

Thermodynamic Study of Crystalline and Quasicrystalline Al–Mn Alloys

A. I. Zaitsev^a, N. E. Zaitseva^a, N. A. Arutyunyan^b, K. B. Kalmykov^b, and M. Yu. Yazvitskii^a

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The currently available data on the thermodynamic properties, formation conditions, and stability of quasicrystals are very scarce. The Gibbs energies and entropies have not been studied at all. The scanty data available to date hinder attempts to determine definitely the nature of quasicrystals and to understand what state (stable, metastable, or labile) quasicrystals correspond to and whether a quasicrystal may be the stable ground state of an alloy. Only one work [1] was devoted to measurements of the heat capacity of the Al₈₆Mn₁₄ alloy in quasicrystalline and equilibrium crystalline states in a wide temperature range (310–730 K). It was found [1] that the heat capacity of a quasicrystal systematically exceeded the heat capacity of a crystal by 2–3 J/(mol K). This regularity may indicate that the quasicrystalline state should be thermodynamically stabilized with increasing temperature and that the stabilization is entropic in nature. This conclusion agrees well with the theoretical concepts [2] of the entropic nature of stabilization of quasicrystals owing to phason defects.

To solve the problems stated and realize the possibility of directly comparing the thermodynamic characteristics of an alloy in quasicrystalline and crystalline states, in this work, we experimentally studied in detail the formation conditions, stability, and thermodynamic properties of icosahedral (ico) and decagonal (deca) quasicrystalline phases in the Al–Mn system. Simultaneously, we determined the thermodynamic properties of equilibrium crystalline Al–Mn alloys over a composition range of 0–26 at % Mn and in a wide temperature range (628–1193 K). The measurements were performed by Knudsen mass spectrometry with the use of Knudsen double cells made of vacuum-fused tantalum, niobium, or molybdenum. To prevent the interaction of the alloys under study and the reference with the material of the effusion cells, boron nitride, zirconium

diboride, or titanium diboride was plasma-deposited on their inner surfaces. Ag (99.99%), Cu (99.999%), or Ca (99.9%) was used as the reference. The experimental procedure was described elsewhere [3, 4].

The initial ingots were smelted from Mn and Al (99.99%) in an electric arc oven with a water-cooled copper stool and a nonconsumable tungsten electrode in a purified argon atmosphere. The ingots were remelted three times to ensure homogeneity. The quasicrystals were synthesized by melt-spinning onto a water-cooled copper wheel rotating at a speed of 15–32 m/s with quenching from the temperatures 1153–1323 K (~50 K above the liquidus). The samples were obtained in the form of bands (brittle fragments in all cases) ~30–50 μm thick and ~10 mm wide. To obtain equilibrium crystalline compositions, the initial ingots or bands were subjected to long-term homogenizing annealing in evacuated quartz ampoules. The phase compositions were determined by X-ray powder diffraction with a STADI-P diffractometer using Cu_{Kα1} or Co_{Kα} radiation. The attainment of equilibrium in an alloy was judged by the constancy of its phase composition on further increase in the annealing duration. As a result, the following stable crystalline phases were found in the composition–temperature range studied: Al₆Mn, λ, μ, and Al₁₁Mn₄. We obtained completely homogeneous samples of icosahedral and decagonal quasicrystalline phases containing 20 and 22 at % Mn, respectively.

Experimental determination of the thermodynamic properties of the quasicrystalline and crystalline Al–Mn alloys is complicated by a number of circumstances. In the concentration range of interest, the temperature range of the coexistence of crystalline phases in the Al–Mn system is limited by the temperature of peritectic melting of the μ phase (1196 K). The standard effusion techniques allowed us to measure only the aluminum and manganese vapor pressures over two-phase alloys Al₁₁Mn₄ + μ at the highest possible temperatures. The measured vapor pressures (ion current intensities) of Mn and Al over alloys and metals and the Gibbs energies of their phase transitions [5] gave a possibility to calculate the partial thermodynamic func-

^a Bardin Central Research Institute for Iron and Steel Industry, Vtoraya Baumanskaya ul. 9/23, Moscow, 105005 Russia

^b Moscow State University, Vorob'evy gory, Moscow, 119992 Russia

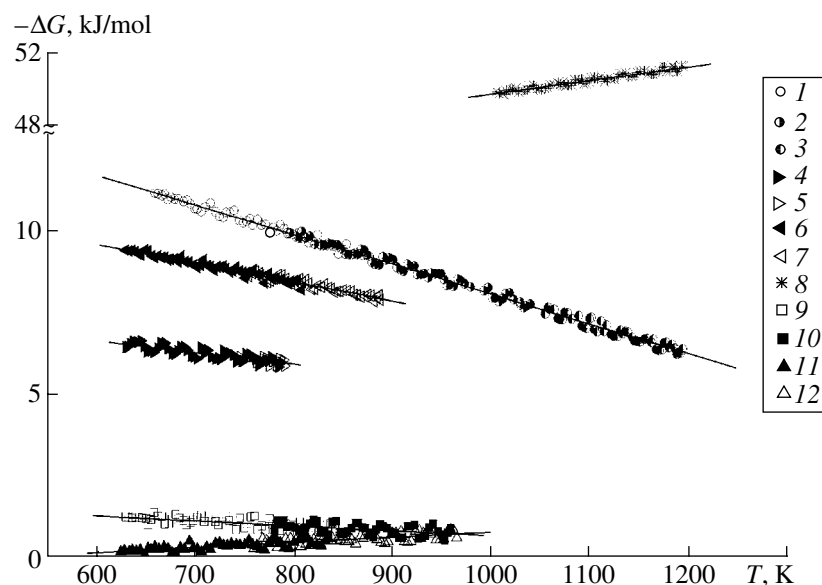
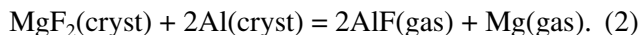


Fig. 1. Partial Gibbs energies of Al and Mn in their heterogeneous alloys found under various experimental conditions ($x(\text{Mn})$; phase composition; material of the effusion cell; material covering the inner surface of the cell; diameter of the effusion orifice, mm; and type of fluoride additive) from the measured vapor pressures of (3) aluminum and (8) manganese (in both runs, 0.220, $\text{Al}_{11}\text{Mn}_4 + \mu$, Ta, ZrB_2 , 0.227), as well as $\Delta G(\text{Al})$ determined in the equilibrium studies with fluoride additives: (1) 0.254, $\text{Al}_{11}\text{Mn}_4 + \mu$, Nb, BN, 0.201, NaF; (2) 0.220, $\text{Al}_{11}\text{Mn}_4 + \mu$, Ta, BN, 0.174, NaF; (4) 0.200, ico ($+\text{Al}_{11}\text{Mn}_4$), Mo, TiB_2 , 0.218, NaF; (5) 0.200, ico ($+\text{Al}_{11}\text{Mn}_4$), Nb, BN, 0.154, MgF_2 ; (6) 0.220, deca ($+\text{Al}_{11}\text{Mn}_4$), Ta, ZrBr_2 , 0.270, NaF; (7) 0.220, deca ($+\text{Al}_{11}\text{Mn}_4$), Nb, BN, 0.178, MgF_2 ; (9) 0.195, $\mu + \lambda$, Mo, ZrBr_2 , 0.243, NaF; (10) 0.185, $\mu + \lambda$, Nb, BN, 0.162, MgF_2 ; (11) 0.160, $\lambda + \text{Al}_6\text{Mn}$, Ta, ZrBr_2 , 0.257, NaF; (12) 0.147, $\lambda + \text{Al}_6\text{Mn}$, Mo, ZrBr_2 , 0.190, MgF_2 .

tions of the components (Fig. 1). Clearly, this information is insufficient for the complete thermodynamic description of the crystalline state. The coexistence range for quasicrystalline phases is limited by even lower temperatures of $\sim 600\text{--}800$ K. To extend the measuring range to lower temperatures, we used an original procedure based on initiating and studying equilibria of reactions between alloys under consideration and special additives yielding volatile products. A certain amount of sodium or magnesium fluoride was added to a sample in an effusion cell. The following reactions are predominant [4]:



The partial thermodynamic functions of Al (Fig. 1) were calculated from the measured partial pressures (ion currents) of AlF and Na (or Mg) over the mixtures of the fluorides with the Al–Mn alloys and pure aluminum with the use of equations for the equilibrium constants of reactions (1) and (2) [4]. These calculations did not require the ionization cross sections of gaseous molecules, which provided much more precise results.

For each of the fields of equilibrium between two crystalline phases ($\text{Al}_{11}\text{Mn}_4 + \mu$, $\mu + \lambda$, $\lambda + \text{Al}_6\text{Mn}$), the measurements were performed for several alloys of different composition under various experimental conditions (the effusion cell material, the type of material covering the inner surface of the cell, the effusion ori-

fice area, the reaction additive and its amount, etc.). With increasing temperature, fluoride additives were varied in the order NaF, MgF_2 . The thermodynamic characteristics found were independent of the experimental conditions (Fig. 1), which was indicative of the attainment of equilibrium during measurements and allowed us to simultaneously process the data found for each heterogeneous field (Table 1). The determination of the partial thermodynamic characteristics of both components in the field of coexistence of the $\text{Al}_{11}\text{Mn}_4$ and μ phases provided a possibility to directly calculate their integral thermodynamic functions (Table 2). The thermodynamic characteristics of the other intermediate phases were found using the Gibbs–Duhem equation (Table 2). The calculations were performed for the stoichiometric compositions $\text{Al}_{11}\text{Mn}_4$ ($x(\text{Mn}) = 0.267$), μ ($x(\text{Mn}) = 0.2$), λ ($x(\text{Mn}) = 0.18$), and Al_6Mn ($x(\text{Mn}) = 0.143$). The existence of the homogeneity range for the μ phase and the limited measuring range of the stability temperatures for the high-temperature polymorph of $\text{Al}_{11}\text{Mn}_4$ were neglected. The errors caused by these factors were minor.

Complete data on the thermodynamic properties of the Al-based Al–Mn phases (Table 2) were obtained for the first time. Only the enthalpy had been studied previously. Kubaschewski and Heymer [6] found by direct reaction calorimetry that the enthalpies of formation of the alloys containing 14.2, 20, and 26.7 at % Mn at 573–623 K were -12.38 , -21.67 , and -21.21 kJ/mol,

Table 1. Partial thermodynamic functions of the components in the heterogeneous Al–Mn alloys referenced to fcc Al and α -Mn

Phase field	T , K	n	Component	$-\Delta H$, J/mol	$-\Delta S$, J/(mol K)
$\text{Al}_{11}\text{Mn}_4 + \mu$	658–1193	168	Al	$17\,147 \pm 97$	9.08 ± 0.11
	1004–1193	66	Mn	$42\,102 \pm 549$	-7.63 ± 0.50
$\mu + \lambda$	628–958	110	Al	$2\,208 \pm 220$	1.54 ± 0.28
	628–958		Mn	$110\,858 \pm 222$	22.54 ± 0.27
$\lambda + \text{Al}_6\text{Mn}$	623–964	103	Al	813 ± 251	-1.59 ± 0.31
	623–964		Mn	$115\,620 \pm 240$	36.80 ± 0.29
ico (+ $\text{Al}_{11}\text{Mn}_4$)	628–789	64	Al	$8\,810 \pm 394$	3.59 ± 0.55
	628–789		Mn	$64\,990 \pm 332$	7.45 ± 0.44
deca (+ $\text{Al}_{11}\text{Mn}_4$)	628–886	95	Al	$13\,039 \pm 173$	5.76 ± 0.23
	628–886		Mn	$53\,380 \pm 207$	1.49 ± 0.24

Table 2. Thermodynamic functions of formation of the quasicrystalline and crystalline phases of the Al–Mn system from fcc Al and α -Mn

Phase	$x(\text{Mn})$	Temperature range, K	$-\Delta_f H$, J/mol	$-\Delta_f S$, J/(mol K)
$1/15\text{Al}_{11}\text{Mn}_4$	0.267	658–1193	$23\,810 \pm 163$	4.62 ± 0.16
μ	0.20	658–1193	$22\,138 \pm 135$	5.74 ± 0.14
λ	0.18	628–958	$20\,145 \pm 123$	5.32 ± 0.13
$1/7\text{Al}_6\text{Mn}$	0.143	623–964	$15\,837 \pm 111$	3.90 ± 0.12
ico	0.20	628–789	$20\,046 \pm 158$	4.36 ± 0.19
deca	0.22	628–886	$21\,914 \pm 138$	4.82 ± 0.14

respectively. In a later work [7], where a similar procedure was used, the standard enthalpy of formation of Al_6Mn was determined to be a more negative value: $\Delta_f H_{298}(1/7\text{Al}_6\text{Mn}) = -15.1 \pm 1.0$ kJ/mol. Taking into account the difference in measuring temperature ranges, the values found in [6, 7] are in good agreement with the data of Table 2.

To obtain convincing evidence of the correctness and reliability of the found thermodynamic characteristics of the intermediate phases, we calculated the phase equilibria in the Al–Mn system using the thermodynamic functions of the melt from [8] and the Gibbs energies of phase transitions of the components from [5]. The results obtained (Fig. 2) virtually coincide with the independent data determined by the methods of physicochemical analysis in [9–12] and of the generalizing work [13].

The sensitivity of the procedure developed allowed us to directly measure the thermodynamic properties of quasicrystalline phases. Samples of the ico ($x(\text{Mn}) = 0.2$) and deca ($x(\text{Mn}) = 0.22$) phases were studied. Ion current intensities were continually recorded with increasing temperature of an alloy. The unit of the double effusion cell was equipped with a differential thermocouple. This allowed us to perform double control and record thermal effects corresponding to transformations of the samples. In addition, to confirm that an

alloy retained a quasicrystalline structure, some measurements were interrupted. After removing a fluoride additive, the samples were analyzed by X-ray powder diffraction. The decomposition temperatures of the icosahedral and decagonal phases fixed in many runs for various samples virtually coincided and were 792 ± 3 and 886 ± 2 K, respectively, which is in good agreement with the data of [12, 14].

To determine and substantiate the calculation scheme for thermodynamic functions of quasicrystalline phases, long-term isothermal experiments were carried out at temperatures much lower (~ 70 – 100 K) than the limits of their thermal stabilities. In all cases, the consumption of aluminum in the reaction with fluoride additions led to the precipitation of $\text{Al}_{11}\text{Mn}_4$ crystals, which was shown by X-ray powder diffraction. Therefore, based on the measured ion current intensities (vapor pressures) of AlF and Na (or Mg), we found the partial functions of aluminum for the fields of metastable equilibrium between quasicrystalline phases and the $\text{Al}_{11}\text{Mn}_4$ compound (Table 1), as well as the thermodynamic properties of the quasicrystalline phases with the use of the equations of the appropriate reactions (Table 2). The composition of the icosahedral quasicrystals studied coincides with that of the μ phase, whereas the decagonal quasicrystals consist of two phases: μ and $\text{Al}_{11}\text{Mn}_4$. The Gibbs energy of this two-

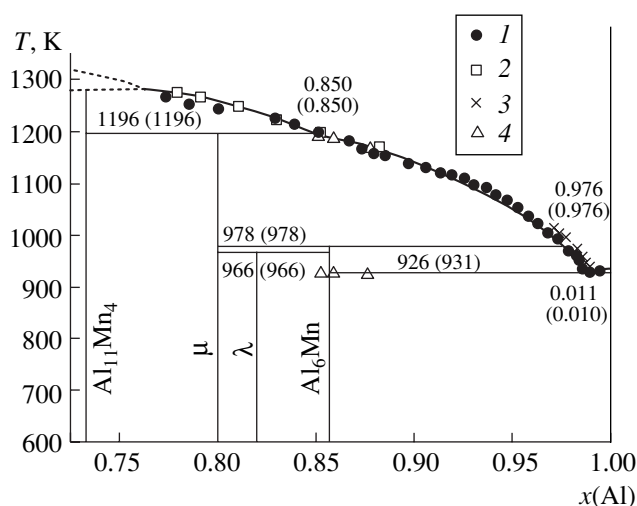


Fig. 2. Phase diagram of the Al–Mn system. Lines designate the calculation data; dots stand for the experimental data of (1) [9], (2) [10], (3) [11], and (4) [12]. The calculated coordinates of special points are shown without parentheses, and the coordinates in parentheses are the recommendations of [13].

phase mixture derived from the data for the μ and $\text{Al}_{11}\text{Mn}_4$ phases (Table 2) can be described by the equation $\Delta_f G(\text{crystal}, x(\text{Mn}) = 0.22) = -(22637 \pm 107) + (5.41 \pm 0.11)T$. The reliability of the data obtained is confirmed by the coincidence of the enthalpies of the phase transitions from the ico and deca phases to equilibrium crystals derived from these data (2092 ± 208 and 723 ± 175 J/mol, respectively) and the enthalpy values ~ 2000 and 600 J/mol, respectively, found in independent DSC studies [14]. The temperatures of metastable congruent melting of icosahedral and decagonal quasicrystals calculated based on the data of Table 2 and the thermodynamic properties of the melt [8] were 1185 and 1227 K, respectively. These data virtually coincide with $T_m(\text{ico}, x(\text{Mn}) = 0.20) = 1183 \pm 20$ K and $T_m(\text{deca}, x(\text{Mn}) = 0.20) = 1238 \pm 20$ K, which were found by Knapp and Follstaedt [15] with the use of an original rapid electron-beam heating technique.

Comparison of the thermodynamic functions determined for the Al–Mn alloys in quasicrystalline and equilibrium crystalline states shows that the decagonal phase is more stable than the icosahedral quasicrystals, which also agrees with the available experimental data [12, 14]. The most important result of the study performed is the conclusion that the difference between the Gibbs energies of both types of quasicrystals and equilibrium crystalline compositions increases with decreasing temperature (Fig. 3). This is evidence in favor of the conclusion that the stabilization of quasicrystals is entropic in nature and that quasicrystals, like metallic glasses, are only an intermediate state between a liquid and a crystal and cannot be the stable ground state of an alloy.

Therefore, complete reliable data on the thermodynamic properties of the icosahedral and decagonal qua-

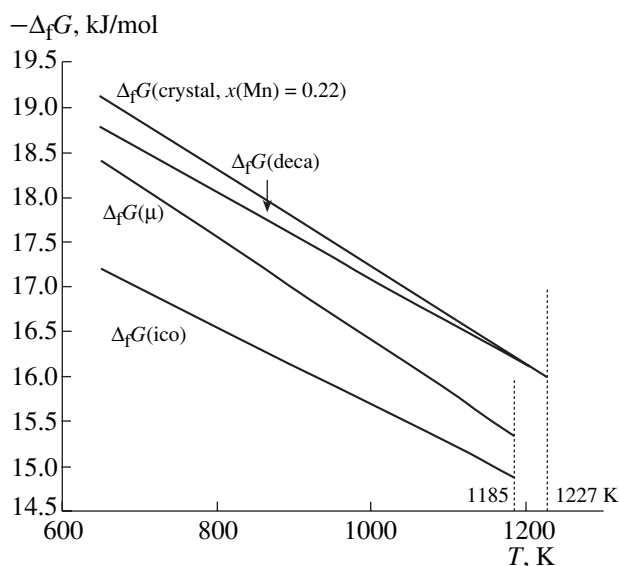


Fig. 3. The Gibbs energies of the quasicrystalline and crystalline Al–Mn alloys of the same composition.

sicrystalline and crystalline phases on the basis of Al in the Al–Mn system were obtained for the first time. A direct comparison of these data was performed. The decagonal phase was found to be more stable than the icosahedral quasicrystals, and the difference between the Gibbs energies of both types of quasicrystals and equilibrium crystalline compositions increased with decreasing temperature. We have obtained evidence in favor of the entropic nature of stabilization of the quasicrystals and the concept that they, like metallic glasses, are only the intermediate state between liquid and crystal and cannot be the stable ground state of an alloy.

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