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MIXED CRYSTALS AND ITS ELIMINATION

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Abstract: Prisms, cut from mixed crystals of thallium halides, as they are used at present for infrared spectroscopy, show optical inhomogeneity which causes an undesirable decrease of resolution. By chemical, X-ray diffraction, and thermal analysis it was possible to trace the cause of this defect to the use of incorrect data of the minimum melting points of the compositions from which the crystals were grown. The melting points of the thallium halides and of their binary systems have been redetermined, and crystals grown from compositions corresponding to the accurate minimum melting points hav been found to be entirely homogeneous. The lattice constants and thermal expansion coefficients of the new mixed crystals have been measured.

Mixed thallium halide crystals* have been used in recent years in infrared spectroscopy for absorption cells, radiation receiver windows, polarizers[1],

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* Mixed crystals of thallium halides, known under the code names KRS-5 (44 mole % TlBr + 56 mole % TlI) and KRS-6 (60 mole % TlCl + 40 mole % TlBr) were grown first by R. Koops (Optik 3, 298 (1948)) in the senior author's (A.S.) laboratory at the Carl Zeiss Optical Works, Jena, Germany, during World War II. Improvements of the crystals were made by the senior author during subsequent years at the Engineer Research and Development Laboratories, Fort Belvoir, Va.

1) R. T. Lageman, J. Opt. Soc. Amer. 41, 1063 (1951).

and prisms[2,3]. The advantage of these materials is their very low water solubility, good transparency over a very wide spectral range (from visible up to 40μ for prisms and up to 60μ for windows), and sufficient hardness (about two times that of NaCl) for optical working to obtain surfaces of desired quality. The disadvantages are high refractive indices (2.2 to 2.6) which cause high reflection loss, and plasticity which may lead to deformation of finished surfaces. The reflection loss can be partially eliminated by proper nonreflecting coatings, but only over a comparatively small wavelength range. Plastic deformation can be avoided if the crystals are properly handled during optical working.[4]

The refractive index data of thallium bromo-iodide mixed crystals of various compositions have been reported for a few visible spectral lines by Barth.[5] Hettner and Leisegang,[6] and Tilton, Plyler and Stephens[7] determined the refractive indices in infrared for compositions corresponding to the minimum melting point. Their data differ considerably and the difference cannot be explained satisfactorily. Furthermore, Plyler[8] found that prisms of thallium bromo-iodide crystals did not have the expected resolution, a fact indicating optical inhomogeneity. A preliminary study of Plyler's prism[9] disclosed that

2) E. K. Plyler, J. Res. U. S. Nat. Bur. Stand. 41, 125 (1948).
3) W. L. Hyde, J. Chem. Phys. 16, 744 (1948).
4) A. Smakula and M. W. Klein, J. Opt. Soc. Amer. 40, 748 (1950).
5) T. Barth, Amer. Mineral. 14, 358 (1929).
6) G. Hettner and G. Leisegang, Optik 3, 305 (1948).
7) L. W. Tilton, E. K. Plyler, and R. E. Stephens, J. Res. U. S. Nat. Bur. Stand. 43, 81 (1949).
8) E. K. Plyler and N. Acquista, ibid. 49, 61 (1952).
9) A. Smakula and M. W. Klein, unpublished.

the refractive index showed a slight variability from end to end. The object of the present investigation was to find out the cause of the optical inhomogeneity and if possible to eliminate it.

Mixed Crystal Formation

In case of complete mutual solubility of two components, three types of solid solutions are possible:

1. The melting point may change monotonically with the composition.

2. The melting point goes through a maximum.

3. The melting point goes through a minimum.

Because of the difference of the solidus and liquidus curves large homogeneous crystals can be grown only from the melts of type 2 and 3, and even in this case only if the composition corresponds to the maximum or minimum of the melting point where the solidus and liquidus curves coincide.

Thallium halides belong to the 3rd group of solid solutions. Thallium chloride and bromide form stable mixed crystals in all proportions, but thallium bromide and iodide, only if the amount of bromide exceeds ca. 20 percent. If the concentration of bromide is smaller the mixed crystals are stable only at high temperature; they decompose slowly at room temperature to orthorhombic TlI and cubic TlBr.

According to Moenkemeyer[10] the binary system of TlCl + TlBr has a minimum melting point at 413°C for the composition 60 mole % TlCl and

10) K. Moenkemeyer, Neues Jahrb. Mineral. Geol. Pal. 22 Beilage-Band, (1906).

40 mole % TlBr, and of TlBr + TlI at 411°C for 42 mole % TlBr and 58

mole % TlI. Later measurements by Koops[11] agree for TlCl + TlBr, but place

the minimum melting point composition for TlBr + TlI at 44 mole % TlBr and

56 mole % TlI.

Optical Inhomogeneity

For our investigation we prepared crystals of 60 mole % TlCl + 40

mole % TlBr and 42 mole % TlBr + 58 mole % TlI. The crystals, 2 cm in

diameter and up to 12 cm long, were grown by the Bridgman method, which

consists in lowering sealed Pyrex crucibles 0.5 mm/hr through a temperature

gradient 10°C/cm. Prisms were cut from different zones and the refractive

index for λ = 0.589 μ was determined. The refractive index of a thallium bromo-

iodide crystal varied linearly from 2.629 to 2.623 between the bottom, where

the crystal starts to grow, and the top. This difference might be caused by an

inhomogeneous distribution of impurities, or an inhomogeneous composition of

the crystal.

Chemical Analysis

To explain such a large difference in the refractive index by an inhomo-

geneous distribution of impurities would require an impurity content of at least

one percent. As a spectroscopic analysis showed, our crystals contained not

more than a few hundredths percent of impurities. Some visible impurities

were concentrated on the top of the crystals causing a dark zone well separated

11) R. Koops, Optik 3, 298 (1948).

from the rest. No discontinuous change of the refractive index between the dark

and the bright portion of the crystal was observed. Thus impurities cannot be

held responsible for the optical inhomogeneity.

To investigate the other possibility (that the inhomogeneity in the refrac-

tive index is caused by an inhomogeneous chemical composition) of the crystal,

we analyzed the bottom and top of a thallium bromo-iodide crystal. The halogens

were separated from thallium by distillation with H_2SO_4 and subsequent absorp-

tion in Na_2SO_3 solution (Fig. 1). Iodide was then oxidized to iodate with bromine[12]

and determined iodometrically. Thallium was titrated with potassium bromate.[13]

TABLE 1

COMPOSITION OF A THALLIUM BROMO-IODIDE
CRYSTAL FROM CHEMICAL ANALYSIS.

Material	TlBr	TlI
Melt	41.86 mole %	58.14 mole %
Crystal bottom	41.7 " "	58.3 " "
Crystal top	45.0 " "	55.0 " "

Table 1 shows that the concentration of iodide is about 3 percent higher at the

bottom than at the top of the 12 cm. long crystal.

Lattice Constant Variation

For further investigation of the inhomogeneity, we made a lattice constant

determination with a High Precision Geiger-Counter X-ray spectrometer.* This

12) E. Viebock and C. Brecher, Ber. 63, 2818 (1930).
13) E. Zintl and G. Rienacker, Z. anorg. Chem. 153, 278 (1928).
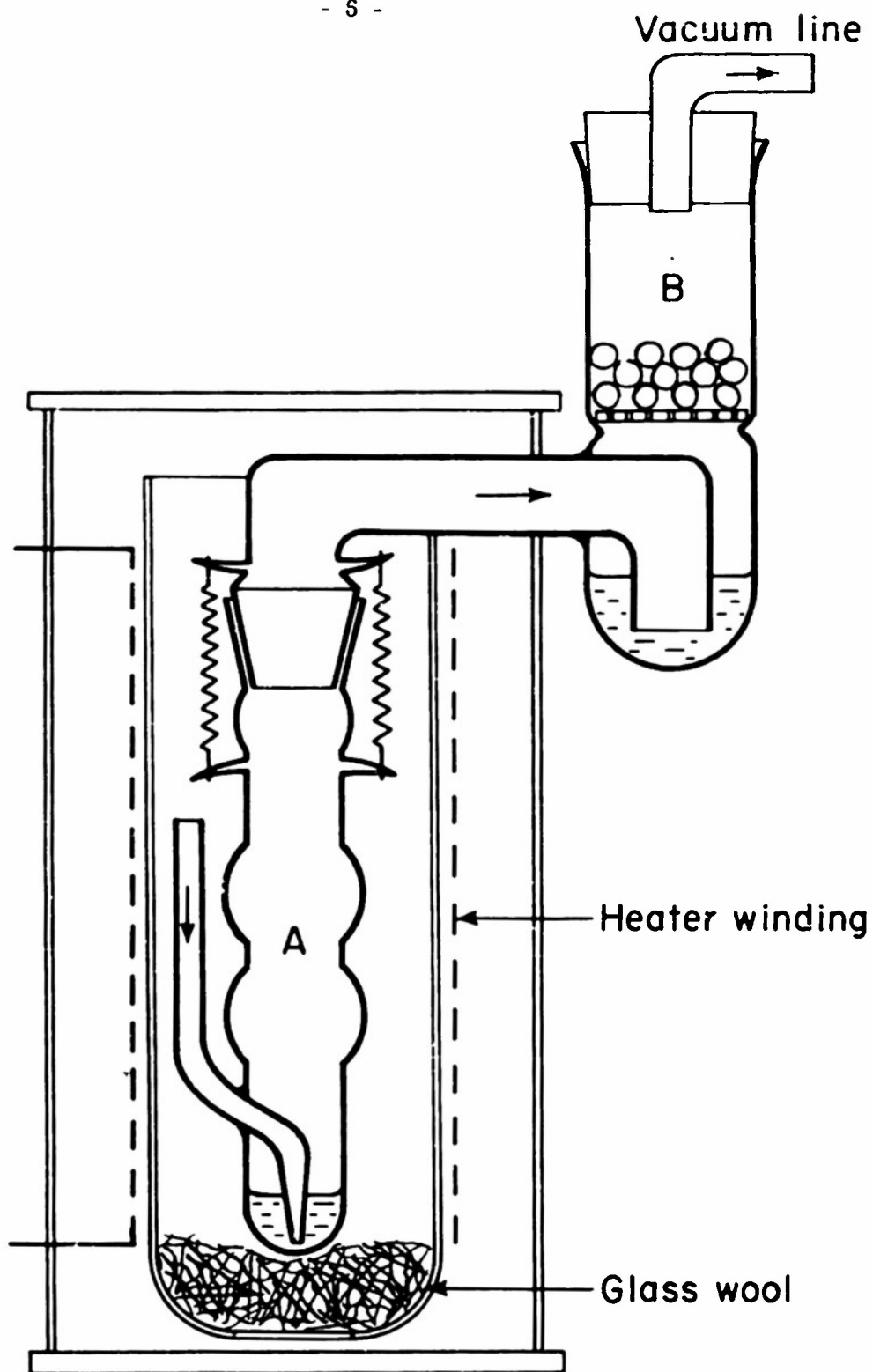* North American Philips Company, Inc., Mount Vernon, N.Y.

Vacuum line

B

Heater winding

A

Glass wool

Fig. 1. Apparatus for halogen separation by distillation.
(A) reaction vessel, (B) absorption cell.

instrument permits a direct reading of diffracticn angles (2 θ) to 0.01° with a

precision of ∓ 0.0025°. The samples were taken at several points along the

cylinder axis of the crystal in the form of fine filings (200 mesh) and annealed

in vacuo 15 h. at 200°C. Special care was taken to insure that the sample in the

spectrometer sample holder was optically flat by heating the filings in a glass

sample holder under slight pressure on an optical flat. The filings then adhere

without any binder. A special constant temperature chamber (Fig. 2) kept the

temperature within ± 0.05°C.[14] As an example, the lattice constants obtained

on one crystal each of thallium chloro-bromide and thallium bromo-iodide are

given in Table 2. For both cases the lattice constant decreases continuously

TABLE 2

LATTICE CONSTANT VARIATION ALONG THE GROWING DIRECTION OF THALLIUM HALIDE MIXED CRYSTALS

A. Thallium chloro-bromide 60 mole % TlC¹ + 40 mole % TlBr		
Height of the Crystal	(hkl) = (321) 2 θ	Lattice Constant A
0.0 cm (bottom)	95.066	3.90694
3.5 " (top)	95.130	3.90496
B. Thallium bromo-iodide 42 mole % TlBr + 58 mole % TlI		
0.0 cm (bottom)	72.289	4.12962
4.2 "	72.343	4.12696
9.3 "	72.395	4.12440
11.3 " (top)	72.419	4.12322

14) A. Smakula and J. Kalnajs, Progress Report No. X, ONR Contract N5ori-0781, Lab. for Ins. Res., MIT, Nov. 1951, p. 15 and No. XI, May 1952, p. 27.

a) Specimen
b) Sample holder
c) Jacket
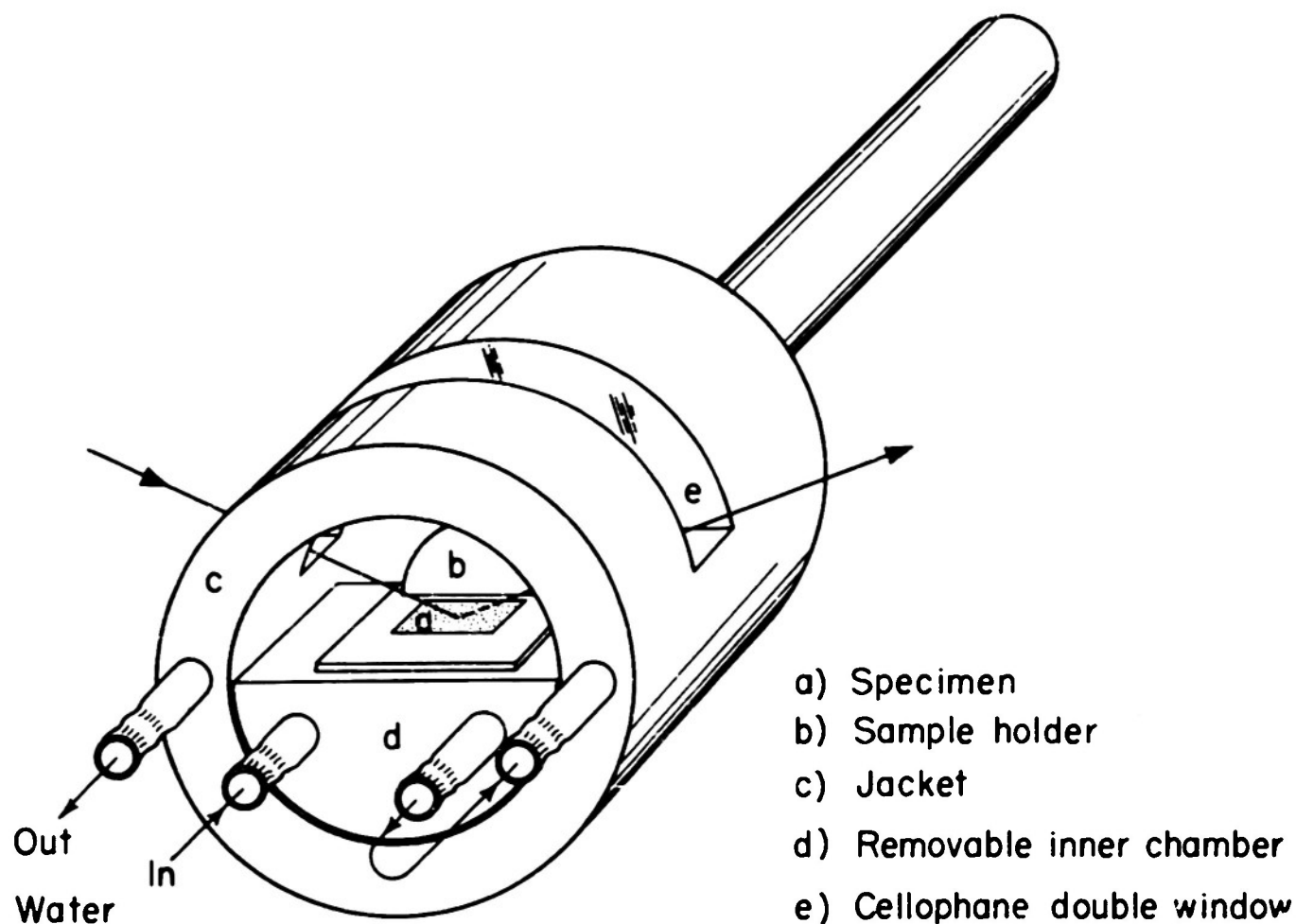d) Removable inner chamber
e) Cellophane double window

Fig. 2. Constant temperature chamber for x-ray spectrophotometer.

from the bottom to the top of the crystal. The rate of decrease depends on the

speed of the crystal growing (at a speed of 10mm/hr the rate is only half of that

at 1mm/hr), but unfortunately, at such a high speed one cannot obtain single

crystals.

According to Barth and Lunde[15] the lattice constant of thallium bromo-iodide increases with the amount of iodide as shown in Fig. 3. As the amount of TlI increases, the lattice constant rises somewhat faster than linearly and reaches its maximum deviation from linearity of 0.5 percent at the composition which corresponds exactly to the minimum melting point. The deviation of the lattice constant or molecular volume from the linearity indicates that the cohesive forces are influenced greatly by the polarization of the ions.

Investigation of Segregation

After it was definitely established that the optical inhomogeneity is caused by a change in chemical composition, the next step was to find out why this change takes place. The effect might be caused by segregation of the components in the melt or in the solid state during the growing process while the mass is kept for days in a temperature gradient. Segregation in a temperature gradient is known as the Ludwig-[16] Soret[17] effect, or thermal diffusion effect, and has been observed in melts[18] and solids.[19]

To check the segregation, a melt of a composition 42 mole % of TlBr + 58 mole % of TlI was kept in a glass tube (10 cm long) in a temperature gradient (16.5°C/cm) for 120 h. and then quenched rapidly. The lattice constant

15) T. Barth and G. Lunde, Z. phys. Chem. 122, 293 (1926).
16) C. Ludwig, Wiener Akad. Ber. 20, 539 (1856).
17) C. Soret, Ann. chim. phys. (5) 22, 293 (1881).
18) M. Ballay, Rev. Met. 25, 427 (1928).
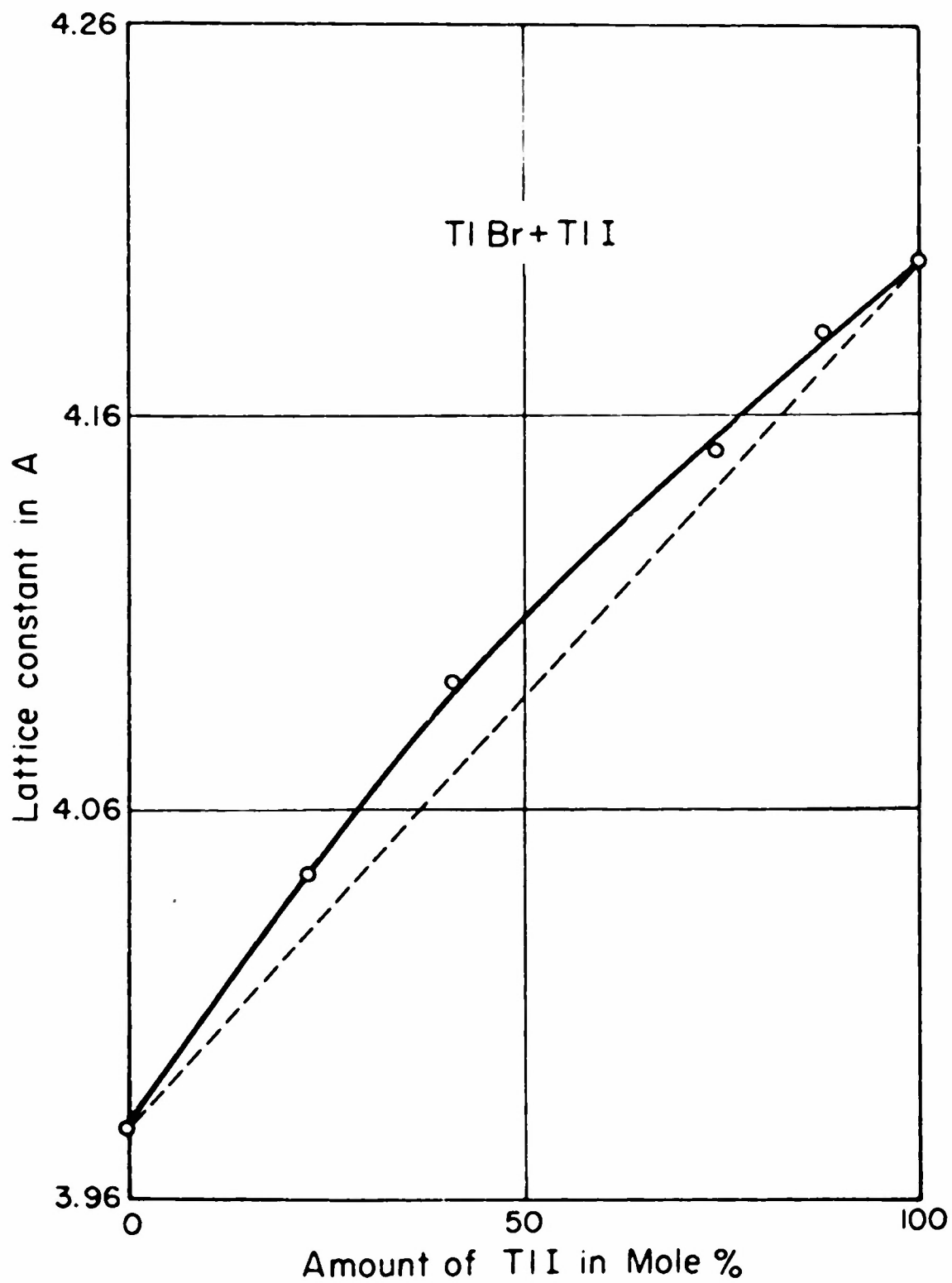19) H. Reinhold and R. Schulz, Z. phys. Chem. A164, 241 (1933).

Fig. 3. Lattice constant of TlBr + TlI system.

measurements showed no deviation along the sample. The possibility of thermal diffusion in the solid was checked by keeping a crystal (10 cm long) in a strong temperature gradient (23°C/cm) for 150 h. No change of the lattice constant was detected.

Phase Diagram Determination

After these negative results we decided to check the phase diagrams by the cooling method for both binary systems (TlCl + TlBr and TlBr + TlI). Samples of 20 to 30 gm. were melted in a Pyrex vessel with a narrow tubing to prevent oxidation and cooled down at the rate 15°C/hr while the melt was being stirred with the thermocouple glass tubing until it solidified (Fig. 4). The temperature was measured with an iron-constantan thermocouple calibrated against the melting point of Zn (419.5°C) standard sample.* The accuracy of reading the thermocouple e.m.f. was increased by factor five by using a partial compensation and amplification of fractional millivolts (Fig. 5). The results are given in Figs. 6 and 7. Our freezing points are considerably higher than those reported by Moenkemeyer and Koops and the minima are shifted. The freezing points of thallium halides are given in Table 3, and the minimum freezing points of the binary systems in Table 4.

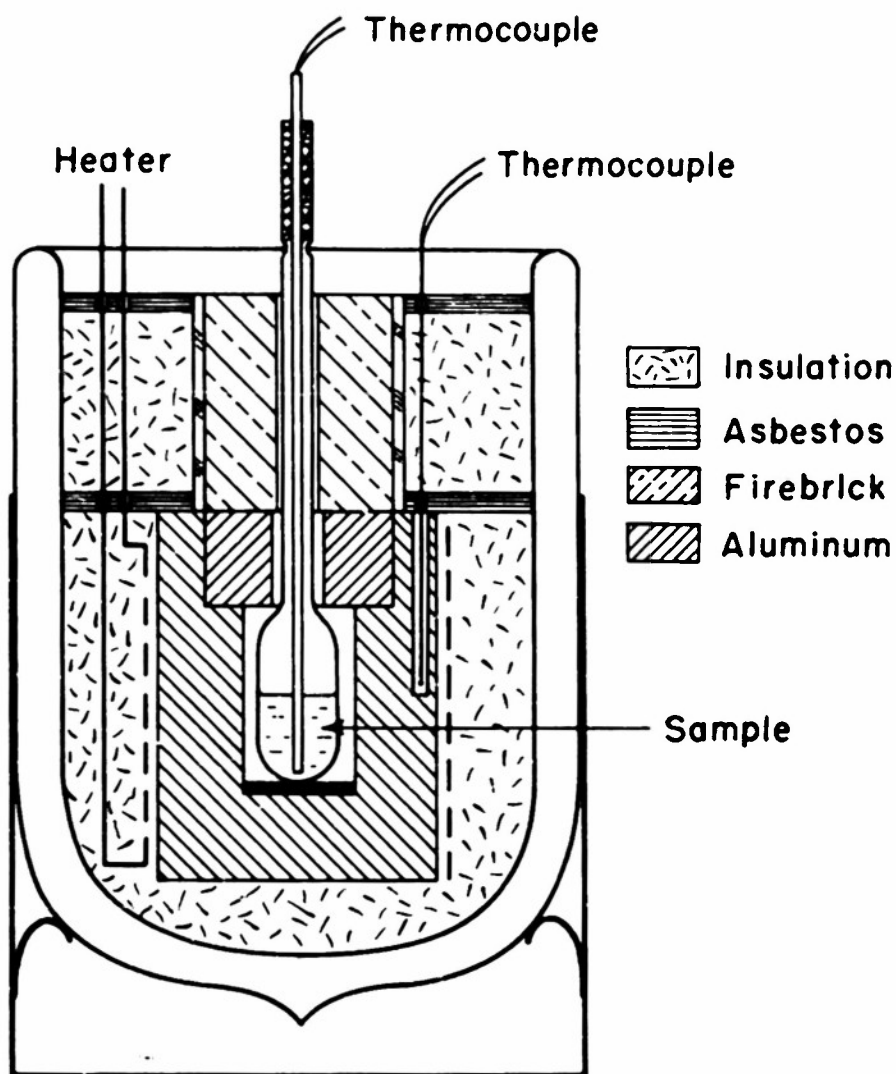* From the U. S. National Bureau of Standards, Washington, D. C.

Fig. 4. Apparatus for freezing-point determination.

Lattice Constants of the New Compositions

After adjusting the accurate minimum melting points, crystals of binary

systems were grown and the lattice constants at different positions along the

growing direction determined. As can be seen from Table 5 the greatest devia-

tion of the lattice constant along the crystal length is now not more than 5×10^{-5}
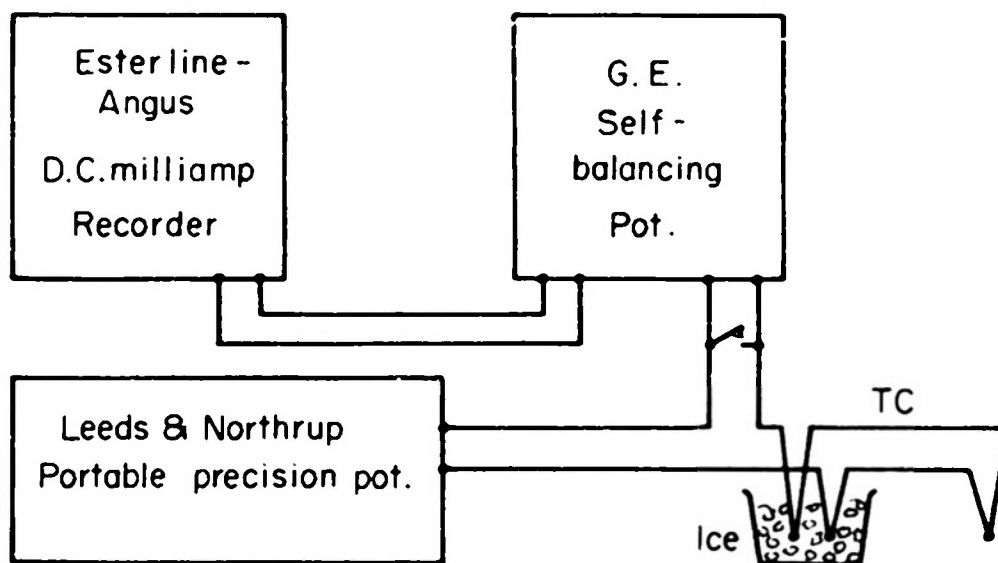
Fig. 5. Circuit diagram for freezing-point determination.

TABLE 3

FREEZING POINTS OF THALLIUM HALIDES

Material	Freezing Point	Reference
TlCl	426°C	10)
	430	20)
	430.2	Present work
TlBr	450	10)
	456	20)
	460	21)
	460.5	Present work
TlI	431	10)
	440	20)
	442.5	Present work

20) H. von Wartenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922).
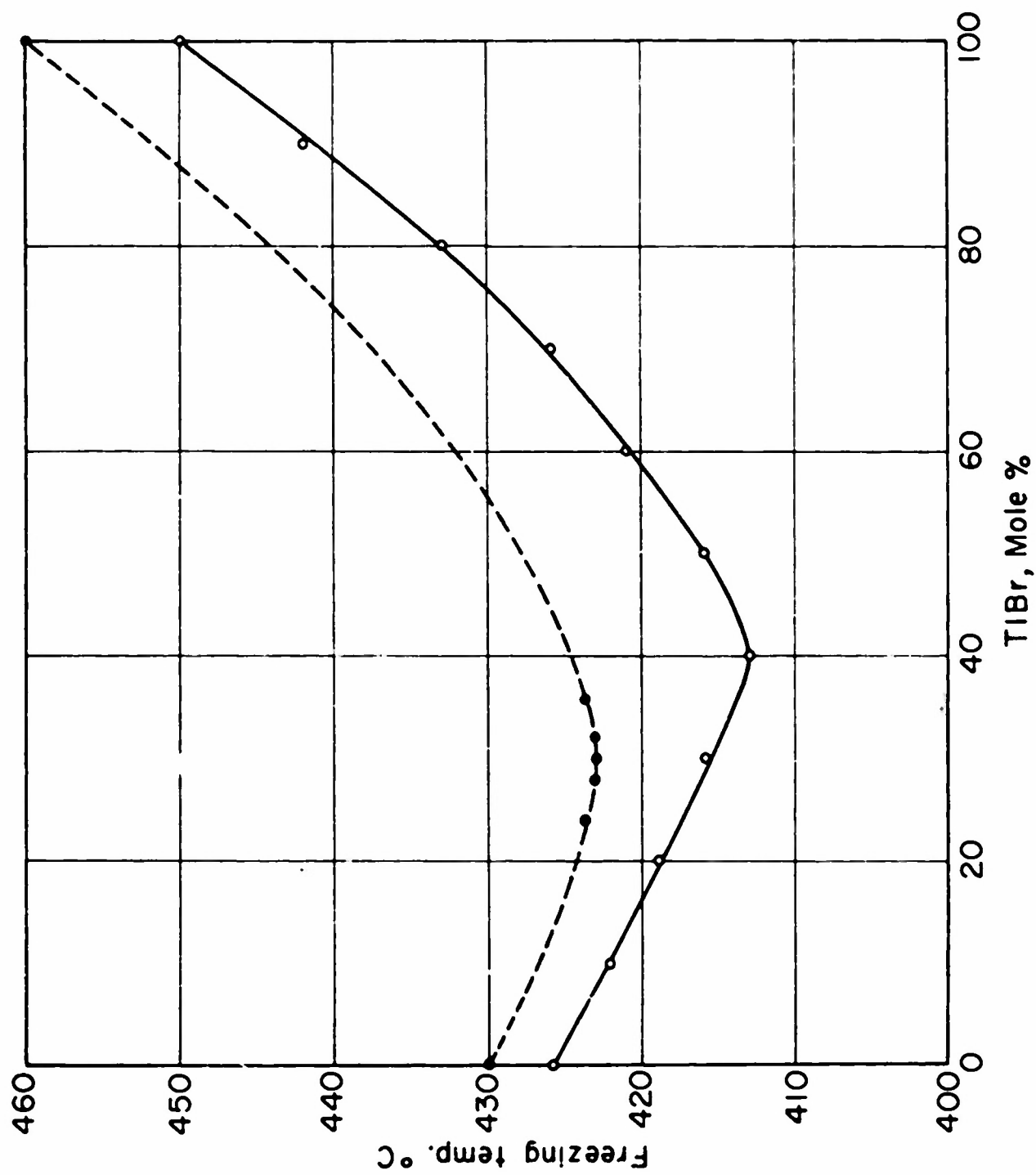21) Handbook of Chemistry and Physics, 1950, p. 583.

Fig. 6. Freezing temperatures of TlCl + TlBr system; upper curve, our measurements; lower curve, Moenkemeyer's data.[10]
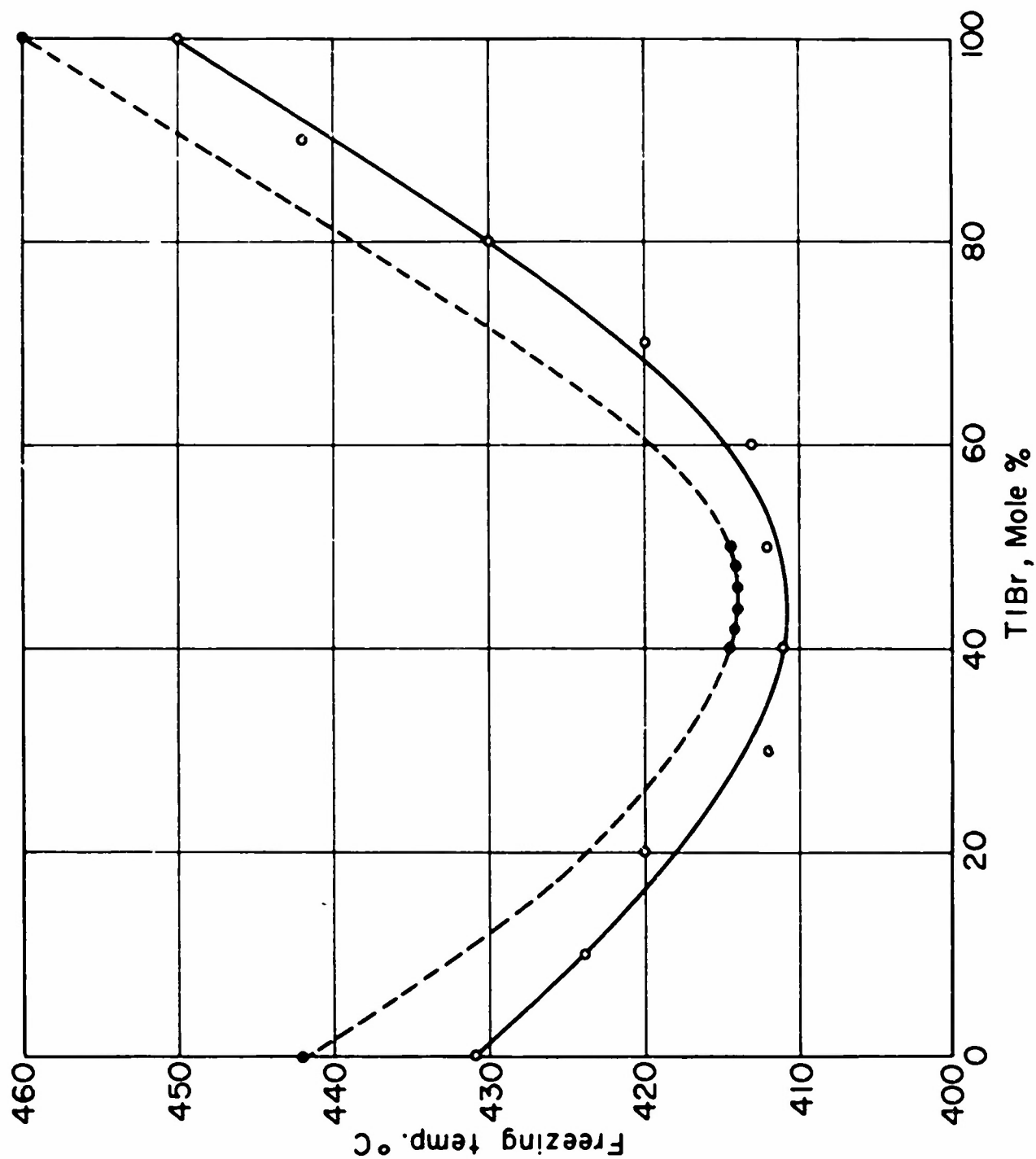
Fig. 7. Freezing temperatures of TlBr + TlI system; upper curve, our measurements; lower curve, Moenkemeyer's data.[10]

TABLE 4

MINIMUM FREEZING POINTS OF THE
BINARY SYSTEMS OF THALLIUM HALIDES

Material	Composition Mole %	Freezing Point	Reference
TlCl + TlBr	60 + 40	413°C	10), 11)
	60 + 40	423.5	22)
	70 + 30	422.97	Present work
TlBr + TlI	42 + 58	411	10)
	42 + 58	414.5	22)
	44 + 56	411	11)
	46 + 54	413.96	Present work

TABLE 5

LATTICE CONSTANT ALONG THE GROWING DIRECTION
OF THE CRYSTALS: 70 mole % TlCl + 30 mole % TlBr, and
46 mole % TlBr + 54 mole % TlI

70 mole % TlCl + 30 mole % TlBr			46 mole % TlBr + 54 mole % TlI		
Height	2θ	Lattice Constant	Height	2θ	Lattice Constant
0 mm.	95.631°	3.88946A	0 mm.	72.521°	4.11824A
10	95.630	3.88948	40	72.520	4.11829
35	95.632	3.88943	80	72.521	4.11824
70	95.631	3.88946			

which corresponds to the accuracy of our measurements.

The lattice constant values given in Table 5 are relative since they have

been computed from only one diffraction angle without elimination of systematic

errors. To obtain lattice constants of high accuracy with the Geiger-Counter

X-ray spectrometer, it is necessary to extrapolate the data to $2\theta = 180°$.

22) A. Smakula, Physical Properties of Optical Crystals, Office of Technical
Services, U. S. Department of Commerce, 1952.

Since diffraction lines of sufficient intensity could be obtained with our instrument only up to $2\theta = 145^{\circ}$, the direct extrapolation to 180° is not very accurate. According to Taylor and Sinclair[23] a plot of the lattice constant, computed from different diffraction angles, against $f(\theta) = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ gives a straight line. Using this method, our data are plotted in Fig. 8 for thallium chloro-bromide, and in Fig. 9 for thallium bromo-iodide. Although the lines are not entirely straight, they are quite good for the purpose of extrapolation. Values thus obtained are given in Table 6.

TABLE 6

LATTICE CONSTANTS AND LINEAR COEFFICIENT OF THERMAL EXPANSION OF THALLIUM HALIDE CRYSTALS

Crystal	Freezing Point	Lattice Constant 25.0°C	Expansion Coefficient x 10^6 25°-35°C
TlCl	429.9$_6$°C	3.8423A	62 ± 3 54.6 24) 53.5 25)
SlBr	459.9$_8$	3.9858	61 ± 2
TlI (cubic)	442.2	4.198 26)	
TlI (orthorh.)	175 (trans)*	5.263 4.591 12.929	67 17 39
TlCl + TlBr (70+30 mole %)	422.90	3.8893	51 ± 1
TlBr + TlI (46+54 mole %)	413.96	4.1170	49 ± 1

23) A. Taylor and H. B. Sinclair, Proc. Phys. Soc. (London) 57, 126 (1945).

24) M. Straumanis and A. Ievins, "Die Prazisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode," J. Springer, Berlin, 1940.

25) P. G. Hambling, Acta Cryst. 6, 98 (1953).

26) T. Barth, Z. phys. Chan. 131, 105 (1927).

* The transition temperature is given from low temperature (orthorhombic) to high (cubic). Only for this direction is the transition temperature constant. In opposite direction the transition temperature varies and may drop to 155°C.
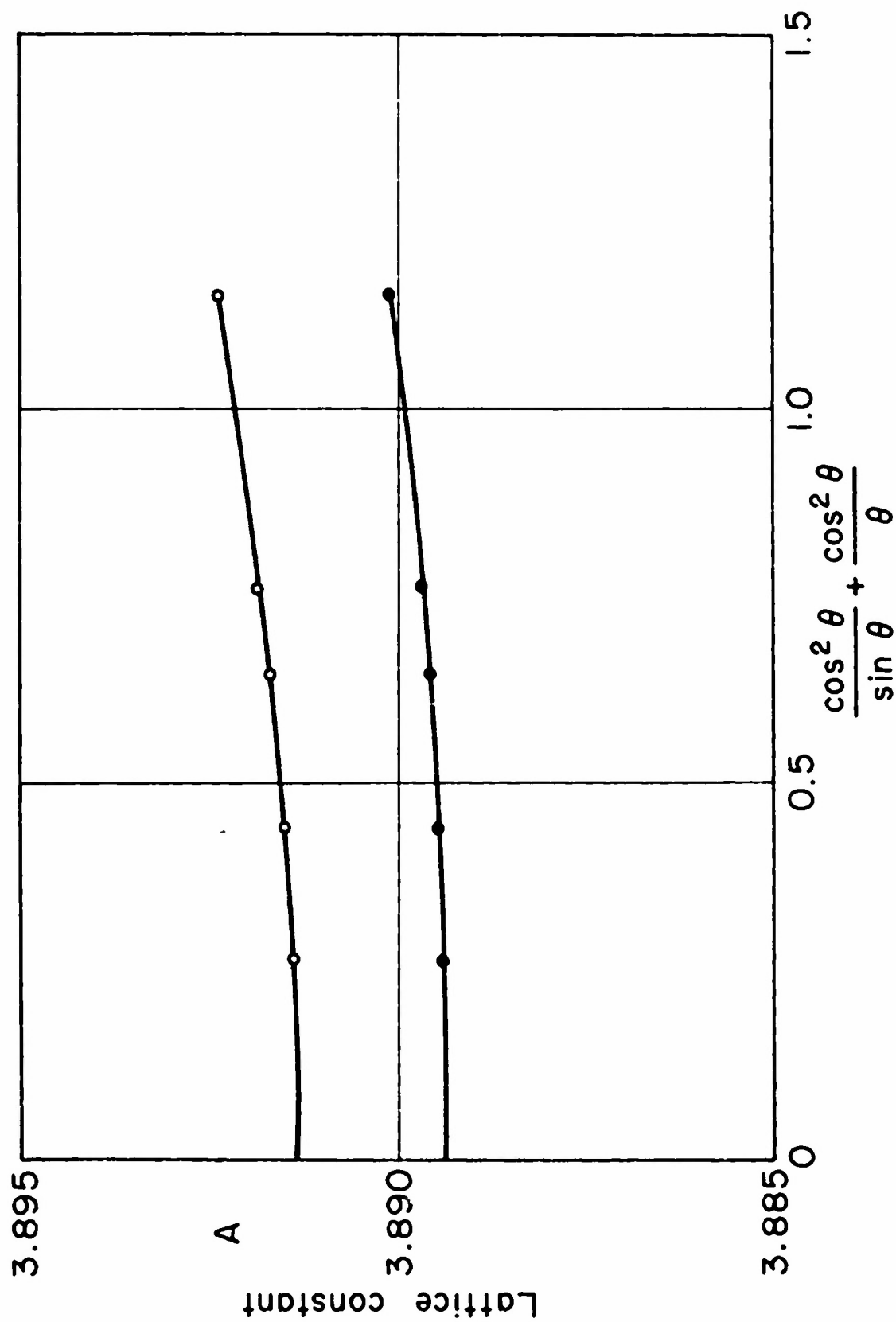
Fig. 8. Graphical extrapolation of lattice constant of the mixed crystal of 70 mole % TlCl + 30 mole % TlBr. Upper curve at 35.8°C; lower curve at 25.0°C.
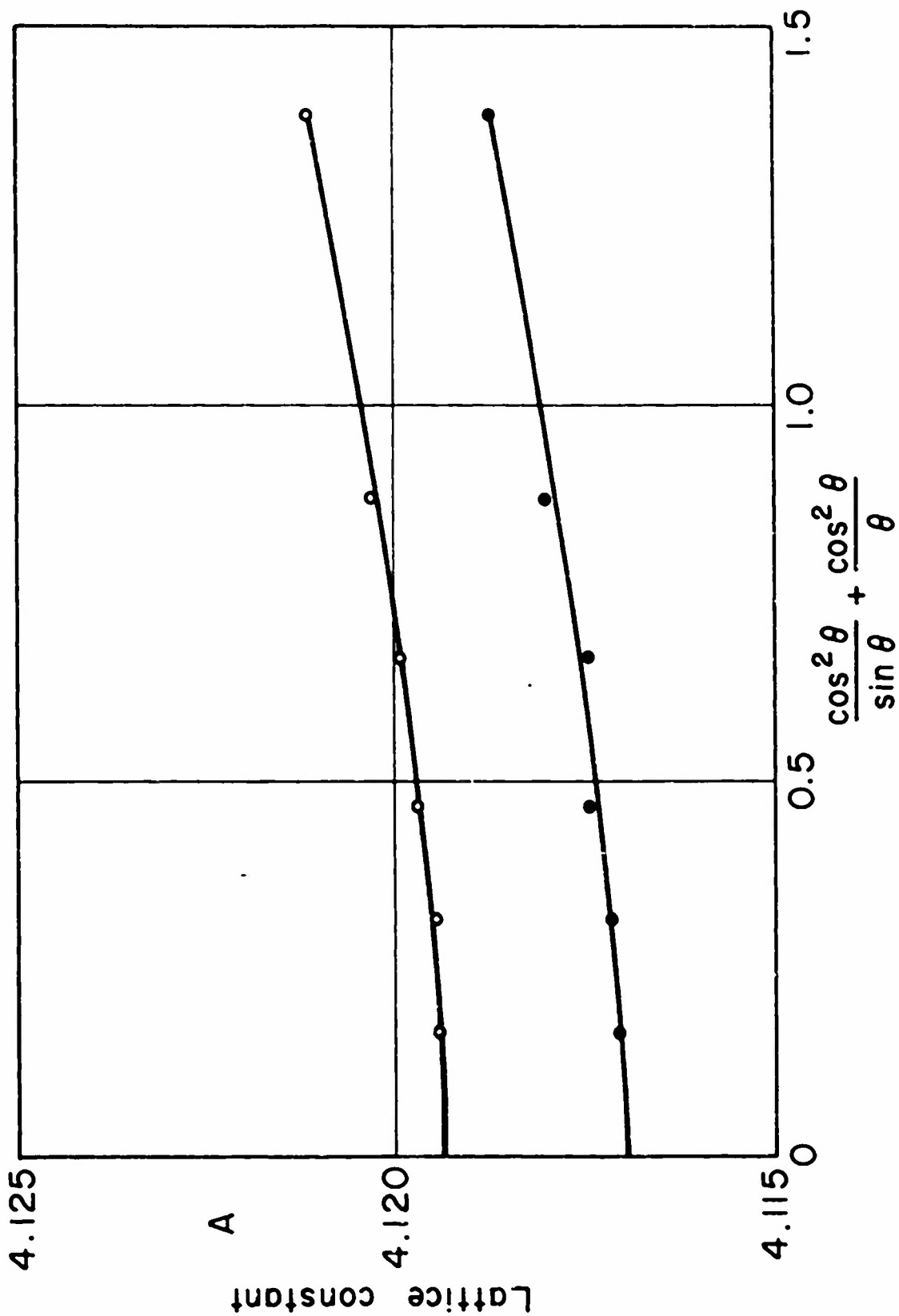
Fig. 9. Graphical extrapolation of lattice constant of the mixed crystal of 46 mole % TlBr + 54 mole % TlI. Upper curve at 36.6°C; lower curve at 25.0°C.

For computing the lattice constants we used $\lambda_{CuK\alpha}$ = 1.54050Å.[27] Our data agree with those given by Straumanis and Ievins.[24]

The lattice constants were determined at 25.0° and 35.0°C and from these data the thermal expansion coefficients (Table 6) computed. The data for TlI are less accurate than the others because the extrapolation to 180° could not be used. The expansion coefficient of thallium chloro-bromide crystals is somewhat lower than those of the pure components. A comparison of thallium bromo-iodide with its components is not possible because thallium iodide is orthorhombic in this temperature range. On the other hand, it has to be mentioned that Kantola[28] found a higher expansion coefficient for mixed potassium chloride and bromide than in pure components. Generally the known lattice constants vary considerably (Table 6) and further measurements are necessary for explanation of the variation.

Conclusions

Our results show that the optical inhomogeneity of mixed thallium halide crystals grown to date was caused by the incorrect composition of the melt. If the composition corresponds exactly to the minimum of the melting point, large, single, mixed crystals can be grown which are perfectly homogeneous. Using the lattice constant as an indicator for the homogeneity of the crystals, we can conclude that the refractive index variation in the new crystals is less than 1×10^{-5}..

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27) W. L. Bragg, Acta Cryst. 1, 46 (1948).

28) M. Kantola, Publ. State Inst. Techn. Res. (Finland) Nos. 2 and 3 (1947).

INHOMOGENEITY OF THALLIUM HALIDE
MIXED CRYSTALS AND ITS ELIMINATION

Errata Sheet

for Technical Report 67, Lab. Ins. Res., M. I. T.

Page 8, Fig. 2, "spectrophotometer" should be "spectrometer."

Page 17, Table 6, "SlBr" should be "TlBr;"

the freezing point of TlCl should be 430. 2°C instead of 429. 9_{6}^{o}C;

that of TlBr 460. 5, instead of 459. 9_{8};

and that of TlI (cubic) 442. 5 instead of 442. 2.

Page 20, line 11. "lattice constants" should be "linear expansion coefficients."