PHYSICAL REVIEW VOLUME 173, NUMBER 3 15 SEPTEMBER 1968

Effect of Pressure on the Polymorphism and Melting Points of the Thallous Halides

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(Received 16 May 1968)

The phase diagrams of the thallous halides were studied to 40 kbar by means of differential thermal analysis. Orthorhombic TlF II transforms at 81°C to TlF I, which was found to crystallize with a tetragonal distortion of the NaCl-type structure. The space group is D_{4h}^{17}-*I4/mmm*, with $a_0=3.771$, $c_0=6.115$ Å at 135°C. TlF I is slightly denser than TlF II. The TlF II-I transition line ends in a triple point I-III-II at 8.3 kbar, 59°C. TlF III is a high-pressure phase that appears at 12.6 kbar at 22°C. The TlF III-II transition line rises slightly with pressure. The melting curve of TlF I rises less steeply with pressure than those of the other thallous halides.

INTRODUCTION

THE high-pressure melting properties of the potassium,[1] rubidium,[2] sodium,[3] and cuprous[4] halides have recently been reported. The present investigation continues this study and is concerned with the determination of the melting curves of the thallous halides to 40 kbar. The melting curves of these substances have not previously been studied. The room-pressure melting points are 322.2,[5] 430.8,[5] 460.0,[5] and 422°C,[5,6] for TlF, TlCl, TlBr, and TlI, respectively.

TlCl and TlBr crystallize in the CsCl-type structure.[7] This structure, with a coordination number of 8, represents the most stable dense configuration for ionic crystals. No phase transitions are therefore expected in TlCl and TlBr at high pressures, and none were observed to ~500 kbar.[8] Under normal conditions TlI II crystallizes in a double-layered orthorhombic structure (D_{2h}^{17}-*Cmcm*).[9] On heating at atmospheric pressure, TlI II transforms to TlI I with the CsCl-type structure[9] at 169°C.[10] TlI I is denser than TlI II, and the TlI II → I transition also occurs at 4.7 kbar, 25°C.[10,11] High-pressure x-ray studies[12,13] have shown that the pressure-induced transition is the same as that occurring at 169°C. TlI has no further high-pressure transitions to 250 kbar.[8] The details of the TlI I-II transition have recently[10] been studied very carefully, and no further work on this subject was carried out in the present investigation.

Under normal conditions, TlF II crystallizes with a unique orthorhombic distortion[14] of the NaCl-type structure. The space group is D_{2h}^{23}-*Fmmm*. The unit cell contains four molecules, and has the approximately equilateral dimensions $a_0=5.180$, $b_0=5.495$, $c_0=6.080$ Å. The thallium atoms are at points of a face-centered lattice with the coordinates $(0,0,0)$; $(\frac{1}{2},\frac{1}{2},0)$; $(\frac{1}{2},0,\frac{1}{2})$; $(0,\frac{1}{2},\frac{1}{2})$; and the fluorine atoms are at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; $(\frac{1}{2},0,0)$; $(0,\frac{1}{2},0)$; $(0,0,\frac{1}{2})$. This is identical to the atomic positions in the NaCl-type structure, and the distortion is therefore completely expressed by the different lengths of the unit-cell constants. The short Tl-F separation along a_0, viz., 2.59 Å, was ascribed to the known high polarizability of thallium ions. It can be expected that the distortion may be somewhat relaxed at higher temperatures, and very recently[5] a transition was discovered at 82°C. The structure of the high-temperature form TlF I is of obvious interest.

CRYSTALLOGRAPHY OF TlF I

Finely powdered TlF was sealed into a thin-walled Lindemann glass capillary, and heated to above the transition temperature by blowing hot air over it. The unit-cell parameters were determined from powder photographs, using Cu *Kα* (Ni filter) radiation. Corrections were made for film shrinkage by photographing the powder pattern of pure CaF_2 on the same film. The powder pattern of TlF I at 135±3°C is shown in Table I. The pattern can be explained on the basis of the following tetragonal unit-cell dimensions:

$$a_0=3.771\pm0.004\text{ Å},$$
$$c_0=6.115\pm0.006\text{ Å},\quad Z=2.$$

The systematic absences hkl for $h+k+l\neq 2n$, $hk0$ for $h+k\neq 2n$, $0kl$ for $k+l\neq 2n$, hhl for $l\neq 2n$, and $00l$

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TABLE I. Powder pattern of TlF I at 135°C.

d_{obs} (Å)	d_{calc} (Å)	hkl	I_{obs}	I_{calc}
3.205	3.210	101	1.0	1.0
3.057	3.057	002	0.9	0.95
2.675	2.667	110	0.5	0.85
2.010	2.010	112	0.8	0.65
1.881	1.885	200	0.4	0.6
1.791	1.793	103	0.5	0.4
1.630	1.626	211	0.4	0.35
1.607	1.605	202	0.2	0.45
1.528	1.529	004	0.2	0.45
1.326	1.326	114	0.1	0.32
1.301	1.299	213	0.1	0.25
1.185	1.187	204	0.1	0.25
1.163	1.163	105	0.2	0.2
1.110	1.111	312	0.1	0.2

for $l \neq 2n$ define a number of space groups. However, the structure of TlF I is related to that of TlF II only if the space group of TlF I is chosen as D_{4h}^{17}-I4/mmm. The relationship between the two structures is more obvious if the larger tetragonal unit cell corresponding to the orientation D_{4h}^{17}-$F4/mmm$ is used. The unit-cell constants then become

$$a_0 = 5.333\text{ Å},$$
$$c_0 = 6.115\text{ Å}, \quad Z = 4$$

as compared with

$$a_0 = 5.180\text{ Å},$$
$$b_0 = 5.495\text{ Å},$$
$$c_0 = 6.080\text{ Å}, \quad Z = 4 \text{ for TlF II}.$$

It is clear that the a and b directions of TlF II are indistinguishable in the case of TlF I. We suggest that the atoms retain their relative positions on transformation, and that, for the smaller tetragonal cell, the thallium atoms are therefore situated on points of a face-centered lattice with the coordinates $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ while the fluorine atoms are at $(0,0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$. This proposed structure was fully substantiated by calculating structure factors for the reflections which were found to agree with the observed intensities quite satisfactorily.

The structure of TlF I is a compromise between the NaCl-type structure and the structure of TlF II, with the distortion somewhat relaxed. As in the case of TlF II this distortion is expressed only by the different lengths of the unit axes. The Tl-F separation perpendicular to c_0 is 2.65 Å, i.e., only slightly longer than in the case of TlF II. To our knowledge the structure of TlF I is unique to date, although extremely simple.

EXPERIMENTAL

The TlF was obtained from Amend Drug and Chemical Co., and had a purity of 99.9%. The other chemicals were obtained from Hopkin and Williams, with stated purities of 99%. The salts were thoroughly dried before use.

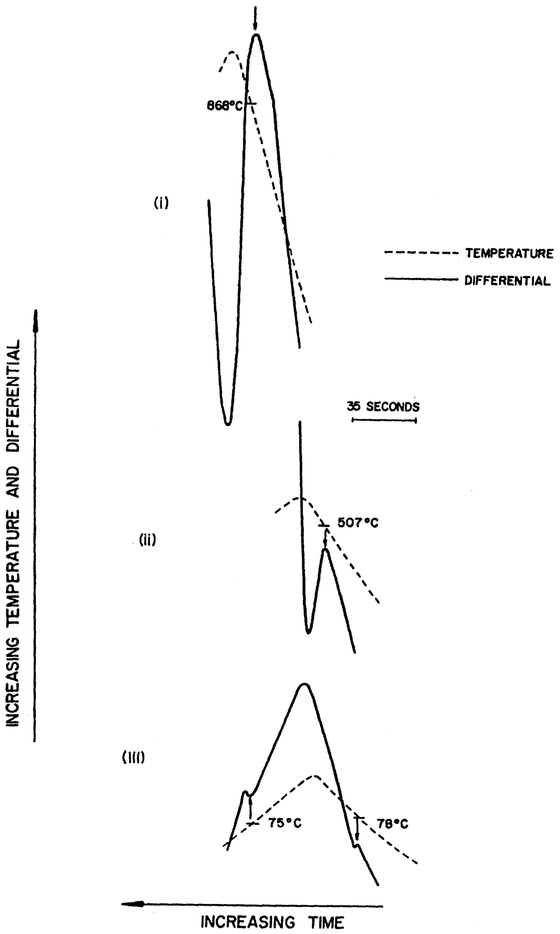

FIG. 1. Typical DTA signals obtained. (i) TlI I melt at 29.6 kbar, 868°C. The melting signals of TlCl and TlBr were similar to this. (ii) TlF I melt at 33.3 kbar, 507°C. (iii) TlF II-I transition at 1.3 kbar, 76.5°C. The signals associated with the TlF III-I transition were similar in nature, but slightly smaller.

Pressures up to 40 kbar were generated in a piston-cylinder device.[15] The furnace assembly was similar to that used by Klement *et al.*[16] Phase changes were detected by means of differential thermal analysis (DTA) using Chromel-Alumel thermocouples below ~950°C, and Pt-(Pt-10%Rh) thermocouples at higher temperatures. Corrections were made for the effect of pressure on the thermocouples.[17] The salts were contained in metal capsules which incorporated thermocouple wells.[1] Where necessary, the axial gradient along the sample capsule was reduced by sandwiching the capsule between two insulated metal plugs.[18] Typical DTA signals obtained are shown in Fig. 1. Capsules of Ni and Monel

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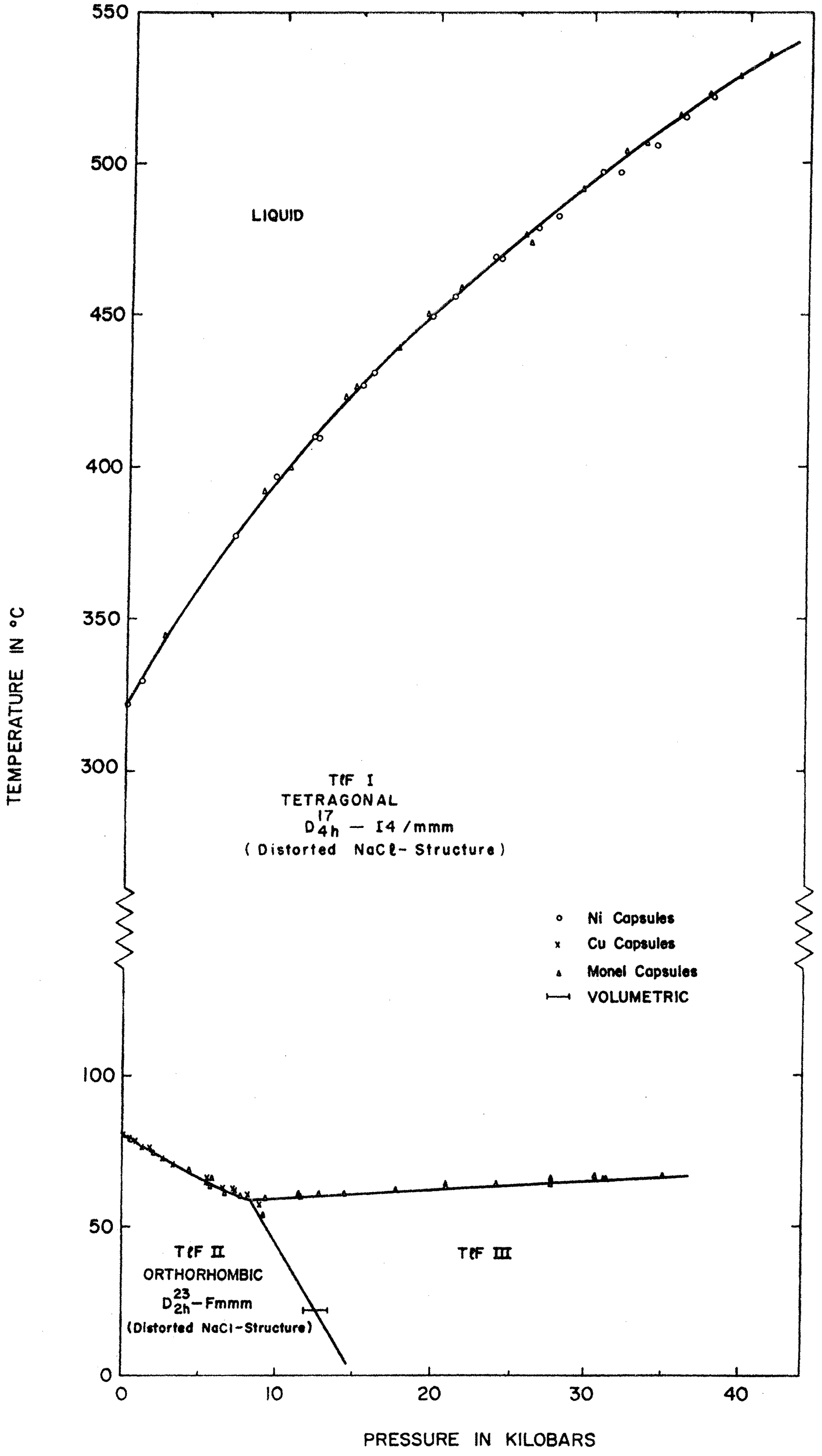

Fig. 2. Phase diagram of TlF to 42 kbar.

TABLE II. Phase relations of the thallous halides.

Phase change	Fit	Standard deviation
TlF II-I	$t(°\text{C})=81-3.51P+0.111P^2$	0.7°C
TlF III-I	$t(°\text{C})=59+0.30(P-8.3)$	0.6°C
TlF II-III	$t(°\text{C})=59-8.6(P-8.3)$	...
TlF I-liquid	$P/13.93=(T/595.4)^{4.507}-1$	1.6°C
TlCl I-liquid	$P/6.603=(T/704.2)^{3.466}-1$	3.1°C
TlBr I-liquid	$P/8.303=(T/733.2)^{3.078}-1$	7.4°C
TlI I-liquid	$P/8.77\ =(T/715.2)^{3.160}-1$	6.6°C
TlI II-I[a]	$t(°\text{C})=156-53P$	...

[a] Reference 10.

were used for TlF, with no trace of reaction with the capsule material. Molten TlF reacted strongly with Cu capsules. The other halides were studied in Ni, Cu, and stainless-steel capsules. There was no trace of reaction in Cu, but after many melting/freezing cycles some contamination was evident in Ni and in stainless-steel capsules. Contaminated points were discarded. Each phase boundary was based on at least three separate runs. The results of different runs were consistent. The heating rate was in the range 0.7–2.0°C/sec. Temperatures could be determined to ±1–3°C. Sliding friction was determined by comparing results obtained on increasing and on decreasing pressure. The pressure obtained in this way were further corrected for the effect of nonsymmetrical pressure losses. The procedure has been described elsewhere.[19] The corrected pressures are believed accurate to better than ±0.5 kbar. The points plotted represent the mean of heating and cooling in the case of solid-solid transitions, and melting temperatures in the case of solid-liquid phase changes.

EXPERIMENTAL RESULTS

Thallous Fluoride

The phase diagram of TlF is shown in Fig. 2. The II-I transition yielded very small but sharp DTA signals, with ~2°C hysteresis between heating and cooling [Fig. 1(iii)] for heating/cooling rates of 0.18–1.2°C/sec. Neither the II → I nor the I → II transition temperature depended on the rate of temperature change. Our zero-pressure transition temperature was 81±1°C, being the mean of ten determinations, in good agreement with the earlier value of 82°C.[5] The II-I transition line falls with pressure to 8.3 kbar, 59°C. The DTA signals obtained at higher pressures are slightly smaller, and the transition temperature increases with pressure. The point at 8.3 kbar, 59°C, is clearly a triple point TlF I-III-II, as shown in Fig. 2. This explanation requires a pressure-induced transition TlF II-III at room temperature.

About 20 g of TlF was precompressed at ~3 kbar in a pill press slightly smaller in diameter than the pressure vessel. This solid slug was then wrapped in a thin lead foil and inserted into the pressure vessel, the walls of which were coated with Molykote to minimize friction. Stoppers of unfired pyrophyllite were used at the upper end of the bore of the pressure vessel to prevent extrusion of the sample when pressure was applied. The displacement of the piston was measured as a function of pressure, using a dial gauge readable to 0.0001 in. The volume change of the TlF II-III transition can be expected to be ~0.1% (see below), and it was important to adhere to a tight time schedule and to increase pressure in small regular steps. A transition can be recognized by inspecting the plot of piston displacement against pressure.

The expected TlF II-III transition was found at 22°C, 12.6±0.8 kbar on increasing and on decreasing pressure. The volume change was ~0.1%, which proved to be just observable by means of our technique.

The melting curve of TlF I was followed to 41.2 kbar without the appearance of any new phases, and rises with pressure. The DTA signals on melting were strong and sharp [Fig. 1(ii)].

The phase relations of TlF are summarized in Table II. The polymorphic phase boundaries were fitted to simple power series, and the melting curve to the Simon equation[20]

$$P=A[(T/T_0)^c-1],$$

where T and T_0°K are the melting points at P kbar and at room pressure, respectively, and A and c are adjustable constants; A and c were determined by means of Babb's method.[21]

The latent heat of the II-I transition is 92 cal/mole.[5] The present initial slope of the transition line is −3.51°C/kbar. Applying the Clapeyron relation, the volume change on transformation is found to be

$$\Delta v_{\text{II-I}}=-0.038\ \text{cm}^3/\text{mole}.$$

This represents a fractional volume decrease of only 0.14%. If the assumption is made that not more than some 70% of the entropy is carried by the III-I transition, the volume change associated with it can be estimated, using the observed slope of 0.30°C/kbar. We find

$$\Delta v_{\text{III-I}}=0.002\ \text{cm}^3/\text{mole}.$$

This represents a fractional volume increase of ~0.008%. From the additive relations at the triple point it follows that

$$\Delta v_{\text{II-III}}=-0.040\ \text{cm}^3/\text{mole}.$$

TlF III is therefore 0.15% denser than TlF II along the II-III transition line. From the slope of the II-III transition line it further follows that near the triple point

$$\Delta H_{\text{II-III}}\simeq 36\ \text{cal/mole}.$$

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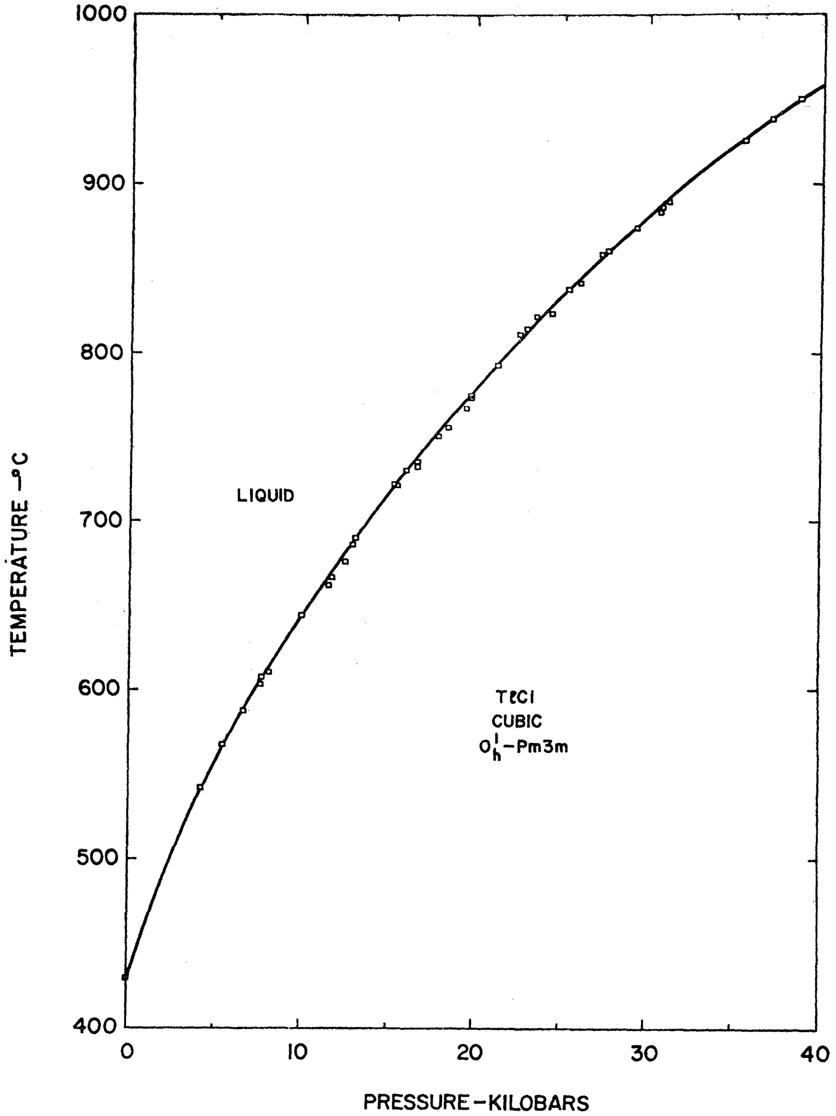

FIG. 3. Melting curve of TlCl to 40 kbar.

The initial slope of the melting curve of TlF I is given by

$$(dT/dP)_{P=0}=T_0/Ac=19.3^{\circ}\mathrm{C/kbar}$$

by differentiation of the Simon equation. The latent heat of melting is 3.315 kcal/mole.[5] The volume change on melting of TlF I is then found to be

$$\Delta v_{\mathrm{I-liq}}=4.5\ \mathrm{cm^3/mole}.$$

Thallous Chloride, Thallous Bromide, and Thallous Iodide

The melting DTA signals [Fig. 1(i)] were strong, sharp, and very similar in nature for the three thallous halides having the CsCl-type structure. The data are shown in Figs. 3–5. The melting curves rise very steeply with pressure. The experimental points, fitted to the Simon equation, are given in Table II.

Using the initial slopes of the melting curves together with the known[5] latent heats of melting, the volume changes upon melting can be obtained, and are shown in Table III. These values are compared with directly determined volume changes[22] in the cases of TlBr and TlI I.

TABLE III. Melting parameters of TlCl, TlBr, and TlI I at zero pressure.

Compound	ΔH_{fus} (kcal/mole)	T_0/Ac (deg/kbar)	Δv_{fus} (cm^3/mole) Calculated	Observed
TlCl	3.72[a]	30.8	6.81	···
TlBr	3.92[a]	28.7	6.42	6.9[b]
TlI I	3.52[a]	25.8	5.31	6.4[b]

[a] See Ref. 5.
[b] See Ref. 22.

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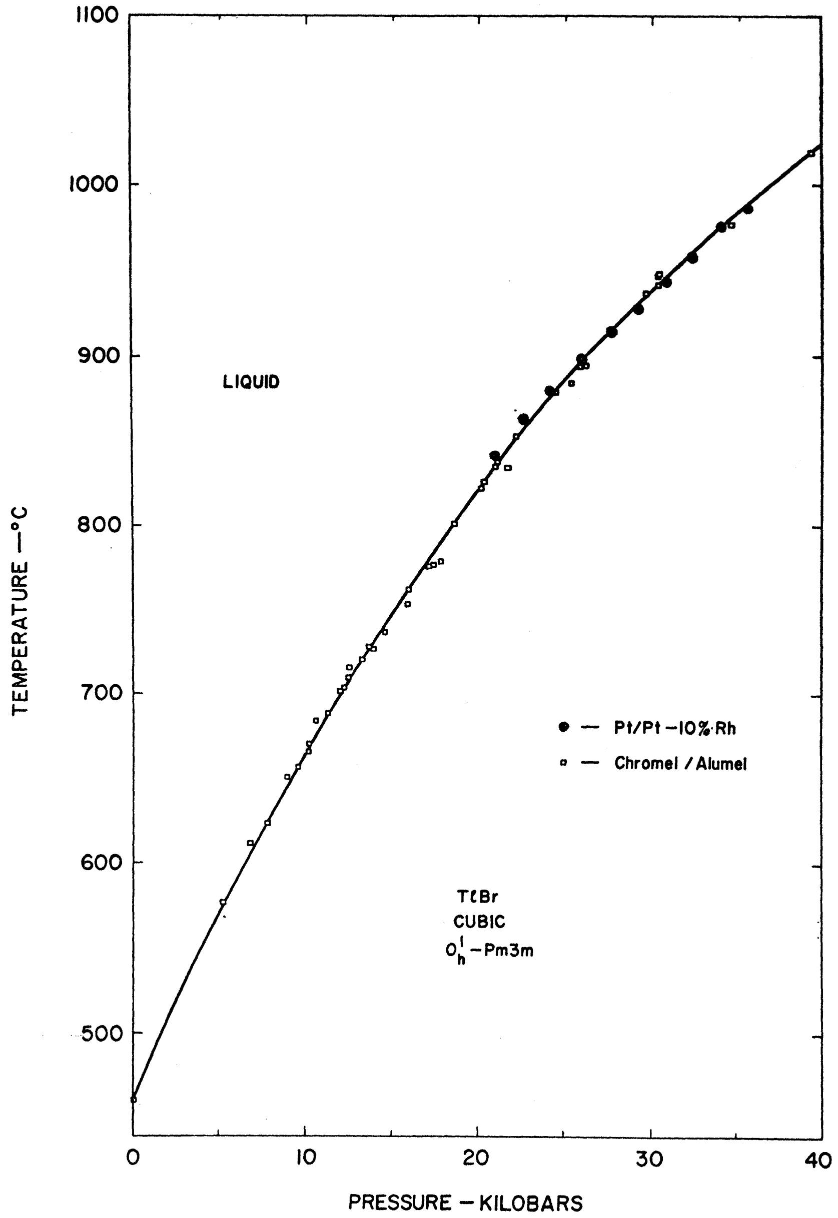

FIG. 4. Melting curve to TlBr to 40 kbar.

DISCUSSION

The TlF II-I transition should not be compared to the TlI II-I transition, although the stability fields of TlF II and TlI II are very similar. In the case of TlF we are dealing with distorted NaCl-type structures with octahedral coordination, while in the case of TlI the structures are distorted and undistorted CsCl-type structures with coordination number approximately 8. However, the structures of TlF II, TlF I, and TlI II are probably all stabilized mainly by the large polarizability of the Tl ion. If this had not been the case, TlI would always have had the undistorted CsCl-type structure, while TlF would have crystallized with the undistorted NaCl-type structure.

The structure of TlF I represents a compromise between the structures of TlF II and NaCl. If TlF I had not melted at a comparatively low temperature, one could presumably have expected a further transition of TlF I to a high-temperature phase with exactly the NaCl-type structure. It is, in fact, possible that such a phase boundary may branch off from the melting curve at some higher temperature and pressure. TlF I, II, and III are almost exactly equally dense at the I-III-II triple point. There is no change in coordination number at the II-I transition, and the small volume change at the II-III transition shows that there is almost certainly no change in coordination number at this transition either. TlF III can certainly not possess a dis-

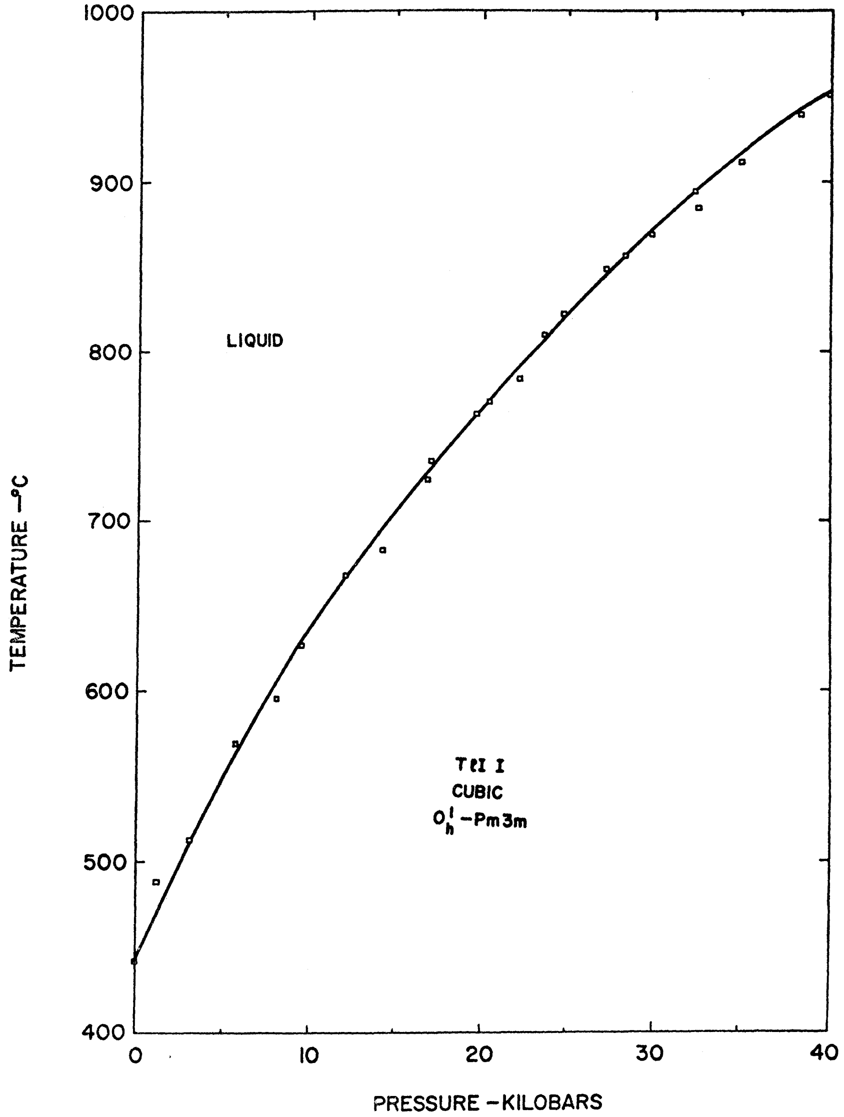

Fig. 5. Melting curve of TlI I to 40 kbar.

torted CsCl-type structure with approximate coordination number of 8, and must be considered as having a slightly different distortion of the NaCl-type structure than TlF II or I. It is, for instance, possible that its structure may be related to those of the high-pressure forms of PbS, PbSe, and PbTe,[23] i.e., orthorhombic, space group $D_{2h}{}^{16}$-*Pbnm*. At very much higher pressures it is probable that TlF I and III will convert to denser phases with eightfold coordination.

The initial slope of the melting curve of TlF I is considerably lower than those of the melting curves of TlCl, TlBr, and TlI I. This is similar to the behavior encountered for the potassium,[1] rubidium,[2] and sodium[3] halides. In the alkali halide cases this was shown to be due to the anomalously high densities of the fluoride melts because of dimerization. However, the curvature of the melting curve of TlF I is more reminiscent of the curvature of the melting curves of NaCl and NaBr than of NaF, and it can be concluded that there is no positive evidence of dimerization in the melt of TlF on the basis of the present results. The low initial slope must be ascribed merely to the fact that the octahedrally coordinated solid is considerably less dense than the CsCl-type solid phases of the other thallous halides, and that the volume change upon melting can therefore be expected to be smaller.

The melting curves of TlCl, TlBr, and TlI I are strikingly similar (Tables II and III). The initial slopes as well as the volume changes upon melting decrease regularly in this order, while the entropy changes upon melting are roughly the same for all three substances. The agreement between the directly determined volume

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changes and those calculated by means of the Clapeyron relation is excellent compared to the comparatively poor agreement[24] for some of the alkali halides. The present discrepancy is ~10%, and is in the usual direction, i.e., the direct determination of Δv yields too high a value, or the latent heat is too low. The consistency of this discrepancy was first pointed out by Clark.[25] The present good agreement can perhaps be ascribed to the fact that the latent heats and volume changes are all based on very recent determinations.[5,22]

ACKNOWLEDGMENTS

The authors would like to thank Mrs. Martha C. Pistorius for writing the computer programs used in fitting the data. Dr. J. C. A. Boeyens was of considerable assistance with the crystallography. We are indebted to Dr. G. Gafner and Dr. E. Rapoport for valuable discussions. J. Erasmus and his staff and G. O'Grady and his staff kept the equipment in good repair, and were responsible for the manufacture of the furnace parts. Calculations were carried out on the IBM System 360 of the National Research Institute for Mathematical Sciences.

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PHYSICAL REVIEW VOLUME 173, NUMBER 3 15 SEPTEMBER 1968

Tuning of PbSe Lasers by Hydrostatic Pressure from 8 to 22 μ

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(Received 20 February 1968)

This paper reports the tuning by hydrostatic pressure of the wavelength of emission of a PbSe laser from 7.5 to 22.3 μ in the infrared. Also discussed are the possibilities for further extension of the emission wavelength, the physical studies thereby rendered possible, the possibility of tunable devices, and the extension of similar ideas and techniques to other semiconductors of the PbSe family.

1. INTRODUCTION

THE results of many experimental[1] and theoretical[2] studies have shown that the face-centered cubic lead chalcogenides PbS, PbSe, and PbTe are semiconductors with small direct energy gaps at the point L of the Brillouin zone, and with large matrix elements for electronic transitions under the influence of electromagnetic radiation. Laser action has been demonstrated in all three of these semiconductors.[3] Separate series of experiments have shown that the pressure coefficients of the energy gaps of all three substances are negative and have about the same vlaue.[4–8] Cal-

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[†] Research supported by the U. S. Office of Naval Research under Contract No. Nonr 1866(10).

[‡] Operated with support from the U. S. Air Force.

[1] Original papers and older references are to be found in the *Proceedings of the Seventh International Conference on Semiconductors* (Dunod Cie., Paris, 1964).

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[4] The probability of a negative pressure coefficient of the fundamental gap may be inferred from the positive temperature coefficient of between 4 and 5×10^{-4} eV/°K found in all three materials. If this temperature coefficient is regarded as composed of two parts, the first stemming from the increase in volume with increasing temperature, the second from changes in the electron-phonon interaction, and if, following the theory of Fan (Ref. 5) we accept that the second contribution is inherently negative for minimal gaps, we are led to calculate an equivalent *negative* pressure coefficient of at least -15×10^{-6} eV/bar.

In fact, experimental studies of the effect of hydrostatic pressure on the transport (Ref. 6) and optical properties (Ref. 7) have been interpreted to correspond to coefficients of about -9×10^{-6} eV/bar only, implying that, in this case at least, the contribution to the temperature coefficient of the electron-phonon interaction is positive and therefore the effect considered by Fan is not the dominant one (Ref. 8).

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[8] For further brief comment on this difficulty, see Paul *et al.*, Ref. 6, p. 719. For a recent attempt to establish a different theory of electronic band energies in the presence of electron-phonon interaction, which could permit both positive and negative coefficients, see S. C. Yu, thesis, Harvard University, 1964 (unpublished).