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Thermal properties of tetragonal ZrO_2 at low temperatures

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Specific-heat (1.7—25 K) and thermal-conductivity (1.7—45 K) measurements are reported on Y_2O_3-stabilized tetragonal ZrO_2. As in cubic ZrO_2, an Einstein-type excess specific heat (62 cm^{-1}) is found above 7 K, and the amplitude of this term agrees well with the oxygen-vacancy concentration (1.4%). A second excess specific heat below 5 K is found (as in the cubic form), due to the electric quadrupole moment of the hafnium impurity which contributes a Schottky term ($\delta = 50$ mK). The Debye temperatures obtained from the Einstein and Schottky fits are 515 and 507 K, respectively. As in the cubic form of ZrO_2, the thermal conductivity displays two *glasslike* features: (1) a plateau near 50 K and (2) a quadratic dependence, $K \sim 10^{-5} T^2$ $W\,cm^{-1}K^{-1}$ at the lowest temperatures. The accumulated evidence suggests that the oxygen conductivity and the low-temperature thermal properties of ZrO_2 are determined by the oxygen vacancies and are relatively insensitive to whether the host zirconia lattice is cubic or tetragonal.

I. INTRODUCTION

As early as 1899, Nernst[1] observed oxygen conductivity in zirconia (ZrO_2+9 wt. % Y_2O_3), and this material remains of great interest today for fuel-cell and oxygen-sensor applications. Nature has contrived to make ZrO_2 an elusive material to study because a destructive tetragonal-monoclinic martensitic transformation occurs at 1170 °C.[2] Consequently, the bulk of the data reported on ZrO_2 has involved the *cubic* fluorite structure which is stabilized by significant amounts of alkaline-earth or rare-earth oxides. In addition to stabilizing the cubic phase, these additive oxides also create oxygen vacancies in ZrO_2, and it is generally agreed that the large oxygen conductivity in stabilized zirconia is due to these oxygen vacancies.

The low-temperature properties of superionic and fast-ion conductors have attracted considerable recent interest. The specific heats[3] and thermal conductivities[4] of the silver and alkali-metal β-aluminas have recently been reported, and the excess specific heats in these materials have been correlated with Raman frequencies in the (28—82)-cm^{-1} range; these frequencies are also evident in the microwave spectra.[5] In particular, the specific heat and thermal conductivity[6–8] of a cubic ZrO_2 containing 8 wt. % Y_2O_3 have been measured at low temperatures. Here, it was found that this oxygen conductor displayed the following properties associated with *amorphous* materials at low temperatures[9]: (1) A maximum in C/T^3, where C is the specific heat, (2) a *linear* term in the specific heat, $C_t \simeq 10^{-5} T$ $J\,cm^{-3}K^{-1}$, (3) a "plateau" in the thermal conductivity near the temperature of the maximum in C/T^3, (4) a quadratic T dependence of the thermal conductivity (K) below about 3 K, $K \simeq 10^{-4} T^2$ $W\,cm^{-1}K^{-1}$, and (5) a frequency-dependent minimum in the dielectric constant at approximately 100 mK. These glasslike properties are generally attributed to a two-level tunneling excitation with a constant density of states resulting from the massive topological disorder in glasses.[9] (We remark here that these *same* glasslike properties have also been observed recently in undoped ferroelectric crystals.[10])

Techniques have recently been developed for stabilizing

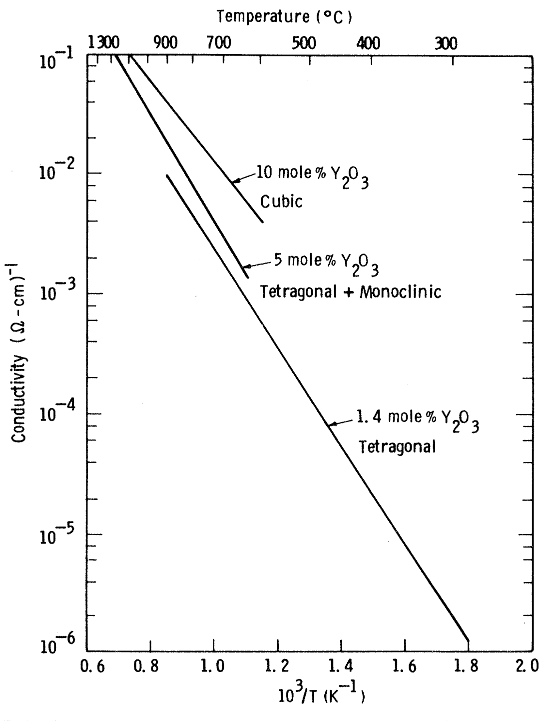

FIG. 1. Oxygen conductivity in Y_2O_3-stabilized, cubic and tetragonal ZrO_2.

the tetragonal phase of ZrO_2 at room temperature. This has been accomplished[11] by taking advantage of fine-particle technology [(100—300)-Å particle size] with minor Y_2O_3 doping, and these tetragonal zirconias have been shown to have remarkable mechanical properties.[12] The grain size of these sintered polycrystalline sample is less than 0.3 μm. The oxygen conductivity of a tetragonal ZrO_2 containing 2.4 wt. % (1.4 mol %) Y_2O_3 was recently measured,[13] and these conductivity data are shown in Fig. 1 compared to various Y_2O_3-stabilized cubic zirconias.

Because the Y_2O_3-stabilized cubic ZrO_2 displayed glasslike low-temperature behavior and because the stabilized tetragonal ZrO_2 has also been shown to be an oxygen conductor roughly equivalent to the cubic ZrO_2, a low-temperature investigation of this tetragonal phase was undertaken with the idea that it may shed additional light on these fast-ion conductors in general and on their glasslike properties in particular.

II. EXPERIMENTAL METHODS AND RESULTS

A disc of tetragonal ZrO_2 was prepared by the methods reported elsewhere.[11] This zirconia contained 2.4 wt. % Y_2O_3, and an x-ray analysis confirmed the tetragonal phase. The disc (4.742 gm) was first used for a specific-heat measurement (1.7—27 K). Next, a bar sample was cut from the disc for a thermal-conductivity measurement (1.7—50 K).

The specific-heat[14] and thermal-conductivity[15] methods have been described previously. Briefly, the specific-heat measurements were made in an adiabatic calorimeter by the pulse method. The $\Delta T/T$ values were maintained at about 3%, and the addenda constituted 1.68 wt. %. As a percentage of the total heat capacity, the addenda contributed 8.0% at 1.7 K and 11.6% at 27 K, and the overall uncertainty in the specific-heat method is approximately less than ±5%. The thermal-conductivity data were measured in the same calorimeter by the linear heat flow, two-thermometer method. The ZrO_2 bar had an A/l ratio of 6.96×10^{-2} cm, and the uncertainty in the method is approximately ±5%, due primarily to the uncertainty in measuring the separation of the thermometers.

The measured specific-heat data are shown in Fig. 2, where the data are plotted as C/T^3 to display the non-Debye features. A Debye "background" of $\simeq 3.5$ ergs $g^{-1}\,K^{-1}$ is shown (see below also), and two features are evident: (1) a maximum in C/T^3 at about 22 K, and (2) a rapid rise in C/T^3 with decreasing temperature wherein C/T^3 achieves values more than an order of magnitude larger than the Debye-background value.

The measured thermal-conductivity data are shown in Fig. 3. Here also, two features are apparent: (1) The K data appear to approach a plateau at about 50 K, but the data were not obtained at a high enough temperature to resolve this plateau, and (2) at the lowest temperatures, the data follow a T^2 regime, as indicated in Fig. 3.

III. DATA ANALYSES AND DISCUSSION

The maximum in C/T^3 at 22 K in Fig. 2 was assumed to be due to an Einstein term, following the behavior found in the β-aluminas[3] and in cubic ZrO_2,[6]

$$C=C_D(\Theta_D/T)+3Rrx^2e^x(e^x-1)^{-2},\quad x=\hbar\omega/kT \quad (1)$$

where C_D and Θ_D are the Debye function and temperature, respectively, R is the gas constant, r is the number of Einstein oscillators per formula weight, and ω is the Einstein frequency. The data in Fig. 2 above 9 K were fit to Eq. (1) using a three-level fitting program (i.e., for Θ_D, r, and ω) which incorporated the Debye function, and this fit is shown in Fig. 4. Here, $C_{ex}=C-C_D$, and an excellent fit to the data are obtained over 3 orders of magnitude in $T^2C_{ex}/3R$. The high-temperature form of Eq. (1) is used for plotting this fit in Fig. 4, and this imparts a slight curvature. The fitting parameters are

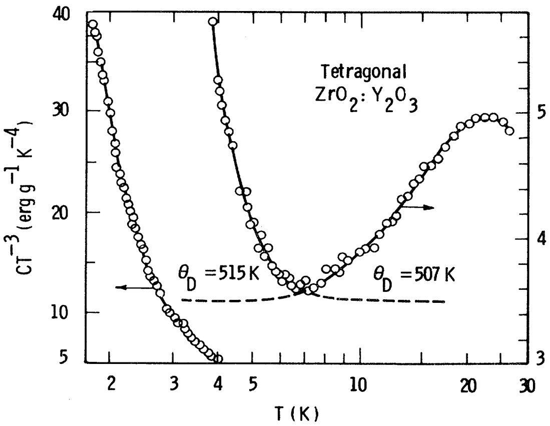

FIG. 2. Specific-heat data plotted as C/T^3 for Y_2O_3-stabilized tetragonal ZrO_2. Debye temperatures shown resulted from separate fittings of the data (see text) and the dashed curves indicate the correpsonding C/T^3 backgrounds.

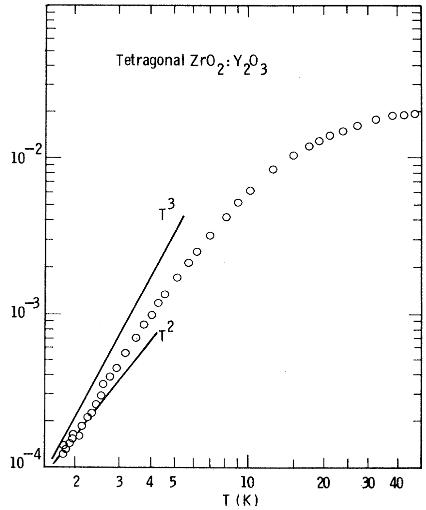

FIG. 3. Thermal-conductivity data for Y_2O_3-stabilized tetragonal ZrO_2. Low-temperture T^2 and T^3 slopes are indicated.

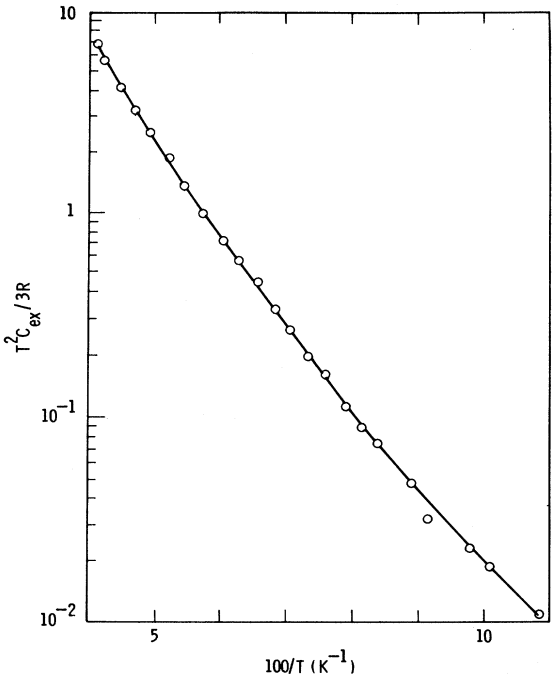

FIG. 4. Fit of the Fig. 2 data above 9 K to the Einstein model, Eq. (1). Fitting parameters are given in the text and Einstein oscillators are attributed to the oxygen vacancies.

$$\Theta_D = 507, \quad \omega = 62.3, \quad r = 0.0148 ,$$

where Θ_D (in K) is normalized to one atom per molecule, and ω is in cm^{-1}. For comparison, the corresponding parameters for *cubic* ZrO_2 are $\Theta_D = 475$ K, $\omega = 61.7$ cm^{-1}, and $r = 0.0492$.[6]

There is a very good correlation between these two forms of Y_2O_3-stabilized ZrO_2 regarding the Einstein terms. Not only are the frequencies nearly the same, but the r values agree very well with oxygen-vacancy concentrations (i.e., 1.4 mol % in the tetragonal form, 4.3 mol % in the cubic form). This leaves little doubt that the oxygen vacancies are responsible for the Einstein-type excess specific heat. Moreover, Raman data on *undoped* ZrO_2 show *no* frequencies below 100 cm^{-1}.[16]

The rapid rise in C/T^3 below 5 K in Fig. 2 is far too large to be due to a linear tunneling term. This tetragonal ZrO_2 has a residual hafnium content, as did the first cubic ZrO_2 measured at low temperatures.[6] In the latter case, a similar rise in C/T^3 below 5 K was observed, and this was attributed to the large electric quadrupole moment of Hf which gives rise to a Schottky term,

$$C_{\text{Sch}} = Rg_0g_1(g_0+g_1)^{-2}(\delta/T)^2 . \qquad (2)$$

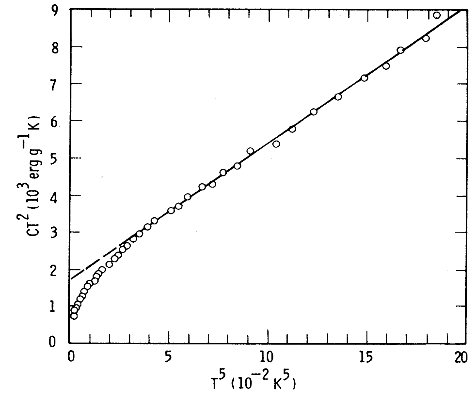

FIG. 5. Fit of the Fig. 2 data below 5 K to the Schottky model, Eq. (2). Deviation below $T^5 \sim 300$ may be due to the high-temperature approximation to the Schottky term.

Equation (2) is the high-temperature form of the two-level Schottky term where g_0 and g_1 are the degeneracies of the two-level system of energy separation δ. We have no reason to choose a two-level system over, say, a three-level system; what is important is the T^{-2} form common to a multilevel Schottky term. The data in Fig. 2 below 5 K follow the Schottky term (added to the Debye background) quite well, and this fit is shown in Fig. 5 where CT^2 vs T^5 is plotted. The fitting parameters are

$$\Theta_D = 515, \quad \delta = 50.1 ,$$

in K and mK, respectively. The degeneracies were set equal in Eq. (2) in this fit (i.e., $g_0 = g_1$); the energy separation δ is not very sensitive to the degeneracies because of the cancellation in Eq. (2). Also, the form of Eq. (2) assumes one Schottky system per molecule, so the fitted δ value is the lower limit of the energy separation.

The experimental data in Fig. 5 deviate from the Schottky fit at the lowest temperatures for this tetragonal zirconia. This is in contrast to the case of the cubic zirconia[6] where the data followed CT^2 vs T^5 to the lowest temperatures. In this latter case, an energy separation $\delta = 37.8$ mK was found (the data were fitted the same as here). Consequently, the deviation in Fig. 5 may simply be due to the use of the high-temperature form [Eq. (2)] for the tetragonal form where the energy separation δ is larger, but this was not pursued.

There is little doubt that the Schottky terms in the cubic and tetragonal zirconias are due to the hafnium content (approximately 2—3 wt. %), for the following reason: An Y_2O_3-stabilized cubic zirconia refined to *reduce* the hafnium has been measured,[7,8] and it was found that the Schottky term, while still present, was considerably reduced. Two isotopes of hafnium have large electric quadrupole moments: ^{177}Hf (18.4 at. % abundance) and ^{179}Hf (13.8 at. % abundance), each of which has a quadrupole moment of 3×10^{24} $e \cdot cm^2$.

The Debye temperatures determined from the Einstein and Schottky fits agree quite well, 515 and 507 K, respectively, and these values are indicated in Fig. 2. The Schottky term makes a negligible contribution in the temperature range of the Einstein fit, and vice versa.

The specific-heat measurements on the hafnium-refined cubic zirconia[7,8] revealed a *linear tunneling* term, $C_t = 10.6T$ ergs $g^{-1} K^{-2}$. This term, if present in the tetragonal zirconia, would represent about 9% of C/T^3 in Fig. 2 at 2 K. An attempt was made to resolve this tunneling term from the Fig. 2 data by subtracting the Debye background (using the Debye temperature determined from the Einstein fit), and the excess specific heat was plotted at T^2C_{ex} vs T^3 (i.e., C_{ex} was set equal to the tunneling term plus a Schottky term). The resulting fit, which was equivalent to the fit shown in Fig. 5, yielded $C_t = 26.5T$ ergs $\text{g}^{-1}\,\text{K}^{-2}$ and an energy separation $\delta = 34.3$ mK. This fitting was appealing in that the coefficient of the tunneling term and the energy separation are both very similar to the values determined in cubic zirconia. However, this cannot be taken as evidence for a tunneling term in tetragonal zirconia because of the equivalence of the fittings.

The thermal-conductivity data in Fig. 3 display a T^2 regime below about 2.5 K with $K \simeq 4\times10^{-5}T^2$ $\text{W cm}^{-1}\,\text{K}^{-1}$. For Y_2O_3-stabilized cubic zirconia, the thermal conductivity follows $K \simeq 8\times10^{-5}T^2$ $\text{W cm}^{-1}\,\text{K}^{-1}$ down to 0.3 K.[8] Therefore, the two forms of stabilized zirconia have approximately the same thermal conductivities which follow the glasslike T^2 dependence; moreover, the magnitudes of the coefficients are similar to those of *glasses* (see above).

The data in Fig. 3 strongly suggest a "plateau" region in the thermal conductivity around 40 K, but the data would have to be determined at higher temperatures to demonstrate this plateau convincingly (thermometer-sensitivity considerations limited the data here to approximately 50 K). In the case of the stabilized cubic zirconia,[8] thermal-conductivity data up to 100 K resolved a plateau region of about 40—60 K.

IV. CONCLUSIONS

The measurements reported here on Y_2O_3-stabilized tetragonal ZrO_2 and elsewhere[6-8] on Y_2O_3-stabilized *cubic* ZrO_2 demonstrate several common features. An excess specific heat above about 8 K is similar in origin and frequency to the Einstein-type excess specific heat found in the β-aluminas, and the frequencies found in the two forms of ZrO_2 agree very well (62.3 and 61.7 cm^{-1}, respectively). Moreover, the amplitudes of the Einstein terms in these two zirconias agree well with oxygen-vacancy concentrations as determined from the Y_2O_3 contents, and this fact strongly suggests that this excess specific heat is due to the oxygen vacancies. The tetragonal ZrO_2 has a slightly larger Debye temperature (511 ± 5.7 K) than the cubic form[6] (473 ± 3.5 K). The hafnium content in both forms of ZrO_2 gives rise to a Schottky contribution below about 6 K which masks the glasslike tunneling contribution; the Schottky energy separations (assumed to be two level) are 37.8 and 50.1 mK in the cubic and tetragonal forms, respectively. Finally, thermal-conductivity measurements on the two forms of ZrO_2 reveal similar *glasslike* behavior, a plateau in K around 50 K, and $K \sim 10^{-4}T^2$ below about 3 K.

The findings reported here and elsewhere suggest that the oxygen conductivity and the low-temperature thermal properties of Y_2O_3-stabilized ZrO_2 are predominantly determined by the oxygen vacancies and are relatively insensitive to whether the host zirconia lattice is cubic or tetragonal.

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