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Heat capacities of $Al_{62.5}Cu_{25}Fe_{12.5}$ quasicrystals and B2 related crystals[1]

Lan Wang[a], Zhi-Cheng Tan[a,*], Jiao-Biao Zhang[a], Shuang-He Meng[a],
Li-Ming Zhang[b,d], Qing-Gang Zhou[b], Chuang Dong[b,c]

[a]Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Academia Sinica, Dalian 116023, China
[b]Department of Materials Engineering, Dalian University of Technology, Dalian 116024, China
[c]State Key Laboratory for Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian 116024, China
[d]Laboratorie de Science et Génie de Matèriaux Mètalliques, Ecole des Mines de Nancy, Parc de Saurupt, F-54042, Nancy, France

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Abstract

The heat capacities of two $Al_{62.5}Cu_{25}Fe_{12.5}$ samples containing icosahedral quasicrystals and B2 related crystals respectively were measured with a high-precision automatic adiabatic calorimeter over the temperature range of 75–385 K. The heat capacities of both samples increase with temperature. At the low temperature range, the heat capacity of the quasicrystalline sample is higher than that of the B2 approximate. However, the heat capacity of the B2 sample becomes higher above 254.987 K. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heat capacity; $Al_{62.5}Cu_{25}Fe_{12.5}$; Quasicrystal; B2 structure; Adiabatic calorimeter

1. Introduction

Quasicrystals are special intermetallic compounds which possess long-range quasiperiodic orientational order and non-crystallographic symmetries [1]. Since its discovery, extensive researches have been carried out to characterize the properties of this new kind of materials [2,3]. However, little has been done on their specific heat properties which provide important information about critical and supercritical phenomena. Quasicrystals often coexist or can be transformed to some related crystalline phases. Among these related structures, the B2 type (CsCl type) is the simplest one which forms the basic structure units for all related crystals [4–6]. In the present communication, we report an investigation on high-precision specific heat measurements of Al–Cu–Fe samples containing respectively icosahedral quasicrystals and a related B2 crystalline phase with the same composition. Both are stable phases over the temperature range of our experiments.

2. Experimental

2.1. Adiabatic calorimetry

The heat capacity measurements were carried out by means of a high-precision automatic adiabatic calorimeter over the temperature range of 75–

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*Corresponding author. Fax: +86-411-4691570; e-mail: tzc@ms.dicp.ac.cn

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385 K. The masses of the samples used in our experiments amounted to 52.4021 and 59.3764 g for crystals and quasicrystals, respectively, which are equivalent to 1.3189 and 1.4945 mol based on their molar mass of 39.731 g mol^{-1}. The construction of the calorimeter has been described previously in detail [7]. Briefly, the calorimeter included a sample cell, a thermometer, a calorimeter heater, two adiabatic shields, two sets of eight-junction chromel-copel thermocouples and a high vacuum system. The calorimeter cell is made of gold-plated copper with a wall of 0.3 mm thickness. The size of the cell is 33 mm in diameter and 60 mm high. The mass of the empty cell is about 50 g and the internal capacity is 50 cm^3. A platinum resistance thermometer which was made by the Instrument Manufactory of Yunnan, China, and calibrated on the basis of the ITS-90 by the Station of Low Temperature Metrology, Academia Sinica, with an uncertainty of about 1 mK, and a heater assembly were inserted in the central entrant well of the cell. After loading the sample into the cell, the up-cover and body was sealed with soldering tin. The cell was evacuated, and then a small amount of helium gas was introduced through a copper capillary tubing on the up-cover to promote the heat transfer. Finally, the container was sealed by pinching off the tubing. Two adiabatic shields surrounded the cell and controlled its temperature. The whole calorimetric system was kept in a vacuum, and its residual pressure was 10^{-3} Pa.

In order to verify the reliability of the calorimeter, the molar heat capacities of α-Al_2O_3 were measured in the range of 80–400 K. Deviation of the experimental results from the smoothed curve lies within $\pm 0.1\%$, while the inaccuracy is within $\pm 0.2\%$, as compared with those of the National Bureau of Standards [8] in the whole temperature range.

2.2. Sample preparation and characterization

This investigation was performed on $Al_{62.5}Cu_{25}Fe_{12.5}$ samples of nominal composition. The Al–Cu–Fe system contains a stable icosahedral quasicrystalline phase [9], as well as a variety of crystalline phases including a B2-type phase.

The $Al_{62.5}Cu_{25}Fe_{12.5}$ alloy was prepared from pure constituents in an inductive furnace under argon atmosphere. The ingots, solidified under cooling rates of 10^1–10^2 K s^{-1}, are referred to as "as-cast" materials. To obtain the complete quasicrystalline phase, the as-cast ingots were annealed at 1033 K for 10 h and then cooled in air with a rate of 50 K/min. The ingots were ground into fine powders by ball milling, with a ball-to-powder weight ratio of 2:1. The sample 1 powder contains largely icosahedral phase ranging from 30 to 55 μm in size. The sample 2 powder is of B2 structure obtained from sample 1 after annealing at 1133 K for 10 h and then cooled in air with a rate of about 60 K min^{-1}.

Structural investigations were carried out with a KRISTALLOFLEX X-ray diffractometer using Co K_α radiation (λ=0.178897 nm). The X-ray diffraction patterns of sample 1 and sample 2 are shown in Figs. 1 and 2, respectively, which indicate that sample 1 has a large range field contain icosahedral quasicrystalline and B2 phases, while sample 2 only possesses the B2 structure.

3. Result and discussion

The experimental data of molar heat capacities of $Al_{62.5}Cu_{25}Fe_{12.5}$ quasicrystalline and B2 samples are shown in Fig. 3. The molar heat capacities in quasi-crystalline and crystalline states for 75–385 K can be illustrated (see Tables 1 and 2) respectively by the following equations:

For $Al_{62.5}Cu_{25}Fe_{12.5}$ quasicrystals:

$$C_{p,\mathrm{m}}\ (\mathrm{J\,K^{-1}mol^{-1}}) = 21.294493 + 5.543514x - 3.761955x^2 + 2.576019x^3 - 1.320895x^4\ (\mathrm{J\,K^{-1}mol^{-1}}).$$

For $Al_{62.5}Cu_{25}Fe_{12.5}$ B2 crystals:

$$C_{p,\mathrm{m}}\ (\mathrm{J\,K^{-1}mol^{-1}}) = 20.967921 + 7.5553088x - 4.005433x^2 + 1.621542x^3 - 0.88143x^4\ (\mathrm{J\,K^{-1}mol^{-1}}).$$

In the two equations, T represents the measurement temperature and x is equal to $(T$–230)/155.

The heat capacity curves of the two samples rise with increasing temperature in a smooth and continuous manner. No phase transition and thermal anomaly were observed, indicating that both the quasicrystalline and the B2 crystalline $Al_{62.5}Cu_{25}Fe_{12.5}$ phases are stable over the temperature range of

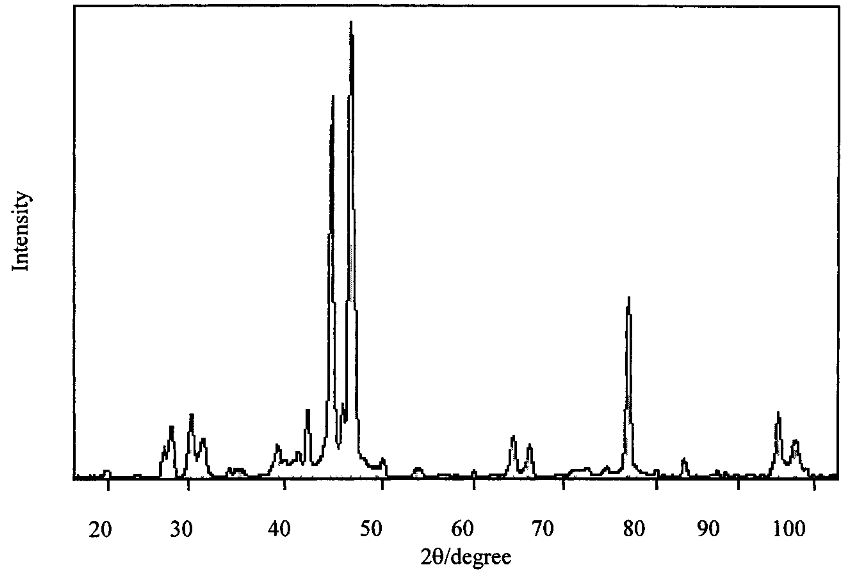

Fig. 1. XRD pattern of quasicrystal sample.

75–385 K. Below a critical temperature of 254.987 K, the heat capacity of the $Al_{62.5}Cu_{25}Fe_{12.5}$ quasicrystal is higher than that of the B2 crystals. This reveals that the quasicrystals are in a higher energy state. Therefore, the quasicrystals are less stable than the B2 crystals. On the contrary, above 254.987 K, the heat capacity of the $Al_{62.5}Cu_{25}Fe_{12.5}$ B2 crystals are higher, so the quasicrystals are more stable. The heat capacities of the two substances are all equal to 22.100 J K^{-1} mol^{-1} at the critical temperature. At

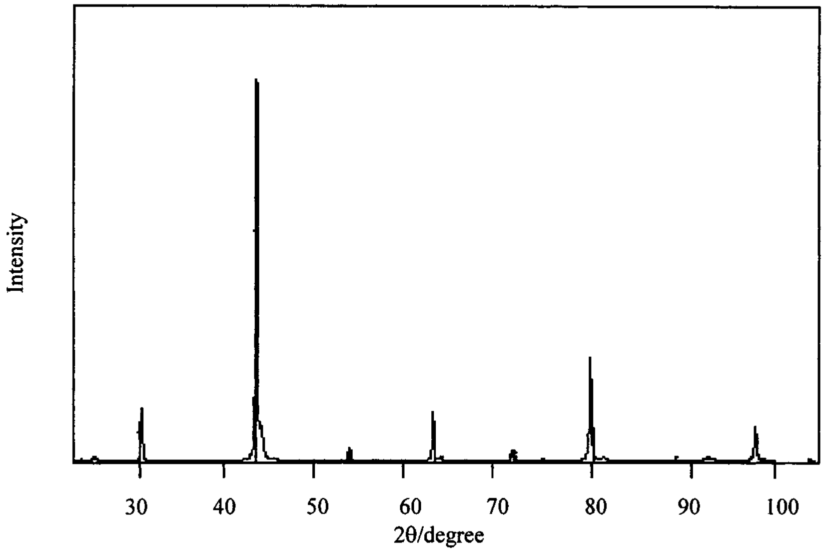

Fig. 2. XRD pattern of B2 related crystal sample.

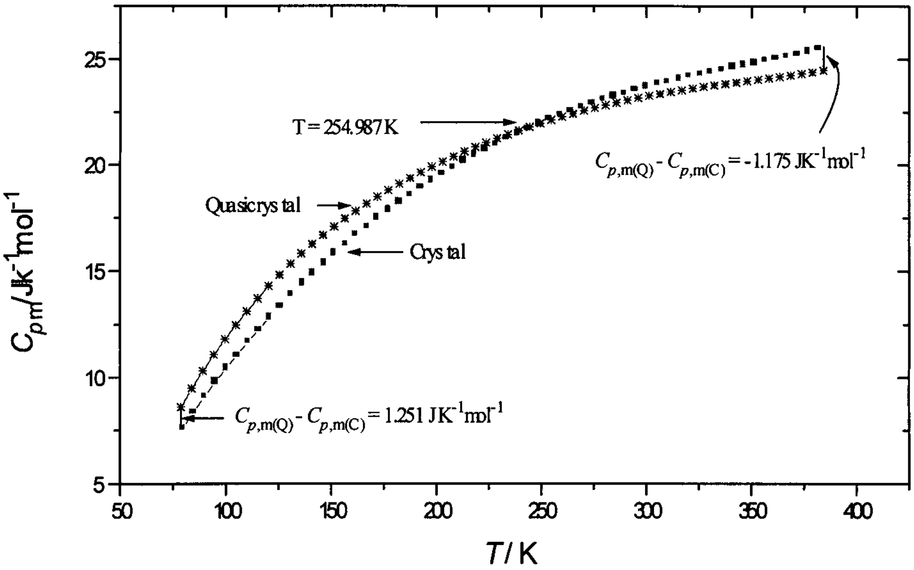

Fig. 3. $C_{p,m}=f(T)$ curves of $Al_{62.5}Cu_{25}Fe_{12.5}$ B2 crystal and quasicrystal samples.

Table 1
The experimental molar heat capacities of $Al_{62.5}Cu_{25}Fe_{12.5}$ quasicrystals (M=39.731 g mol^{-1})

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
78.773	8.596	220.128	20.77
80.494	8.897	222.640	20.85
82.178	9.152	225.141	20.98
83.973	9.520	227.623	21.12
85.875	9.808	230.758	21.45
87.913	10.15	232.500	21.67
90.083	10.45	234.963	21.89
92.208	10.73	237.413	21.61
96.990	11.47	239.426	21.74
99.423	11.77	246.328	21.36
101.804	12.11	248.954	21.74
104.139	12.40	251.783	21.88
106.431	12.77	254.605	21.88
108.686	12.97	257.416	21.93
110.908	13.24	260.216	22.11
118.669	14.16	263.195	22.15
121.272	14.37	266.355	22.39
123.838	14.72	269.506	22.46
126.364	15.06	272.614	22.48
136.107	15.87	275.772	22.56
138.497	16.06	278.892	22.64
140.872	16.28	282.002	22.69
143.574	16.51	285.101	22.79
145.574	16.70	288.188	22.82
147.895	16.86	291.260	22.92
150.196	17.01	294.317	23.08
152.478	17.16	297.372	23.13
154.743	17.29	300.628	23.10
156.991	17.45	304.078	23.29
159.550	17.22	307.520	23.36
161.435	17.84	310.956	23.28
163.635	17.96	314.380	23.35
165.821	18.07	317.796	23.50
167.994	18.20	321.206	23.56
170.155	18.41	321.206	23.60
172.303	18.25	324.607	23.75
174.438	18.53	328.001	23.77
176.564	18.59	331.389	23.84
181.084	18.88	334.774	23.82
183.784	19.04	338.159	23.87
186.465	19.13	341.546	23.98
189.129	19.34	344.937	23.96
191.783	19.42	348.336	23.87
194.420	19.45	351.739	24.05
197.041	19.68	355.147	24.06
199.651	19.82	357.898	24.04
202.250	20.03	361.994	24.13
204.839	20.11	365.368	24.17
207.414	20.21	368.731	24.28
209.979	20.29	372.089	24.26
212.533	20.30	377.162	24 .37
215.074	20.52	383.904	24.48
217.605	20.75		

Table 2
The experimental molar heat capacities of $Al_{62.5}Cu_{25}Fe_{12.5}$ crystals (M=39.731 g mol^{-1})

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})
79.659	7.573	223.414	20.65
82.368	7.957	227.023	21.07
84.991	8.388	230.548	22.71
87.543	8.731	234.072	21.42
90.307	9.117	237.621	21.69
93.273	9.550	241.074	22.88
96.156	9.936	244.514	21.70
99.300	10.45	248.000	21.74
102.697	10.87	251.477	21.82
106.010	11.22	254.936	22.01
109.237	11.62	258.375	22.17
112.490	11.96	261.798	22.28
115.478	12.30	265.203	22.40
118.506	12.64	268.824	22.62
121.479	12.97	272.660	22.75
124.401	13.22	276.478	22.88
127.688	13.64	280.279	23.05
131.330	14.02	284.062	23.19
134.909	14.32	287.824	23.39
138.426	14.70	291.565	23.54
141.884	14.99	295.289	23.62
145.292	15.28	299.006	23.64
148.650	15.66	302.715	23.76
151.962	15.88	306.413	23.84
155.236	16.15	313.763	24.06
158.471	16.43	317.420	24.18
161.667	16.65	321.065	24.21
164.829	16.92	324.701	24.30
167.958	17.15	328.325	24.39
171.057	17.37	331.838	24.44
174.126	17.64	335.542	24.56
177.169	17.82	339.136	24.63
180.183	18.04	342.722	24.71
183.173	18.24	346.301	24.77
186.139	18.45	349.872	24.86
189.567	18.68	353.433	24.95
193.452	18.91	356.981	25.06
197.301	19.18	360.518	25.11
201.116	19.40	364.048	25.23
204.900	19.58	367.576	25.17
208.654	19.769	371.102	25.26
212.384	19.961	374.634	25.19
216.089	20.18	378.172	25.19
219.767	20.39	381.682	25.61

this temperature, they have the same energy state and identical stability. The absolute heat capacity difference between the quasicrystals and the B2 crystals, $\Delta C_{p,\mathrm{m}}=C_{p,\mathrm{m}\ (\mathrm{quasicrystal})}-C_{p,\mathrm{m}\ (\mathrm{crystal})}$, decreases from 1.251 J K^{-1} mol^{-1} at 75 K to 0 at the critical temperature. At the ending temperature of the experiment, 385 K, this difference is -1.175 J K^{-1} mol^{-1}. The relative difference, $\Delta C_{p,\mathrm{m}}/C_{p,\mathrm{m}\ (\mathrm{crystal})}$, changes first from 18.29% (75 K) to 0 (259.987 K), then to -4.61% (385 K). The interpretation of such changes with temperature will be the subject of further studies.

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