

Heat capacity and thermodynamic properties of thallose fluoride from 5 to 445 K†

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The heat capacity of TlF has been determined from 6 to 445 K. The nature of the structural transition at 356.3 K, and the excess entropy found ($0.225 \text{ cal K}^{-1} \text{ mol}^{-1}$, in reasonable accord with that of Cubicciotti and Eding) are discussed. The derived thermodynamic functions permit a re-evaluation of the thermodynamics of the gaseous system, give better concordance with spectroscopic data, and yield a Gibbs energy of formation:

$$\Delta G_f^\circ(298.15 \text{ K}) = -(72.8 \pm 0.1) \text{ kcal mol}^{-1}.$$

1. Introduction

The monofluorides of thallium, potassium, rubidium, cesium, and silver constitute a class of binary fluorides for which CsCl-type structures would be expected if the radius-ratio criterion obtained. However, all have NaCl-type structures except TlF which has an orthorhombically distorted variant.⁽¹⁻⁴⁾ Moreover, orthorhombic TlF is reported to be a soft plastic phase⁽⁴⁾ which transforms at 355 K⁽⁵⁻⁷⁾ to a tetragonal lattice, i.e. a less distorted variant of the NaCl structure.^(4, 6, 8) Despite the lower symmetry of TlF and the uncertainty as to the exact nature of the distortion of the lower-temperature structure, a heat capacity determination of the deviation from the harmonic model of lattice vibrations is of great interest because of the extremely large disparity in ion masses. Intermediate-temperature adiabatic calorimetry permits delineation of the nature of the small lattice transformation already detected by enthalpy increment determination.⁽⁵⁾

2. Experimental

LOW-TEMPERATURE DETERMINATIONS

These measurements were made in the previously described Mark II adiabatic cryostat⁽⁹⁾ with a gold-plated copper calorimeter (laboratory designation W-42, about 93 cm^3 capacity). Temperatures determined with a capsule-type, platinum-resistance thermometer (laboratory designation A-5) are considered to be in accord with the thermodynamic temperature scale within 0.03 K from 10 to 90 K and within 0.04 K

† This work was performed under the auspices of the U.S. Atomic Energy Commission.

from 90 to 350 K. The heat capacity of the empty calorimeter was determined separately with appropriate small corrections for the slight differences in the amounts of helium and Apiezon-T grease on the loaded and on the empty calorimeter. The heat capacity of the sample varied between 98 and 82 per cent of the total. The calorimetric sample had a mass of 404.38 g, buoyancy corrections having been made on the basis of a density of 8.36 g cm^{-3} .⁽¹⁰⁾ Helium gas (about 101 Torr at 300 K) was used to enhance thermal contact between calorimeter and sample.†

HIGHER-TEMPERATURE DETERMINATIONS

These were made in the intermediate-range Mark IV calorimetric apparatus⁽¹¹⁾ with silver calorimeter W-22. Measurements on the 349.03 g calorimetric sample were made only to 445 K because tests indicated that the sample would be corrosive in the fusion region. Approximately 74 per cent of the total heat capacity was that of the sample. All determinations of mass, potential, current, time, and temperature over both ranges are ultimately based upon calibrations by the National Bureau of Standards.

PREPARATION AND PURITY OF SAMPLE

For this study, thallos fluoride was supplied by Dr D. Cubicciotti of the Stanford Research Institute. The preparation and analysis of the finely-divided calorimetric sample was described in detail by Keneshea and Cubicciotti.⁽¹²⁾ Three thallium analyses of the sample by the modified chromate method gave results of (91.57 ± 0.08) mass per cent of Tl (theoretical, 91.49 mass per cent of Tl). No ion peaks corresponding to species containing hydrogen were reported by the above authors in the mass spectrometric vaporization studies. Final confirmation of purity must await fractional fusion of the calorimetric sample (preferably in platinum).

3. Thermal properties

The experimental heat capacities for thallos fluoride are presented in chronological sequence at the mean temperatures of determination in table 1. Temperature increments employed in the measurements may usually be inferred from the differences in the adjacent mean temperatures. These results have been adjusted for "curvature" occasioned by the finite temperature increments employed in the measurements and are considered to have a probable error which decreases from about 3 per cent at 5 K to 0.5 per cent at 10 K and to less than 0.1 per cent above 20 K. All the results presented herein are based upon a defined thermochemical calorie of 4.184 J, an ice temperature of 273.15 K, and a molar mass of $223.3684 \text{ g mol}^{-1}$ for TlF. Results from several series of determinations taken to ascertain the enthalpy increment through the transition region have been summarized in table 2.

The smoothed heat capacities and thermodynamic functions obtained by integrating these results with a high-speed digital computer are given in table 3 at selected temperatures. The heat capacities in this table were taken from a smooth curve which was obtained by a least-squares fit of a polynomial to the experimental points. The

† Throughout this paper $\text{cal} = 4.184 \text{ J}$, $\text{Torr} = (101.325/760) \text{ kN m}^{-2}$, $\text{Å} = 0.1 \text{ nm}$.

thermodynamic functions have a probable error of less than 0.1 per cent above 100 K. An additional digit beyond those significant is given in table 3 for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin or for isotopic mixing contributions and are hence practical values for use in chemical thermodynamic calculations.

Figure 1 presents the low-temperature heat capacity of TlF together with smooth curves for CsF,⁽¹³⁾ KF,⁽¹⁴⁾ and NaF.⁽¹⁵⁾ Relative to these other fluorides, the lower-temperature portion of the curve for TlF appears quite normal. However, above 150 K the curve appears to deviate markedly from that of CsF as if a premonitory transitional or anharmonic contribution were involved. Above 220 K a significant deviation beyond the harmonic limit of $6R$ begins to appear.

TABLE 1a. Heat capacity of thallos fluoride in Mark IV cryostat

$\langle T \rangle$ K	ΔT K	C_p cal K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	ΔT K	C_p cal K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	ΔT K	C_p cal K ⁻¹ mol ⁻¹
		Series I	343.06	10.04	13.37			Series X
304.05	5.83	12.84	349.07	1.99	13.48	354.32	3.19	15.31
310.62	7.31	12.93	351.05	1.98	13.53	356.13	0.42	150
			353.67	3.27	13.65	357.70	2.71	18.8
		Series II	355.69	0.78	42	359.36	0.62	12.95
			356.17	0.17	200	359.98	0.63	12.89
320.72	10.28	13.03	356.66	0.78	42	360.60	0.62	13.06
330.94	10.18	13.18	358.05	2.00	13.29	361.22	0.63	12.82
341.05	10.06	13.35	360.07	2.04	12.94	361.85	0.63	12.97
351.00	9.84	13.72	362.10	2.05	12.82			
359.02	6.23	24.38	364.15	2.05	12.86			
367.09	9.91	13.54						Series XI
		Series III		Series VII		361.98	0.63	12.78
329.75	5.65	13.11	404.67	10.03	13.22	362.61	0.63	12.76
334.38	5.53	13.17	414.65	9.96	13.31	363.23	0.64	12.66
339.98	5.59	13.28	424.57	9.90	13.40	363.85	0.62	12.90
345.54	5.55	13.39	434.43	9.83	13.49	364.47	0.62	12.98
351.06	5.51	13.49	444.21	9.78	13.57	365.09	0.63	12.94
						365.72	0.62	13.04
						366.34	0.62	12.92
		Series IV		Series VIII				Series XII
353.98	3.89	17.63	356.12	0.13	34			
356.33	0.81	81	356.21	0.04	122	365.17	1.43	12.88
358.67	3.85	13.31	356.25	0.04	103	366.60	1.43	12.84
362.55	3.96	12.87	356.29	0.04	154	368.01	1.42	12.95
			356.32	0.04	121	369.42	1.41	12.94
		Series V	356.37	0.06	80	370.84	1.42	12.91
374.45	10.20	12.99				372.25	1.42	13.00
384.60	10.13	13.08						
394.71	10.09	13.14						
404.75	10.03	13.23	356.12	8.36	23			Series XIII
			362.76	4.95	12.92	324.45	9.36	13.08
			367.06	3.66	12.92	333.75	9.27	13.22
		Series VI	370.71	3.65	12.94	342.97	9.17	13.38
335.02	2.02	13.21	374.35	3.64	13.00			
337.04	2.02	13.18	377.99	3.63	13.00			

TABLE 1b. Heat capacity of thallos fluoride in Mark II cryostat

$\langle T \rangle$ K	C_p cal K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal K ⁻¹ mol ⁻¹	$\langle T \rangle$ K	C_p cal K ⁻¹ mol ⁻¹
	Series I	312.47	12.92	19.17	2.359	26.51	3.471
114.64	9.995	322.09	13.03	20.85	2.636	29.09	3.814
125.93	10.36	331.59	13.15			31.88	4.169
141.59	10.77	340.98	13.28			34.93	4.538
156.93	11.09					38.32	4.925
166.01	11.25					42.29	5.349
175.33	11.41		Series II	5.29	0.111	46.78	5.807
184.89	11.54	5.53	0.130	6.29	0.183	51.52	6.267
194.32	11.67	6.08	0.167	7.27	0.289	56.55	6.716
203.65	11.78	6.97	0.260	8.28	0.430	62.41	7.219
213.15	11.90	7.85	0.367	9.38	0.625	69.03	7.714
222.99	12.01	8.59	0.488	10.48	0.816	75.90	8.172
232.89	12.12	9.33	0.615	11.64	0.993	83.45	8.652
242.69	12.22	10.22	0.779	12.82	1.209	91.67	9.083
252.60	12.32	11.28	0.931	13.96	1.428	100.29	9.454
262.62	12.41	12.39	1.125	15.16	1.653	109.43	9.814
272.69	12.51	13.52	1.341	16.54	1.899	119.36	10.15
282.82	12.62	14.71	1.568	18.12	2.177	129.69	10.46
292.83	12.72	16.04	1.813	19.84	2.470	139.73	10.72
302.71	12.82	17.56	2.083	21.74	2.772	149.54	10.94
				24.00	3.117		

TABLE 2. Enthalpy of transition determinations

T_1 K	T_2 K	$H(T_2) - H(T_1)$ cal mol ⁻¹	$H(370 \text{ K}) - H(332 \text{ K})$ cal mol ⁻¹
347.55	363.85	294.30	580.34
348.00	364.18	292.40	580.23
347.65	363.83	292.30	580.07
348.42	367.66	331.90	580.44
348.01	367.27	331.78	579.70
340.20	359.67	338.81	580.95

Average value : 580.3 ± 0.4

$$\begin{aligned} \{H^\circ(370 \text{ K}) - H^\circ(332 \text{ K})\}(\text{lattice})/\text{cal mol}^{-1} &= 500.0 \\ \Delta H_t/\text{cal mol}^{-1} &= 80.3 \pm 0.5 \\ T_t &= 356.3 \text{ K} \\ \Delta S_t/\text{cal K}^{-1} \text{ mol}^{-1} &= 0.225 \pm 0.001 \\ \Delta C_{p,t}(\text{lattice})/\text{cal K}^{-1} \text{ mol}^{-1} &= -0.67 \end{aligned}$$

TABLE 3. Thermodynamic functions for thallos fluoride

$\frac{T}{K}$	C_p cal K ⁻¹ mol ⁻¹	S° cal K ⁻¹ mol ⁻¹	$H^\circ(T) - H^\circ(0)$ cal mol ⁻¹	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal K ⁻¹ mol ⁻¹
5	0.096	0.032	0.118	0.008
10	0.722	0.252	1.886	0.064
15	1.613	0.711	7.696	0.198
20	2.501	1.300	18.030	0.398
25	3.253	1.940	32.451	0.642
30	3.931	2.594	50.439	0.913
35	4.546	3.247	71.656	1.200
40	5.111	3.891	95.818	1.496
45	5.635	4.524	122.70	1.797
50	6.124	5.143	152.11	2.101
60	7.009	6.340	217.9	2.709
70	7.781	7.480	291.9	3.310
80	8.441	8.563	373.1	3.899
90	8.995	9.590	460.4	4.475
100	9.457	10.562	552.7	5.036
110	9.843	11.482	649.3	5.580
120	10.173	12.354	749.4	6.109
130	10.462	13.179	852.6	6.621
140	10.720	13.964	958.5	7.118
150	10.951	14.712	1066.9	7.599
160	11.155	15.43	1177.4	8.066
170	11.333	16.11	1289.9	8.519
180	11.485	16.76	1404.0	8.959
190	11.618	17.38	1520	9.386
200	11.736	17.98	1636	9.801
210	11.849	18.56	1754	10.205
220	11.963	19.11	1873	10.597
230	12.079	19.65	1994	10.979
240	12.194	20.16	2115	11.351
250	12.304	20.66	2237	11.713
260	12.404	21.15	2361	12.067
270	12.492	21.62	2485	12.412
280	12.577	22.07	2611	12.749
290	12.670	22.52	2737	13.078
300	12.782	22.95	2864	13.400
320	13.034	23.78	3122	14.023
340	13.287	24.58	3385	14.620
350	13.50	24.96	3519	14.905
356.3	^a (200)	25.20	3603	15.09
356.3	^a (200)	25.43	3683	15.09
360	13.11	25.56	3731	15.20
380	13.02	26.26	3990	15.76
400	13.19	26.93	4252	16.30
273.15	12.52	21.76	2525	12.52
298.15	12.76	22.87	2841	13.34

^a Assuming the transition to be entirely isothermal.

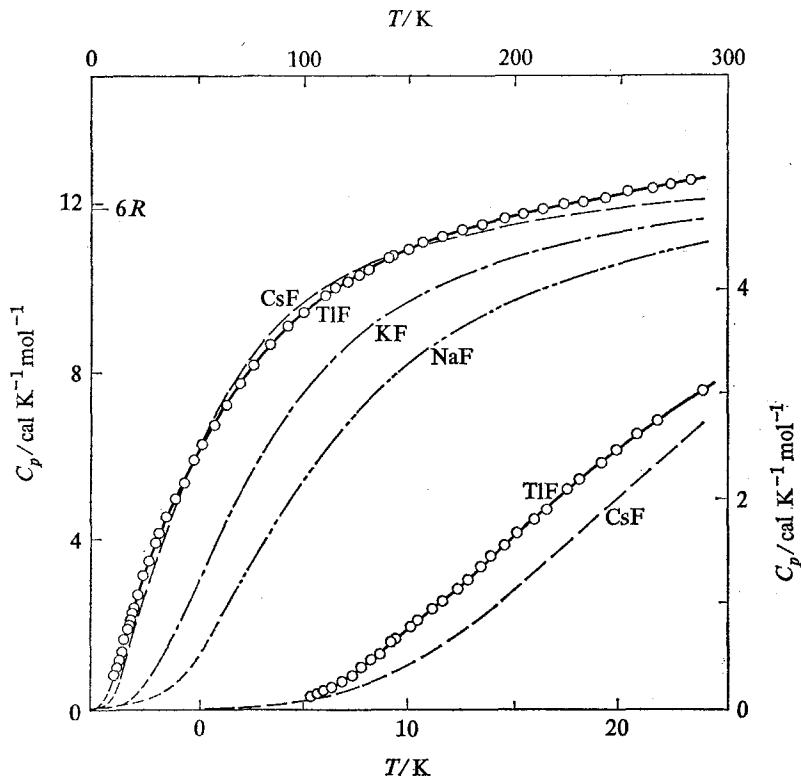


FIGURE 1. Low-temperature heat capacities of TlF and (nearly isostructural) alkali fluorides. The curve $\text{---}\circ\text{---}\circ\text{---}\circ\text{---}\circ\text{---}$, represents the experimental values for TlF; --- , the smoothed curve for CsF;⁽¹³⁾ $\text{---}\cdot\text{---}\cdot\text{---}\cdot\text{---}\cdot\text{---}$, the curve for KF;⁽¹⁴⁾ and $\text{---}\cdot\text{---}\cdot\text{---}\cdot\text{---}$, the curve for NaF.⁽¹⁵⁾ Extrapolations are represented by dotted lines.

A small but abrupt transition occurs at 356.3 K at which the lower-temperature crystal II phase (orthorhombic) undergoes transformation to the crystal I phase (tetragonal). Our results in this region are depicted in figure 2. The transition shows a slight premonitory rise prior to the relatively sharp peak with a heat capacity greater than $200 \text{ cal K}^{-1} \text{ mol}^{-1}$. On cooling at a rate of 2 K min^{-1} the major break in the cooling curve occurs at 353 K and may represent the temperature at which the rate of transformation is greatest. From the enthalpy increments summarized in table 2, we calculate $\Delta H_t = (80.3 \pm 0.5) \text{ cal mol}^{-1}$ and $\Delta S_t = (0.225 \pm 0.001) \text{ cal K}^{-1} \text{ mol}^{-1}$ on the basis of lattice heat capacities obtained by smooth extrapolations of the curves for crystal phases I and II of TlF. The position of these curves on figure 2 may be deduced from $\Delta C_{p,t}(\text{lattice})$ in table 2. High-temperature enthalpy determinations have also been reported by Cubicciotti and Eding.⁽⁵⁾ Their heat capacity equation derived by differentiation of their enthalpies for crystal II phase is:

$$C_p/\text{cal K}^{-1} \text{ mol}^{-1} = 12.31 + 2.62 \times 10^{-3}(T/\text{K}).$$

They also reported the existence of a small transition at a temperature of $(355 \pm 1) \text{ K}$

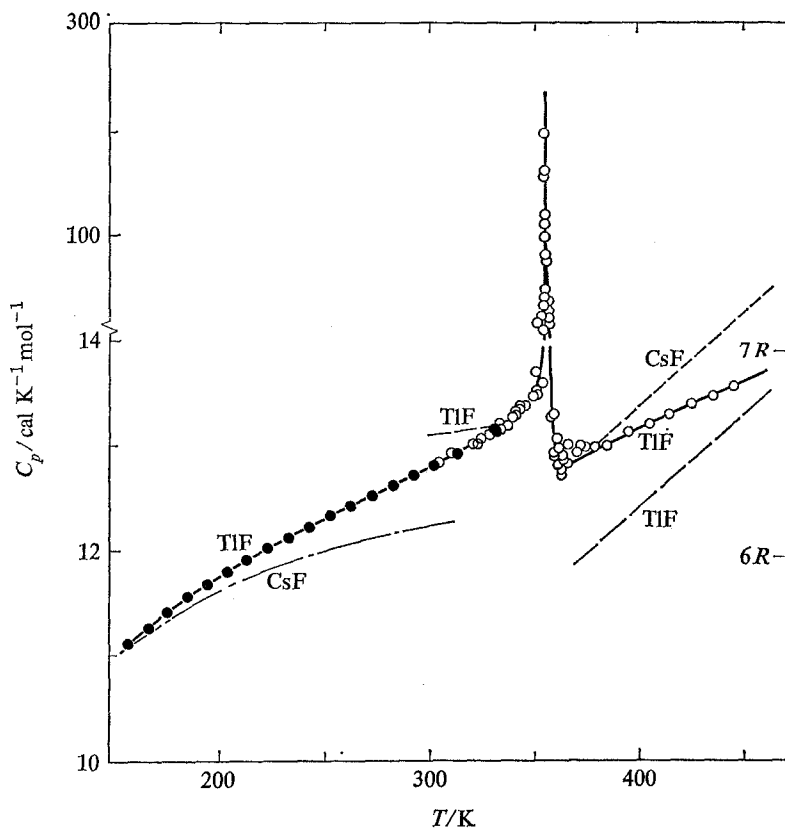


FIGURE 2. The intermediate-temperature heat capacities of TlF. The heat capacities of TlF derived by differentiation of the drop calorimetric data of Cubicciotti and Eding⁽⁵⁾ (—) have been included as have the similarly derived values for CsF⁽¹⁶⁾ (---). The cryogenic data for CsF⁽¹³⁾ (- · - · -) are also shown for comparison.

determined by thermal analysis with $\Delta H_t = 92 \text{ cal mol}^{-1}$ and $\Delta S_t = 0.26 \text{ cal K}^{-1} \text{ mol}^{-1}$. The heat capacity for the crystal I phase is:

$$C_p / \text{cal K}^{-1} \text{ mol}^{-1} = 5.29 + 17.78 \times 10^{-3}(T/\text{K}).$$

Their curves are also shown in figure 2. Their values accord with ours within the combined precision indices of the two sets. The heat capacity of crystal II derived from drop calorimetry⁽⁵⁾ agrees reasonably well if allowance is made for the short temperature range (55 K) available for enthalpy determinations and the apparently few determinations made. The heat capacities over the common temperature range of measurement (370 to 450 K) for crystal I, however, are seriously divergent both in magnitude and in trend. The high-temperature (373.15 to 976 K) drop-calorimetric data of Shpil'rain and Kagan⁽¹⁶⁾ on CsF are indeed parallel to those on TlF by Cubicciotti and Eding⁽⁵⁾ but despite claims to the contrary⁽¹⁶⁾ the heat capacities of CsF obtained by differentiation of the enthalpy equation⁽¹⁶⁾ do not join smoothly

(see figure 2) with the low-temperature adiabatic—calorimetric values for CsF by Paukov and Rakhmenkulov.^(1,3) These discrepancies occasion concern about the reliability of the higher-temperature drop-calorimetric data on both substances and suggest the desirability of adiabatic calorimetric determinations to higher temperatures.

4. Discussion

THE STRUCTURAL TRANSITION

The exact nature of the distortion of crystal II from the ideal NaCl-type has been the subject of considerable dispute. A summary of space groups and other crystallographic data assigned to crystal II by various investigators is given in table 4.

TABLE 4. Structural data on TlF

Space group	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{cm}^3 \text{mol}^{-1}$ ^a	Reference
Phase II—Orthorhombic					
D_{2h}^{32} — Fmmm	5.180	5.495	6.080	26.06	1
C_{2v}^{18} — Fmm2	—	—	—	—	2
C_{2v}^4 — Pma2	5.175	5.488	6.092	26.05	3
C_{2v}^5 — Pca2 ₁	5.190	5.506	6.092	26.21	4
Space group	$a/\text{\AA}$	$c/\text{\AA}$	$t/^\circ\text{C}$	$V/\text{cm}^3 \text{mol}^{-1}$ ^a	Reference
Phase I—Tetragonal					
D_h^7 — I4/mmm	3.771	6.115	135	26.18	6
—	3.783	6.092	145	26.25	4
—	3.804	6.120	100	26.67	8

^a While the molar volumes V computed from the X-ray data for TlF crystal phases I and II might seem at first glance to indicate a *positive* value for ΔV_t , the slope of the I–II boundary curve in the phase diagram of Pistorius *et al.*⁽⁶⁾ is clearly *negative*, indicating a *negative* value for this increment. ($\Delta V_t = -0.0333 \text{ cm}^3 \text{mol}^{-1}$ when adjustment is made for the new value of ΔH_t determined in this work.)

Although the space-group is by no means certain, the original assignment by Ketelaar⁽¹⁾ is ruled out. However, all later authors are in agreement that the structure is at least approximately face-centered orthorhombic. Two additional considerations concerning the crystal structure determinations seem necessary. First, the X-ray determinations as well as the i.r. and Raman work were carried out only near 300 K and second, the heat capacity of crystal II begins to deviate appreciably from that of CsF at temperatures above about 150 K. If the apparent excess heat capacity is in fact associated with the transition process, part of the confusion in the X-ray work might be due to a breakdown of conditions for systematic absences. Similarly, one might expect the selection rules for i.r. absorption and Raman scattering to be relaxed by the onset of a disordering process. Crystal structure determinations, i.r.,

and Raman studies at liquid nitrogen temperatures may provide more clear-cut indications of the true space-group. Neutron diffraction may prove to be the best technique for refining the fluorine parameters in the TlF structures; elucidation of the structures of the two phases of PbO, a substance formally isoelectronic to TlF, was thus achieved. PbO does show a transition at 762 K from the low-temperature, red, tetragonal form to the high-temperature, yellow, orthorhombic form with an associated entropy of transition ($0.23 \text{ cal K}^{-1} \text{ mol}^{-1}$)⁽¹⁷⁾ very close to that of TlF ($0.225 \text{ cal K}^{-1} \text{ mol}^{-1}$). However, crystallographic investigations⁽¹⁸⁻²⁰⁾ do not reveal a close relationship between these two transitions. Indeed, that in PbO apparently involves a decrease in symmetry.

A further peculiar feature of crystal II is apparent from the i.r. absorption spectrum determined by Ruoff and Weidlein.⁽²⁾ These authors detected an intense absorption band at 474.5 cm^{-1} which they attribute to the presence of TlF molecules in the crystal lattice not as an intrinsic property of crystal II but rather as an "impurity". Since their sample (unlike most of the others) was formed by a sublimation process, such contamination might have resulted during the final stage of purification. Nevertheless, it would be most interesting to determine whether this band occurs even in samples of TlF purified by other methods (e.g. deposition from solution, zone melting, etc.) and if so, whether there is any connexion between the appearance of this band and the onset of the transition to phase I.†

The crystallographic properties of phase I are also given in table 4. The consensus of this work seems to be that phase I is a body-centered tetragonal (equivalently, "face-centered tetragonal") lattice, very simple related crystallographically to phase II. It appears as if the transformation merely involves the disappearance of the 0.315 \AA disparity in the a and b axes of orthorhombic phase II. Indeed the a parameter for phase I (face-centered cell) is almost exactly the average of a and b for phase II. This slight shift is consistent with the small negative volume increment (0.11 per cent) for the transition II to I determined from the phase diagram of Pistorius and Clark.⁽⁶⁾ Dilatometric measurements by Tranquard *et al.*⁽⁷⁾ on polycrystalline samples, appear to indicate an increase in volume for the II to I transition, however, this interpretation has not been encouraged by the authors⁽²¹⁾ and is irreconcilable with the high pressure data unless the assumption is made that there was some preferential alignment of the crystallites in the dilatometric sample.‡

THE THERMODYNAMIC SITUATION

As was suggested by Murad *et al.*⁽²²⁾ the entropy of TlF(c) at 298 K derived by Keneshea and Cubicciotti⁽¹²⁾ from their vaporization results ($25.9 \pm 0.4 \text{ cal K}^{-1} \text{ mol}^{-1}$), is somewhat high compared with measured calorimetric values on other crystalline thallium halides. Kelley and King⁽²³⁾ have estimated $S^\circ = (22 \pm 1) \text{ cal K}^{-1} \text{ mol}^{-1}$ at 298 K in good accord with an estimate of $(22 \pm 2) \text{ cal K}^{-1} \text{ mol}^{-1}$ by Hildenbrand.⁽²⁴⁾ On the basis of the calorimetrically determined entropy for the crystal at 298.15 K and a spectroscopic value for the gaseous monomer, Keneshea and Cubicciotti⁽²⁵⁾ have re-evaluated their vaporization results. This had led to sub-

†, ‡ See "Notes added in proof" on p. 581.

stantial revision of the entropies and formation data of the gaseous species and generally better concordance with spectroscopic data.

The enthalpy of formation of TIF(c) at 298.15 K has been reported by Cubicciotti and Withers⁽²⁶⁾ as $-(77.8 \pm 1)$ kcal mol⁻¹. Combination of this value with the entropies of thallium and fluorine⁽²⁷⁾ and the data from the present investigation yields an entropy of formation ΔS_f° and a Gibbs energy of formation ΔG_f° of $-(16.69 \pm 0.05)$ cal K⁻¹ mol⁻¹ and $-(72.8 \pm 0.1)$ kcal mol⁻¹, respectively, for the crystal II phase at 298.15 K.

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NOTES ADDED IN PROOF

† A private communication from Dr A. Ruoff indicates that the band at 474.5 cm^{-1} appears also in TlF samples which have been sublimed, melted, and carefully cooled below fusion. Moreover, this band appears with surprising intensity even at liquid nitrogen temperatures.

‡ In subsequent (privately communicated) results, Professor Tranquard has indicated that the above sample was a mold-cast bar and may have possessed preferential orientation. However, more recent dilatometric measurements in his laboratory on compressed powders indicate a decrease in length for the II to I transition in accord with the high pressure data.