

Contribution of Interstitial Defects and Anharmonicity to the Premelting Increase in the Heat Capacity of Single-Crystal Aluminum

E. V. Safonova^a, R. A. Konchakov^a, Yu. P. Mitrofanov^a, N. P. Kobelev^b,
 A. Yu. Vinogradov^c, and V. A. Khonik^a

^a Voronezh State University, Universitetskaya pl. 1, Voronezh, 394043 Russia

^b Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia

^c Norwegian University of Science and Technology NTNU, N-7491 Trondheim, Norway

e-mail: konchakov.roman@gmail.com

Received May 5, 2016

With the use of experimental data on the temperature dependence of the concentration of interstitial atoms, it has been shown within the interstitial theory that the premelting nonlinear increase in the heat capacity of aluminum can be caused by the intense generation of interstitial defects in a dumbbell configuration.

DOI: 10.1134/S0021364016120134

A significant nonlinear increase in the heat capacity of simple metals near their melting temperature is now reliably established for both fusible and refractory metals [1–7]. Figure 1 exemplifies several temperature dependences of molar heat capacity of aluminum taken from various works. Despite a noticeable spread of experimental data, which is apparently due to the methods of the measurement of the heat capacity (e.g., adiabatic [3, 5] and isothermal [6] calorimetry) and to the different degrees of purity of the experimental samples, the mentioned increase at temperatures $T > 800$ K is quite pronounced. As was mentioned more than once, the nature of this increase is still generally unclear [8].

The heat capacity at constant pressure C_p can be written in the form [6, 9, 10]

$$C_p = C_v + VT\gamma^2 K_T, \quad (1)$$

where V is the molar volume, T is the absolute temperature, γ is the thermal expansion coefficient, and K_T is the isothermal bulk modulus. The heat capacity of a monatomic metal at constant volume C_v can be represented as the sum of various contributions:

$$C_v = C^{\text{qh}} + C^{\text{ah}} + C^{\text{el}} + C^{\text{vac}} + C^{\text{int}}, \quad (2)$$

where C^{qh} is the Debye heat capacity, C^{ah} is the contribution to the heat capacity owing to the anharmonicity of vibrational motion of atoms, C^{el} is the electronic heat capacity, and C^{vac} and C^{int} are contributions from equilibrium point defects, namely, vacancies and interstitial atoms, respectively. We emphasize that all attempts at the interpretation of the premelting non-

linear increase in the heat capacity completely ignore interstitial defects, arguing this by their low concentration [11, 12]. Indeed, the statement that the equilibrium concentration of interstitial defects is negligibly low was included even in modern textbooks on physical materials science (see, e.g., [13]). Correspondingly, in addition to the obvious contributions C^{qh} and C^{el} , only the vacancy and anharmonic contributions are included.

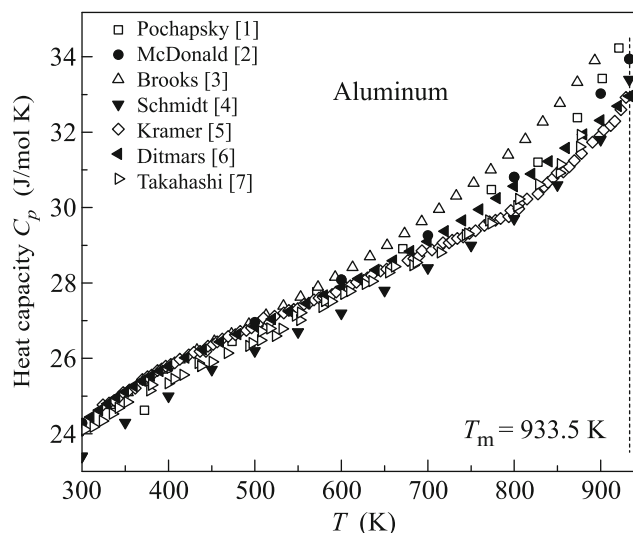


Fig. 1. Temperature dependence of the molar heat capacity C_p of aluminum taken from [1–7]. The vertical dashed straight line indicates the melting temperature.

The authors of [1, 3, 9] attribute the premelting nonlinear increase in the heat capacity to anharmonicity because vacancies ensure only about 1% of the observed excess increase in the heat capacity above the contributions C^{qh} and C^{el} . Correspondingly, they conclude that anharmonicity makes a positive contribution to the heat capacity. On the contrary, the authors of [4, 14, 15] state that contribution of anharmonicity to the heat capacity is positive. At the same time, the authors of molecular dynamics simulation of single-crystal aluminum [10] conclude that the contribution of anharmonicity to the heat capacity is no more than several percent.

Thus, the origin of the nonlinear increase in the high-temperature heat capacity of metals is currently under discussion. We believe that the problem is in the incorrect inclusion of the contribution to the heat capacity from equilibrium point defects and anharmonicity. Meanwhile, the difference between these contributions is incompletely definite. Some authors believe [16] that the contribution from vacancies cannot be separated from the contribution from anharmonicity. We propose a method for solving the indicated problem by the correct inclusion of the contribution from interstitial defects.

The most stable configuration of an interstitial defect in monatomic fcc, bcc, and hcp metals is the dumbbell (split) configuration [17–19]. The main property of interstitial dumbbells is their capability of efficiently interacting with shear stress field, initiating additional inelastic deformation. This results in a decrease in the shear modulus as compared to the defect-free crystal, which, according to the main equation of Granato's interstitial theory [20], can be described by the equation

$$G = G_{\text{perf}} \exp(-\beta n^{\text{int}}), \quad (3)$$

where G and G_{perf} are the shear moduli of the crystal containing interstitial defects with the concentration n^{int} and the perfect (defect-free) crystal, respectively, and β is the dimensionless shear susceptibility, which is 27 for aluminum [21].

Equation (3) demonstrates that the concentration of interstitial dumbbells can be determined from precise measurements of the shear modulus. Such measurements recently performed with single-crystal aluminum [22] revealed that the intense generation of interstitial dumbbells begins above ≈ 870 K. In this case, their contribution near the melting temperature T_m is lower than the contribution of vacancies only by a factor of 2–3. The temperature dependence of the contribution of interstitial dumbbells obtained in [22] is shown in Fig. 2 in comparison with the contribution of vacancies according to the data reported in [23].

An increase in the contribution of interstitial dumbbells with the temperature is due both to Arrhenius thermal activation and to a decrease in their formation enthalpy (in view of a decrease in the shear

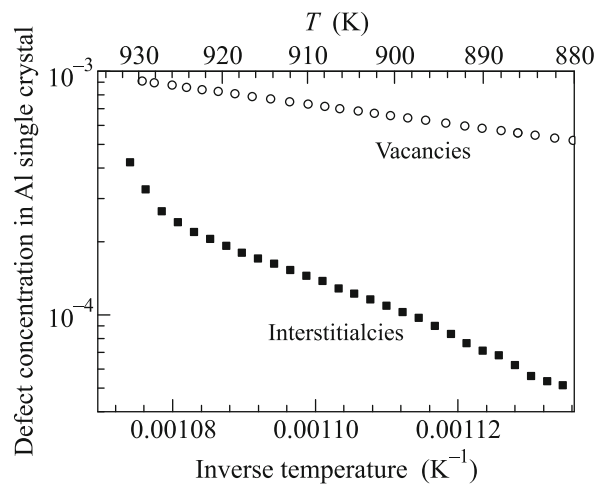


Fig. 2. Temperature dependence of the concentration of interstitial dumbbells n^{int} [22] and vacancies n^{vac} [23] in aluminum.

modulus with increasing temperature), which, together with a large formation entropy, significantly reduces the Gibbs energy, so that, near T_m , it is only slightly higher than the Gibbs energy of vacancies [22]. Correspondingly, the contribution of interstitial dumbbells near T_m is only slightly lower than the contribution of vacancies, as is shown in Fig. 2.

Thus, the necessity of the inclusion of the contribution of interstitial dumbbells to the heat capacity becomes obvious. This contribution can be estimated within the interstitial theory [20], according to which the enthalpy of interstitial dumbbells H_f^{int} is related to their contribution n^{int} as

$$dH_f^{\text{int}}/dn^{\text{int}} = \alpha\Omega G, \quad (4)$$

where $\alpha \approx 1$ is the dimensionless parameter and Ω is the volume per atom. Then, interstitial dumbbells contribute to the molar heat capacity, which can be represented in the form

$$C^{\text{int}} = \alpha\Omega G N_a \frac{dn^{\text{int}}}{dT}, \quad (5)$$

where N_a is the Avogadro number. The vacancy contribution to the heat capacity can be estimated by the formula

$$C^{\text{vac}} = H_f^{\text{vac}} N_a \frac{dn^{\text{vac}}}{dT}, \quad (6)$$

where H_f^{vac} is the enthalpy of formation of vacancies [23] and n^{vac} is the contribution of vacancies.

Figure 3 shows the contributions of interstitial dumbbells and vacancies to the heat capacity of single-crystal aluminum calculated by Eq. (5) with allowance

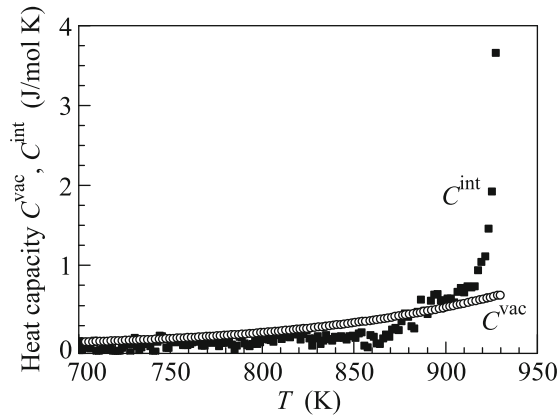


Fig. 3. Contribution from interstitial dumbbells C^{int} and vacancies C^{vac} to the molar heat capacity of aluminum.

for the temperature dependence of G [22] and by Eq. (6) with $H_f^{\text{vac}} = 0.67$, respectively.

It is seen that the contribution of interstitial dumbbells to the heat capacity increases sharply at $T > 870$ K because, as was mentioned above, their concentration increases rapidly when approaching T_m . Thus, the neglect of the contribution of interstitial defects to the heat capacity is too rough an approximation.

To take into account all terms in Eq. (2), we determine the anharmonic, C^{ah} , and electron, C^{el} contributions to the heat capacity. Figure 4 shows the temperature dependences of C^{ah} and C^{el} for aluminum taken from [4, 15, 24, 25].

The electronic heat capacity C^{el} depends on the temperature almost linearly, so that the negative anharmonic contribution C^{ah} is mainly compensated by the positive contribution from electronic excitations. In further calculations, we used more detailed and accurate data (as compared to [4, 15, 25]) on the electronic and anharmonic contributions to the heat capacity reported in [24].

To calculate the quantity $VT\gamma^2K_T$ in Eq. (1), the temperature dependences of the molar volume V , thermal expansion coefficient γ , and isothermal bulk modulus K_T for aluminum were taken from [26], [27], and [28], respectively. Figure 5 shows (line 1) the experimental temperature dependence of the heat capacity taken from [5] and the heat capacity calculated by the formula

$$C_p = C^{\text{qh}} + C^{\text{ah}} + C^{\text{el}} + C^{\text{vac}} + C^{\text{int}} + VT\gamma^2K_T, \quad (7)$$

(line 2) with and (line 3) without the contribution of interstitial dumbbells C^{int} . The difference between lines 1 and 3 is seen at temperatures above 850 K, which increases when approaching the melting temperature T_m . This difference is eliminated by the inclusion of the contribution of interstitial dumbbell to the heat capacity (line 2).

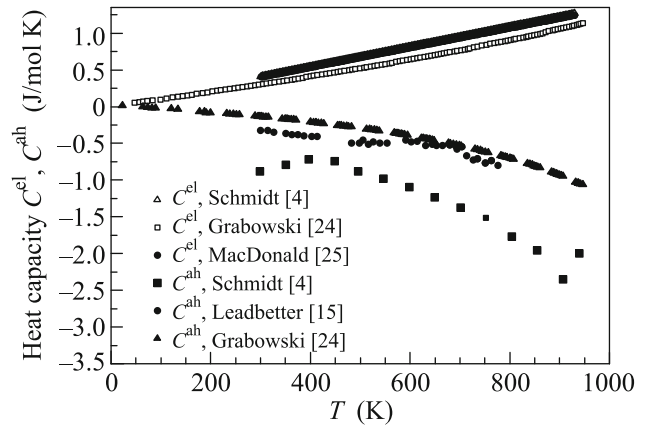


Fig. 4. Electronic, C^{el} , and anharmonic, C^{ah} , contributions to the molar heat capacity of aluminum [4, 15, 24, 25].

A slight difference between lines 1 and 2 immediately near the melting temperature can be explained as follows. The anharmonic contribution to the heat capacity of aluminum was taken from [24], where it was calculated from ab initio simulation in terms of the second derivative of the free energy with respect to temperature, and the functional form of the free energy was constructed with the inclusion of only vacancies. The simulation was performed in [24] for a system of 500 atoms, which seems insufficient for the accurate inclusion of the heat capacity of interstitial dumbbells. Meanwhile, the concentration of interstitial dumbbells near T_m is $\approx 10^{-4}$ (Fig. 2). Consequently, the adequate inclusion of the generation of interstitial dumbbells and their contribution to the heat capacity requires a much larger model system of about 10^4 atoms rather than of 500 atoms (which is sufficient for the simulation of the vacancy contribution

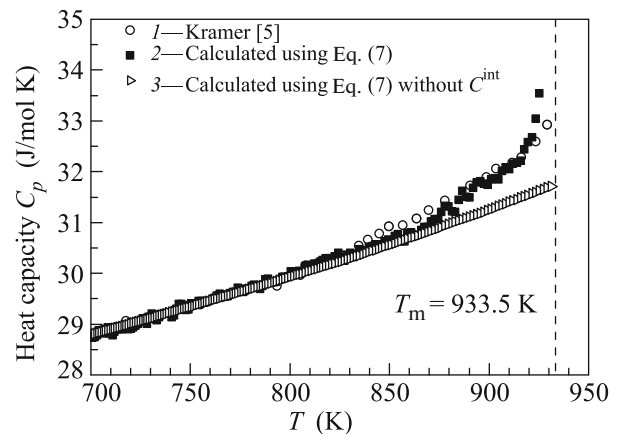


Fig. 5. Temperature dependences of the molar heat capacity of aluminum calculated by Eq. (7) (line 2) with and (line 3) without the contribution of interstitial defects in comparison with the data reported in [5].

to the heat capacity. Therefore, the calculation of the heat capacity by Eq. (7) with the contribution C^{ah} taken from [24] (overestimated in absolute value) gives the C_p value near T_m overestimated as compared to the experimental value.

The correlation of the intense generation of interstitial dumbbells with a sharp nonlinear increase in the heat capacity of aluminum indirectly confirms the interstitial mechanism of melting of simple substances, as was implied by Granato's interstitial theory [20]. Since interstitial dumbbells provide the most stable configuration of interstitial defects and exist in all basic monatomic crystal lattices, it is reasonable to expect a similar correlation for any other simple metals. The fundamental difficulty for testing such an assumption is the necessity of the precise measurement of the shear modulus near the melting temperature, which is a very difficult experimental problem. For this reason, we analyzed only the heat capacity of single-crystal aluminum, for which reliable experimental data on the temperature dependence of the shear modulus (and, correspondingly, the temperature dependence of the concentration of interstitial dumbbells) were obtained [22].

As far as we know, the premelting nonlinear increase in the heat capacity of metals was not previously attributed to the generation of interstitial defects because it was believed that their equilibrium concentration is too low. The results obtained in this work indicate that the interstitial defects in the dumbbell configuration should be taken into account when analyzing a high-temperature increase in the heat capacity.

This work was supported by the Ministry of Education and Science of the Russian Federation (assignment no. 3.114.2014/K).

REFERENCES

1. T. E. Pochapsky, *Acta Metall.* **1**, 747 (1953).
2. R. A. McDonald, *J. Chem. Eng.* **12**, 115 (1967).
3. C. R. Brooks and R. E. Bingham, *J. Phys. Chem. Solids* **29**, 1553 (1968).
4. U. Schmidt, O. Vollmer, and R. Kohlhaas, *Z. Naturforsch., A: Phys. Sci.* **25**, 1258 (1970).
5. W. Kramer and J. Nolting, *Acta Metall.* **20**, 1353 (1972).
6. D. A. Ditmars, C. A. Plint, and R. C. Shukla, *Int. J. Thermophys.* **6**, 499 (1985).
7. Y. Takahashi, T. Azumi, and Y. Sekine, *Thermochim. Acta* **139**, 133 (1989).
8. J. Rogal, S. V. Divinski, M. W. Finnis, A. Glensk, J. Neugebauer, J. H. Perepezko, S. Schuwalow, M. H. F. Sluiter, and B. Sundman, *Phys. Status Solidi B* **251**, 97 (2014).
9. R. C. Shukla and C. A. Plint, *Int. J. Thermophys.* **1**, 299 (1980).
10. M. Forsblom, N. Sandberg, and G. Grimvall, *Phys. Rev. B* **69**, 165106 (2004).
11. R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **117**, 52 (1960).
12. R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **129**, 1533 (1963).
13. G. Gottshtain, *Physicochemical Foundations of Material Science* (BINOM. Labor. Znaniy, Moscow, 2009) [in Russian].
14. J. M. Keller and D. C. Wallace, *Phys. Rev.* **126**, 1275 (1962).
15. A. J. Leadbetter, *J. Phys. C* **1**, 1489 (1968).
16. Y. Kraftmakher, *Phys. Rep.* **299**, 79 (1998).
17. V. V. Kirsanov and A. N. Orlov, *Sov. Phys. Usp.* **27**, 106 (1984).
18. P. Ehrhart, P. Jung, H. Schultz, and H. Ullmaier, *Atomic Defects in Metals*, Vol. 25 of *Landolt-Börnstein New Series III*, Ed. by O. Madelung (Springer, Berlin, 1991).
19. W. G. Wolfer, in *Comprehensive Nuclear Materials*, Ed. by R. Konings (Elsevier, Amsterdam, The Netherlands, 2012), Vol. 1, p. 1.
20. A. V. Granato, *J. Phys. Chem. Solids* **55**, 931 (1994).
21. C. A. Gordon and A. V. Granato, *Mater. Sci. Eng. A* **370**, 83 (2004).
22. E. V. Safonova, Yu. P. Mitrofanov, R. A. Konchakov, A. Yu. Vinogradov, N. P. Kobelev, and V. A. Khonik, *J. Phys.: Condens. Matter* **28**, 215401 (2016).
23. R. W. Siegel, *J. Nucl. Mater.* **69–70**, 117 (1978).
24. B. Grabowski, L. Ismer, T. Hickel, and J. Neugebauer, *Phys. Rev. B* **79**, 134106 (2009).
25. R. A. MacDonald and W. M. MacDonald, *Phys. Rev. B* **24**, 1715 (1981).
26. N. Saunders, X. Li, A. P. Miodownik, and J. P. Schille, in *Essential Readings in Light Metals*, Ed. by J. Grandfield (Wiley, New Jersey, USA, 2013), Vol. 3, p. 519.
27. A. Debernardi, M. Alouani, and H. Dreyse, *Phys. Rev. B* **63**, 064305-1 (2001).
28. J. L. Tallon and A. Wolfenden, *J. Phys. Chem. Solids* **40**, 831 (1979).

Translated by R. Tyapaev