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Low-temperature specific heat of a ZrO_2:Y_2O_3 oxygen conductor

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The specific heat of a partially stabilized ZrO_2:Y_2O_3 ceramic containing 4.3% oxygen vacancies is reported between 2 and 15 K. An excess specific heat above 6 K attributed to the oxygen vacancies is accurately described by an Einstein term with an oscillator frequency of 62 cm^{-1}. A second excess specific heat below 5 K follows a Schottky term ($\delta = 38$ mK) and is believed due to the electric quadrupole moment of the hafnia impurity. The Debye temperatures obtained from the Einstein and Schottky fits are 475 and 470 K, respectively. No evidence for a tunneling contribution to the specific heat was found.

I. INTRODUCTION

The group-IV*A* oxides, ZrO_2, HfO_2, CeO_2, and ThO_2, have large oxygen conductivities when doped with either alkaline-earth oxides, Sc_2O_3, Y_2O_3, or rare-earth oxides.[1] In fact, as early as 1899, Nernst[2] observed oxygen conductivity in a $ZrO_2 + 9$-wt.% Y_2O_3 solid solution. Doping serves two complementary purposes; First, the dopants stabilize the cubic fluorite structure (in ZrO_2 and HfO_2); and second, the presence of di- or trivalent cations on the cation sublattice causes the formation of oxygen vacancies to preserve electrical neutrality. Oxygen conduction occurs principally via these vacancies.

Materials with large ionic conductivities have received considerable recent attention both as a way of studying diffusion mechanisms in the presence of a large concentration of diffusing ions and as potential materials for energy-storage, fuel-cell, and oxygen-sensing systems. Although the ionic conductivity is appreciable mainly above room temperature, low-temperature studies can provide information on the conduction mechanisms which are often masked at higher temperatures due to the vagaries of sample preparation. For example, the low-temperature specific heats of the silver and alkali-metal β-aluminas have recently been measured.[3] An excess specific heat was found which could be correlated with Raman frequencies in the 28- to 82-cm^{-1} range, and these frequencies are also evident in the microwave conductivity spectra.[4] At the lowest temperatures a specific-heat term linear in the temperature was found and interpreted as the cation-tunneling contribution.[3] The low-temperature thermal conductivities of several β-aluminas have also been reported (0.1–300 K).[5]

The purpose of this paper is to report the first low-temperature measurements on an oxygen conductor, Y_2O_3-stabilized ZrO_2, and to investigate what similarities may exist with other fast-ion conductors.

II. EXPERIMENTAL METHOD AND RESULTS

The sample measured contained 8-wt.% Y_2O_3 and had a nominal composition $Zr_{0.913}Y_{0.087}O_{1.957}$, containing 4.3% oxygen vacancies.[6] These types of stabilized zirconias typically have ionic conductivities $\sim 0.1\ \Omega^{-1}cm^{-1}$ at 1000 °C and activation energies ~ 0.9 eV.[1] A careful x-ray scan of the sample in the neighborhood of the $2\theta \sim 30°$ region where the monoclinic peaks are especially prevalent[7] did not reveal any trace of the monoclinic phase. Strictly speaking, the 8-wt.% Y_2O_3 addition is not quite large enough to fully stabilize zirconia against the monoclinic phase, so the sample has to be considered partially stabilized. However, it is not unusual to find no x-ray trace of the monoclinic phase in these types of zirconias.

The disc-shaped sample (4.304 g) was fixtured with a 458-Ω heater, carbon-chip resistor thermometer, and a Manganin thermal link. The addenda contributed 6–15% of the total heat capacity. The pulse calorimeter described previously[8] was used. The $\Delta T/T$ values were maintained $< 3\%$, and the uncertainty of the method is believed $< \pm 5\%$.

Specific-heat data plotted as CT^{-3} vs T^2 are shown in Fig. 1 in the range 2–15 K. The data are plotted as CT^{-3} to emphasize the non-Debye contributions to the specific heat.

The CT^{-3} data in Fig. 1 have a minimum at about 6 K. Following the behavior found in the β-aluminas,[3] we assume that the CT^{-3} rise above 6 K is due to an Einstein term above the Debye background,

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

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,

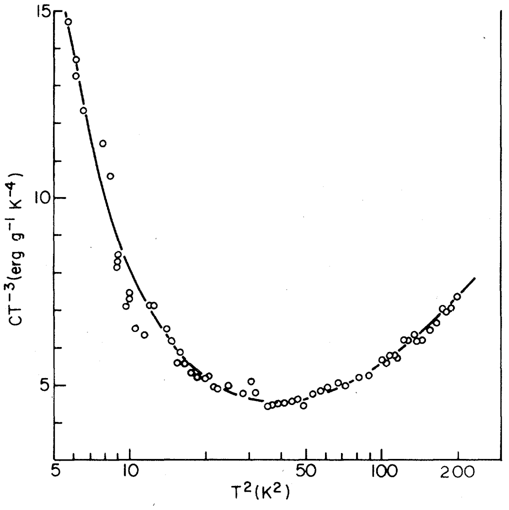

FIG. 1. Specific heat of $ZrO_2 + 8$-wt.% Y_2O_3 plotted as CT^{-3} to emphasize the non-Debye contributions above and below about 6 K ($T^2 \simeq 35$).

and ω is the Einstein frequency. The fit of the $T > 6$ K data to Eq. (1) is shown in Fig. 2, and an excellent fit was obtained over four orders of magnitude in $T^2 \times (C_{\text{exp}} - C_D)$. The fitting parameters are

$$\Theta_D = 475 \text{ K} ,$$

$$\omega = 61.7 \text{ cm}^{-1}, \text{ Einstein fit, } 6 < T < 15 \text{ K} , \quad (2)$$

$$r = 0.0492 ,$$

where Θ_D is normalized to one atom per molecule. The fitting parameters in Eq. (2) have an uncertainty $< \pm 2\%$.

The Einstein term is believed due to the oxygen vacancies because Raman data[9] on *pure* ZrO_2 show *no* frequencies below about 100 cm^{-1}. Moreover the r value in Eq. (2) agrees very well with the nominal oxygen-vacancy concentration, 4.3%.

The rapid rise in CT^{-3} below about 5 K in Fig. 1 was first believed to be the tunneling contribution, but the 2–5 K data could not be satisfactorily fit to either a linear or an Einstein term. These data do follow a high-temperature Schottky term,

$$C_{\text{Sch}} = R g_0 g_1 (g_0 + g_1)^{-2} (\delta/T)^2, \quad T >> \delta , \quad (3)$$

added to the Debye background, where g_0, g_1 are the degeneracies of a two-level system of energy separation δ. The form of Eq. (3) is the $T >> \delta$ expansion for a two-level system, although we have no reason to choose a two-level system over, say, a three-level system. What is important to the T^{-2} dependence of the Schottky term, and in Fig. 3 are shown the data below 5 K plotted as CT^2 vs T^5. The higher-temperature Einstein term ($\omega = 61.7$ cm^{-1}) makes a negligible contribution in this temperature range.

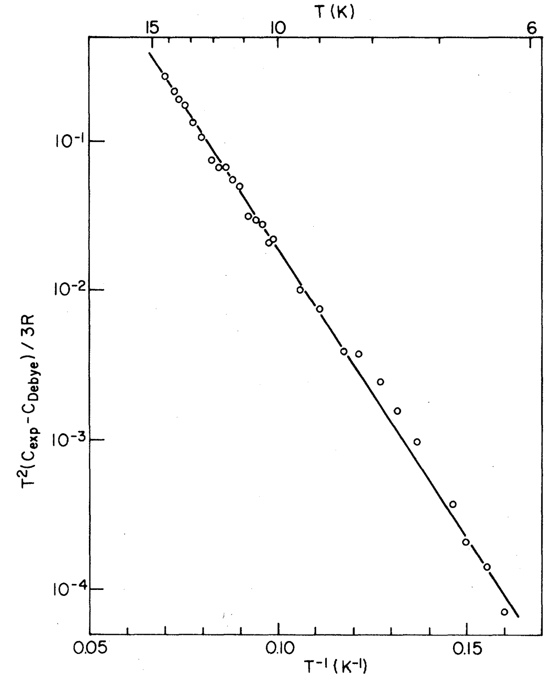

FIG. 2. Fit of the $T > 6$ K data of Fig. 1 to an Einstein term, Eq. (1). The fitting parameters are given to Eq. (2), and the Einstein oscillators are attributed to the oxygen vacancies.

The curve drawn in Fig. 3 results from a least-squares fit; the slope is proportional to Θ_D^{-3} and the intercept is $T^2 C_{\text{Sch}}$. The fitting parameters are given in Eq. (4), assuming $g_0 = g_1$ [the energy separation δ is not very sensitive to the degeneracies because of

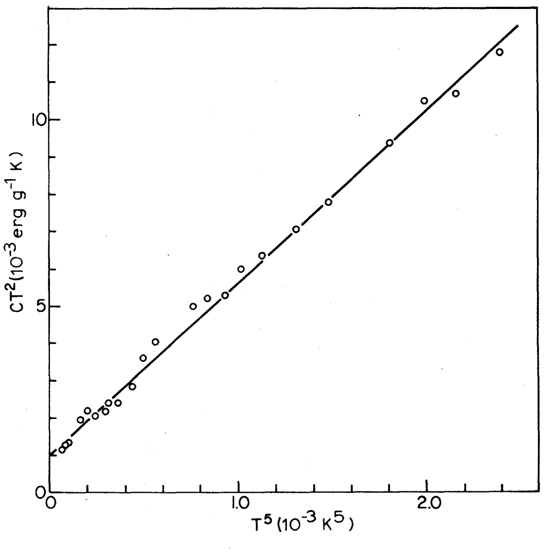

FIG. 3. Fit of the $T < 5$ K data of Fig. 1 to the Schottky term, Eq. (3). An assumed two-level scheme gives a fitted energy separation of 38 mK.

the cancellation in Eq. (3)].[10]

$$\Theta_D = 470\ \text{K, Schottky fit}\ , \quad \delta = 37.8\ \text{mK},\ 2 < T < 5\ \text{K}\ . \tag{4}$$

III. DISCUSSION

The measured specific-heat data of the oxygen conductor ZrO_2 + 8-wt.% Y_2O_3 are accurately described by an Einstein term above ~6 K (Fig. 2) and a Schottky term below ~5 K (Fig. 3), both added to a Debye background. The Debye temperatures from the two fits agree to within ±0.5%, which indicates that the Schottky term is negligible in the Einstein range $T > 6$ K, and vice versa.

The lowest Raman frequency reported for pure ZrO_2 is 102 cm^{-1} and this frequency shows no temperature dependence between 300 and 1500 K.[9] This A_g Raman mode would make its largest contribution at about 35 K but is negligible in the temperature range below 15 K compared to the 61.7 cm^{-1} mode in Fig. 2. The latter mode is believed to be a localized excitation associated with the oxygen vacancies, because, as noted above, the r value, Eq. (2), agrees very well with the expected oxygen vacancy concentration. This result corresponds to a random motion of the oxygen vacancies, implying independent Einstein oscillators for which the phonon mode is dispersionless. The 62 cm^{-1} Einstein mode found in Na β-alumina by infrared and Raman measurements[11] was similarly interpreted.

The Schottky term, Fig. 3, corresponds to an (two-level) energy separation ~38 mK, Eq. (4), although we cannot reliably infer the specific heat in the mK temperature range from this result. This Schottky term is in contrast to the case of the β-aluminas where a term linear in T was found between 1.3 and 3 K and interpreted as the tunneling contribution.

The smallness of the energy separation, 38 mK, suggests a nuclear effect, namely a quadrupole moment interaction with an electric field gradient.[12] The 8-wt.% Y_2O_3 sample measured is a is a mixture of the cubic and tetragonal phases containing Y^{3+} cations randomly occupying Zr^{4+} sites. The electric quadrupole moment of ^{89}Y, however, is zero, and the moment of ^{91}Zr has not been measured. The zirconia composition measured does contain 2–3 wt.% hafnia,[13] and two isotopes of hafnia have large electric quadrupole moments: ^{177}Hf (18.4% abundance) and ^{179}Hf (13.8% abundance), each of which has a quadrupole moment of 3 in units of $e \times 10^{24}$ cm^2. Therefore, the Schottky term is presumably due to the hafnia impurity in the tetragonal phase.

The tunneling contribution to the specific heat of the β-aluminas is believed due to the glasslike disorder of the alkali or silver ions and the different potential-energy minima at different sites. In these cationic conductors the tunneling term is $C' \simeq 10^{-3} T$ (cal $mole^{-1}$ K^{-1}).[3]

There is no evidence of a tunneling term in the Schottky plot for ZrO_2:Y_2O_3, Fig. 3. If a tunneling term exists in zirconia, it is considerably smaller than in the β-aluminas. For example, the *total* specific heat of ZrO_2:Y_2O_3 in the range 2–6 K is $\simeq (2-6) \times 10^{-4}$ cal $mole^{-1}$ K^{-1} (Fig. 1).

If a tunneling term exists in zirconia, the limit of the density of tunneling states can be estimated using the formalism developed in Ref. 3,

$$C'T \simeq \tfrac{1}{6}(\pi k)^2 P(0) x\ , \tag{5}$$

where x is the total number of different tunneling configurations and $P(E)$ is the probability distribution that the energy difference between accessible sites is E. Using the $P(0)$ function of Ref. 3,

$$\frac{C'}{T} \propto \left[\frac{e_1^2 a}{\epsilon} \left(n_1 + \frac{e_2^3}{e_1^3} n_2 \right)^{2/3} \right]^{-1}\ , \tag{6}$$

where n_1, e_1 and n_2, e_2 are the density and charge of the mobile O^{2-} ions and compensating centers, ϵ is the dielectric constant, and a is the lattice parameter [the geometric factor x in Eq. (5) is on the order of unity].

It seems reasonable that a tunneling contribution would be no larger than about 5% of the total specific heat at the lowest temperatures in view of the excellent Schottky plot, Fig. 3. Using $\epsilon = 12$ (for zircon), $a \simeq 5 \times 10^{-8}$ cm, and arbitrarily setting $n_2 \sim 0.1 n_1$ (the β-alumina case), we find that $n_1 > 3 \times 10^{23}$ cm^{-3} (note that C' varies inversely with n_1). For comparison, $n_1 \simeq 2.5 \times 10^{21}$ cm^{-3} in the β-aluminas.

This estimated limit for ZrO_2:Y_2O_3 is physically unrealistic (there are 2.7×10^{22} molecules/cm^3 in ZrO_2). Two explanations are possible: First, the tunneling term may be absent in anionic conductors. Second, there are strong dipole-dipole interactions between the O^{2-} ions because of the large oxygen polarizability, and these interactions were neglected in deriving the distribution $P(0)$ used here.

In conclusion, the measurements reported here on ZrO_2:Y_2O_3 demonstrate an excess specific heat above 6 K which is similar both in origin and frequency to the Einstein-type excess specific heat found in the β-aluminas. The Schottky contribution below 5 K appears to be a spurious effect due to the hafnia impurity and may be masking a tunneling contribution. If a tunneling term is present in ZrO_2:Y_2O_3, it is certainly much smaller than in the β-aluminas. Specific-heat measurements at much lower temperatures or on hafnia-free zirconia are needed to establish the presence of a tunneling term. Finally, the localized excitations associated with the oxygen vacancies in ZrO_2:Y_2O_3 are in the 10^{11}-Hz range and should be reflected in the thermal conductivity at low temperatures.[14]

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