Heat capacities of Cr_5Te_8 and Ni_5Te_8 from 325 to 930 K [☆]

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Abstract

Heat capacities of monoclinic $Cr_5Te_8(m)$ and hexagonal $Ni_5Te_8(hex)$ have been measured from 325 to 930 K using an adiabatic scanning calorimeter. For monoclinic $Cr_5Te_8(m)$ the λ-type heat capacity anomaly was observed at 815 K, presumably due to the order–disorder of chromium atoms and vacancies in chromium tellurides. The transition entropy change of the $Cr_5Te_8(m)$ sample obtained in this experiment compared reasonably well with that calculated on the basis of the order–disorder transition from vacancy-ordered Cr_5Te_8-type to vacancy-ordered Cr_3Te_4-type crystal structures. For the hexagonal $Ni_5Te_8(hex)$ sample two excess heat capacities were observed around 400 K and above 700 K. The excess heat capacity at low temperature may be connected to the order–disorder of nickel atoms and vacancies in this structure and that at high temperature may be related to the activation processes such as defect formation, electron excitation and electron–hole pair formation.

Keywords: Cr_5Te_8; Excess heat capacity; Heat capacity; Ni_5Te_8; Order–disorder transition

1. Introduction

Tellurium is a corrosive fission product having a fission yield of about 1% in a fast breeder reactor and may attack the inner surface of fuel cladding made of stainless steel in the presence of oxygen, cesium, iodine, etc. [1,2]. The presence of

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tellurium in the gap between cladding and fuel has been reported by some investigators [3,4]. For the evaluation of the reaction between stainless steel cladding and fission product tellurium, the thermodynamic data of iron, chromium and nickel tellurides are necessary, but they are lacking [5].

The heat capacities of the stoichiometric Cr_5Te_6, Cr_3Te_4 and Cr_2Te_3 samples have been measured in the temperature range 5–350 K by Grønvold and Westrum [6]. Above room temperature, heat capacity data of the stoichiometric Cr_3Te_4 have been reported between 298 and 950 K by Grønvold [7], and the λ-type transition from monoclinic $Cr_3Te_4(m_l)$ to monoclinic $Cr_3Te_4(m_h)$ has been observed at 903 K, presumably connected with disordering of vacancies in the grossly defective structure. The experimental order–disorder transition entropy change (2.22 J K^{-1} mol^{-1}) for $Cr_{0.75}Te$ was in reasonable agreement with the theoretical value (2.88 J K^{-1} mol^{-1}) calculated by assuming disordering of 1/4 mol of chromium atoms and vacancies. Recently, we have measured the heat capacities of monoclinic $Cr_5Te_8(m)$ ($CrTe_{1.528}$, $CrTe_{1.576}$ and $CrTe_{1.590}$) and trigonal $Cr_5Te_8(tr)$ ($CrTe_{1.609}$) phases in the temperature range 220–900 K [8]. For monoclinic $Cr_5Te_8(m)$ and trigonal $Cr_5Te_8(tr)$ phases, the heat capacity anomalies were first observed at about 800 K. However, the transition entropy changes for $Cr_5Te_8(m)$ and $Cr_5Te_8(tr)$ phases obtained experimentally were considerably smaller than those calculated from the entropy changes due to the partial disordering of chromium vacancies limited to the layer distributed in an orderly way over every second chromium layer.

However, heat capacities of the nickel tellurides at compositions of $NiTe_{1.1}$, $NiTe_{1.5}$ and $NiTe_{2.0}$ have been measured from 5 to 350 K by Westrum et al. [9], and no evidence of thermal anomalies has been observed. Grønvold et al. [10] have reported the quasi-isothermal transformation at low temperature and the λ-type transformation at high temperature from heat capacity measurements of $Ni_{3.00}Te_2$ and $Ni_{2.86}Te_2$ between 298 and 900 K. The heat capacity of Ni_3Te_4 has also been measured between 298 and 950 K by Grønvold [7] and a slightly enhanced heat capacity has been observed in the region 350–500 K, indicating only a slight tendency for vacancy ordering. However, the heat capacity of $Ni_5Te_8(hex)$ has not yet been measured.

In this paper, heat capacities of monoclinic $Cr_5Te_8(m)$ and hexagonal $Ni_5Te_8(hex)$ were measured between 325 and 930 K using an adiabatic scanning calorimeter to determine quantitatively the order–disorder transition mechanism for $Cr_5Te_8(m)$ and to obtain new heat capacity data for $Ni_5Te_8(hex)$ which was also used for the heat capacity baseline for $Cr_5Te_8(m)$.

2. Experimental

2.1. Sample preparation

The starting materials used for sample preparation were high-purity chromium (99.99%), nickel (99.9%) and tellurium (99.999%). The monoclinic $Cr_5Te_8(m)$ and hexagonal $Ni_5Te_8(hex)$ specimens were prepared using a method similar to that

used to prepare $Cr_5Te_8(m)$ and $Cr_5Te_g(tr)$ samples in an earlier study [8]. The chromium (or nickel) and tellurium were weighed to obtain the stoichiometric composition. The mixture of chromium (or nickel) and tellurium obtained was evacuated and sealed in a quartz tube. It was heated to 1273 K over a period of 7 days, kept at that temperature for 5 days and cooled slowly to room temperature over a period of 2 weeks. The sample was finely crushed and then tempered for 5 days at 1073 K in another quartz tube. It was slowly cooled to 673 K, kept at this temperature for 10 days and cooled slowly to room temperature over a period of 1 week. The crushed 16–20 g sample was loaded into a sample holder made of quartz, and sealed in a quartz vessel filled with helium gas at 20 kPa, then annealed at 673 K for 20 days and cooled slowly to room temperature over a period of 8 days to obtain a highly ordered phase.

The $Cr_5Te_8(m)$ sample prepared was a monoclinic single phase and the lattice parameters ($a = 1.3535$ nm, $b = 0.7822$ nm, $c = 1.1994$ nm and $\beta = 90.40$) measured in this experiment were in good agreement with those ($a = 1.3530$ nm, $b = 0.7836$ nm, $c = 1.1994$ nm and $\beta = 90.36$) reported by Ipser et al. [11]. An X-ray diffraction pattern of the $Ni_5Te_8(hex)$ sample showed a hexagonal single phase and the lattice parameters ($a = 0.3883$ nm and $c = 0.5331$ nm) obtained in this experiment were in good agreement with those ($a = 0.3882$ nm and $c = 0.5331$ nm) measured by Barstad et al. [12].

2.2. Heat capacity measurement

Heat capacities of monoclinic $Cr_5Te_8(m)$ and hexagonal $Ni_5Te_8(hex)$ specimens were measured in the temperature range 325–930 K using an adiabatic scanning calorimeter [13]; in this calorimeter the power supplied to the sample was measured continuously, and the heating rate was kept constant regardless of the type and amount of the sample. The heating rate chosen was 2 K min^{-1}, and the measurement was carried out between 325 and 930 K under a pressure of about 130 Pa of air by using a 16–20 g sample sealed in a quartz vessel filled with helium gas at 20 kPa. The heating rate and adiabatic control were usually maintained within ± 0.005 K min^{-1} and ± 0.01 K, respectively. The heat capacity measurement was conducted within an imprecision of $\pm 3\%$ and an inaccuracy of $\pm 2\%$.

3. Results and discussion

3.1. Heat capacity of monoclinic $Cr_5Te_8(m)$

The result of heat capacity measurement of monoclinic $Cr_5Te_8(m)$ is shown in Fig. 1. The peak of the heat capacity anomaly for $Cr_5Te_8(m)$ is seen at 815 K, which is in good agreement with the peak temperature of 815 K for $CrTe_{1.590}(m)$ in our previous study [8]. In our previous paper, similar heat capacity anomalies were also observed at 841, 842 and 815 K for monoclinic $Cr_5Te_8(m)$ ($CrTe_{1.528}$, $CrTe_{1.576}$ and $CrTe_{1.590}$, respectively) and at 776 K for trigonal $Cr_5Te_8(tr)$ ($CrTe_{1.609}$),
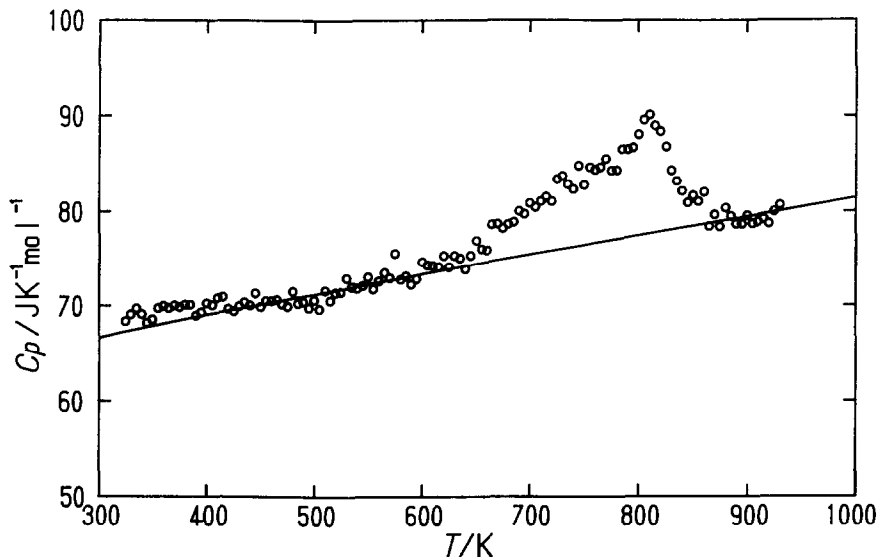
Fig. 1. Heat capacity of monoclinic $Cr_5Te_8(m)$.

presumably due to the order–disorder of chromium atoms and vacancies in chromium tellurides. However, the transition entropy changes of $Cr_5Te_8(m)$ and $Cr_5Te_8(tr)$ samples obtained experimentally in our previous study were rather smaller than those calculated from the entropy changes due to the partial disordering of chromium vacancies originally limited to every second chromium layer [8]. Two reasons are considered for the difference between experimental and theoretical values: one is an estimation of the baseline of heat capacity used for the calculation of transition entropy change and the other is whether the theoretical model used for the calculation is correct or not.

For the estimation of the baseline of heat capacity of $Cr_5Te_8(m)$ and $Cr_5Te_8(tr)$ specimens in our previous paper [8], the polynomial equation was applied to all heat capacity data except those in the temperature range 600–850 K involving heat capacity anomaly without any experimental confirmation. In this study, by applying the Kopp–Neumann rule the baseline of heat capacity C_p for $Cr_5Te_8(m)$ is assumed to be equal to that for $Ni_5Te_8(hex)$ shown in Fig. 3, as will be discussed later, because the heat capacities of chromium and nickel are about the same and the crystal structure of $Cr_5Te_8(m)$ is similar to that of $Ni_5Te_8(hex)$. As seen in Fig. 1 the baseline of heat capacity of $Cr_5Te_8(m)$ determined from heat capacity data of $Ni_5Te_8(hex)$ is fitted well in lower and higher temperature regions. The transition enthalpy (ΔH) and entropy (ΔS) changes in this study calculated on the basis of this baseline are 1.36 kJ mol^{-1} and 1.80 J K^{-1} mol^{-1}, respectively, whose values are slightly larger than those of 1.07 kJ mol^{-1} and 1.42 J K^{-1} mol^{-1} in our previous study [8]. The transition entropy change obtained in this experiment is still smaller than that (6.88 J K^{-1} mol^{-1}) calculated theoretically in our previous paper [8].

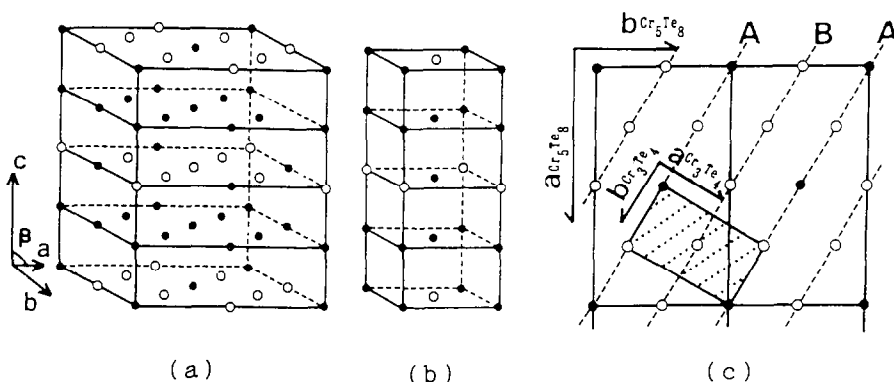Fig. 2. Schematic illustrations of (a) Cr_5Te_8-type and (b) Cr_3Te_4-type crystal structures are shown. Only chromium sites are depicted. Filled and open circles indicate chromium atoms and vacancy sites, respectively; (c) shows the transition mechanism from Cr_5Te_8-type to Cr_3Te_4-type crystal structures in the partially filled chromium vacancy layer. **a** and **b** are the unit cell vectors for Cr_5Te_8-type and Cr_3Te_4-type crystal structures [14].

Let us consider three models for theoretical calculation of the order–disorder phase transition for the monoclinic $Cr_5Te_8(m)$. The schematic illustrations of Cr_5Te_8-type and Cr_3Te_4-type crystal structures are shown in Figs. 2(a) and (b), respectively, where only chromium sites are depicted. In the figure filled and open circles indicate chromium atoms and vacancy sites, respectively. Fig. 2(c) shows the transition mechanism from Cr_5Te_8-type to Cr_3Te_4-type crystal structures in the partially filled chromium vacancy layer. In Fig. 2(c) **a** and **b** are the unit cell vectors for Cr_5Te_8-type and Cr_3Te_4-type crystal structures. This transition mechanism was first proposed for the phase transition from V_5S_8-type to V_3S_4-type crystal structures by Oka et al. [14] and was confirmed by high temperature X-ray and DTA methods. In the model A the λ-type transition entropy is calculated on the basis of a one-dimensional order–disorder transition on the A axis shown in Fig. 2(c) for $CrTe_{1.6} = (4/5)CrTe\{(Cr_{1/4}\Box_{1/4})\Box_{1/2}\}Te$, where $\Box$ indicates chromium vacancies, from vacancy-ordered Cr_5Te_8-type to vacancy-ordered Cr_3Te_4-type crystal structures as

$$\Delta S_A = -(2/5)R(0.5 \ln 0.5 + 0.5 \ln 0.5)$$

$$= 2.31 \text{ J K}^{-1} \text{ mol}^{-1} \tag{1}$$

where R is the gas constant. This model A is considered simply to estimate the transition entropy change, although the phase transition does not exist in a one-dimensional system as has been pointed out in the literature [15].

In model B for a two-dimensional phase transition, it is assumed that the disorder affects only the intra layer involving chromium vacancies limited to every second chromium layer for $CrTe_{1.6} = (4/5)(CrTe)\{(Cr_{1/4}\Box_{3/4})Te\}$ shown in Fig. 2(a). The entropy change ΔS_B from the completely ordered $Cr_5Te_8(m)$ phase to the

partially disordered phase where chromium atoms and vacancies are randomly distributed only in every second layer is given by the equation

$$\Delta S_B = -(4/5)R(\{(1/4)\ln(1/4) + (3/4)\ln(3/4)\}$$

$$= 3.74 \text{ J K}^{-1}\text{ mol}^{-1} \tag{2}$$

In contrast, in model C for a three-dimensional phase transition, disorder among all chromium atoms and vacancies is assumed for $CrTe_{1.6} = (8/5)\{(Cr_{5/8}\,\square_{3/8})Te\}$. The entropy change ΔS_C from the completely ordered $Cr_5Te_8(m)$ phase to the completely disordered phase is calculated from the equation

$$\Delta S_C = -(8/5)R\{(5/8)\ln(5/8) + (3/8)\ln(3/8)\}$$

$$= 8.80 \text{ J K}^{-1}\text{ mol}^{-1} \tag{3}$$

The theoretical transition entropy change of model A ($\Delta S_A = 2.31$ J K^{-1} mol^{-1}) for $CrTe_{1.6}(m)$, i.e. $Cr_5Te_8(m)$, calculated from Eq. (1) is in reasonably good agreement with that obtained from the experimental value ($\Delta S = 1.80$ J K^{-1} mol^{-1}). The small difference suggests that the completely ordered phase at low temperature is not formed in spite of slowly cooling the sample, or that the partially ordered phase still remains even at high temperatures at which measurements were made in this study. It may be noted that the experimental entropy change for $Cr_5Te_8(m)$ in this study is about 78% of the theoretical value for model A, because the experimental entropy change for $Cr_3Te_4(m)$ reported by Grønvold [7] was also about 77% of the theoretical value which was calculated by assuming disordering 1/4 mol of chromium atoms and vacancies.

3.2. Heat capacity of Ni_5Te_8(hex)

The result of heat capacity measurements of hexagonal Ni_5Te_8(hex) is shown in Fig. 3, where the baseline of heat capacity is determined by the following procedures. The heat capacity C_p of Ni_5Te_8(hex) is generally expressed by the sum

$$C_p(T) = C_h + C_d + C_e + C_{ah} + \Delta C \tag{4}$$

where C_h is the harmonic term of the lattice vibration, C_d is the dilational term, C_e is the electronic term, C_{ah} is the anharmonic term of the lattice vibration and ΔC is the excess heat capacity. Each term of heat capacity in Eq. (4) obtained by the following procedures is shown in Fig. 3.

The harmonic term of the lattice vibration for $NiTe_y$ ($y = 1.6$), i.e. $(1/5)Ni_5Te_8$ can be calculated from

$$C_h = 3RD(\theta_D/T)(1 + y) \tag{5}$$

where R is the gas constant, $D(\theta_D/T)$ is the Debye function and θ_D is the Debye temperature which is estimated to be 286.9 K from heat capacity data at low temperature for three different $NiTe_y$ samples [9] by applying Debye's cubic law.
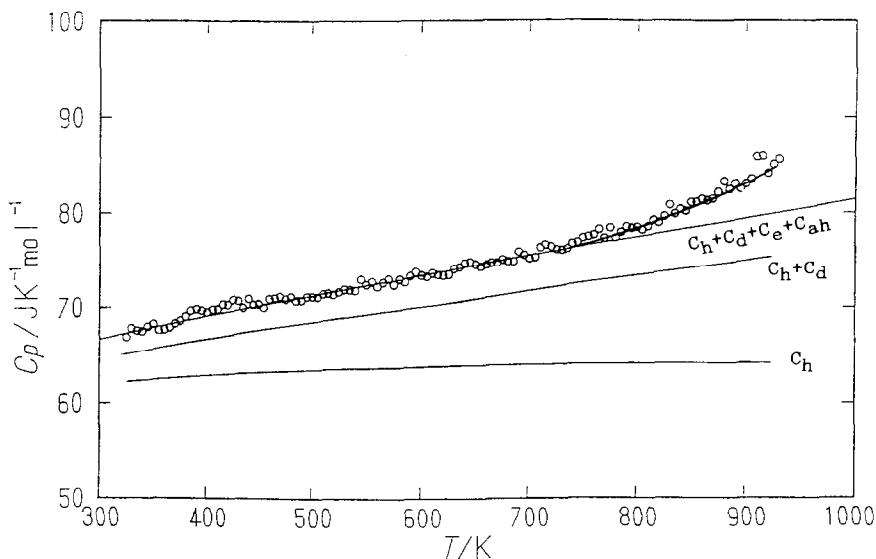
Fig. 3. Heat capacity of hexagonal Ni_5Te_8(hex).

The dilational term of the molar heat capacity C_d can be estimated from the Nernst–Lindemann equation [16], which is expressed as

$$C_d = A(T/T_m)\{C_p/(1+y)\}^2(1+y) \tag{6}$$

where A is the universal constant equal to 0.0051 K mol J^{-1}, and T_m is the melting point of Ni_5Te_8(hex) ($T_m = 1014$ K [17]).

By assuming that the excess heat capacity ΔC is negligibly small in the temperature range 500–700 K, the electric and anharmonic terms are then calculated from the experimental heat capacity data C_p and the values of C_h and C_d in this temperature range by using the equation

$$(C_e + C_{ah}) = C_p - (C_h + C_d) = (\gamma + b)T \tag{7}$$

where γ and b are the coefficients of the electronic and anharmonic terms, respectively. The value of this sum is calculated from the linear regression line of Eq. (7) in the temperature range 500–700 K. The baseline of the heat capacity shown in Fig. 3 is calculated as the sum of Eqs. (5)–(7). In Fig. 3, two excess heat capacities for Ni_5Te_8(hex) are seen around 400 K and above 700 K.

For the excess heat capacity at low temperature, a similar small excess heat capacity was observed in the 340–370 K region for the stoichiometric Ni_3Te_4(hex) by Grønvold [7] who suggested that this may be connected with a slight tendency for vacancy ordering. Since both Ni_5Te_8 and Ni_3Te_4 samples have the same hexagonal crystal structure, the excess heat capacity anomaly of hexagonal Ni_5Te_8(hex) may be related to the order–disorder of nickel atoms and vacancies in this structure.

The excess heat capacity ΔC in Eq. (4) for Ni_5Te_8(hex) at high temperature may be fitted by the equation

$$\Delta C = (\xi \Delta H^2/RT^2) \exp(-\Delta H/RT) \tag{8}$$

where ξ and ΔH are entropy and enthalpy terms, respectively, for activation processes such as defect formation, electron excitation and electron–hole pair formation. The enthalpy value could be obtained as $\Delta H = 97.98$ kJ mol^{-1} in Eq. (8) by computer curve fitting. A similar excess heat capacity at high temperature seems to be seen for Ni_3Te_4(hex) as reported by Grønvold [7], although he did not mention anything at all about excess heat capacity at high temperature.

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