

ZrTe₅ and HfTe₅: The Heat Capacity and Derived Thermophysical Properties from 6 to 350 K

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The heat capacities of ZrTe₅ and HfTe₅ have been measured by adiabatic shield calorimetry from 6 to 350 K on samples carefully shielded to minimize the contact between the sample and oxygen during all stages of preparation and measurements. Since ZrTe₅ and HfTe₅ are isostructural and their molecular volumes are almost identical, the small differences between their heat capacities are due essentially solely to mass effects. There is absolutely no indication of any excess contribution to the heat capacities of these compounds below 350 K. The effective thermodynamic dimension of ZrTe₅ and HfTe₅ is estimated to be between one and two. The molar heat capacity, entropy, and enthalpy at 298.15 K are 18.32*R*, 31.96*R*, and 4155.7*R* · K for ZrTe₅, and 18.77*R*, 32.99*R*, and 4276.8*R* · K for HfTe₅. © 1989 Academic Press, Inc.

Introduction

In recent years low-dimensional solids have been the subject of growing attention, because such compounds exhibit a series of interesting—as well as useful—properties. Their low dimensionality is a result of high anisotropy in chemical bonding which in turn causes anisotropy in physical properties, such as electrical conductivity, magnetic behavior, etc.

The low-dimensional polytellurides of zirconium and hafnium have a relatively short, but hectic, history. (The prefix poly emphasizes the existence of bonding Te–Te interactions in the structural arrangement.)

ZrTe₃ was first reported by McTaggart and Wadsley (1, 2) in 1958. In an attempt to synthesize HfTe₃, Brattås and Kjekshus (3) initially obtained (in 1971) HfTe₅ which forms much more readily than HfTe₃. Soon afterwards the same authors (4) succeeded in the preparation of ZrTe₅ which is somewhat more difficult to obtain than ZrTe₃. The ease of preparation is accordingly reversed from ZrTe₃ versus ZrTe₅ to HfTe₃ versus HfTe₅.

ZrTe₃ and HfTe₃ crystallize (5) with the ZrSe₃-type structure (6) and ZrTe₅ and HfTe₅ take the HfTe₅-type structure (7, 8). The ZrSe₃- and HfTe₅-type atomic arrangements are indeed very closely related.

Both arrangements contain trigonal prismatic rods as rigid building blocks. In the HfTe_5 -type structure these building blocks are linked together by zigzag chains of tellurium atoms, the latter TeIII arrangement closely resembling the structural building blocks of elementary Te. The coordination around the M ($M = \text{Zr}$ or Hf) atoms is slightly different in the ZrSe_3 - and HfTe_5 -type structures. The coordination polyhedron may in a useful zeroth approximation be regarded as plain and bicapped trigonal prismatic, respectively. Neighboring rods are directly connected to each other in the ZrSe_3 -type structure. The fact that both atomic arrangements, to the zeroth approximation, can be regarded as made up from the thus defined trigonal prismatic rods is clearly reflected in the interatomic distances [292–297 pm for the strongest M -Te bonds and 276–278 pm for the strongest Te-Te bonds within the rods versus 311 and 291 pm, respectively, for the (weaker) rod joints (5–8)]. The conclusions of the bond distance analysis are confirmed and strengthened by Raman spectroscopic studies of single crystal and powder samples of ZrTe_3 , ZrTe_5 , HfTe_3 , and HfTe_5 (9–11).

Hence according to the useful zeroth approximation these compounds can be regarded as pseudo-one-dimensional. An improved approximation takes into account the somewhat weaker bonds which link the trigonal prismatic rods together, and a distinct two-dimensional layer character becomes apparent. Between the layers there are large voids and only van der Waals interactions. An interesting question is, therefore, whether these substances will behave as one-, two-, or three-dimensional solids in the thermodynamic sense.

Much of the excitement about these compounds is occasioned by the observation in 1980 of the so-called giant resistivity anomalies (12–14) in the vicinity of 150 and 80 K for ZrTe_5 and HfTe_5 , respectively. In fact

the anomalies manifest themselves in the various electrical transport properties [viz., in the temperature dependencies of dc and ac resistance, Hall coefficients, and thermoelectric power (12–20)]. The anomalies are also reflected in magnetic susceptibility (15, 16, 21–23) and detected by time-dependent perturbed angular correlation (TDPAC) measurements (24, 25). However, the anomalies could not be confirmed by Raman spectroscopy (10, 11, 26–28), powder X-ray and neutron diffraction (8), or experimental (21, 29) or theoretical (30, 31) studies of electronic band structure. The only structural manifestation of the anomalies is recorded by Skelton *et al.* (17) who reported maxima in the intensity of some *very weak* additional reflections [forbidden in the space group assigned to the HfTe_5 -type structure (7)] at the temperatures concerned. Accurate heat capacity measurements are described herein on well made and carefully characterized ZrTe_5 and HfTe_5 samples to reveal whether or not such anomalies are present. The heat capacity measurements (by a high resolution dc relaxation technique) of Sambongi *et al.* (32) on (orthorhombic single-crystal specimens of) ZrTe_5 leave some vague indications that this could be the case. Excess contributions, amounting to some 2% of the total heat capacity, were observed in the vicinity of 90 and 135 K. The ~ 90 K feature was attributed to a monoclinic phase (32). However, this monoclinic phase was not found by others despite extensive investigations (11, 23–28). [According to Brill and Sambongi (33) there is an anomaly in Young's modulus for ZrTe_5 at ~ 90 K (also ascribed to the monoclinic phase), but this parameter lacks an anomaly at ~ 150 K.] The ~ 135 K feature was assumed (32) to be of the same origin as the anomalies in the electrical transport properties and two different explanations were advanced (both involving changes in the electronic band structure).

Experimental

Sample Provenance and Characterization

Polycrystalline samples of ZrTe₅ and HfTe₅ were synthesized in six batches, each amounting to about 25 g, from the elements (99.9% Zr and Hf, from Koch-Light Laboratories, turnings from crystal bars; 99.999% Te, from Koch-Light Laboratories, lumps). The mixtures of the elements were heated in evacuated, sealed silica-glass tubes. After an initial heat treatment of the compounds at 500°C for 7 days and cooling to room temperature for 1 day, each sample batch was carefully crushed and subjected to two corresponding annealing cycles. The different batches of each compound were finally crushed, mixed, and annealed at 500°C for about 10 days before being cooled to room temperature over a 1-day period. Great care was taken to minimize the contact between the samples and oxygen during all stages of this procedure (34).

Powder X-ray diffraction data for the different samples were collected at room temperature with an 80-mm-diameter Guinier camera, using CuK α_1 radiation and silicon as internal standard, $a(298.15\text{ K}) = 543.1065\text{ pm}$ (35). Unit cell dimensions were derived by the method of least squares using the program CELLKANT (36). The resulting unit cell dimensions are $a = 398.78(5)$, $b = 1453.4(3)$, $c = 1372.8(2)$ pm for ZrTe₅ and $a = 397.09(5)$, $b = 1450.2(3)$, $c = 1372.6(2)$ pm for HfTe₅ and are in excellent agreement with previous results for the two compounds (8).

Calorimetric Technique

The heat capacities of ZrTe₅ and HfTe₅ were measured in a new adiabatic calorimetric cryostat [laboratory designated Mark XIII (37)] over the temperature range 5.3 to 350 K. The same gold-plated, oxygen-free, high-conductivity (OFHC) copper calorimeter (laboratory designation W-139)

was used for both samples. The calorimeter has a mass of 13.21 g and an internal volume of 23 cm³. The temperature of the calorimeter was measured with a Leeds & Northrup platinum encapsulated resistance thermometer in an entrant well. The thermometer was calibrated by the U.S. National Bureau of Standards against IPTS-48 and is considered to reproduce the thermodynamic temperature scale within 0.03 K from 5 to 300 K.

About 62.5 g of ZrTe₅ sample and about 61.8 g of HfTe₅ sample were put in the calorimeter. This represents about 0.086 mole and about 0.0757 mole of ZrTe₅ and HfTe₅, respectively, when 729.224 and 816.5 g · mole⁻¹ are selected as the molar masses. To facilitate rapid thermal equilibration 2.67 and 3.20 kPa at 300 K of helium gas was introduced after evacuation for the ZrTe₅ and the HfTe₅ experiments, respectively. To avoid exposure to oxygen, the loading and the unloading of the calorimeter were performed in an oxygen-free atmosphere of a glove box. At no time was the sample exposed to an atmosphere that contained more than 3 ppm of oxygen. The calorimeter containing each sample was sealed in the inert atmosphere and then reopened on the vacuum line for the evacuation and the introduction of helium. The calorimeter was then sealed, placed in the cryostat, and cooled. The heat capacity of the empty calorimeter represented 10% of the total heat capacity at temperatures below 50 K and about 25 to 30% at higher temperatures.

Results and Discussion

The heat capacity data for ZrTe₅ and HfTe₅ are listed in Table I and plotted in Fig. 1. No special contributions other than that of the lattice contribution are observed in the entire temperature range of the experiments. Thermodynamic functions at selected temperatures for ZrTe₅ and HfTe₅ are listed in Table II. Since the report on

previous determination (32) of the heat capacity for $ZrTe_5$ does not provide numerical molar heat capacity values, comparison of the results of the current study with those of the earlier determination is not feasible.

Thermal equilibrium at the lowest temperatures was difficult to obtain because of low thermal diffusivity within the calorimeter. Since the samples were finely divided powders with very large surface area, much of the helium introduced to enhance thermal diffusivity at low temperatures may have been absorbed on the sample surface,

and hence poor thermal diffusivity occurs. Consequentially the temperature inside the calorimeter was not uniform, the copper calorimeter and the sample portion close to the heater tended to be warmer than the sample portions which were further from the heater or the calorimeter walls. Since adiabatic conditions are hard to maintain at very low temperatures rapid thermal equilibrium is essential to obtain high-quality data. Several attempts to improve the experimental results, during the course of the experiments, were made. No significant im-

TABLE I
MOLAR HEAT CAPACITIES OF ZIRCONIUM AND HAFNIUM PENTATELLURIDES
($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Zirconium pentatelluride, $MW = 729.224 \text{ g} \cdot \text{mole}^{-1}$									
Series I		339.166	18.497	102.069	14.399	93.462	13.877	17.808	1.758
		344.276	18.624	106.143	14.629	98.182	14.155	18.641	1.933
290.458	18.196	347.910	18.541	110.217	14.833	103.128	14.464	19.519	2.121
294.311	18.398			114.299	15.038			20.441	2.324
299.403	18.322	Series II		118.389	15.235	Series V		21.407	2.541
304.482	18.430			122.482	15.419			22.419	2.771
309.564	18.456	162.037	16.673	126.581	15.595	7.344	0.105	23.481	3.018
314.648	18.443	165.943	16.763	130.683	15.768	8.440	0.153	24.594	3.280
319.728	18.442	171.007	16.856	134.790	15.920	8.953	0.298	25.765	3.557
324.788	18.488	176.070	16.959	139.317	16.072	9.664	0.377	26.992	3.851
329.873	18.544	181.135	17.050	144.258	16.212	10.491	0.494	28.278	4.157
334.959	18.588	186.204	17.132	149.193	16.342	11.306	0.628	29.631	4.481
340.067	18.641	191.272	17.198	154.137	16.465	12.178	0.749	31.049	4.820
345.234	18.573	196.340	17.267	159.081	16.596	13.070	0.876	32.537	5.172
248.142	17.880	201.408	17.344	164.030	16.718	13.959	1.026	34.101	5.539
252.644	17.918	206.476	17.405	168.983	16.821			35.743	5.917
257.729	17.931	211.547	17.486			Series VI		37.467	6.302
262.811	18.011	216.622	17.560	Series IV				39.280	6.694
267.895	18.045	221.694	17.619			6.001	0.054	41.185	7.093
272.974	18.082	226.776	17.679	50.390	8.860	6.562	0.080	43.187	7.499
278.049	18.147	231.859	17.733	52.181	9.167	7.270	0.121	45.005	7.859
283.144	18.206	236.936	17.773	54.768	9.598	7.963	0.179	46.926	8.230
288.227	18.241	242.018	17.819	57.470	10.004	8.658	0.263	49.228	8.657
293.314	18.250	247.101	17.861	60.306	10.445	9.295	0.352	51.641	9.074
298.400	18.289	252.184	17.916	63.287	10.871	10.031	0.456	54.177	9.503
303.486	18.401	257.267	17.927	66.422	11.281	10.957	0.579	56.846	9.911
308.584	18.386	262.338	17.988	69.725	11.656	11.966	0.672	59.649	10.344
313.673	18.440			73.201	12.031	12.976	0.870	62.595	10.776
318.768	18.430	Series III		76.855	12.417	13.918	1.027	65.694	11.192
323.860	18.485			80.697	12.805	14.922	1.204	68.959	11.574
328.951	18.528	94.743	13.951	84.734	13.193	15.903	1.384	72.397	11.948
334.050	18.580	97.988	14.143	88.984	13.552	16.903	1.577	76.025	12.218

TABLE I—Continued

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Hafnium pentatelluride, MW = 816.5 g · mole ⁻¹									
Series I		Series II		10.144	0.487	52.542	9.655	118.308	15.736
				11.053	0.591	55.922	10.238	123.407	15.953
223.506	18.065	5.767	0.026	12.114	0.767	59.327	10.775	128.515	16.161
229.343	18.114	6.367	0.048	13.200	0.932	62.987	11.310	133.634	16.347
235.560	18.193	6.934	0.074	14.308	1.129	66.901	11.854	138.762	16.515
241.782	18.243	7.589	0.137	15.552	1.364	70.836	12.324	143.897	16.665
247.998	18.255	8.143	0.211	16.928	1.636	75.046	12.770	149.035	16.801
254.216	18.302	8.682	0.247	18.324	1.924	79.511	13.243	154.436	16.930
260.435	18.371	9.337	0.301	19.743	2.231	83.991	13.682	160.100	17.070
266.643	18.446	10.063	0.466	21.171	2.551			165.765	17.196
272.851	18.517	10.975	0.583	22.746	2.919	Series IV		171.429	17.314
279.066	18.555	11.984	0.745	24.459	3.330			177.104	17.421
285.277	18.612	13.062	0.910	26.183	3.749	68.498	12.055	182.786	17.530
291.491	18.676	14.294	1.127	27.926	4.181	72.438	12.503	188.464	17.615
297.688	18.772	15.644	1.382	29.817	4.652	76.413	12.910	194.143	17.710
303.897	18.848			31.850	5.162	80.402	13.337	199.834	17.790
310.111	18.901	Series III		33.895	5.668	84.650	13.744	205.527	17.862
316.333	18.930			36.139	6.210	89.160	14.117	211.472	17.934
322.548	18.980	6.848	0.032	38.577	6.783	93.690	14.433	217.678	18.004
328.758	19.030	7.572	0.126	41.030	7.337	98.241	14.713	223.884	18.064
335.012	19.102	8.015	0.189	43.686	7.912	103.056	14.987	230.097	18.126
341.393	19.137	8.507	0.365	46.542	8.510	108.129	15.254	236.305	18.211
347.634	19.145	9.277	0.279	49.416	9.081	113.213	15.504	242.508	18.293

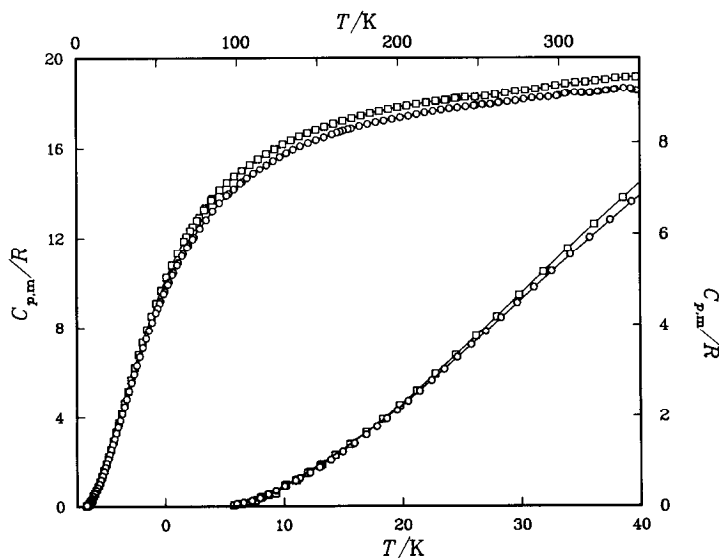
FIG. 1. Molar heat capacities of ZrTe₅ (○) and HfTe₅ (□).

TABLE II
THERMODYNAMIC PROPERTIES AT SELECTED TEMPERATURES FOR ZIRCONIUM AND HAFNIUM
PENTATELLURIDES ($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$)

T/K	$C_{p,m}^{\circ}/R$	$\Delta_0^T S_m^{\circ}/R$	$\Delta_0^T H_m^{\circ}/R \cdot K$	$\Phi_m^{\circ}(T, 0)/R$	T/K	$C_{p,m}^{\circ}/R$	$\Delta_0^T S_m^{\circ}/R$	$\Delta_0^T H_m^{\circ}/R \cdot K$	$\Phi_m^{\circ}(T, 0)/R$
Zirconium pentatelluride					Hafnium pentatelluride				
0	0.0	0.0	0.0	0.0	0	0.0	0.0	0.0	0.0
10	0.437	0.121	0.921	0.029	10	0.431	0.102	0.806	0.021
15	1.214	0.438	4.955	0.107	15	1.260	0.428	4.960	0.097
20	2.227	0.921	13.474	0.247	20	2.287	0.926	13.742	0.239
25	3.375	1.540	27.445	0.442	25	3.461	1.561	28.077	0.438
30	4.570	2.260	47.302	0.684	30	4.698	2.300	48.455	0.685
35	5.747	3.054	73.11	0.965	35	5.939	3.118	75.00	0.974
40	6.847	3.894	104.64	1.278	40	7.105	3.988	107.71	1.296
45	7.858	4.759	141.43	1.617	45	8.192	4.889	145.98	1.645
50	8.791	5.637	183.10	1.975	50	9.190	5.804	189.48	2.015
60	10.402	7.386	279.29	2.731	60	10.879	7.636	290.19	2.799
70	11.692	9.090	390.03	3.519	70	12.219	9.417	405.91	3.618
80	12.740	10.722	512.3	4.318	80	13.303	11.122	533.7	4.451
90	13.610	12.275	644.2	5.116	90	14.157	12.740	671.2	5.283
100	14.284	13.745	783.9	5.907	100	14.822	14.268	816.2	6.105
110	14.821	15.13	929.5	6.683	110	15.360	15.71	967.2	6.914
120	15.300	16.44	1080.1	7.442	120	15.810	17.06	1123.1	7.703
130	15.740	17.69	1235.4	8.183	130	16.210	18.34	1283.3	8.473
140	16.090	18.87	1394.6	8.904	140	16.550	19.56	1447.1	9.222
150	16.370	19.99	1557.0	9.606	150	16.830	20.71	1614.0	9.950
160	16.610	21.05	1721.9	10.288	160	17.070	21.80	1783.6	10.657
170	16.840	22.06	1889.2	10.951	170	17.280	22.85	1955.4	11.343
180	17.040	23.03	2058.7	11.596	180	17.470	23.84	2129.2	12.010
190	17.190	23.96	2229.8	12.222	190	17.640	24.79	2304.7	12.658
200	17.310	24.84	2402.3	12.831	200	17.790	25.70	2481.9	13.287
210	17.450	25.69	2576.2	13.424	210	17.920	26.57	2660.5	13.899
220	17.600	26.51	2751.4	14.000	220	18.030	27.40	2840.3	14.494
230	17.720	27.29	2928.1	14.561	230	18.130	28.21	3021.1	15.07
240	17.810	28.05	3105.8	15.11	240	18.210	28.98	3202.8	15.64
250	17.880	28.78	3284.2	15.64	250	18.290	29.73	3385.3	16.19
260	17.970	29.48	3463.4	16.16	260	18.370	30.45	3568.7	16.72
270	18.080	30.16	3643.7	16.66	270	18.460	31.14	3752.8	17.24
280	18.160	30.82	3824.9	17.16	280	18.570	31.81	3938.0	17.75
290	18.230	31.46	4006.8	17.64	290	18.680	32.47	4124.2	18.25
298.15	18.320	31.96	4155.7	18.02	298.15	18.770	32.99	4276.8	18.64
300	18.350	32.08	4189.6	18.11	300	18.790	33.10	4311.6	18.73
310	18.440	32.68	4373.6	18.57	310	18.890	33.72	4500.0	19.20
320	18.450	33.27	4558.1	19.02	320	18.970	34.32	4689.3	19.67
330	18.530	33.83	4743.0	19.46	330	19.050	34.91	4879.4	20.12
340	18.640	34.39	4929.0	19.89	340	19.120	35.48	5070.	20.56
350	18.540	34.93	5115.	20.31	350	19.160	36.03	5262.	21.0

provement was noted as a result of these attempts. The data reported in Tables I and II are the best data that could be obtained from our experiments. Above about 11 K

these problems disappeared completely and the thermal equilibration time was reduced to 15 min on the average.

The thermodynamic functions were eval-

uated by extrapolating the experimental heat capacity curves to 0 K and by integrating with the computer program FITAB-2 (38). The extrapolation for $ZrTe_5$ was from 6.0 to 0 K and the resultant entropy and enthalpy at 10 K are $0.121R$ and $0.92R \cdot K$, respectively. The extrapolation for $HfTe_5$ was from 5.8 to 0 K and at 10 K the resultant entropy and enthalpy are, respectively, $0.102R$ and $0.81R \cdot K$.

For both compounds the experimental results at temperatures higher than 11 K are very good and the heat capacity curves are smooth and nearly similar over the entire range. No anomalous behavior can be identified in either compound at any temperature. All the points that were used for the calculation of thermodynamic functions fit the integrated polynomial within the experimental error ($\pm 0.1\%$ for temperatures larger than 15 K). The experimental heat capacity for $HfTe_5$, however, is larger than that for $ZrTe_5$ at temperatures above 10 K. Since the two major factors that affect lattice heat capacity are the molar volumes [as demonstrated by the volumetric theory (39, 40)] and the molar masses of the lattice components, this result is to be expected because the atomic mass of hafnium is about twice as large as that of zirconium and their radii are almost identical as a consequence of the "lanthanide contraction". These phenomena make Hf and Zr candidates for examination of the contributions due to mass effects on thermodynamic properties (in some respects these materials are more suitable than isotopes for such

studies because of the larger mass difference). The compound with the larger molar mass is expected to reach the Dulong–Petit limit at lower temperatures, if all other factors remain the same. (Other factors may include vibrational characteristics, structural details, etc.) The mass effect on the heat capacities of $ZrTe_5$ and $HfTe_5$ is illustrated in Fig. 1, where the curve for $HfTe_5$ is above that for $ZrTe_5$ for all temperatures higher than 10 K. Since the compounds are isostructural and their molar volumes are almost identical, the differences in their heat capacities (ca. 3%) is entirely a mass effect.

To examine the experimental results in greater detail the heat-capacity data were fitted by the recently developed Komada–Westrum model (41) for evaluation of lattice heat capacity. This model, which is computer-aided, calculates an approximation to the phonon density of states function, based upon the lattice heat capacity and several parameters of physical origin. The approximated density of states function is then used to calculate an apparent characteristic temperature, Θ_{KW} , for the substance. Once Θ_{KW} is established, an estimated lattice heat-capacity value for any given temperature can be calculated. For both $ZrTe_5$ and $HfTe_5$ the Θ_{KW} 's are reasonably constant between 20 and 250 K (Fig. 2). This result illustrates that the lattice is the sole contributor to the observed heat capacity over that region. Hence if the reported anomalies in physical properties are present in our samples of $ZrTe_5$ and $HfTe_5$

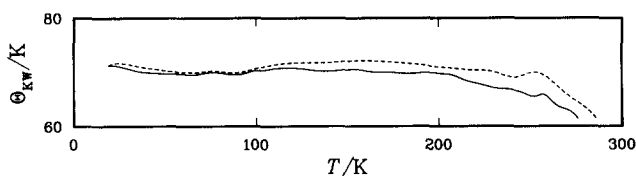


FIG. 2. Apparent characteristic temperatures Θ_{KW} for $ZrTe_5$ (—) and $HfTe_5$ (---). Θ_{KW} starts to drop at high temperatures as the heat capacity approaches (and eventually exceeds) the Dulong–Petit limit (see text).

they do not produce heat-capacity anomalies. There is certainly no evidence for a Schottky contribution in any temperature region for either compound. The possibility of structural phase transitions is also ruled out by the present results in combination with the earlier findings (8, 10, 11, 26–28). This conclusion is further supported by the smoothness of the heat-capacity curves throughout the entire temperature range studied. It is, therefore, not clear why Sambongi *et al.* (32) observed anomalous heat-capacity contributions for ZrTe_5 , but it is tempting to question whether these experiments were performed on contaminated samples, whether gas absorption may change the physical parameters, etc. At temperatures larger than 250 K, the Komada–Westrum approximation, with C_p as input instead of C_V , is no longer applicable because the measured values exceed the Dulong–Petit limit.

Close investigation of the low-temperature portion of the heat-capacity curves does not reveal the familiar Debye-like be-

havior. In an attempt to characterize the electronic contribution to the low-temperature heat capacity, C_p/T versus T^2 and C_p/T versus T plots were drawn (Fig. 3). The experimental data are clearly not linear against either T , T^2 , or T^3 . Extrapolation of either curve in Fig. 3 to 0 K gives a negative intercept. The low-temperature heat capacity is seen to be larger than expected according to the Debye model. This variance explains the nonlinearity and wavelike appearance of Θ_{KW} at low temperatures since the Komada–Westrum (41) model is consistent with Debye behavior at low temperatures. Such behavior at low temperatures is, however, not to be expected for low-dimensional solids such as ZrTe_5 and HfTe_5 .

The nonlinearity of the heat capacities with T^3 at low temperatures (Fig. 3) confirms that ZrTe_5 and HfTe_5 are not three-dimensional, and as already pointed out the heat capacities of the compounds are not linear against either T^2 or T . As evident from Fig. 1 the C_p curves are concave up-

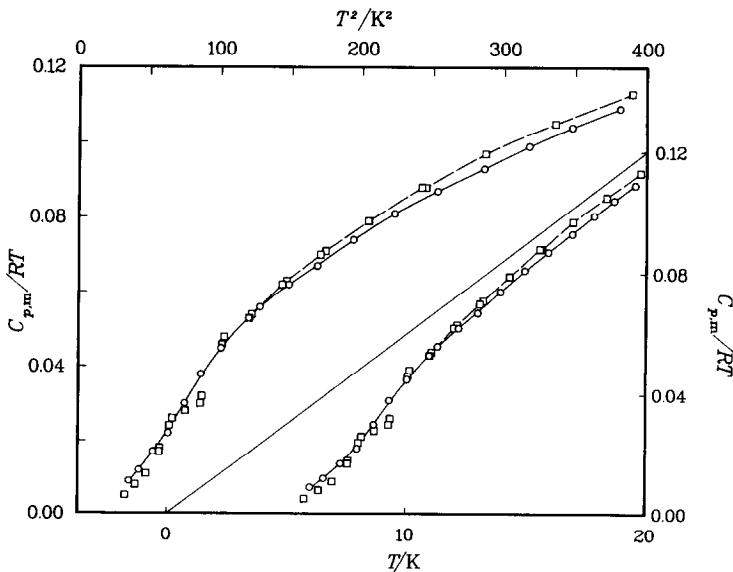


FIG. 3. $C_{p,m}/R \cdot T$ versus T^2 and $C_{p,m}/R \cdot T$ versus T between 0 and 20 K for ZrTe_5 (○) and HfTe_5 (□).

ward at the low-temperature end. Figure 3 shows that C_p/T is concave downward over the same temperature region. The effective thermodynamic dimension of ZrTe₅ and HfTe₅ is, therefore, somewhere between one and two, which is consistent with the structures of these compounds.

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