

# Correlation of spectral and heat-capacity Schottky contributions for $\text{Dy}_2\text{O}_3$ , $\text{Er}_2\text{O}_3$ , and $\text{Yb}_2\text{O}_3$ <sup>a)</sup>

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A self-consistent interpretation of the Raman and infrared spectra and the heat-capacity measurements on  $\text{Dy}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$ , which have the cubic (bixbyite) structure, is presented. New spectra recorded at 10, 80, and 300 °K on oriented single crystals of each oxide are compared with published spectral data and interpretations. Most of the data are consistent with earlier interpretations. However, several additional crystalline-electric-field split levels have been found for ions in the  $C_{3i}$  sites that, together with the established CEF-split levels for ions in the  $C_2$  sites, now provide a total picture for the CEF splitting of the ground-state manifolds. These values allow calculation of the total Schottky contribution to the heat capacity.

Experimental Schottky heat-capacity values are independently derived by the volume-weighted lattice-contribution scheme. Correlation between optical data and heat-capacity measurements is found to be excellent. Further confirmation of the analysis is found in the agreement (to within 3%) between observed and calculated CEF splitting for the lanthanide ions on  $C_2$  sites.

## I. INTRODUCTION

The cubic lanthanide sesquioxides possess two inequivalent cation sites,  $C_2$  and  $C_{3i}$ , the latter with inversion symmetry. They have been of scientific and technological interest for many years in part because the lattice itself is an excellent host material for some of the most powerful lasers built.<sup>1-3</sup> Since the early sixties, lasers have made possible the study of many low probability nonlinear optical phenomena,<sup>4</sup> including vibrational and electronic Raman scattering.<sup>5-7</sup> Coherent, polarized, and tuneable excitation sources permit identification through electronic Raman scattering and double-photon absorption of crystal-field states of lanthanide ions in sites having inversion symmetry.<sup>6-8</sup> Moreover, energy transfer between inequivalent cation sites in the cubic lanthanide sesquioxides has been investigated quantitatively using laser excitation sources.<sup>9</sup>

The Schottky contributions to the heat capacity have been successfully resolved recently by Chirico *et al.* for the lanthanide trihydroxides<sup>10-14</sup> and for the hexagonal lanthanide trichlorides<sup>15</sup> through application of a lattice-heat-capacity approximation technique based on a volume-weighted interpolation between the heat capacities of compounds containing S-type ground states (i. e., interpolated from the  $\text{La}^{+3}$ ,  $\text{Gd}^{+3}$ , and  $\text{Lu}^{+3}$  analogs). In view of these results the heat-capacity data of Justice and Westrum for the lanthanide sesquioxides<sup>16-19</sup> provide an important check on the assignments made to the crystal-field split [SL]  $J$ -levels for lanthanide ions in both  $C_2$  and  $C_{3i}$  cation sites as deduced from Raman and optical spectra.<sup>8, 20-25</sup> Such a check is particularly valu-

able in the interpretation of the Raman scattering experiments, which, in certain cases, exhibit vibrational and electronic spectral peaks of similar magnitude.<sup>8, 23</sup> Moreover, a recent comprehensive study of the  $\text{Ln}^{+3}$  crystal-field splitting of the  $4f^n$  [SL]  $J$ -manifolds in both  $C_2$  and  $C_{3i}$  sites in  $\text{Y}_2\text{O}_3$  provides an additional independent check of the experimentally deduced Stark splittings.<sup>26</sup> In addition, these crystal-field calculations make possible further interpretation or reinterpretation of EPR, Mössbauer, and heat-capacity data.<sup>27-31</sup>

We present a self-consistent interpretation of the Raman and optical spectra with the heat-capacity measurements of concentrated (i. e., 100%)  $\text{Dy}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$ <sup>18</sup> by analyzing unpublished, infrared and electronic Raman scattering data as well as extant data.<sup>20-25</sup> The deduced Stark splitting for both sites are then compared with the crystal-field calculations of Chang, Gruber, Leavitt, and Morrison.<sup>26</sup>

## II. SAMPLE PROVENANCE AND SPECTROSCOPIC TECHNIQUES

Single crystals several cm in length and width and several mm in thickness were cleaved from 6.0 by 1.0 cm rods of oxides (99.99%  $\text{R}_2\text{O}_3$ ) grown by D. M. Johnson at Douglas Aircraft Company, Santa Monica, California, in the mid-sixties using a modified flame-fusion technique. Crystal axes and planes were established using standard x-ray crystallographic techniques. Crystals selected for their size and clarity were further cut and polished. The oxides of Dy, Er, and Yb were found to have the cubic  $C$  (bixbyite) modification ( $T_n^7$ ,  $1a3$ ). The elementary cell contains sixteen formula units with the thirty-two cations distributed 24 in  $C_2$  sites and 8 in  $C_{3i}$  sites. The local axes of the  $C_{3i}$  sites are found in the  $[111]$ ,  $[\bar{1}\bar{1}\bar{1}]$ ,  $[1\bar{1}\bar{1}]$ , and  $[\bar{1}\bar{1}1]$  directions, respectively. The  $C_2$  axes are parallel to  $[100]$ ,  $[010]$ , or  $[001]$ .

Infrared spectra (5 to 400 wave numbers) on powdered

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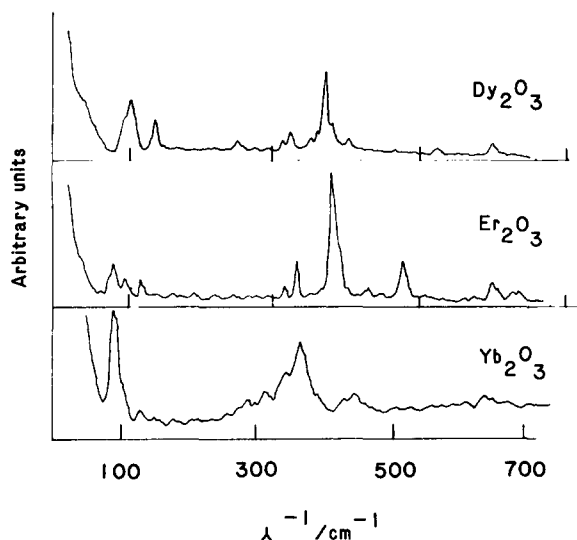


FIG. 1. Raman spectra of Dy<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub> observed at 80 °K. Intensities are relative to each spectrum and incident excitation was chosen so that all Raman-active modes are observable. The horizontal axes for each spectrum (in cm<sup>-1</sup>) increase to the right away from that of the excitation source frequency.

mulls of the oxides were recorded in the mid-seventies by JBG at Washington State University using a Beckman FS-720 Fourier interference spectrophotometer. Samples were cooled to 80 K using a liquid nitrogen conduction dewar. A Cary-14 spectrophotometer and Perkin-Elmer-301 spectrometer recorded single-crystal and powdered mull data between 10 000 and 4000 and between 4000 and 250 cm<sup>-1</sup>, respectively. Samples were cooled to 15 K using a liquid helium conduction dewar. These measurements were recorded by Gruber, Henderson and Muramoto at Douglas Aircraft (later McDonnell Douglas Astronautics) Company, Santa Monica, California between 1965 and 1969. Part of these data, including the single-crystal spectra, were reported earlier.<sup>24,25</sup> The remaining unpublished data are included here since they also aid in the interpretation of the following Raman data and observed Schottky contributions reported earlier by Justice and Westrum.<sup>16-19</sup>

Two-photon absorption and scattering experiments on the oxides of Dy, Er, and Yb were first begun by JBG at Washington State University in 1969 with assistance from Stoner and Olsen<sup>32-34</sup> and continued from 1975 through 1980 at North Dakota State University with assistance from Larson, Daly, and Schmidt.<sup>34-36</sup> Details on the experimental design and early data were first described in 1971 by JBG.<sup>8</sup> Much data were recorded since then but not analyzed. With the recent collaboration involving Leavitt and Morrison,<sup>26</sup> who began to calculate crystal field splittings for the rare earth ions in both C<sub>2</sub> and C<sub>3i</sub> sites, it became possible to identify electronic Raman transitions and thus to once again examine the Schottky contributions to the heat capacity data reported by Justice and Westrum.<sup>16-19</sup>

The Raman scattering experiments reported here follow the approach described earlier by Schaack and Koningstein<sup>22</sup> in the use of symmetry types and choice

of coordination axes. Raman spectra were recorded with a 1.0 m McPherson Czerny-Turner spectrograph, equipped with a 1100 mm<sup>-1</sup> grating. Optical path lengths up to 1.0 cm in oriented crystals could require up to 15 h exposure time in order to pick up weak lines or bands. Measurements were carried out at 10, 80, and 300 K. In addition to the use of a 60 mW helium-neon laser and a 100 mW argon-ion laser, many of the Raman-active vibrational levels could be seen using the traditional A-H6 1 kW high-pressure, mercury arc lamp. The exciting wavelength was selected according to the optical properties of the samples and produced Raman spectra similar to that reported by Schaack and Koningstein<sup>22</sup> and by Lejus and Michel.<sup>23</sup> For that reason we include only a representative figure of the Raman spectra (see Fig. 1) for the reader to compare with similar details appearing in earlier publications.<sup>22,23</sup>

### III. RESULTS OF SPECTRAL STUDIES

Table I presents Raman-active (A<sub>g</sub>, E<sub>g</sub>, and T<sub>g</sub> symmetries) and infrared-active (T<sub>u</sub> symmetry) phonon and electronic transitions for Dy<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub> at 10 K. Symmetry labels for phonon transitions are taken from Schaack and Koningstein<sup>22</sup> and agree with the interpretation of our data. The assignments to electronic transitions Γ<sub>n</sub>(C<sub>2</sub>) and Γ<sub>n</sub>(C<sub>3i</sub>) are based on unpublished infrared and Raman data as well as on the absorption spectra of Dy<sub>2</sub>O<sub>3</sub> reported by Henderson, Muramoto, Henderson, and Gruber<sup>24</sup> and Er<sub>2</sub>O<sub>3</sub> published by Gruber, Henderson, Muramoto, Rajnak, and Conway.<sup>17</sup> The Yb<sub>2</sub>O<sub>3</sub> data have not been reported previously.<sup>35</sup> The electronic Raman scattering data reported here add new information especially regarding Dy<sub>2</sub>O<sub>3</sub> and essentially confirm the previous assignments by Bloor and Dean,<sup>20</sup> by Dean and Bloor,<sup>21</sup> by Schaack and Koningstein,<sup>22</sup> and by Lejus and Michel.<sup>23</sup> In fact, to show the correlation, Table I includes also previously published values (in parentheses) together with our data. A general shift of Raman spectra from approximately 3 to 8 cm<sup>-1</sup> occurs between 10 and 300 K. Electronic Raman lines are generally weak and appear to be more easily detected for ions in C<sub>3i</sub> symmetry than for those in C<sub>2</sub> symmetry. Reasons for these observed intensities have been given earlier.<sup>7,8,37,38</sup>

### IV. THE SCHOTTKY HEAT-CAPACITY CONTRIBUTIONS

Resolution of Schottky contributions in lanthanide compounds requires an evaluation of the much larger "lattice" (vibrational) contribution to the total measured heat capacities. In view of its previous success, the volume-weighted lattice-approximation technique<sup>10-15</sup> has been applied. The lattice heat capacities of the C-type lanthanide sesquioxides may be expressed as

$$C_p(\text{lattice, Ln}_2\text{O}_3) = (1 - f)[C_p(\text{Gd}_2\text{O}_3^*)] + f[C_p(\text{Lu}_2\text{O}_3)], \quad (1)$$

where  $f$  is defined as

$$f(\text{Ln}_2\text{O}_3) = \frac{V(\text{Ln}_2\text{O}_3) - V(\text{Gd}_2\text{O}_3)}{V(\text{Lu}_2\text{O}_3) - V(\text{Gd}_2\text{O}_3)}, \quad (2)$$

TABLE I. Raman and optical spectra for Dy<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>.

Transition	Dy <sub>2</sub> O <sub>3</sub>	Transition	Er <sub>2</sub> O <sub>3</sub>	Transition	Yb <sub>2</sub> O <sub>3</sub>
		$\Gamma_n(C_2)$	38 (39) <sup>a</sup>		
		$\Gamma_n(C_{3i})$	41 (41) <sup>a</sup>		
$\Gamma_n(C_{3i})$	66 (66) <sup>a</sup>	$\Gamma_n(C_2)$	75 (75) <sup>a</sup>		
$\Gamma_n(C_2)$	74 (78) <sup>a</sup>	$\Gamma_n(C_{3i})$	80 (80) <sup>a</sup>		
		$\Gamma_n(C_2)$	88 (89) <sup>a</sup>		
$T_u$	88 (88) <sup>a</sup>	$T_u$	90 (90) <sup>a</sup>	$T_u$	83 (83.2) <sup>b</sup>
$T_u$	98 (96) <sup>a</sup>	$T_u$	96 (95, 97) <sup>a</sup>	$T_u$	90 (90) <sup>a</sup>
$T_g$	101	$T_g$	100 (99.7) <sup>b</sup>	$T_g$	99 (99.2) <sup>b</sup>
		$T_u$	100 (101) <sup>a</sup>		
$T_u$	106	$T_u$	105 (106) <sup>a</sup>	$T_u$	103
$A_g + T_g$	128	$A_g + T_g$	122 (123.2) <sup>b</sup>	$A_g + T_g$	122 (121.0) <sup>b</sup>
$T_u$	129 (128) <sup>a</sup>	$T_u$	128 (128) <sup>a</sup>	$T_u$	125 (125) <sup>a</sup>
$T_u$	135 (134) <sup>a</sup>	$T_u$	135 (134) <sup>a</sup>	$T_u$	134 (132) <sup>b</sup>
$T_u$	146 (146) <sup>a</sup>	$T_u, E_g$	147 (146) <sup>a,c</sup>	$T_u$	140
		$\Gamma_n(C_2)$	159 (165) <sup>a</sup>		
		$\Gamma_n(C_{3i})$	168 (168) <sup>a,c</sup>		
$T_u$	186 (184) <sup>a</sup>	$T_u$	184 (183) <sup>a</sup>	$T_u$	183
$\Gamma_n(C_2)$	261	$\Gamma_n(C_2)$	265 (298) <sup>b</sup>		
				$E_g$	304 (305) <sup>b</sup>
$T_g$	316				
$T_u$	320	$T_g$	322 (322) <sup>c</sup>		
$\Gamma_n(C_{3i})$	326	$\Gamma_n(C_{3i})$	328 (328) <sup>c</sup>		
		$T_u$	334 (335) <sup>b</sup>	$\Gamma_n(C_{3i})$	334 (334) <sup>b</sup>
$E_g$	340	$E_g$	338 (337.9) <sup>b</sup>	$T_u$	341 (341) <sup>b</sup>
$\Gamma_n(C_2)$	355	$T_g$	359 (359) <sup>c</sup>	$A_g + T_g$	359 (358) <sup>b</sup>
		$T_u$	375 (375) <sup>b</sup>		
$T_g$	375	$A_g + T_g(T_g)$	381 (384.1) <sup>b</sup>	$\Gamma_n(C_2), T_u$	388 (388) <sup>b</sup>
$E_g$	386	$E_g$	391 (390) <sup>c</sup>		
		$T_u$	395 (395) <sup>b</sup>		
$T_g$	400	$\Gamma_n(C_{3i})$	405, 416 (417) <sup>c</sup>	$T_u$	405 (405) <sup>b</sup>
$\Gamma_n(C_{3i})$	423			$T_g$	418 (420) <sup>b</sup>
		$T_g$	436 (436) <sup>c</sup>	$T_g$	443 (443) <sup>b</sup>
		$T_u$	475 (475) <sup>c</sup>		
		$T_g; \Gamma_n(C_{3i})$	485 (484) <sup>b</sup>	$T_u$	488 (490) <sup>b</sup>
$\Gamma_n(C_2)$	505	$\Gamma_n(C_2)$	490		
$\Gamma_n(C_{3i})$	512	$\Gamma_n(C_2)$	505		
$T_g$	520				
		$T_u$	566 (565) <sup>b</sup>	$T_u$	570 (573) <sup>b</sup>
		$\Gamma_n(C_{3i})$	580	$\Gamma_n(C_2)$	595 (595) <sup>b</sup>
$\Gamma_n(C_2), T_g$	602	$T_g$	600 (598.3) <sup>b</sup>		
				$T_g$	620 (621) <sup>b</sup>
$\Gamma_n(C_{3i})$	682				
$\Gamma_n(C_2)$	746			$\Gamma_n(C_{3i})$	740
$\Gamma_n(C_{3i})$	834			$T_u$	820
$\Gamma_n(C_{3i})$	965			$\Gamma_n(C_{3i})$	980
				$\Gamma_n(C_2)$	1021

<sup>a</sup>Numbers in parentheses are infrared spectra from Refs. 20 and 21.

<sup>b</sup>Numbers in parentheses are Raman spectra from Ref. 22.

<sup>c</sup>Numbers in parentheses are Raman spectra from Ref. 23; labels  $\Gamma_n(C_2)$  and  $\Gamma_n(C_{3i})$ , refer to Stark level assignments for Ln<sup>3+</sup> ions in C<sub>2</sub> (see Refs. 24, 25) and C<sub>3i</sub> (see Ref. 26) sites, respectively; Raman active ( $A_g$ ,  $E_g$ , and  $T_g$ ) and infrared active ( $T_u$ ) phonon transitions serve as labels for vibrational spectra.

where  $V$  is the molar volume. The superscript in Eq. (1) indicates that the cooperative magnetic contribution to the heat capacity of Gd<sub>2</sub>O<sub>3</sub> has been deleted. This contribution is usually quite small above 10 K in Gd<sup>3+</sup> compounds; however, it is clear from Fig. 2 that it is significant to at least 75 K. Because of this unusually large cooperative magnetic contribution, the lattice contribution calculated from Eq. (1) must be considered less reliable in this temperature region. This is partially offset by the reduced magnitude of the lattice con-

tribution at low temperatures. Although the fractional variations of the lattice contributions across the lanthanide sesquioxides is relatively smaller than it is for the trihydroxides and trichlorides, the maximum difference between the interpolated volume-weighted lattice heat capacity ( $C_p/R$ ) and the linear in atomic number approximation used earlier is approximately 0.1 per mole of Ln<sub>2</sub>O<sub>3</sub>.

The calorimetrically derived Schottky contributions

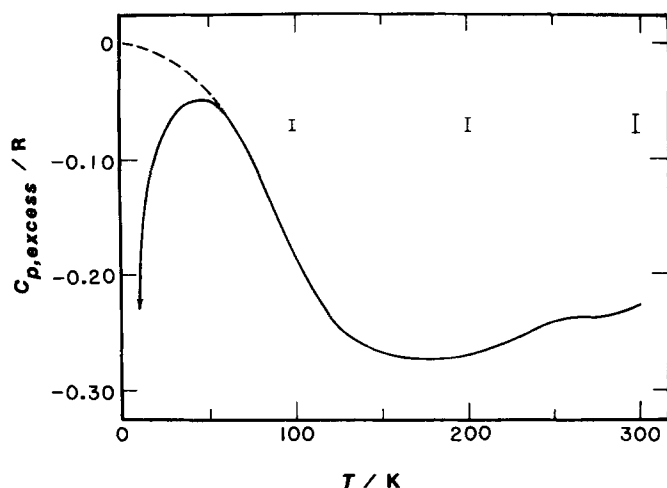


FIG. 2.  $C_p(\text{Lu}_2\text{O}_3) - C_p(\text{Gd}_2\text{O}_3)$ , total —. Estimate of  $C_p(\text{Lu}_2\text{O}_3) - C_p(\text{Gd}_2\text{O}_3)$ , lattice ———.

to the heat capacities of Dy<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub> are represented by the uninterrupted curves in Figs. 3–5, respectively. The error bars in the figures reflect not only the uncertainties in the heat-capacity data but also those in determining the lattice contribution.

## V. INTERPRETATION OF DATA

Table II presents the observed crystalline electric field splitting of the ground state manifold  $[SL]J$  for the ions Dy<sup>3+</sup>(4f<sup>9</sup>), Er<sup>3+</sup>(4f<sup>11</sup>) and Yb<sup>3+</sup>(4f<sup>13</sup>) in both C<sub>2</sub> and C<sub>3i</sub> cation sites in the cubic (bixbyite) lattice of the rare earth oxide R<sub>2</sub>O<sub>3</sub>. The experimental values listed in column 4 are based on the unpublished infrared data appearing in Table I. Assignments to these values have been verified against the references cited in Table I also. In column 7 the experimental values are derived

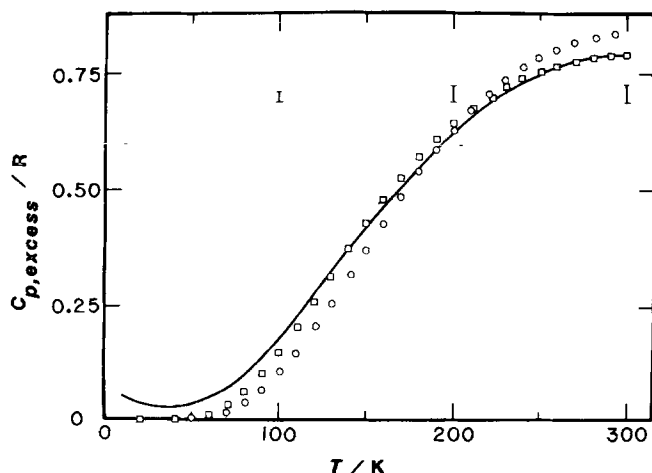


FIG. 3. Calorimetric Schottky contribution, i.e.,  $C_p(\text{Yb}_2\text{O}_3) - [0.90 C_p(\text{Lu}_2\text{O}_3) + 0.10 C_p(\text{Gd}_2\text{O}_3)$ , correction for magnetic ordering] —. Spectroscopic Schottky contributions calculated from Stark levels  $\square\square\square\square$ : C<sub>2</sub>=0, 388, 595, 1021; C<sub>3i</sub>=0, 334, 740, 980. Theoretically derived Schottky contribution with "lattice sum" C<sub>2</sub> levels  $\circ\circ\circ\circ$ : C<sub>2</sub>=0, 469, 567, 996, and C<sub>3i</sub> levels above.

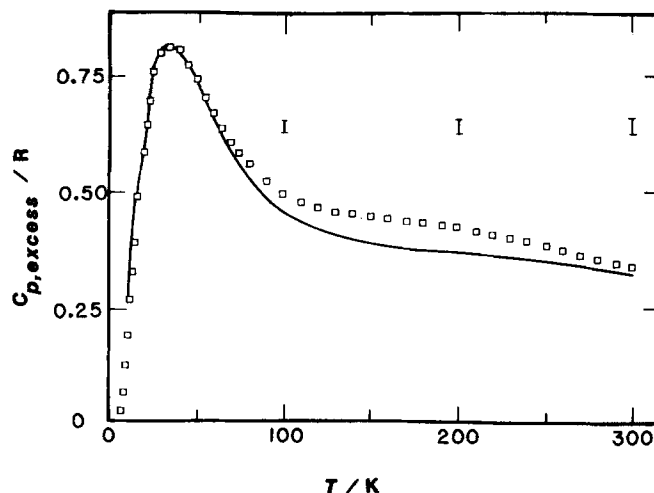


FIG. 4. Calorimetric Schottky contribution, i.e.,  $C_p(\text{Er}_2\text{O}_3) - [0.64 C_p(\text{Lu}_2\text{O}_3) + 0.36 C_p(\text{Gd}_2\text{O}_3)]$  —. Spectroscopic Schottky contribution calculated from Stark levels  $\square\square\square\square$ : C<sub>2</sub>=0, 38, 75, 88, 159, 265, 490, 505; C<sub>3i</sub>=0, 41, 80, 168, 359 (or 328), 416, 485, 580.

from the Raman spectra (see Fig. 1). Identification of levels is based on orientation-dependent studies<sup>22</sup> and agreement with assignments reported elsewhere.<sup>9,22,23</sup>

The calculated Schottky contributions to the heat capacities (represented by Figs. 3 through 5) are based on the levels appearing in columns 5 and 8 in Table II. These values are identical—save for the Z<sub>8</sub> level in Dy<sub>2</sub>O<sub>3</sub>—to the levels identified from the various spectroscopic measurements as Kramers' doublets associated with the CEF splitting of the ground state manifold of the lanthanide ions in both the C<sub>2</sub> and the C<sub>3i</sub> sites. The agreement between spectroscopic and thermal Schottky contribution to the total heat capacity lends assurance to the consistency of assignments to the CEF levels. The Z<sub>8</sub> level at 1080 cm<sup>-1</sup> used in the Schottky calculation for Dy<sub>2</sub>O<sub>3</sub> was observed in the absorption

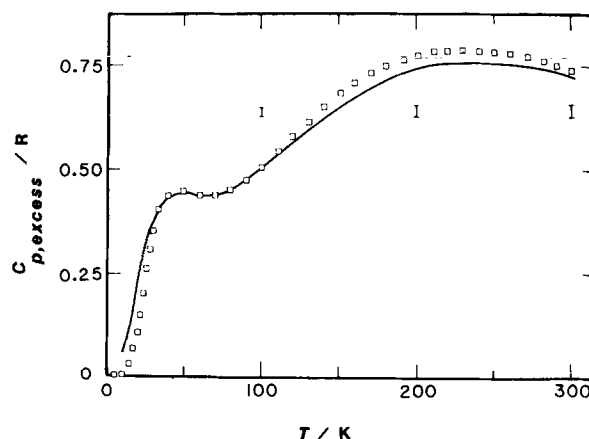


FIG. 5. Calorimetric Schottky contribution, i.e.,  $C_p(\text{Dy}_2\text{O}_3) - [0.36 C_p(\text{Lu}_2\text{O}_3) + 0.64 C_p(\text{Gd}_2\text{O}_3)$ , correction for magnetic ordering] —. Spectroscopic Schottky contribution calculated from Stark levels  $\square\square\square\square$ : C<sub>2</sub>=0, 74, 261, 355, 505, 602, 746, 1080; C<sub>3i</sub>=0, 66, 326, 423, 512, 682, 834, 965.

TABLE II. Stark levels for ground state manifolds: C<sub>2</sub> and C<sub>3i</sub> sites.

Oxide	[SL]J	Z <sub>n</sub>	C <sub>2</sub> sites			C <sub>3i</sub> Sites	
			E (cm <sup>-1</sup> ), Sp. <sup>a</sup>	E (cm <sup>-1</sup> ), Sch. <sup>b</sup>	E (cm <sup>-1</sup> ) calc. <sup>c</sup>	E (cm <sup>-1</sup> ), Sp <sup>d</sup>	E (cm <sup>-1</sup> ), S
Dy <sub>2</sub> O <sub>3</sub>	<sup>6</sup> H <sub>15/2</sub>	1	0	0	0 <sup>e</sup>	0	0
		2	74	74	74	66	66
		3	261	261	263	326	326
		4	355	355	368	423	423
		5	505	505	505	512	512
		6	602	602	606	682	682
		7	746	746	728	834	834
		8	...	1080	830	965	965
Er <sub>2</sub> O <sub>3</sub>	<sup>4</sup> I <sub>15/2</sub>	1	0	0	0 <sup>f</sup>	0	0
		2	38	38	36	41	41
		3	75	75	73	80	80
		4	88	88	89	168	168
		5	159	159	166	328	328
		6	265	265	262	416	416
		7	490	490	485	485	485
		8	505	505	507	580	580
Yb <sub>2</sub> O <sub>3</sub>	<sup>2</sup> F <sub>7/2</sub>	1	0	0	0 <sup>g</sup>	0	0
		2	388	388	410	334	334
		3	595	595	586	740	740
		4	1021	1021	1014	980	980

<sup>a</sup>Assignments based on unpublished infrared data described in text and verified from assignments and spectra reported in references included in Table I.

<sup>b</sup>Energy levels used to calculate the Schottky contribution to the heat capacity appearing in Figs. 3–5.

<sup>c</sup>Energy levels calculated using first-order perturbation theory as described in Refs. 1 and 2. Normalization of CEF parameters follow Wybourne's treatment of crystal-field theory in Ref. 39.

<sup>d</sup>Assignments based on unpublished electronic Raman scattering data described in text and verified from assignment and spectra reported in references included in Table I.

<sup>e</sup> $B(k, m)$ ;  $B(2, 0) = -259.0$ ;  $B(2, 2) = -654.9$ ;  $B(4, 0) = -1384$ ;  $RB(4, 2) = -1410$ ;  $IB(4, 2) = 413.8$ ;  $RB(4, 4) = 835.5$ ;  $IB(4, 4) = -815.3$ ;  $B(6, 0) = 75.10$ ;  $RB(6, 2) = 275.5$ ;  $IB(6, 2) = 22.64$ ;  $RB(6, 4) = 503.1$ ;  $IB(6, 4) = -400.3$ ;  $RB(6, 6) = -6.365$ ;  $IB(6, 6) = -76.10$  all in cm<sup>-1</sup>; standard deviation for 38 levels is 5.6 cm<sup>-1</sup>.

<sup>f</sup> $B(k, m)$ ;  $B(2, 0) = -149.7$ ;  $B(2, 2) = -678.0$ ;  $B(4, 0) = -1389$ ;  $RB(4, 2) = -1061$ ;  $IB(4, 2) = 239.0$ ;  $RB(4, 4) = 712.3$ ;  $IB(4, 4) = -852.4$ ;  $B(6, 0) = 252.1$ ;  $RB(6, 2) = 270.6$ ;  $IB(6, 2) = 119.2$ ;  $RB(6, 4) = 180.0$ ;  $IB(6, 4) = -218.1$ ;  $RB(6, 6) = -23.50$ ;  $IB(6, 6) = -41.58$  all in cm<sup>-1</sup>; standard deviation for 46 levels is 7.9 cm<sup>-1</sup>.

<sup>g</sup> $B(k, m)$ ;  $B(2, 0) = -173.0$ ;  $B(2, 2) = -726.9$ ;  $B(4, 0) = -1118$ ;  $RB(4, 2) = -1066$ ;  $IB(4, 2) = 340.4$ ;  $RB(4, 4) = 529.9$ ;  $IB(4, 4) = -711.1$ ;  $B(6, 0) = 189.4$ ;  $RB(6, 2) = 140.2$ ;  $IB(6, 2) = -30.70$ ;  $RB(6, 4) = 350.3$ ;  $IB(6, 4) = -310.4$ ;  $RB(6, 6) = -106.0$ ;  $IB(6, 6) = -44.75$  all in cm<sup>-1</sup>; standard deviation for 7 levels is 4 cm<sup>-1</sup>.

spectrum of concentrated Dy<sub>2</sub>O<sub>3</sub> by Henderson *et al.*<sup>24</sup> It should be noted that the energy of this level is not in good agreement with the calculated value of 830 cm<sup>-1</sup> (see Table II). The relatively high energy of the Z<sub>8</sub> level together with the high degeneracy of the <sup>6</sup>H<sub>15/2</sub> ground J manifold render the Schottky heat capacity relatively insensitive to the positioning of this level. If the calculated Z<sub>8</sub> energy value had been employed in the Schottky calculation, only a small increase would obtain in the calculated Schottky heat capacity relative to those shown in Fig. 5 above 100 K. The positive deviations of the calorimetrically derived Schottky contributions at low temperatures from those calculated from the spectral data (see Figs. 3–5) are almost certainly due to cooperative magnetic contributions, which are ignored—except in the case of Gd<sub>2</sub>O<sub>3</sub>—in the current treatment. At higher temperatures the deviations rarely exceed the estimated experimental uncertainties.

Projected measurement of the heat capacity of C-type Eu<sub>2</sub>O<sub>3</sub> should provide an improved estimate of the lattice contribution (since there are no magnetic contributions) as well as a reliable check of the resolution of the

Schottky contribution reported here (cf. Ref. 11). Moreover, the absence of very low-lying electronic states (i. e., < 150 cm<sup>-1</sup>) implies that the Schottky contribution is relatively insensitive to small errors in the energies of these sites.

A further confirmation of such assignments is found by comparing the recent crystal-field splitting calculations for these ions in both sites<sup>26</sup> with the reported experimental splittings. Column 6 in Table II presents the calculated CEF splitting for the lanthanide ions in the C<sub>2</sub> sites. The calculations make use of first-order perturbation theory as developed by Judd and Wybourne in the early sixties.<sup>1,39</sup> Normalization of CEF parameters follows Wybourne's treatment<sup>39</sup> of CEF theory. A least-squares fitting of calculated to observed levels has established a set of crystal-field parameters  $B_{n,m}$  for Dy<sup>3+</sup>, Er<sup>3+</sup>, and Yb<sup>3+</sup> in C<sub>2</sub> sites. These parameters are found in footnotes e, f, and g of Table II with a standard deviation for each calculation. A point-charge and dipole lattice sum calculation originally developed by Morrison and Leavitt<sup>40</sup> has been extended to include calculations for ions in both C<sub>2</sub> and C<sub>3i</sub> sites for many of

the expected CEF levels up to 40 000 cm<sup>-1</sup> for all lanthanide ions in the Y<sub>2</sub>O<sub>3</sub> (bixbyite) lattice. Our intent here is simply to indicate that calculations expected to be published soon substantiate the experimental assignments made here. With the agreement between spectroscopic and heat capacity data relevant to Schottky contributions, it now appears that with the aid of the forthcoming lattice-sum calculations, CEF parameters, and wave functions, further interpretation or reinterpretation will be possible for existing and published EPR, Mössbauer, and heat-capacity data on the cubic lanthanide sesquioxides.

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