Heat Capacity of Pure and Doped V_2O_3 Single Crystals*

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Heat capacities have been measured for single crystals of V_2O_3, either pure or doped with 1 and 1.4 mole % Cr_2O_3 and Al_2O_3 over the temperature range 100–700°K. V_2O_3 undergoes a fairly sharp transition at low temperatures (~170°K) but fails to exhibit any thermal anomaly above 300°K. The thermal behavior of $(M_xV_{1-x})_2O_3$, $M = Cr$, Al, is manifested by two transitions: one at low temperatures, 170–180°K for $x = 0.01$ and 180–190°K for $x = 0.014$, and the other at high temperatures. For $x = 0.01$, the high-temperature (H-T) anomaly extended over the range 325–345°K (Cr-doped V_2O_3) and 345–365°K (Al-doped V_2O_3), respectively. The corresponding ranges for $x = 0.014$ were found to be 260–280°K and 270–290°K, respectively. Further, the H-T anomaly was characterized by a large hysteresis (~50°K). The values of lattice heat capacity of pure and doped V_2O_3 were, however, found to be almost the same and could be empirically represented by the Debye (D)–Einstein (E) function $D(580/T) + 4E(\theta/T)$ with θ values 430°K ($T = 100$–230°K) and 465°K ($T > 230$°K), respectively. Further, the enthalpy change ΔH associated with the H-T anomaly in doped V_2O_3 ($80 \leqslant \Delta H \leqslant 510$ J/mole) was 5–10 times smaller than the ΔH corresponding to the lower-temperature transition. The results cited here appear incompatible with the Mott transition model that has been invoked to explain the H-T anomaly.

Introduction

Vanadium sesquioxide doped with 1 at% chromium has been a particularly challenging material because of its anomalous electrical properties slightly above room temperature. McWhan and co-workers (1, 2) have regarded the anomaly as a manifestation of electronic correlation effects accompanying a Mott transition, while Zeiger (3) and Honig et al. (4) claim that it is either unnecessary or inappropriate to invoke a Mott transition to explain the observations. Thus it appears that the origin of the change in electrical conduction in the transition close to room temperature is still in doubt.

It is well known that there exist three polymorphic modifications of $(Cr_{0.01}V_{0.99})_2O_3$. At temperatures above 375°K, one encounters the β-corundum phase. Between approximately 375 and 275°K it coexists with the intermediate α-corundum form; the latter is the sole phase in the range below 275 to about 150°K. Below this region an abrupt transition occurs to the low-temperature γ-monoclinic phase. Previous thermal studies (4) on powdered $(Cr_{0.01}V_{0.99})_2O_3$ single crystals had indicated a very small enthalpy change in the region of the α–β transformation. Subsequently, evidence was uncovered suggesting that the state of aggregation plays a role in determining the relevant thermodynamic parameters. Therefore, a thorough study of heat capacity at constant pressure (C_p) of V_2O_3 doped with 1 and 1.4 mole %

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Cr$_2$O$_3$ or with Al$_2$O$_3$ was undertaken to gain further insight into this problem. The requisite single crystals were obtained by arc-melting techniques.

Another unresolved issue pertains to the structure of pure V$_2$O$_3$ above room temperature. X-ray measurements originally reported by McWhan and Remeika (1) were subsequently questioned by Chandrashekhar et al. (5), whose work on powdered V$_2$O$_3$ specimens showed a small splitting in the principal X-ray Bragg reflection peaks. This was interpreted as showing either that the α- and β-corundum structures coexisted over a considerable temperature range or else that there was an incipient transformation from the corundum structure to a configuration of lower symmetry in the range from 450 to at least 700°K. However, careful subsequent measurements on single crystals and on powders by Robinson (6, 7) failed to turn up any evidence for splittings of the X-ray diffraction peaks, thus confirming the earlier work (1). A series of heat capacity measurements was, therefore, also undertaken to obtain independent evidence with respect to this question.

Experimental

V$_2$O$_5$ (United Mineral and Chemical Corp., purity 99.995%) was reduced to V$_2$O$_3$ by heating in flowing, purified hydrogen gas at 1000°C for about 12 hr. The starting materials were V$_2$O$_3$ needles carefully grown from this powder and high-purity Cr$_2$O$_3$ and Al$_2$O$_3$. Single crystals were grown by the conventional arc-melting technique described by Fan and Reed (8). The total impurity content as determined by mass spectrometric analysis was of the order of 100 ppmw (principally, W, 30 ppmw; Ti, 30 ppmw) in Cr-doped samples and 200 ppmw (principally, Na, 100 ppmw; Fe, 50 ppmw; Mg, 20 ppmw; Si, 20 ppmw) in Al-doped crystals.

Heat capacities at constant pressure (C_p) were measured on a Perkin–Elmer Differential Scanning Calorimeter (DSC-2) over the temperature range 100–700°K, generally at heating or cooling rates of 10°/min. Frequently a rate of 1.25°/min was also used. Measure-

ments were carried out on unannealed needles as grown from the tri-arc furnace, plates and disks cut from large single crystals grown from molten needles, or powdered needles of plates. Specimens of pure V$_2$O$_3$ and or (M_xV$_{1-x}$)$_2$O$_3$ (M = Al, Cr; x = 0.01, 0.014) were examined. All the samples were precooled to 200°K to ensure conversion to the α form prior to the measurements. Sapphire was used as the reference standard.

Results

All the relevant data are summarized in Table I and Figs. 1 and 2. The $\bar{T}_h$ and $\bar{T}_l$ values refer to the midpoint of the α–β and α–γ transitions while ΔT indicates the span of the ranges.

Inspection of Fig. 1 and Table I leads to the following conclusions dealing with various aspects of the transition:

I. Transitions in Pure V$_2$O$_3$

Pure V$_2$O$_3$ exhibits a fairly sharp transition around 170°K (T increasing). This can be correlated with the antiferromagnetic → paramagnetic transformation and with the corresponding change in crystal structure. This transition has been studied in detail and is reviewed elsewhere (9). On cooling, a hysteresis of 18°K was observed, displacing the transition to a range about 151°K.

Anderson (10) reported a value* of 2900 J/mole for the enthalpy of transition, while the value obtained in the present measurements ($\sim$ 2000 J/mole) is considerably lower. The reason for this discrepancy is not clear. However, this matter was pursued further by repeatedly measuring the heat capacity of sample #3 through the transition region. The value of the enthalpy of transition (ΔH) remained practically unchanged (cf. Table I).

There is some question concerning the order of this low-temperature (L–T) transition. The marked hysteresis indicates that the phase change is first order; yet the width of the transition was observed to be $\sim$10°K. The calculated value of dT_c/dp using the Clausius–Clapeyron equation was found to be $-4.1 \times$

*The ΔH values cited here refer to joules per mole of V$_2$O$_3$ or to joules per mole of (M_xV$_{1-x}$)$_2$ O$_3$ throughout.

TABLE I

CALORIMETRIC DATA PERTAINING TO TRANSITIONS IN V_2O_3 AND ITS ALLOYS WITH Al_2O_3 AND Cr_2O_3

Nominal composition/ state of aggregation	Low-temperature transition				High-temperature transition			
	Heating		Cooling		Heating		Cooling	
	$\bar{T}_l$ (°K) ΔT	ΔH^a (J/mole)	$\bar{T}_l$ (°K) ΔT	ΔH^a (J/mole)	$\bar{T}_h$ (°K) ΔT	ΔH^a (J/mole)	$\bar{T}_h$ (°K) ΔT	ΔH^a (J/mole)
V_2O_3								
# 1 powder	170 10	2010	152 9	2100	NO	NO	NO	NO
2 plate	168 7	1950	150 6	2050	NO	NO	NO	NO
3 powder run 1	173 10	2025	NM	NM	NM	NM	NM	NM
2		2000	NM	NM	NM	NM	NM	NM
3		1995	NM	NM	NM	NM	NM	NM
$(Al_{0.01}V_{0.99})_2O_3$								
# 1 powder	176 10	2600	164 7	2540	353 14	80	310 12	130
2 plate	175 6	1990	164 8	1950	360 30	260	293 26	490
3 plate	174 5	2010	164 5	1900	345 10	240	304 12	330
4 plate	174 6	1970	163 8	1920	349 12	175	305 15	210
5 needle	174 15	1990	164 13	1900	360 20	160	322 15	330
6 needle	174 15	1990	164 13	1900	356 20	280	316 16	510
$(Cr_{0.01}V_{0.99})_2O_3$								
needle	176 16	1990	165 10	2050	335 20	160	266 18	330
$(Al_{0.014}V_{0.986})_2O_3$								
needle	184 6	2420	172 7	2310	280 20	360	225 10	320
$(Cr_{0.014}V_{0.986})_2O_3$								
needle	186 12	2435	174 12	2360	270 20	150	210 20	150

[a] Precision ±80 J. NO = Not observed. NM = Not measured. ΔH values correspond to endothermic transitions while heating and exothermic transitions while cooling.

10^{-3} deg/bar; the directly measured values were reported as -3.1×10^{-3} deg/bar (11) and -3.8×10^{-3} deg/bar (12), respectively. Since the calculated and experimental values of dT_c/dp are in fair agreement this seems to indicate that the transition at low temperatures is close to being of first order.

Careful searches for a heat capacity anomaly in pure V_2O_3 in the high-temperature range, 300–700°K, failed to reveal any unusual features. Conceivably, failure to detect an anomaly could be ascribed to the broadness of the α–β transition, as reported in the X-ray studies by Chandrashekhar et al. (5). On the other hand, the absence of the heat capacity anomaly correlates well with the inability by Robinson (6, 7) to detect an anomaly in this range by X-ray diffraction measurements.
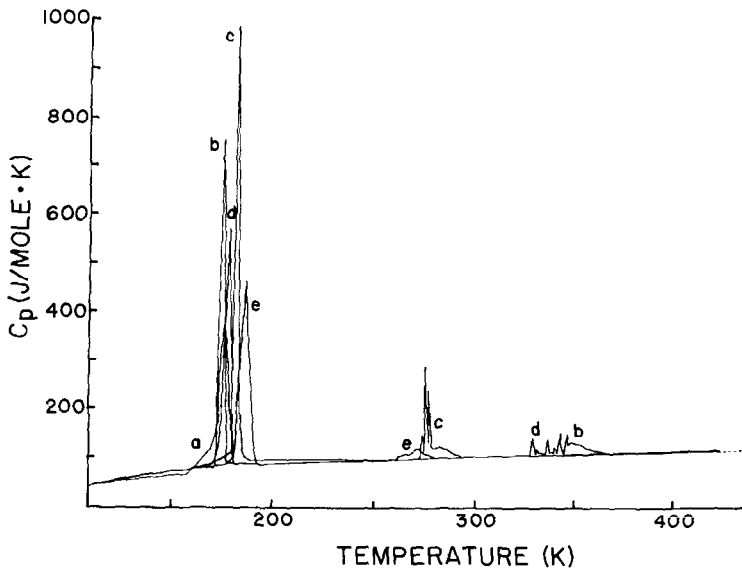
FIG. 1. Temperature variation of heat capacity (C_p) of pure and doped V_2O_3 with increasing temperature (T): (a) V_2O_3; (b) $(Al_{0.01}V_{0.99})_2O_3$ #2; (c) $(Al_{0.014}V_{0.986})_2O_3$; (d) $(Cr_{0.01}V_{0.99})_2O_3$; (e) $(Cr_{0.014}V_{0.986})_2O_3$.
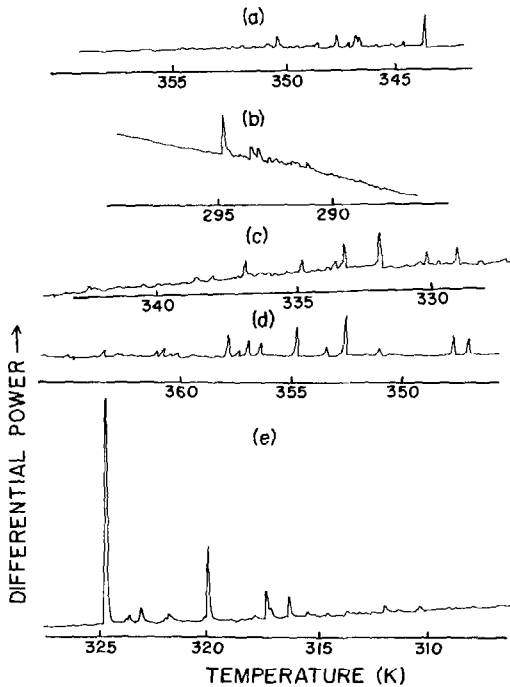

FIG. 2. Details of the high-temperature transition in doped V_2O_3 at 1.25°/min scanning rate: (a) $(Al_{0.01}V_{0.99})_2O_3$ #2 plate (T increasing); (b) $(Al_{0.01}V_{0.99})_2O_3$ #2 (T decreasing); (c) $(Cr_{0.01}V_{0.99})_2O_3$ needle (T increasing); (d) $(Al_{0.01}V_{0.099})_2O_3$ #6 needle (T increasing); (e) $(Al_{0.01}V_{0.99})_2O_3$ #6 needle (T decreasing).

We are inclined to adopt the second viewpoint and question the reliability of the findings reported in (5).

II. Hysteresis Effects in $(M_xV_{1-x})_2O_3$

Large hysteresis effects were observed in both transitions for samples containing either 1 or 1.4 at% Al or Cr. The hysteresis was as large as 50°K for the high-temperature (H-T) anomaly corresponding to the α–β transformation, but considerably smaller (~11°K) for the α–γ transition. As discussed later, we believe this to be a particularly important finding pertaining to the nature of both transitions. Both the temperatures and the hysteresis effects correlate well with comparable measurements of the electrical transitions in both temperature ranges.

In view of the hysteresis, precooling to 200°K is essential to ensure the conversion of the β phase into the α form; otherwise, no sizeable anomaly is observed in the first heating cycle of the DSC scans.

III. Heat Capacity Data for V_2O_3 and $(M_xV_{1-x})_2O_3$

The temperature variation of C_p for both Cr- and Al-doped samples is similar in many

respects. The values of lattice heat capacity are almost the same for all three systems and approach the Dulong–Petit limiting value near 500°K. Following Kelley and King (13) the lattice contribution was empirically fitted to an equation corresponding to a combination of Debye (D)–Einstein (E) functions through the equation

$$C_p \approx C_v = \mathrm{D}\left(\frac{580}{T}\right) + 4\mathrm{E}\left(\frac{\theta}{T}\right)$$

with θ values 430°K ($T = 100$–230°K) and 465°K ($T > 230$°K), respectively. This relation is useful in calculating the lattice heat capacity at any desired temperature between 100 and 700°K.

In the empirical fits cited above a Debye temperature $\theta_\mathrm{D} = 580$°K was used, as a rough average between the lower limiting values of 585°K, reported by Wenger and Keesom (14) and of 575°K calculated from the data supplied in (15). These θ_D values greatly exceed the quantity $\theta_\mathrm{D} = 275$°K reported by Anderson (10) on the basis of much earlier work.

IV. Effect of Dopant Concentrations on Transition Temperatures

As the dopant concentration was changed from $x = 0.010$ to 0.014 in $(M_xV_{1-x})_2O_3$, all transition temperatures were altered. For $M = \mathrm{Cr}$, the H-T anomaly shifted from 325–345°K down to 260–280°K; for $M = \mathrm{Al}$, the corresponding shift occurred from 345–365 to 270–290°K. For the L–T transition, there was an increase in range from 170–180 to 180–190°K for both Cr- and Al-doped specimens when x was increased from 0.010 to 0.014. All of the above ranges refer to measurements taken with increasing temperature. Corresponding alterations were encountered when the specimens were cooled, as may be noted by inspection of Table I. With an increase in doping from $x = 0.010$ to 0.014 the hysteresis in the L-T range remained unaltered, but the hysteresis was slightly increased in the H-T range.

V. Enthalpies of Transition in Doped V$_2$O$_3$

The enthalpy change (ΔH) of the L-T transition is 5 to 10 times greater than that of

the corresponding H-T transformation; results obtained with a 10°/min scanning rate indicated that typical values of ΔH for the α–β transition fall in the range of 125–335 J/mole, although values as low as 80 J/mole (for powdered specimens) and as high as 510 J/mole were occasionally encountered; the corresponding enthalpy values of the α–γ transformation were in the range ~2000 J/mole for $x = 0$ and 0.01[1] and in the range ~ 2400 J/mole for $x = 0.014$.

VI. Effects of State of Subdivision and Sample Treatment

The size and shape of the H-T anomaly was affected by the state of aggregation of the sample, i.e., whether the specimen consisted of powder, needles, or plates. The results also depended on the details of the thermal treatment, viz., whether the material was virgin or whether it had previously been cycled through the transition(s).

Powdering the sample increased the temperature range over which the H-T anomaly was observed, and thus resulted in greater uncertainty with respect to determining the base line; as a result the lattice heat capacity was overestimated. Estimates of ΔH values thus became less reliable. For example, the value of ΔH for one powdered 1 at% Al-doped V$_2$O$_3$ sample was observed to be low (~80 J/mole) compared with that obtained for single crystal specimens with the same nominal composition in the form of needles or plates (cf. Table I). The ΔH value for sample #5 needle dropped from 160 to 80 J/mole on powdering. The low ΔH values (80 and 130 J/mole) of the powdered 1 at% Al-doped sample agree favorably with those (~100 J/mole) reported earlier on powdered 1 at% Cr-doped V$_2$O$_3$ (4).

The slight differences in $\bar{T}_h$ and $\bar{T}_l$ values encountered for different samples are probably due to small changes in composition caused by the subtle variation of conditions during crystal growth.

[1] As shown in Table I, there occurred one conspicuous exception whose significance is not understood. For one powdered $(\mathrm{Al}_{0.01}V_{0.99})_2O_3$ specimen, ΔH was 2600 J/mole.

The width of the $\alpha-\gamma$ transition temperature range also varied irregularly between 5 and 15°, depending on whether powder, needles, or plates were used. This indicates that the degree of crystalline perfection plays a role in determining the thermal parameters for the L-T transition.

VII. Thermal History Effects

The dependence of ΔH values for the H-T transition on the thermal history was examined for 1 at% Al-doped samples. The values obtained during the cooling cycles were greater than those observed during the heating cycles. However, no definite correlation could be established between ΔH values and details of thermal treatment in passing through the H-T range. For example, sample #2, which had been cycled once through the L-T and H-T transitions, exhibited almost identical ΔH values at the H-T anomaly as did #6, which was virgin. Similarly, although samples #2, 3, and 4 were grown from the same melt, neither the H-T range nor the enthalpy of transformation was identical. By contrast, the L-T transition characteristics always remained the same, indicating that there was no fundamental problem with the homogeneity of the melts.

VIII. High-Temperature Transition at Slow Scanning Rate

In order to study the H-T transition more closely, a slower rate (1.25°/min) was employed in the relevant temperature ranges. Figure 2 depicts the results obtained with 1 at% Cr-doped V_2O_3 needle and with two 1 at% Al-doped V_2O_3 samples with different states of aggregation. The H-T anomaly is seen to be composed of many discrete peaks occurring at slightly different temperatures and spread over a relatively broad temperature range ($\sim20-30°K$). This particular feature cannot be ascribed to an instrumental effect since it was not observed when other first-order transitions were studied under the same conditions. The phenomenon is very likely associated with the presence of domains of rather sizeable dimensions.

Traces obtained for different 1 at% Al-doped samples under the same conditions are

similar but not identical. This indicates that the course of the transition via formation of domains is sensitive to slight variations in composition and details of microstructure. Similarly, the traces for any particular sample, say #5, were not reproducible in different cycles, in that the peaks occurred in different arrangements and sequences; nevertheless, the H-T range where these peaks occurred remained almost the same.

The observations during heating and cooling also differed in detail. The transition on cooling was marked by relatively greater sharpness in peaks and the bulk of the (H-T) transition took place over a narrower temperature range of about 3 to 7°. Thus, the detailed course of the transition seems to be a strong function of crystal imperfections and relative rates of nucleation and propagation of the emerging phases in the host lattice. Similar observations were made by Chandrashekhar and Sinha (16), while reporting on the high-temperature X-ray diffraction studies on $(Cr_{0.01}V_{0.99})_2O_3$.

ΔH values encountered with 1.25°/min scanning rate in the H-T range for 1 at% Al-doped samples were smaller (130–250 J/mole) compared to those observed when the faster rate (10°/min) was employed. This inequality is presumably caused by the broadening of the transition range at slower rates and the consequent unreliability in the accurate determination of base lines.

Similar observations can be made concerning the thermal behavior of 1.4 at% Cr- and Al-doped V_2O_3.

IX. Comparison of Thermal and X-Ray Analysis in Doped V_2O_3

The high-temperature ($\alpha-\beta$) transition range, observed in C_p vs T plots of 1 at% Cr-doped V_2O_3, is small ($\sim20-30°K$), whereas the X-ray diffraction studies of McWhan and Remeika (1) and of Chandrashekhar and Sinha (16) indicate the range to be much broader ($\sim200°K$). However, as is shown in these X-ray studies, the greater part of the transition appears to take place within a 20° interval after the onset of the $\alpha-\beta$ transformation. It is only a small remainder of the transition that is still detectable with X-ray

diffraction over an additional 150 to 180° interval. X-ray studies again indicate, in conformity with the thermal measurements, that the transition is a function of crystal imperfections and relative rates of nucleation and propagation of the emerging phase(s) in the host lattice. Similar comments should apply to V_2O_3 samples doped with 1 at% Al.

X. Effects of Sample Preparation Techniques

Preliminary experiments show that no significant changes in heat capacity properties are encountered when specimens are prepared by $TeCl_4$ vapor transport techniques rather than by arc-melting.

Discussion

In light of the previous suggestions (1, 2) that the H-T anomaly in $(Cr_{0.01}V_{0.99})_2O_3$ is to be interpreted as a manifestation of the Mott transition, considerable significance should be attached to the following findings reported above: (a) The H-T heat capacity anomaly was not entirely reproducible, but depended somewhat on the thermal history of the sample. (b) Very large H-T hysteresis effects ranging between 30 and 50°K were found. (c) Many discrete peaks were encountered in the heat capacity measurements (see Fig. 2) between 345 and 365°K while heating and between 325 and 310°K while cooling for 1 at% Al-doped V_2O_3 samples. This is ascribed to the occurrence of domains undergoing a first-order α–β corundum phase transition. (d) Finally, it has been stated (17) that the magnitude of the entropy change involved in the electron localization accompanying the Mott transition is of the order of 0.2 e.u., which, when converted, is numerically close to the ΔH values for the H-T transition cited in Table I. However, the sign is opposite to what is required: In a Mott transition the electronic localization process is associated with a negative entropy change since the localized electron distribution is a far more ordered configuration than the itinerant state. The Mott insulator is thus at a lower entropy than a narrow-band metal, and the metal–Mott insulator transition should be manifested as an exo-

thermic process. In fact, the measurements reported here clearly show that the transformation is endothermic. Electronic localization, if it occurred, would then have to be overshadowed by other processes, such as lattice expansion, to account for the experimental observations. Alternatively, the presumed electronic localization in principle could be counteracted by spin disordering. Elementary calculations show that such a process should result in an entropy change in the range from 2 to 4 e.u., which is larger by an order of magnitude than the observed value.

These findings strongly suggest that the lattice plays a very active role in the determination of the H-T anomaly, and this, in turn, makes it difficult to accept the Mott transition as a viable model for the interpretation of the effects described above. In particular, the Mott transition depends solely on electron–electron correlations as a driving force; therefore, the crossover from a metallic to a highly correlated electron regime should be a unique function of temperature, so that no hysteresis effects should be in evidence. Moreover, whenever domain effects are encountered one would have to envisage the coexistence in the ground state of itinerant and localized electrons in boundary regions separating the two sets of domains. This in itself runs counter to the very essence of the Mott model, according to which the generation of a few highly mobile charge carriers would be sufficient to convert the remaining carriers to the uncorrelated state. Analogously, the presence of just a small density of correlated charge carriers is unstable against either a complete set of correlated or of independent carriers. Therefore, from the data presented here we conclude that the electrons and the lattice act in concert to determine the nature of the H-T anomaly in 1 at% Cr- and Al-doped V_2O_3.

Acknowledgments

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