Determination of Standard Gibbs Energy of Formation of Al₂Nd by Solution Calorimetry and Heat Capacity Measurement from Near Absolute Zero Kelvin

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The thermodynamic properties of Al₂Nd were investigated by calorimetry. The standard entropy of formation of Al₂Nd at 298 K, $\Delta_f S^o_{298}$(Al₂Nd), was determined from measuring the heat capacities, C_p, from near absolute zero (2 K) to 300 K by the relaxation method. The standard enthalpy of formation of Al₂Nd at 298 K, $\Delta_f H^o_{298}$(Al₂Nd), was determined by solution calorimetry in hydrochloric acid solution. The standard Gibbs energy of formation of Al₂Nd at 298 K, $\Delta_f G^o_{298}$(Al₂Nd), was determined from these data. The results were obtained as follows: $\Delta_f S^o_{298}$(Al₂Nd)/J·K^{-1}·mol^{-1} = −10.7 ± 1.2, $\Delta_f H^o_{298}$(Al₂Nd)/kJ·mol^{-1} = −105.03 ± 27, and $\Delta_f G^o_{298}$(Al₂Nd)/kJ·mol^{-1} = −101.85 ± 27. [doi:10.2320/matertrans.47.2044]

1. Introduction

High melting point metals such as titanium, chromium, molybdenum and tantalum, and their alloys, which have high heat-resistance, have been used as wiring materials for liquid crystal displays (LCD). Recently, large size of the panel with high precision has been desired for LCD, and aluminium and its alloy films have been used for improving the signal delay caused by high electric resistivity of wiring materials.[1–3] Aluminium is a low melting point metal, and the formation of hemispheric hillocks caused by the thermal history including the production process of Al wiring become a subject of discussion.[4–6] Especially, the Al-Nd alloy film has been come into practical use as wiring material,[1] since it has higher heat-resistance than Al while the increase of electric resistivity caused by the addition of Nd is comparatively low. Therefore, thermodynamic data of the Al-Nd binary system are inevitably necessary to design and develop new wiring materials.

Previously Deenadas *et al.* measured the heat capacities, C_p, of the magnetic materials including Al₂Nd in the temperature range of 8–305 K to calculate the third law entropy, S^o_T, by the adiabatic calorimeter[7] and found a peak at 77.2 K, consistent with the ferromagnetic-paramagnetic phase transition.[8,9] However, in order to determine correct S^o_T, the C_p values below 8 K are indispensable.

Recently relaxation method[10–13] has been developed to measure heat capacity, C_p, at very low temperature. Since a small amount (5–30 mg) of a sample is enough to measure C_p, this method[10–13] can change the sample temperature rapidly. In our previous studies,[13–18] the standard entropies of formation at 298 K, $\Delta_f S^o_{298}$, of intermetallic compounds[14–18] and an oxide[13] were determined by measuring C_p from near absolute zero Kelvin (2 K) by the relaxation method.[10–13] In the present study, we have tried to determine $\Delta_f S^o_{298}$ of Al₂Nd from C_p measured from near absolute zero

Kelvin as in the same way of our previous studies.[13–18] In addition, the standard enthalpy of formation at 298 K, $\Delta_f H^o_{298}$, of Al₂Nd was determined by solution calorimetry in hydrochloric acid solution by using a new calorimeter[19] to which new thermoelectric devices are equipped. The standard Gibbs energy of formation at 298 K, $\Delta_f G^o_{298}$, was determined from the obtained $\Delta_f S^o_{298}$ and $\Delta_f H^o_{298}$. Furthermore, electric resistivity, ρ, of Al₂Nd was measured to clarify phase transitions. Such a determination of $\Delta_f G^o_{298}$, followed by measuring C_p in the temperature range from 298 K to high temperatures, is attractive since it gives us the Gibbs energy of formation, $\Delta_f G^o_T$, up to the maximum temperature of C_p measurement.[13,18]

2. Experimental

2.1 Preparation of the specimens

Commercial Al (99.99%, High Purity Chemical Institute Co., Japan (HPCI)) and Nd (99.9%, HPCI) were used as starting materials. Figure 1 shows the phase diagram of the Al-Nd binary system.[20] Composition of Al₂Nd is Al-Nd (66.7–33.3 mol%). Since the formulation for one mole of atoms is convenient, it is usual to compare the molar thermodynamic properties of compounds, and Al₂Nd is rewritten as Al₀.₆₆₇Nd₀.₃₃₃. Al₀.₆₆₇Nd₀.₃₃₃ was prepared by
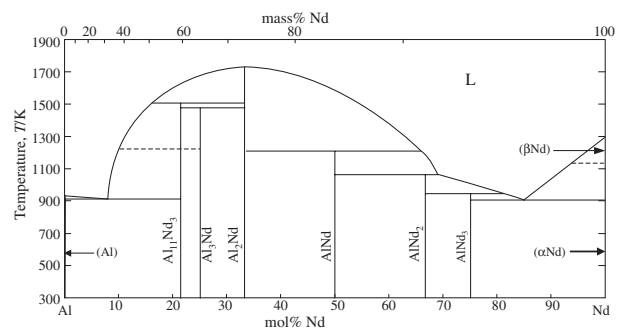

Fig. 1 Phase diagram of the Al-Nd binary system.[20]

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arc-melting the compressed compacts of the mixture of Al and Nd powders in the composition of Al-Nd (68.7–31.3 mol%) with a tungsten electrode in an argon atmosphere. After melting, the sample was vacuum-sealed in silica tube and then subjected to a homogenizing treatment at 673 K for 21 days. The addition of an excess of 2 mol% Al was necessary in order to prepare Al$_{0.667}$Nd$_{0.333}$, since an oxidation loss of Al occurred during arc-melting and heat treatment. The amount of the addition of excess Al was determined from prior experiments. The structure and the composition of the sample were measured by an X-ray diffractometer (XRD, Rigaku, RINT-2200) and an electron microprobe microanalyzer (EPMA, JEOL, JXA-8900R), respectively. The detected XRD peaks of the sample corresponded to Al$_2$Nd and it was homogeneous and single phase. Average of atomic ratio of Al and Nd of five analyses were 0.657 and 0.343, respectively, corresponding to the stoichiometric composition within error. Thus, the sample was submitted to calorimetry.

2.2 Calorimetric methods
2.2.1 C_p at 2–300 K and $\Delta_f S^o_{298}$
The entropy of a material at 298 K, S^o_{298}, based on the third law of thermodynamics is given by

$$S^o_{298} = \int_0^{298} \frac{C_p}{T}\,dT \tag{1}$$

where T is the absolute temperature and C_p is the heat capacity. The heat capacities for Al$_{0.667}$Nd$_{0.333}$ were measured in the temperature range of 2–300 K by using a relaxation method[10–13] instrument (Quantum Design, San Diego, USA). Details of this method were described in our previous studies.[14–18] The measured C_p values were fitted to a polynomial expression as follows:

$$C_p = \sum_{n=1}^{n} a_n T^n. \tag{2}$$

The polynomials were integrated as shown in eq. (1) to determine the S^o_{298} of Al$_{0.667}$Nd$_{0.333}$. The entropy of mixing of Al$_{0.667}$Nd$_{0.333}$, $\Delta_{mix}S_{298}$(Al$_{0.667}$Nd$_{0.333}$), is given by

$$\Delta_{mix}S_{298}(\text{Al}_{0.667}\text{Nd}_{0.333}) = S^o_{298}(\text{Al}_{0.667}\text{Nd}_{0.333})$$
$$- S^o_{298}(\text{Al}) \times 0.667 - S^o_{298}(\text{Nd}) \times 0.333 \tag{3}$$

where S^o_{298}(Al) = 28.275 J·K^{-1}·mol^{-1} and S^o_{298}(Nd) = 71.086 J·K^{-1}·mol^{-1} are the third law entropies of pure Al and Nd and were adopted from the thermochemical tables.[21,22] Consequently, the standard entropy of formation of Al$_2$Nd, $\Delta_f S^o_{298}$(Al$_2$Nd), is obtained as follows:
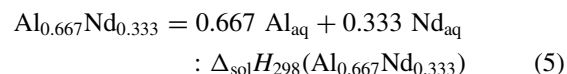
$$\Delta_f S^o_{298}(\text{Al}_2\text{Nd}) = \Delta_{mix}S_{298}(\text{Al}_{0.667}\text{Nd}_{0.333}) \times 3. \tag{4}$$
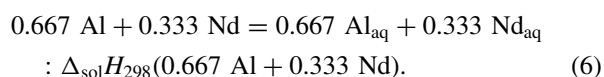
2.2.2 $\Delta_f H^o_{298}$
The enthalpy of solution, $\Delta_{sol}H_{298}$, was measured by using a new Calvet-type calorimeter (Tokyo Rikou, Tokyo, Japan) equipped with a thermo-module composed of p-type thermo-electric semi-conductors of BiSbTe, PbSnTe, SiGe and SnTe, and n-type Bi$_2$(Se,Te)$_3$, PbTe and Gd$_2$Se.[19] Details of the experimental procedures were described in our previous works.[14–18] Previously calorimetric cells in which the samples were dissolved in to acid solution were made from stainless steel (SUS 316) coated with fluorine resin.[14–18] In

the present study, the calorimetric cells were made from all fluorine resin. The mass of Al$_{0.667}$Nd$_{0.333}$ was 65.67 mg. Commercial 5 N (5 mol·dm^{-3}) hydrochloric acid solution (25 ml) was used as a solvent to dissolve Al$_{0.667}$Nd$_{0.333}$.

The chemical reaction during dissolving of Al$_{0.667}$Nd$_{0.333}$ is defined by eq. (5),

$$\text{Al}_{0.667}\text{Nd}_{0.333} = 0.667\,\text{Al}_{aq} + 0.333\,\text{Nd}_{aq}$$
$$: \Delta_{sol}H_{298}(\text{Al}_{0.667}\text{Nd}_{0.333}) \tag{5}$$

where Al$_{aq}$ and Nd$_{aq}$ are aluminium ion and neodymium ion in the solvent, respectively. In the same way for the intermediate phase, the chemical reaction of the mechanical mixtures of the requisite amounts of pure aluminium and pure neodymium, (0.667 Al + 0.333 Nd) is defined by eq. (6), namely

$$0.667\,\text{Al} + 0.333\,\text{Nd} = 0.667\,\text{Al}_{aq} + 0.333\,\text{Nd}_{aq}$$
$$: \Delta_{sol}H_{298}(0.667\,\text{Al} + 0.333\,\text{Nd}). \tag{6}$$

The enthalpy of mixing of Al$_{0.667}$Nd$_{0.333}$, $\Delta_{mix}H_{298}$(Al$_{0.667}$-Nd$_{0.333}$), is defined by subtracting $\Delta_{sol}H_{298}$(Al$_{0.667}$Nd$_{0.333}$) from $\Delta_{sol}H_{298}$(0.667 Al + 0.333 Nd) as follows:

$$\Delta_{mix}H_{298}(\text{Al}_{0.667}\text{Nd}_{0.333}) = \Delta_{sol}H_{298}(0.667\,\text{Al} + 0.333\,\text{Nd})$$
$$- \Delta_{sol}H_{298}(\text{Al}_{0.667}\text{Nd}_{0.333}). \tag{7}$$

The $\Delta_{sol}H_{298}$ values of the intermediate phase and the mechanical mixture were determined as the average of five measurements, and the $\Delta_{mix}H_{298}$ was determined from each average $\Delta_{sol}H_{298}$. Consequently, the standard enthalpy of formation of Al$_2$Nd is obtained by

$$\Delta_f H^o_{298}(\text{Al}_2\text{Nd}) = \Delta_{mix}H_{298}(\text{Al}_{0.667}\text{Nd}_{0.333}) \times 3. \tag{8}$$

In the present study, error was treated by general error propagation theory.[23]

3. Results and Discussion

3.1 C_p in the temperature range of 2–300 K and S^o_{298}
The measured C_p values of Al$_{0.667}$Nd$_{0.333}$ in the temperature ranges of 2–300 and 2–20 K are shown as open circle symbols in Figs. 2 and 3. A λ-type peak (P$_1$) was found at the temperatures of T_1 = 71.8 K, consistent with the ferromagnetic-paramagnetic phase transition.[8,9] Also, the other λ-type peak (P$_2$) was found at the temperatures of T_2 = 3.91 K for the first time.

Table 1 shows the coefficients of the polynomials to fit the measured C_p values of Al$_{0.667}$Nd$_{0.333}$ and the measured C_p values without the two peaks as base lines. In order to obtain enough fitting accuracy, the measured C_p values of nine temperature ranges and the base lines of two temperature ranges were fitted separately. The results of calculations of C_p and base lines using the polynomials are shown as solid lines and dashed lines, respectively, in Figs. 2 and 3. Since the fitting functions represent the measured C_p values well, the third law entropy, S^o_{298}, of Al$_{0.667}$Nd$_{0.333}$ was calculated by eq. (1). Although the C_p values below 2 K were not measured, the integration was performed using the fitting function extrapolated to T = 0.001 K, where the C_p value calculated by the fitting function was almost zero. The result was as follows:
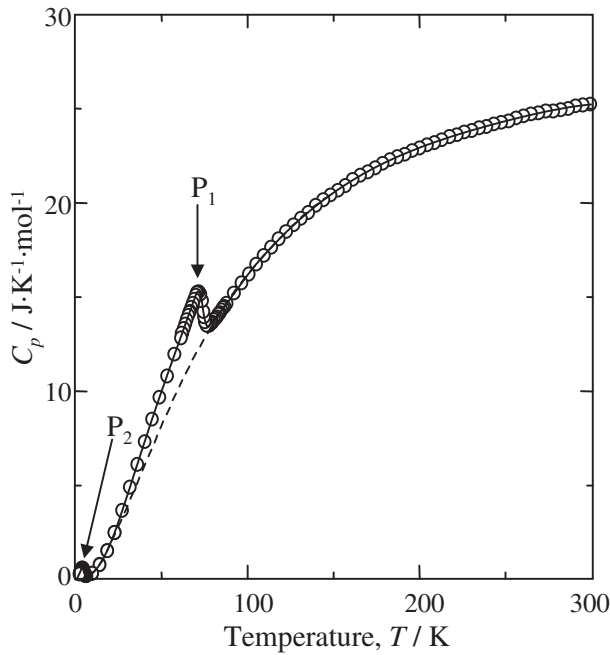
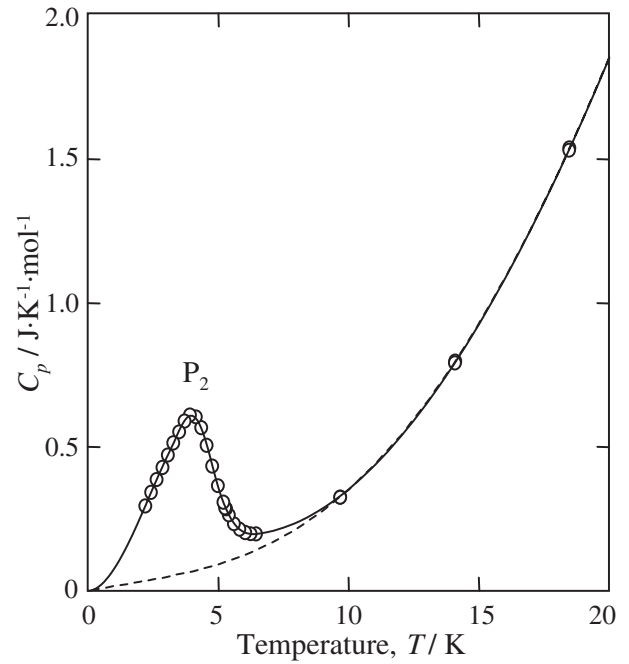Fig. 2 Temperature dependence of heat capacity, C_p, for $Al_{0.667}Nd_{0.333}$ in the temperature range of 0–300 K.

Fig. 3 Temperature dependence of heat capacity, C_p, for $Al_{0.667}Nd_{0.333}$ in the temperature range of 0–20 K.

Table 1 Coefficients of the polynomials to fit the measured C_p values of $Al_{0.667}Nd_{0.333}$ and base lines. $C_p/\text{J·K}^{-1}\text{·mol}^{-1} = a + bT + cT^2 + dT^3 + eT^4 + fT^5 + gT^6$.

Temperature Range/K	a	b	c	d	e	f	g
0–3.272	-6.2332×10^{-6}	6.3919×10^{-3}	8.1999×10^{-2}	-1.2273×10^{-2}	2.7269×10^{-3}	-1.2687×10^{-3}	1.6917×10^{-4}
3.272–5	7.9874	-6.2268	1.1230	2.2999×10^{-1}	-6.8998×10^{-2}	-3.1922×10^{-4}	6.9124×10^{-4}
5–6.434	3.3222	-3.6669×10^{-1}	-1.1851×10^{-1}	3.4063×10^{-3}	2.0204×10^{-3}	2.7481×10^{-4}	-4.5945×10^{-5}
6.434–28	5.7164×10^{-1}	-1.3407×10^{-1}	1.2999×10^{-2}	-2.0166×10^{-4}	2.3154×10^{-6}	2.2362×10^{-8}	-1.0453×10^{-9}
28–70	7.8097×10^{-1}	-1.7660×10^{-1}	1.4543×10^{-2}	-1.1874×10^{-4}	-2.4065×10^{-6}	4.9230×10^{-8}	-2.4465×10^{-10}
70–74	-3.8494×10^{1}	-3.5067×10^{-1}	9.1051×10^{-3}	2.3947×10^{-4}	-1.4950×10^{-7}	5.0728×10^{-9}	-4.5489×10^{-10}
74–77.01	1.0933×10^{2}	-5.1228×10^{-1}	2.4800×10^{-3}	-2.4669×10^{-4}	-1.2786×10^{-6}	-4.2251×10^{-9}	4.6960×10^{-10}
77.01–105	9.9352	4.2117×10^{-2}	-4.5599×10^{-4}	-3.9604×10^{-7}	1.1438×10^{-7}	6.9024×10^{-11}	-5.1507×10^{-12}
105–300	-1.9565×10^{-1}	2.0834×10^{-1}	-3.1551×10^{-4}	-1.7279×10^{-6}	3.2016×10^{-9}	1.6232×10^{-11}	-3.7578×10^{-14}
baseline 0–20	1.5386×10^{-5}	1.8016×10^{-2}	-1.9418×10^{-3}	4.4792×10^{-4}	-8.2393×10^{-6}	1.5126×10^{-9}	—
baseline 20–150	-5.8313×10^{-1}	4.2955×10^{-2}	5.1488×10^{-3}	-6.1262×10^{-5}	2.0148×10^{-7}	5.3634×10^{-10}	-3.2653×10^{-12}

$$S^{\circ}_{298}(Al_{0.667}Nd_{0.333})/\text{J·K}^{-1}\text{·mol}^{-1} = 38.96 \pm 0.39. \quad (9)$$

Previously, C_p of pure copper (99.9999%, Nilaco, Tokyo) was measured, and the deviation of the measured C_p data and the calculated S°_{298} data was less than 1%. Thus, the present C_p and S°_{298} of $Al_{0.667}Nd_{0.333}$ was treated as having an uncertainty of 1% as given in eq. (9). This $S^{\circ}_{298}(Al_{0.667}Nd_{0.333})$ value is slightly higher than the value measured by Deenadas et al. (38.59 J·K^{-1}·mol^{-1}). This discrepancy is due to that Deenadas et al. measured C_p over 8 K. Values of C_p, S°_T and $H^{\circ}_T - H^{\circ}_{298}$ data calculated for different temperatures from the polynomials (Table 1) are summarized in Table 2.

The $\Delta_{\text{mix}}S_{298}$ of $Al_{0.667}Nd_{0.333}$ was given by eq. (3),

$$\Delta_{\text{mix}}S_{298}(Al_{0.667}Nd_{0.333})/\text{J·K}^{-1}\text{·mol}^{-1}$$
$$= -3.58 \pm 0.39. \quad (10)$$

Table 2 Thermodynamic functions for $Al_{0.667}Nd_{0.333}$.

T /K	C_p /J·K^{-1}·mol^{-1}	S°_T /J·K^{-1}·mol^{-1}	$H^{\circ}_T - H^{\circ}_{298}$ /kJ·mol^{-1}
50	9.987	6.158	-5.091
100	16.17	15.57	-4.399
150	20.55	23.04	-3.471
200	22.94	29.31	-2.377
250	24.36	34.59	-1.193
298	25.22	38.96	0
300	25.24	39.12	0.05046

Consequently, the $\Delta_f S^{\circ}_{298}$ of Al_2Nd was obtained by eq. (4),

$$\Delta_f S^{\circ}_{298}(Al_2Nd)/\text{J·K}^{-1}\text{·mol}^{-1} = -10.7 \pm 1.2. \quad (11)$$

This $\Delta_f S^{\circ}_{298}(Al_2Nd)$ value was found to be negative. This is
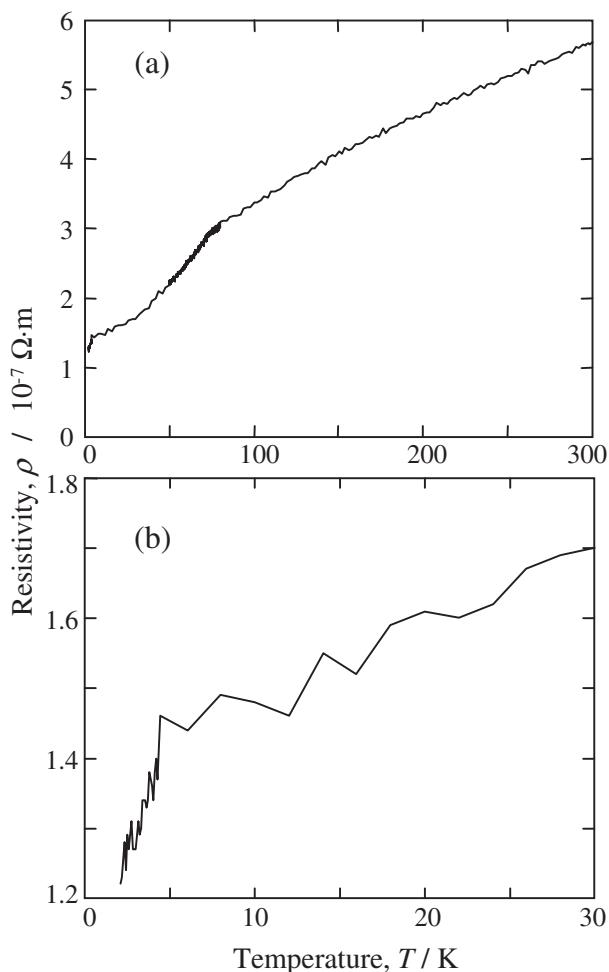
Fig. 4 Electrical resistivity of Al$_{0.667}$Nd$_{0.333}$ in the temperature range of (a) 0–300 K and (b) 0–30 K.

due to the entropy of vibration, $\Delta_f S^{o,vib}$, which generally decreases in a compound due to an increase of lattice vibration frequencies.[24]

3.2 ρ

Figure 4(a) shows ρ of Al$_2$Nd as a function of temperature measured by a four-probe measuring method. ρ decreased at around the temperature of the Curie temperature,[8,9] that is, the temperature of the ferromagnetic-paramagnetic phase transition (P$_1$), resulted from depressing scattering of conduction electrons by spin ordering.[8]

Figure 4(b) shows the detail of ρ of Al$_2$Nd below 30 K. ρ decreased at the temperature corresponding with that of the C_p peak of P$_2$ in Fig. 3. Maple[25] investigated the electronic- and magnetic-properties of NdRh$_6$B$_6$ and found the complicated phase transitions, that is, the superconductive phase transition was caused at 1.91 K, competing with the anti-

ferromagnetic phase transition at 5 K. The local electronic states around neodymium atoms in NdRh$_6$B$_6$ appear to be very complicated. When such complicated electronic states around neodymium atoms are given in Al$_2$Nd, it is possible that complicated phase transitions are caused as a function of temperature. In order to investigate the superconductive and magnetic phase transitions, measurements of magnetic susceptibility and C_p in magnetic field are necessary. Therefore, the mechanism of the phase transition of P$_2$ (Fig. 3) should be further investigated.

3.3 Enthalpy and entropy change of phase transition

The enthalpies and entropies of phase transitions of P$_1$ and P$_2$ were determined using the fitting functions shown in Table 1. The enthalpy of the phase transition (P$_1$) at $T_1 = 71.8$ K was calculated by subtracting the integration of the base line from the integration of the fitting function of C_p from 20.8 to 85.1 K as follows:

$$\Delta_{Tr}H = \int_{20.8}^{85.1} (C_p - C_p(\text{base line}))\mathrm{d}T. \tag{12}$$

The integral interval was the temperatures at which the measured C_p curve turned away from and returned to the base line of C_p. Thus the entropy of phase transition was obtained as follows:

$$\Delta_{Tr}S = \Delta_{Tr}H/T_1. \tag{13}$$

The enthalpy and entropy of the phase transition (P$_2$) at $T_2 = 3.91$ K were calculated in the same way from 0.001 K to 9.67 K.

Table 3 shows the results of thermodynamic values of the phase transitions. For P$_1$, $\Delta_{Tr}H$ and $\Delta_{Tr}S$ were found to be large, compared with simple ferromagnetic-paramagnetic phase transition. It is likely that the phase transition anomaly involves the change of magnetism and excitation into the higher energy crystal field states.[7] Such electronic states appears to be reason for large values of $\Delta_{Tr}H$ and $\Delta_{Tr}S$. For P$_2$, $\Delta_{Tr}H$ and $\Delta_{Tr}S$ should be further discussed by investigating its mechanism by measuring magnetic susceptibility.

3.4 $\Delta_f H^o$ and $\Delta_f G^o$ at 298 K

Table 4 shows the measured $\Delta_{sol}H_{298}$ values and their average values of the intermediate phase (Al$_{0.667}$Nd$_{0.333}$) and the mechanical mixture (0.667 Al + 0.333 Nd). Standard deviations, σ, of (Al$_{0.667}$Nd$_{0.333}$) values and (0.667 Al +

Table 3 The enthalpies and entropies of phase transitions of Al$_{0.667}$Nd$_{0.333}$.

	T/K	$\Delta_{Tr}H$/J·mol^{-1}	$\Delta_{Tr}S$/J·K^{-1}·mol^{-1}
P$_1$	71.8	90.50	1.261
P$_2$	3.91	1.658	0.4241

Table 4 The measured enthalpy of solution ($\Delta_{sol}H$) and their average values ($\Delta_{sol}H_{AV}$) of the intermediate phase (Al$_{0.667}$Nd$_{0.333}$) and the mechanical mixture (0.667 Al + 0.333 Nd).

Sample	Measured $\Delta_{sol}H$/kJ·mol^{-1}					$\Delta_{sol}H_{AV}$/kJ·mol^{-1}
Al$_{0.667}$Nd$_{0.333}$	−543.81	−557.42	−557.54	−542.97	−557.30	−551.81
0.667 Al + 0.333 Nd	−579.41	−587.87	−584.70	−591.83	−590.30	−586.82

0.333 Nd) values were 7.69 and 4.94 kJ·mol^{-1}, respectively. Statistical error is generally given by the ratio of σ to an average value. Therefore, the errors of the present measurements for $Al_{0.667}Nd_{0.333}$ and $(0.667 \ Al + 0.333 \ Nd)$ were 1.4 and 0.84 pct, respectively, convincing enough accuracy. The $\Delta_{sol}H_{298}$ values of $Al_{0.667}Nd_{0.333}$ and $(0.667 \ Al + 0.333 \ Nd)$ were determined as follows:

$$\Delta_{sol}H_{298}(Al_{0.667}Nd_{0.333})/kJ\cdot mol^{-1} = -551.81 \pm 7.7 \quad (14)$$

$$\Delta_{sol}H_{298}(0.667 \ Al + 0.333 \ Nd)/kJ\cdot mol^{-1}$$
$$= -586.82 \pm 4.9. \quad (15)$$

The given error ranges are based on the standard deviation of 5 measurements for each sample. The $\Delta_{mix}H_{298}$ of $Al_{0.667}Nd_{0.333}$ and $\Delta_f H_{298}^o$ of Al_2Nd were obtained by eq. (7) and eq. (8) as follows:

$$\Delta_{mix}H_{298}(Al_{0.667}Nd_{0.333})/kJ\cdot mol^{-1} = -35.01 \pm 9.1 \quad (16)$$

$$\Delta_f H_{298}^o(Al_2Nd)/kJ\cdot mol^{-1} = -105.03 \pm 27. \quad (17)$$

Consequently, the Gibbs energy of mixing of $Al_{0.667}Nd_{0.333}$, $\Delta_{mix}G_{298}$ $(Al_{0.667}Nd_{0.333})$, and the standard Gibbs energy of formation of Al_2Nd, $\Delta_f G_{298}^o$ (Al_2Nd), were determined from eqs. (10), (16), (11) and (17), respectively, as follows:

$$\Delta_{mix}G_{298}(Al_{0.667}Nd_{0.333})/kJ\cdot mol^{-1} = -33.95 \pm 9.1 \quad (18)$$

$$\Delta_f G_{298}^o(Al_2Nd)/kJ\cdot mol^{-1} = -101.85 \pm 27. \quad (19)$$

The errors of ΔS_{298} were negligibly small compared with those of ΔH_{298}. Therefore, the errors of ΔG_{298} are given by the errors of ΔH_{298}.

4. Conclusions

The standard Gibbs energy of Al_2Nd, $\Delta_f G_{298}^o$ (Al_2Nd), was determined by combining the acid solution calorimetry at 298 K with the measurement of the heat capacity in the temperature range of 2–300 K. Such a determination of $\Delta_f G_{298}^o$, followed by measuring C_p in the temperature range from 298 K to high temperatures, is attractive since it gives us the Gibbs energy of formation, $\Delta_f G_T^o$, up to the maximum temperature of C_p the measurement. Therefore, the present results are expected to be useful as basic thermodynamic data of Al-based wiring alloys.

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