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# On the Specific Heat of Nonstoichiometric Ceria

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Ceria ($CeO_2$) can readily be reduced to form a wide range of binary compounds $CeO_y$, $2 \geq y \geq 1.5$. Specific heat measurements at constant $y$ were carried out for the composition range $2 \geq y > 1.714$ and for the temperature range $300\text{ K} < T < 1200\text{ K}$. In this $y$, $T$ region the specific heat exhibits a complex form reflecting various transformations. The results and theoretical evaluations of the specific heat are presented as the temperature is varied from low values ($T \approx 400$ K) where two phases coexist, through several phase transformations to a high temperature $\alpha$ phase. Special features of the specific heat due apparently to increased internal local pressure appearing for small deviations from stoichiometry are also discussed.

## 1. Introduction

$CeO_2$ is readily reduced at low oxygen pressures and elevated temperatures to form so-called nonstoichiometric compounds $CeO_y$ ($2 \geq y \geq 1.5$) (*1–3*). At low temperatures $T \lesssim 722$ K the $CeO_y$ phases form a discrete set of compositions. At elevated temperatures ($T \geq 921$ K, $y > 1.818$) a single phase $CeO_y$ exists for which $y$ may obtain a continuum of values. We recently presented $c_p$ measurements and a discussion of the phase diagram of $CeO_y$ (*3*) (see Fig. 1). The phase diagram was determined from $c_p$ measurements on $CeO_y$ at constant $y$. We were interested mainly in the phase diagram and have concentrated on the temperatures and heats of the transformations. It is the purpose of the present work to discuss, in detail, those $c_p$ measurements over a wide temperature and composition range. In the $c_p$ vs $T$ data (for constant $y$) we identify various regions ordered by increasing temperature. They reflect the two-phase region in which the phases have well-defined compositions; the two-phase region where the composition of one phase is changing with temperature; transformations at fixed temperatures; the binodal line where two phases coexist (e.g., $\alpha$ and $\alpha'$ phases, see Fig. 1) and both change their compositions with temperature; and the high temperature single $\alpha$ phase.

The analysis should contribute to the un-

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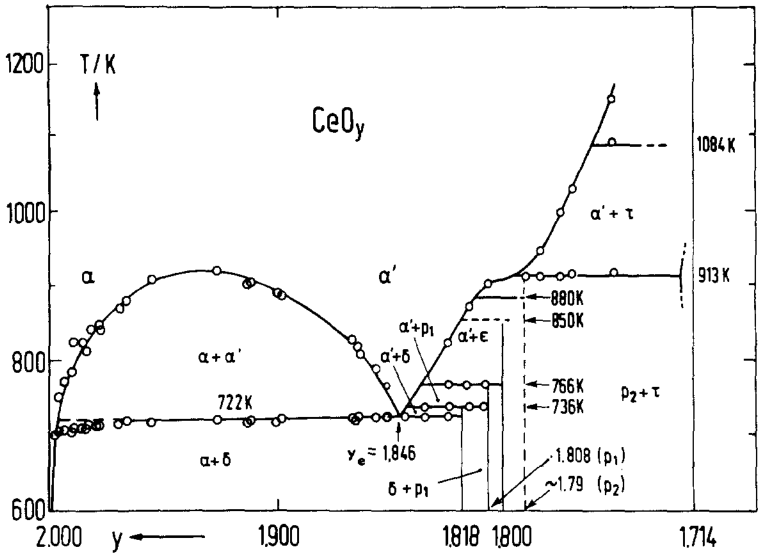

FIG. 1. The phase diagram of $CeO_y$.

derstanding of $CeO_y$ and of other reduced materials having similar nature such as $PrO_2$ and $TbO_2$. It refers also to some general features of the specific heat of binary compounds.

## 2. Experimental

The specific heat was measured in an adiabatic, temperature scanning calorimeter. The composition of the sample was adjusted *in situ* by a gas mixture of $H_2/H_2O$ and determined by weighing. The reader is referred to Ref. (*3*) for a detailed description of the experimental procedure.

## 3. Experimental Results

Figure 2 presents the specific heat of $CeO_2$. As the phase does not change on heating (see Fig. 1) the $c_p$ curve is smooth and represents the lattice contributions.

Figure 3 presents the specific heat of $CeO_{1.925}$. Five regions of interest can be defined (I–V). The phases involved are $\alpha$, $\delta$,

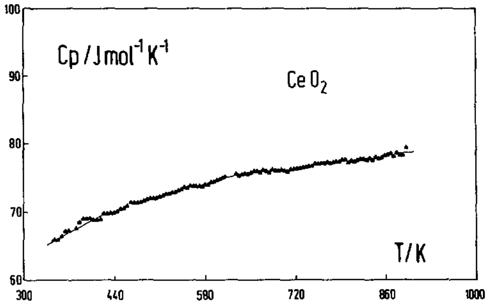

FIG. 2. $c_p$ vs $T$ of $CeO_2$.

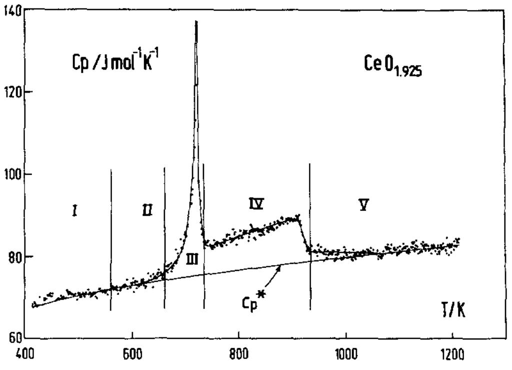

FIG. 3. $c_p$ vs $T$ of $CeO_{1.925}$.

and $\alpha'$. Their existence range is shown in Fig. 1.

Region I: the low temperature region for which the specific heat is determined by the coexisting phases ($\alpha$ and $\delta$).

Region II: the approach to a phase transition where $c_p$ has an additional contribution due to transformation of small amounts of $\alpha$ phase into $\delta$ phase.

Region III: the transformation $\alpha + \delta \rightarrow \alpha + \alpha'$.

Region IV: $c_p$ has the form of a shoulder, and is determined by the coexistence of two phases, $\alpha$ and $\alpha'$, and both change composition and amount with $T$.

Region V: high temperature single-phase region ($\alpha$ phase).

Figure 4 presents the $c_p$ of $CeO_{1.823}$. It exhibits three sharp peaks reflecting the three phase transformations at 722, 736, and 767 K (see Fig. 1). Due to overlap, the data between peaks cannot be resolved and only information on the transitions can be obtained. The same difficulty arises with all $c_p$ measurements exhibiting several phase transformations. Therefore, for clarity, we shall discuss mainly $c_p$ with one transformation as is shown in Fig. 3, measured for $y > y_e = 1.846$.

## 4. Analysis and Discussion

### 4a. Basic Specific Heat

For analysis of the data it is convenient to separate the $c_p$ values into two parts denoted as the basic specific heat $c_p^*$ (see Fig. 3) and the difference $c_p - c_p^* = \Delta c_p$ which is denoted as the excess specific heat. $c_p^*$ represents the contributions due to lattice vibrations but it does not include the heat effects due to phase transformations. The latter contributions are included in $\Delta c_p$. In particular for a single phase in equilibrium $\Delta c_p$ vanishes.

At temperatures high with respect to the Debye temperature, $\theta_D$, the basic specific heat can be written as (*4*),

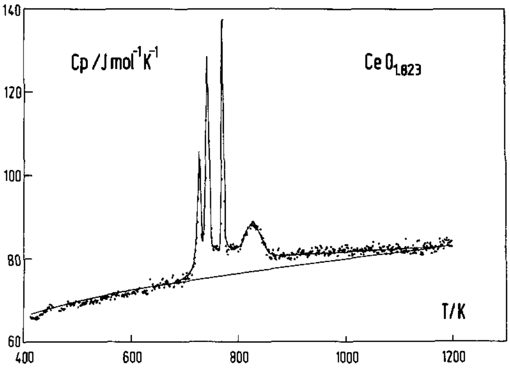

FIG. 4. $c_p$ vs $T$ of $CeO_{1.823}$.

$$c_p^* = a - \frac{c}{T^2} + bT, \qquad (1)$$

which originates from the high temperature Debye specific heat and the anharmonic effects. For $CeO_2$ the constants are $a = 67.95$, $b = 0.0125$, and $c = 9.9 \times 10^5$ where $T$ is in K and $c_p$ in Joule (mole K). If the constant $c$ is interpreted as

$$c = \tfrac{1}{12} a \theta_D^2 \qquad (2)$$

then the data for $CeO_2$ yield a rough estimate for $\theta_D$: $\theta_D = 410$ K. The $c_p$ values for $CeO_2$ agree with those of others within 2% (*5–8*). For $CeO_{1.818}$ ($\delta$ phase at $T \leq 736$ K) one would expect Eq. (1) to hold separately in regions I and V (see Fig. 3). It turns out, however, that a single curve can be fitted to the $c_p$ data of $CeO_y$ with composition close to $y = 1.818$ for both region I and the high temperature side of region V (see Figs. 3, 4). The basic specific heat of $CeO_{1.818}$ when expressed by Eq. (1) for all temperatures has $a = 67.04$, $b = 0.0140$, and $c = 9.9 \times 10^5$. For intermediate compositions $2.00 > y > 1.818$ $c_p^*$ was calculated as a linear combination of the basic specific heat $c_{p,2}^*$ of $CeO_{2.000}$ and $c_{p,1}^*$ of $CeO_{1.818}$ (regardless of the actual composition of the $\alpha$ phase which may deviate somewhat from $CeO_2$ above 560 K):

$$c_p^*(y) = x_2 c_{p,2}^* + x_1 c_{p,1}^* \qquad (3a)$$

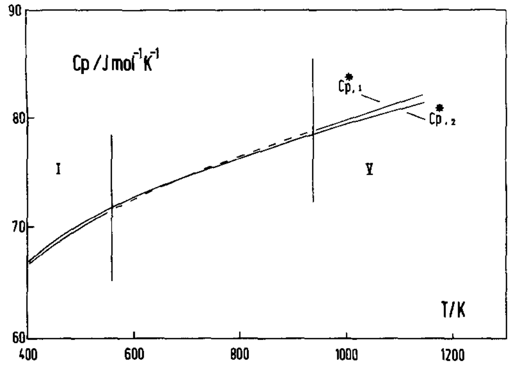

FIG. 5. $c^*_{p,1}$, $c^*_{p,2}$ vs $T$.

where

$$x_1 = \frac{2 - y}{2 - 1.818}, \quad x_2 = \frac{y - 1.818}{2 - 1.818} \quad \text{(3b)}$$

are the calculated mole fractions of $CeO_{1.818}$ and $CeO_{2.000}$, respectively. This can be justified in region I and is plausible also in region V. We then assume that $c^*_p(y)$ can be used for all temperatures.

### *4b. Region I*

In the low temperature region $T < 560$ K and for the composition range $2 \geq y \geq 1.818$ the material can be considered as a mixture of the two phases $CeO_2(\alpha)$ and $CeO_{1.818}(\delta)$. The specific heat is therefore a linear combination of the specific heat of these two phases. It is equal to $c^*_p$ and can be expressed by Eq. (3). In doing so we have neglected possible contributions to $c_p$ due to interactions between the two phases at the $\alpha,\delta$ grain boundaries. Microscopic observations on the used sample show grain sizes between $10^{-6}$ and $5 \times 10^{-6}$ m.

The difference in $c^*_p$ of $CeO_{2.000}$ and $CeO_{1.818}$ in regions I and V is seen in Fig. 5. For low temperature $c^*_{p,2}$ is greater than $c^*_{p,1}$. This difference decreases with $T$. The difference could be understood qualitatively on the basis of the smaller number of anions in the $\delta$ phase. However the difference observed is smaller by a factor 4 than that calculated from the Dulong–Petit relation. With increasing temperature we would expect the difference to increase to approach that of Dulong–Petit. As the opposite occurs we conclude that the material is far from its high temperature limit behavior and that oxygen vacancies in the reduced material introduce low-lying energy levels that are excited in the measured temperature range.

### *4c. Region II*

For $y \lesssim 1.93$ the specific heat for $T \lesssim 670$ K follows practically $c^*_p$. For $y \gtrsim 1.93$, $c_p$ is larger than $c^*_p$ for $T \gtrsim 560$ K. This is shown in Figs. (6, 7) for $y = 1.998$ and $y = 1.982$, respectively. The basic specific heat was calculated as shown in section 4.a. Equation (3) would represent $c^*_p$ if the composition of the $\alpha$ and $\delta$ phase did not deviate from $CeO_{2.000}$ and $CeO_{1.818}$ respectively. However the composition range of the $\alpha$ phase becomes broader for $T > 560$ K. This is shown in Fig. (8). On the other hand the composition range of the $\delta$ phase is quite narrow. Hence for $2 \geq y \geq 1.818$ as $T$ increases (720 K $\gtrsim T \gtrsim$ 560 K) the $\alpha$ component changes its composition and amount; some of it transforms into the $\delta$ phase. This process is associated with heat of transformation which contributes to $c_p$. As $y$ decreases, the fraction of the $\alpha$ phase and its contribution to $c_p$ decrease as well. For $y \lesssim 1.94$ the deviation of $c_p$ from $c^*_p$ can no longer be observed in our measurements.

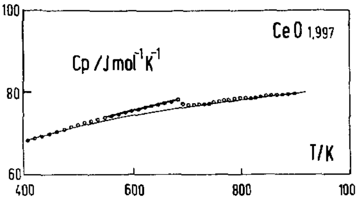

FIG. 6. $c_p$ vs $T$ for $CeO_{1.997}$. ○, measurements; light solid line, calculated $c^*_p$; heavy solid line, calculated $c_p$ ($c_p = \Delta c_p + c^*_p$).

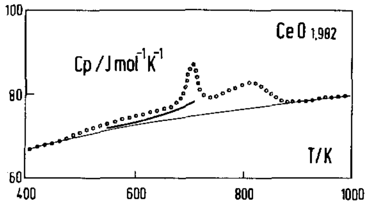

FIG. 7. $c_p$ vs $T$ for $CeO_{1.982}$. O, measurements; light solid line, calculated $c_p^*$; heavy solid line, calculated $c_p$ ($c_p = \Delta c_p + c_p^*$).

We have calculated $\Delta c_p$ using the $\alpha$-phase boundary line shown in Fig. 8. The method used is similar to that applied in discussing region IV and will be presented in Section 4e. The results are shown in Figs. 6, 7. The calculations show that this heat effect does not explain the whole observed deviation from $c_p^*$ (for $1.994 > y \gtrsim 1.96$).

### *4d. Region III*

Region III is the temperature range in which the phase transformation occurs.

*4d.1. Enthalpy of transformation.* The enthalpy of transformation $L$ is represented by the area under the peak above $c_p^*$ (see Fig. 3). Its determination was discussed before (*3*). $L$ changes with the ratio of the two phases undergoing the transformation. Figure 9 shows $L$ at 722 K as a function of composition. The data were fitted with two straight lines as required by the following calculations. At the transformation the $\alpha$ and $\delta$ phases coexist with the $\alpha'$ phase of the eutectic composition, e. Let $H_\alpha$, $H_\delta$, and $H_e$ be the molar enthalpies of the three corresponding phases $\alpha$, $\delta$, and eutectic $\alpha_e'$ at 722 K.[1] The heat of transformation is the difference of enthalpies before and after the transformation. For compositions $y_\alpha > y > y_e$ ($y_e = 1.846$, eutectic composition, $y_\alpha = 1.994$ (*2, 3*)),

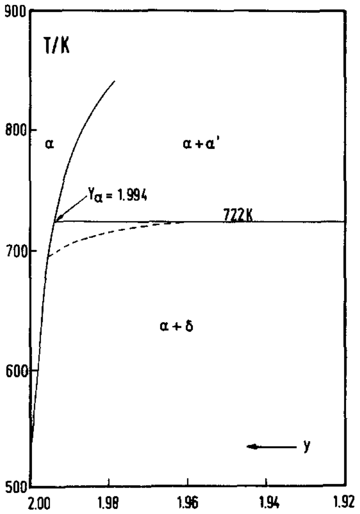

FIG. 8. Expanded section of the phase diagram of $CeO_y$. It exhibits the existence range of the $\alpha$ phase close to 700 K and the depression of the temperature of the transformation $\alpha + \delta \rightarrow \alpha + \alpha_e'$ below 722 K for $y \gtrsim 1.96$ due to nonequilibrium effects (increased local pressure) (dashed line).

$$L = x_\alpha^+ H_\alpha + x_e H_e - x_\alpha^- H_\alpha - x_\delta H_\delta \quad (4)$$

where $x_\alpha^+$, $x_\alpha^-$, $x_\delta$, $x_e$ represent the molar fractions, and $x_\alpha^+$ and $x_\alpha^-$ denote the $\alpha$-phase molar fraction just above and below the transformation, respectively. By the lever rule,

$$x_\alpha^- = (y - y_\delta)/(y_\alpha - y_\delta) \quad (5a)$$

$$x_\delta = (y_\alpha - y)/(y_\alpha - y_\delta) \quad (5b)$$

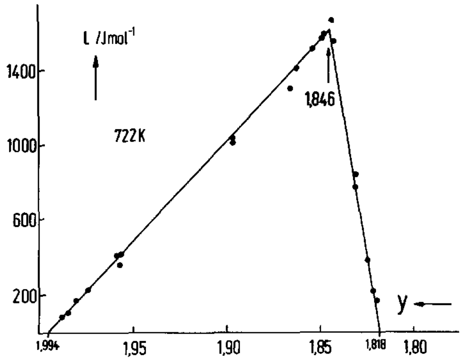

FIG. 9. Heat of transformation $L$ vs composition $y$ for the eutectic transformation at 722 K.

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[1] For brevity the symbols $H_i$ were used instead of $\Delta H_i$. The reader should keep in mind that these enthalpies are fixed values, corresponding to the three-phase equilibrium at 722 K. Only differences of these enthalpies appear in the final relations (*6, 7*).

$$x_\alpha^+ = (y - y_e)/(y_\alpha - y_e) \qquad (5c)$$

$$x_e = (y_\alpha - y)/(y_\alpha - y_e). \qquad (5d)$$

Inserting Eqs. (5a)–(5d) into Eq. (4) yields

$$L = (y_\alpha - y)\left[\frac{H_e - H_\alpha}{y_\alpha - y_e} + \frac{H_\alpha - H_\delta}{y_\alpha - y_\delta}\right], \quad y_\alpha \geq y \geq y_e. \qquad (6)$$

$L$ is linear in $y$. For $y_e \gtrsim y \gtrsim y_\delta$ a similar derivation yields

$$L = (y - y_\delta)\left[\frac{H_e - H_\delta}{y_e - y_\delta} + \frac{H_\delta - H_\alpha}{y_\alpha - y_\delta}\right], \quad y_e \geq y \geq y_\delta. \qquad (7)$$

$L$ is linear in $y$. The straight lines in Fig. 9 are based on Eqs. (6) and (7), which are not independent. Hence from the two measured slopes one relation among $H_\alpha$, $H_e$, and $H_\delta$ can be determined. $H_e$ can be obtained taking into account thermodynamic measurements in the high temperature $\alpha$ phase. Further considerations of this relation will therefore be continued in the discussion of region V.

*4d.2. Nonequilibrium due to increased local pressure.* For $y \gtrsim 1.96$ the temperature of the eutectic (e) transformation $\alpha + \delta \rightarrow \alpha + \alpha'$ is lower than 722 K. The deviation is about 25 K at $y \approx 1.995$, decreasing with smaller $y$ and vanishing at $y \approx 1.96$. This nonequilibrium effect depends on the sample preparation and previous temperature treatment. Further discussion is necessary since this effect does appear in other systems as well and cannot always be avoided.

Let us follow cooling of $CeO_y$, $y_\alpha > y > 1.97$, from the high temperature $\alpha$ phase through the binodal and the $\alpha,\alpha'$ coexistence region toward the eutectic transformation at ~722 K. At the binodal temperature a small amount of the $\alpha'$ phase segregates within the $\alpha$ phase as small grains. As the free molar volume of $\alpha'$ phase is larger than that of the surrounding $\alpha$ phase (*2*) increased local pressure is exerted on the $\alpha'$ grain. When the cooling through the binodal is completed the pressure on a grain has reached $p_0$ and the temperature $T_0$. The values of $p_0$ and $T_0$ may vary from grain to grain. The difference in the molar volumes of $\alpha,\alpha'$ phases, is approximately proportional to the composition difference $y_\alpha - y'_\alpha$ (*2*). The pressure on the enclosed $\alpha$ grain increases therefore if $T$ is lowered. This results in a smearing of the shoulder in $c_p$ (see Fig. 7).

It is only near $y \approx 1.93$, $T \approx 922$ K, i.e., the maximum of the binodale, that the internal pressure can be assumed uniform and at 1 atm because only there (a) $\alpha$ and $\alpha'$ appear in comparable amounts and can hardly exert pressure on each other and (b) the difference in molar volume is negligible. As a consequence the decline of the shoulder in $c_p$ is sharp. This was observed in the experiments (*3*) (see Fig. 3).

The $\alpha'$ grain may be considered in local equilibrium under the elevated pressure at a given temperature. We may then apply the Clausius–Clapeyron equation to the $\alpha'_e$ grain

$$dp/dT = \Delta H/(T\Delta V) \qquad (8)$$

and use it for the $\alpha + \delta \rightarrow \alpha'_e$ (eutectic) transformation. $\Delta H$ is the enthalpy change per mole $\alpha'_e$ phase and $\Delta V$ is the corresponding molar volume change. Since $\Delta H > 0$ and $\Delta V < 0$, under increased pressure the transformation temperature is lowered.

One may assume that the difference in pressure $p_0$ on the various $\alpha'$ grains is not large. Using Eq. (8) with $\Delta H = 1600$ J/mole (*3*) and $\Delta V = -1.5\%$ of the molar volume (*2, 9*) (0.3 $cm^3$/mole) yields for $T = 722$ K and $\Delta T = -25$ K a roughly estimated local pressure $p_0$ of 1 kbar.

### *4e. Region IV*

In region IV $\Delta c_p$ has the shape of a shoulder. It represents the transformation along the binodal line. For $1.994 \geq y \geq y_e$

and 921 K $\geq T \geq$ 722 K a two-phase system exists and we use the indexes $\alpha'$ and $\alpha$ to characterize the right and left side of the miscibility gap, respectively. The molar enthalpy of the $\alpha$ side is $H^\alpha = H^\alpha(T, y^\alpha)$ and

$$\frac{dH^\alpha}{dT} = \left(\frac{\partial H^\alpha}{\partial T}\right)_{y^\alpha} + \left(\frac{\partial H^\alpha}{\partial y^\alpha}\right)_T \frac{dy^\alpha}{dT}. \quad (9)$$

A similar equation holds for the $\alpha'$ side.

With $y$ and $T$ in the miscibility gap the compositions of the two sides are fixed on the binodal line; i.e., $y^\alpha$ and $y^{\alpha'}$ are now defined functions of $T$ given by the binodal line. In this region the total enthalpy can be written as

$$H = x^\alpha H^\alpha + x^{\alpha'} H^{\alpha'}, \quad (10a)$$

with

$$x^\alpha = \frac{y - y^{\alpha'}}{y^\alpha - y^{\alpha'}}, \qquad x^{\alpha'} = \frac{y^\alpha - y}{y^\alpha - y^{\alpha'}}. \quad (10b)$$

$c_p$ is

$$c_p = \frac{dH}{dT} = \frac{dx^\alpha}{dT}(H^\alpha - H^{\alpha'}) + x^{\alpha'}\frac{dH^{\alpha'}}{dT} + x^\alpha \frac{dH^\alpha}{dT} \quad (11)$$

with $H^\alpha$ and $H^{\alpha'}$ functions of $T$ along the binodal line ($H^\alpha = H^\alpha(T, y^\alpha(T))$, $H^{\alpha'} = H^{\alpha'}(T, y^{\alpha'}(T))$).

Combining Eqs. (9), (10a), and, (11) yields

$$c_p = \frac{dx^\alpha}{dT}(H^\alpha - H^{\alpha'}) + x^\alpha \frac{dy^\alpha}{dT}\left(\frac{\partial H^\alpha}{\partial y^\alpha}\right)_T + x^{\alpha'} \frac{dy^{\alpha'}}{dT}\left(\frac{\partial H^{\alpha'}}{\partial y^{\alpha'}}\right)_T + x^\alpha \left(\frac{\partial H^\alpha}{\partial T}\right)_{y^\alpha} + x^{\alpha'}\left(\frac{\partial H\alpha'}{\partial T}\right)_{y^{\alpha'}}. \quad (12)$$

The first three terms reflect the effect of change in composition and are identified as $\Delta c_p$ which represents the shoulder. The last two terms of Eq. (12) are identified as the basic specific heat:

$$c_p(\text{basic}) = x^\alpha \left(\frac{\partial H^\alpha}{\partial T}\right)_{y^\alpha} + x^{\alpha'}\left(\frac{\partial H^{\alpha'}}{\partial T}\right)_{y^{\alpha'}} \quad (13)$$

i.e.,

$$\Delta c_p = c_p - c_p\,(\text{basic}). \quad (14)$$

When $x^\alpha = 0$, $x^{\alpha'} = 1$ or $x^\alpha = 1$, $x^{\alpha'} = 0$, $c_p$ (basic) coincides with $c_p^*$. $c_p$(basic) of Eq. (13) for $y$ is therefore a linear combination of $c_p^*$ of two other compositions $y^\alpha$ and $y^{\alpha'}$. On the other hand, $c_p^*$ was found to be linear in composition (Eq. (3)). $c_p^*(y)$ can therefore be presented as a linear combination of $c_p^*$ of any two other compositions with the appropriate molar fractions. Hence $c_p^*(y)$ equals $c_p$(basic) of Eq. (13),

$$c_p(\text{basic}) = c_p^*, \quad (15)$$

for all temperatures in region IV. In calculating $c_p$ we therefore use Eq. (3) instead of Eq. (13) for $c_p$(basic) but calculate $\Delta c_p$ from the first three terms in Eq. (12).

To calculate $\Delta c_p$ we notice that

$$\left(\frac{\partial H}{\partial y}\right)_T = -\frac{1}{2}[\overline{H}(O_2, y, T) - H(O_2, T)] \quad (16)$$

where $\overline{H}(O_2, y, T)$ is the partial molar enthalpy of $O_2$ in $CeO_y$, i.e., the enthalpy of solution of one mole $O_2$ in $CeO_y$ at $T$. $H(O_2, T)$ is the molar enthalpy of $O_2$ at $T$. For $T_1 >$ 921 K,

$$H(y^1, T_1) - H(y^2, T_2) = \tfrac{1}{2}\int_{y^1}^{y^2} [\overline{H}(O_2, y, T_1) - H(O_2, T_1)]\,dy. \quad (17)$$

$H^\alpha - H^{\alpha'}$ at $T_2 <$ 921 K can be obtained from Eq. (17) if one adds the difference of integrals of $c_p$ along the temperature interval ($T_1 - T_2$) for compositions $y^1 = y^\alpha(T_2)$, $y^2 = y^{\alpha'}(T_2)$. This difference, however, was found to be small and can be neglected. Inserting Eqs. (12), (13), (16), and (17) into Eq. (14) yields

$$\Delta c_p = \frac{dx^\alpha}{dT}\frac{1}{2}\int_{y^\alpha}^{y^{\alpha'}} \overline{H}(O_2, y, T)\,dy - x^\alpha \frac{dy^\alpha}{dT}\frac{1}{2}\overline{H}(O_2, y^\alpha, T) - x^{\alpha'}\frac{dy^{\alpha'}}{dT}\frac{1}{2}\overline{H}(O_2, y^{\alpha'}, T) \quad (18)$$

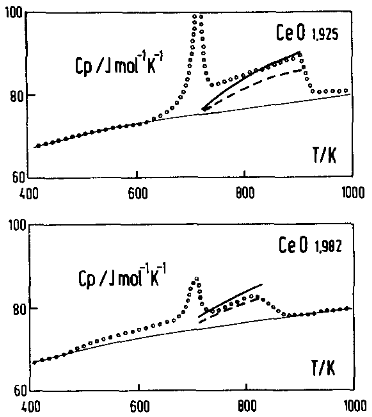

FIG. 10. $c_p$ vs $T$ in region IV (the shoulder). ○, measurements; light solid line, calculated $c_p^*$; heavy solid line, calculated $c_p$ ($c_p = \Delta c_p + c_p^*$) using the partial molar enthalpy of $O_2$ from Bevan and Kordis (*1*); broken heavy solid line, calculated $c_p$ ($c_p = \Delta c_p + c_p^*$) using the partial molar enthalpy of $O_2$ from Campserveux and Gerdanian (*10*).

where the terms containing $H(O_2, T)$ cancel.

We have used $\overline{H}(O_2, y, 1353\ K)$ from Bevan and Kordis (*1*) and from Champserveux and Gerdanian (*10*). The shape of the binodal was taken from Fig. 3. (It differs somewhat from that in Ref. (*3*) though it is based on the same data. It was determined from the temperature corresponding to the middle of the right-hand slope of the shoulder in $c_p$ rather than from the temperature of the peak of the shoulder. The maximum of the binodal is now at $y = 1.934$ and $T = 921$ K.) The fitting of Eq. (18) to the experimental $c_p$ data is shown in Fig. 10.

It was found that the use of $\overline{H}(O_2, y, 1353\ K)$ from Bevan and Kordis (*1*) gives a better fit to $c_p$ than that from Champserveux and Gerdanian (*10*) over a wide range of compositions. In more recent measurements (*11*) the latter authors have found agreement with the result of the free energy of Bevan and Kordis used to determine $\overline{H}(O_2, y, T)$. $\overline{H}(O_2, y, T)$ from Bevan and Kordis therefore must be considered and the fitting of Eq. (18) to our data is satisfying. Equation (18) represents $\Delta c_p$ due to a gradual change in the composition of one or two coexisting phases. It therefore holds, for example, also for the transformation $\alpha' \leftrightarrow \delta$ as $T$ varies in the range 736 K $> T >$ 722 K and the composition is $1.846 > y > 1.818$. Equation (18) was also applied in discussing region II for the $\alpha$, $\delta$ coexistence at 560 K $< T <$ 722 K where $\alpha$ changes its composition with $T$ (see Figs. 6, 7 and the discussion in Sect. 4c).

### 4f. Region V

In region V the sample is in the high temperature $\alpha$ phase. The measurements were carried out in a rather limited temperature range sufficient to determine the phase diagram (*3*). We have already used the $c_p$ data in region V to determine $c_p^*$ in Section 4a. $\Delta c_p$ observed just beyond the shoulder is expected to originate from short range order.

We shall now discuss the calculation of the enthalpy at the eutectic, $H_e$, and of the $\delta$ phase, $H_\delta$, from a knowledge of $H_\alpha$ at 722 K, $\overline{H}(O_2, y, T)$ at 1353 K, $c_p^*$, and the heat of transformation $L$. $H_e$ can be obtained from $H_\alpha$ if the following path in the phase diagram is followed: For composition $y_\alpha$ increase the temperature from 722 to 1353 K, where $\overline{H}(O_2, y, 1353\ K)$ is known (*1*). Then change $y$ to the eutectic composition $y_e$ and finally cool to 722 K. Taking $H_\alpha$ from the literature (*2*), $c_p$ from $c_p^*$ (Eq. (3)), and $\overline{H}(O_2, y, 1353\ K)$ from Bevan and Kordis (*1*) yields $H_e = (-989 \mp 2)$ kJ/mole at $T =$ 722 K.

We have shown in Section 4d, Eqs. (6) and (7), that $H_\alpha$, $H_e$, and $H_\delta$ at 722 K are interrelated. From the slope in Fig. 9 and the values of $H_\alpha$ and $H_e$ we find $H_\delta = (-978 \mp 2)$ kJ/mole at 722 K. $H_\delta$ at 298 K is calculated using $C_p^*$: $H_\delta = (-1006 \mp 2)$ kJ/mole. This is in agreement with the calculated value of $H_\delta = -1033$ kJ/mole by Westrum (*13*).

## 5. Concluding Remarks

We analyzed $c_p$ measurements of reduced ceria ($CeO_y$) for the temperature range $400\ K \lesssim T \lesssim 1000\ K$ and composition range $2.000 > y > 1.818$. $c_p$ was separated into a basic specific heat, $c_p^*$, and an excess one, $\Delta c_p$, reflecting the excess enthalpy associated with phase transformations due to changes in oxygen content. In the low temperature range $c_p(y)$ is a linear combination of the values of the coexisting phases $\alpha$ and $\delta$, the latter having a narrow composition range. For higher temperatures $\Delta c_p$ was calculated as gradual changes in the oxygen content of the phases evolved with $T$. The composition dependence of the enthalpy of transformation, $L$, of three coexisting phases occurring at a single temperature (e.g., $\alpha + \delta \rightarrow \alpha + \alpha'$) was calculated and shown to be linear in $y$. It was used to find a relation among the molar enthalpies of the three coexisting phases. Deviations of the eutectic transformation temperature from a single value 722 K for large $y$ were interpreted as due to pressure exerted on isolated $\alpha'$ grains in the $\alpha$ matrix. The gradual transformation of the $\alpha$ and $\alpha'$ compositions separated by a miscibility gap was shown to result in a shoulder-shaped excess $c_p$.

Further $c_p$ measurements are underway for a detailed determination of $c_p$ in the high temperature $\alpha$ phase. The pressure effect near 722 K will also be examined, and its dependence on sample preparation conditions will be determined. Dilatometry and X-ray diffraction measurements are being utilized.

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