the whole volume of the metal into identical cells with n atoms each and suppose that the lattice of each cell can have N orientations in relation to a common system of coordinates. Neglecting a correlation in the orientation of neighboring cells, let us describe the desired contribution to the free energy per cell in the form

$$F - F_0 = \frac{1}{2}\gamma \sum_{i=1}^{N} \sum_{j=1}^{N} c_i c_j (1-\delta_{ij}) + kT \sum_{i=1}^{N} c_i \ln c_i, \qquad (1)$$

where c_i is the contribution of cells with ith orientation and k is the Boltzmann constant. The first term in (1) takes into account the interaction between the clusters in the neighboring cells in the mean-field approximation. The clusters with the same orientation are thought not to interact with one another, while those with different orientation ($i \neq j$) add to the free energy some contribution proportional to γ and independent of i and j. The value γ has the meaning of the total free energy of the boundary separating a cluster with orientation i from the neighboring clusters with orientations $j \neq i$, $j' \neq i, \ldots$. The entropy $s = -\partial\gamma/\partial T$ and the energy $\varepsilon = \gamma + Ts$ connected with the value γ are assumed constant. The second term in (1) describes the configuration entropy of the system.

The interfaces between disoriented clusters have, probably, a sparser structure than the ideal lattice, therefore their formation can be connected with the elastic energy. However, elastic effects may be lacking if the cluster is nucleated at a vacancy site and the volume of the vacancy Ω_v is distributed along the developed interface. There is a value of n that gives ideal compensation of the volume effect. The formation of such clusters is energetically of the best advantage, and correspondingly their concentration is a maximum. It is these "optimum" clusters that are kept in mind in the model. The possible mechanisms of their formation are discussed in the last section.

The equilibrium state corresponds to a cluster distribution over N orientations such that the right-hand side of (1) is a minimum if the normalization $\Sigma c_i = 1$ is taken into account. At high temperatures, an isotropic state of the system with a chaotic orientation of clusters is to the advantage: $c_1 = \ldots = c_N = N^{-1}$. This state corresponds to a melt in the cluster model. At a certain temperature T_m a preferred orientation of clusters spontaneously arises in one of directions (say, 1) and is enhanced as the temperature decreases. As $T \to 0$ the system approaches the state $c_i = 1$, $c_1 = \ldots = c_N = 0$ corresponding to the ideal crystal.

Let us calculate all the characteristics of melting and premelting within the framework of the above model. Since all orientations are considered equivalent, any state of the

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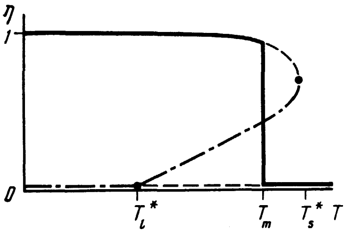

FIG. 1. Temperature dependence of the orientational order parameter. The solid lines denote equilibrium states, the dashed line denotes metastable states, and the dash-dot line indicate absolutely unstable states. The points of the loss of stability of phases are marked.

system is described by a single orientation order parameter η:

$$\eta=(Nc_1-1)/(N-1);\quad c_2=\ldots=c_N=(1-\eta)/N. \tag{2}$$

Minimization of (1) with respect to ($\partial F/\partial\eta=0$) gives

$$\gamma\eta=kT\ln[1+N\eta(1-\eta)^{-1}]. \tag{3}$$

Equation (3) has two solutions (Fig. 1). One of them, $\eta=0$, describes a melt with a free energy

$$F_l(T)=F_0(T)+\gamma(N-1)/2N-kT\ln N. \tag{4}$$

The second solution, $\eta>0$, describes the crystalline state with allowance for the orientational defects, with $\eta\to1$ as $T\to0$. To analyze the $\eta(T)$ dependence, it is simpler to express T from (3) in terms of η:

$$T=\varepsilon\eta[s\eta+k\ln[1+N\eta(1-\eta)^{-1}]]^{-1}. \tag{5}$$

The temperature dependence of the free energy of the crystal $F_s(T)$ is obtained by substituting $\eta(T)$ in (1).

The melting point T_m is determined from the equality $F_l(T)=F_S(T)$ (Fig. 2). Besides T_m, there are points of loss of stability of two phases, T_l^* and T_s^*. They represent the temperature limits of supercooling (superheating) of the melt (the crystal) and are determined from the condition $\partial^2F/\partial\eta^2=0$, i.e.,

$$\xi\ln\xi=N\eta(1-\eta)^{-2},\quad \xi\equiv1+N\eta(1-\eta)^{-1}, \tag{6}$$

together with (3). From (6) and (3), the point of the loss of stability of the melt is

$$T_l^*=\varepsilon(s+kN)^{-1}. \tag{7}$$

The point T_s^* can be found only approximately.

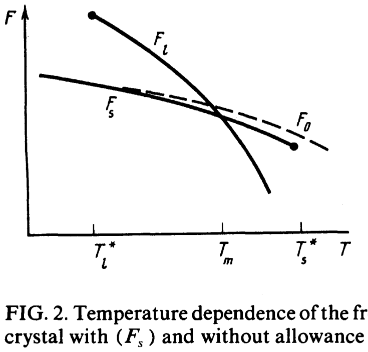

FIG. 2. Temperature dependence of the free energy (F_l) of a melt and of a crystal with (F_s) and without allowance (F_0) for oriented defects.

For the further calculations, let us take into consideration that under real conditions $N\gg1$, with $1-\eta\ll1$ for the crystalline state ($0\leqslant T\leqslant T_s^*$). To find T_m, we assume accordingly $F_s(T)\approx F_0(T)$ i.e., we drop the contribution of the orientational defects to F_s. Then from the condition $F_l(T)=F_s(T)$, using (4), we obtain

$$T_m=\varepsilon(s+2k\ln N)^{-1}. \tag{8}$$

The approximation made gives an error in T_m of order N^{-4}. Further, taking into consideration the smallness of $1-\eta$ and N^{-1} in (3) and (6), we find the point of loss of crystal stability

$$T_s^*=\varepsilon(s+k\ln N)^{-1}. \tag{9}$$

At this point $\eta^*=1-1/\ln N$. Using (4), it is not difficult to find the jumps of the energy (λ) and of the entropy (s_m) at the melting point. This yields, per atom,

$$\lambda=\varepsilon/2n, \tag{10}$$

$$s_m=(\varepsilon+2k\ln N)/2n. \tag{11}$$

Considering the condition $N(1-\eta)^{-1}\gg1$, we obtain from Eq. (3)

$$1-\eta\approx\exp(-\gamma/kT)=\exp(s/k)\exp(-\varepsilon/kT). \tag{12}$$

According to (2), $c_2+\ldots+c_N\approx1-\eta$. Therefore, (12) has the meaning of the concentration of the orientational defects in the crystal or, in other words, the fraction of the atoms belonging to the clusters with disturbed lattice orientation. This value grows with temperature and at the melting point reaches a maximum value equal to $\exp[-\gamma(T_m)/kT_m]=N^{-2}$. (Incidentally, one can see from this result that the conditions $1-\eta\ll1$ and $N\gg1$ are equivalent.)

The received equations allow one to estimate the contribution of the orientational defects to the premelting behavior of the heat capacity, thermal expansion, and other physical properties. For instance, the contribution to the heat capacity per atom is

$$\Delta C=n^{-1}\frac{\partial}{\partial T}[\varepsilon(1-\eta)]=\frac{\varepsilon^2}{nkT^2}\exp\left(\frac{s}{k}\right)\exp\left(-\frac{\varepsilon}{kT}\right). \tag{13}$$

At the melting point this contribution is a maximum and equal to

$$\Delta C_m=\varepsilon^2/nkT_m^2N^2. \tag{14}$$

2. COMPARISON WITH EXPERIMENTAL DATA

The model contains four parameters, n, N, ε and s, which we will consider as fitting parameters. For their calculation on the basis of experimental data one needs four known melting characteristics. For these, let us choose the melting temperature of the metal T_m, the latent heat of melting λ, the volume melting effect $\Delta V/V$ and the surface ten-

TABLE I.

Experimental data					Calculation					
Metal	T_m,K	λ,eV	$\Delta V/V$,%	σ_{sl},N/m	n	ε, eV	ln N	s/k	$\Delta C_m/k$	T_S^*
Al	934	0.112	6.5	0.093	12	2.69	2.98	27.17	0.24	1035
Au	1338	0.130	5.2	0.132	15	3.90	3.48	26.65	0.072	1502
Cu	1358	0.135	4.2	0.177	19	5.13	3.22	37.27	0.161	1470
Ni	1728	0.181	5.4	0.255	15	5.43	2.75	30,81	0.363	1878
Pb	601	0.049	3.6	0.033	22	2.60	3.68	34.98	0.053	648

sion σ_{sl} of the melt–crystal boundary at $T = T_m$. The data necessary for the calculation for several fcc metals are presented in Table I (Ref. 8).

Equations (8) and (10) relate T_m and λ to the desired parameters. Some additional assumptions are needed to find them.

First, as already indicated, an orientational defect is probably generated near a vacancy, fully inheriting its volume Ω_v. A dynamic equilibrium is established between the oriented defects and vacancies and does not affect c_v. Hence, as new defects appear, the crystal volume V increases by a value close to $V(\Omega_v/n\Omega)\ (1-\eta)$, where Ω is the atomic volume. At the melting point this value changes jumpwise by $-v(\Omega_v/n\Omega)\Delta\eta$, where $\Delta\eta$ is the jump of the order parameter. Assuming that this change in the volume completely determines the volume melting effect and taking into account that $\Delta\eta \approx -1$, we obtain

$$\Delta V/V \approx \Omega_v/n\Omega. \tag{15}$$

For the majority of fcc metals, $\Omega_v \approx 0.8\Omega$.

Secondly, one should take into account that $\gamma \approx g_1\sigma(n\Omega)^{2/3}$ where σ has the meaning of the surface tension of the intercluster boundaries and g_1 is a geometric factor depending on the cluster shape. For definiteness sake, let us assume a spherical approximation where $g_1 = (36\pi)^{1/3}$. On the other hand, the value of σ at the melting point can be expressed through σ_{sl}. Indeed, within the framework of the given model the melt–crystal interface between regions with a chaotic and almost ideal orientation of clusters consists of the segments of intercluster boundaries with tension σ. On the basis of this, we can assume $\sigma(T_m) = g_2\sigma_{sl}$. The geometrical factor g_2 takes into account the fact that a melt–crystal interface on a scale of $(n\Omega)^{1/3}$ resembles a cobble-stone pavement rather than a smooth boundary. In the spherical approximation, such a boundary has roughly half the area of the combined intercluster boundaries forming it, hence, $g_2 \approx 1/2$ and thus, $\gamma(T_m) \approx (9\pi/2)^{1/3}\sigma_{sl}(n\Omega)^{2/3}$. Since according to (8) $\gamma(T_m)/kT_m = 2\ln N$, we finally obtain

$$2\ln N \approx (9\pi/2)^{1/3}\sigma_{sl}(n\Omega)^{2/3}/kT_m. \tag{16}$$

The values of n, N, ε and S calculated from equations (8), (10), (15) and (16) are presented in Table I.

The derived values of n show that between one and three coordination spheres can take part in rotation around a central atom (vacancy). The number of orientations N (from 15 to 40) is not as large as could be expected, which is probably connected with the realization of a set of the energetically most advantageous orientations. This is indirectly confirmed by the following consideration. Using the obtained values ε one can estimate the surface energy E of the intercluster boundaries by the equation $\varepsilon = (36\pi)^{1/3} \times E(n\Omega)^{2/3}$. The obtained values (for instance, 0.26, 0.46 and 0.60 N/m for Al, Cu and Ni, respectively) are a little lower than the energies of the grain boundaries of general type but are close to the typical energies of the special boundaries (Ref. 9). At the same time, the entropy of the intercluster boundaries is unusually high. The tabulated values of s pertain to the "surface" atoms of a cluster, so that each has an entropy of order of $sn^{-2/3} \approx 5k$. However, one should keep in mind that this value might be overestimated owing to the roughness of the model. For instance, the cell method takes no account of the entropy due to from the differences in the sizes and shapes of the clusters. When fitted to experiment, this unaccounted-for entropy is ascribed to intercluster boundaries.

Table I shows the maximum contribution of the oriented defects to the heat capacity (14). An analogous value for vacancies calculated by the equation

$$C_m{}^v/k = (\varepsilon_v/kT_m)^2 \exp(s_v/k)\exp(-\varepsilon_v/kT_m), \tag{17}$$

has the same order of magnitude. Thus, $C_m^v/k = 0.055$ and 0.026 for Al and Pb (using the experimental values $\varepsilon_v = 0.73$ and 0.55 eV, $s_v = 1.76$ and $1.60k$ of Ref. 10). Since the vacancy contribution is registered reliably, the value of ΔC_m can also be measured in principle. However, the difficulty is that the contribution of the orientational defects as well as of other premelting structures can manifest themselves only in a narrow interval near T_m. This pertains not only to the heat capacity but also to other values. Using (12) one can evaluate the temperature T_0 above which the contribution of orientational defects prevails the vacancy contribution, from the condition

$$1-\eta(T) = c_v(T) = \exp(s_v/k)\exp(-\varepsilon_v/kT).$$

Thus, this condition gives the values $T_0 = 927$ and 560 K for Al and Pb which are close to T_m.

As a consequence of experimental difficulty, rather few reliable data on premelting were obtained, in spite of many years of effort[3] (for a review of earlier works, see Ref. 11). A shortcoming of the majority of the studies in which premelting effects were observed is that impurities can "blur" the melting point. In this sense, the results of Refs. 12 and 13, obtained for especially pure samples with a thorough evaluation of possible influence of the impurities, seem to be the most reliable.

The electrical resistance R of lead was measured to an accuracy of 10% in the range from 300 K to $T_m = 601$ K in Ref. 12. After separating out the phonon contribution, the $R(T)$ dependence was approximated by a sum of two terms of the form of $b \exp(-\varepsilon/kT)$. The first of them, which made a contribution at all temperatures, corresponded to scattering on vacancies since the value $\varepsilon_1 \approx 0.4$ eV is close to ε_v. Beginning from $T = 540$ K, a contribution of the second term was observed, with $\varepsilon_2 = 1.42$ eV and $b_2 = 10^7 b_1$. The authors attributed the second term to the contribution of new premelting defects containing, according to their estimate, $n \approx 17$ atoms and having an energy and entropy of formation of ε_2 and $s_2 = 16 k$. One can see from the comparison with the data in the table that these values do not contradict the cluster model if its approximate character and the difficulty of separating out the second exponential of the experimental curve are kept in mind.

In Ref. (13) the heat capacity C of mercury was measured to an accuracy of $3 \times 10^{-2}\%$ in the temperature range from 0.721 to $0.997 T_m$. At $T < 0.91 T_m$ the $C(T)$ dependence was described by the sum of an electronic component, a lattice exponential (taking anharmonism into account) and the usual vacancy exponential. At temperatures $0.91 T_m$, the new contribution $C(T)$ appeared, which the authors attributed to oriental defects and described by the equation[4]

$$\Delta C = F(T_s^* - T)^{-1/2}, \tag{18}$$

where $F = \text{const}$. However, they were unable to reach an adequate agreement. The reason of this discrepancy becomes clear if one takes into account the fact that the dependence (18) is valid in narrow neighborhood of the point T_s^*. It can be satisfied near T_m if $T_m \approx T_s^*$. In the particular case of $N = 4$ and $s = 0$ considered in Ref. 4 this is really true but in case of more realistic parameter values the temperatures T_s^* and T_m differ substantially, (Table I). Under such conditions, the exponential dependence (13) should be more precise. It would be possible to check this assumption by reviewing of the data of Ref. 13.

3. DISCUSSION

Thus, at reasonable parameter values the cluster model agrees satisfactorily with the available experimental data on melting and premelting of metals. In contrast to other structural theories, the cluster model describes directly the loss of the long-range order at the melting point and gives a more realistic structure of a melt. The model suggests that oriental lattice defects can arise in a crystal near T_m. Let us discuss the possible mechanisms of their formation.

1. The formation of an "extended" vacancy from a normal vacancy, followed by the transformation "normal vacancy $\rightleftarrows$ "extended" vacancy $\rightleftarrows$ oriented defect." The idea of "extended" point defects was developed by Seeger[14,15] to account for the high-temperature anomalies in silicon but was used later to analyze premelting effects in metals.[12,16] The "extended" vacancy has a non-ordered (liquid-like) structure resulting from strong displacements of 10–20 atoms surrounding the vacancy. The structure is thought either to be unstable to one of the generalized coordinates and considered as an activated complex for vacancy jump,[17,18] or it is assumed to be a stable state separated by potential barriers from the other states. Having a high energy and entropy, the "extended" vacancies originate at high temperatures and are in dynamic equilibrium with the normal vacancies. According to the suggested mechanism, a lattice section with an irregular orientation, i.e., an orientational defect, is produced by a successive crystallization of an "extended" vacancy. After some time, it may again become disoriented and later crystallize with regular orientation or again into an irregular lattice but of another orientation.

2. In the vicinity of T_m, the concentration of vacancies, interstices, and other defects increases. As a result of their interaction, they are ordered and form cell boundaries with disoriented lattices. An analogous mechanism was considered for the melting of two-dimensional crystals.[19,20] It was assumed that as temperature and concentration of the dislocations (in the two-dimensional case, point defects) increase, they line up in dislocation walls. The walls then close on themselves and form the boundaries of disoriented clusters, the number of clusters and the disorientation angles increasing in the vicinity of T_m. Recently such a picture of the two-dimensional melting was revealed by computer simulation by the molecular-dynamics technique.[21] Although the two-dimensional melting has its own distinctive features, one can assume that in the three-dimensional case generation of disoriented crystalline clusters is possible as a result of association of interacting defects.

To choose between these mechanisms as well as to check the adequacy of the model itself, further accumulation of experimental data is required.

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