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ZINC BLENDE TYPE HgTe–MnTe SOLID SOLUTIONS—I

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Abstract—The ternary phase diagram Hg–Mn–Te is discussed with special emphasis on the stability and phase limits of the solid solution range which has the zinc blende type structure. Up to about 80 per cent of the mercury atoms in HgTe can be replaced by manganese atoms with the retention of the zinc blende type structure. The possible concentration of tellurium vacancies in the lattice increases to approximately 13 per cent as the manganese content increases.

1. INTRODUCTION

WE HAVE found that HgTe–MnTe solid solutions of the zinc blende structure-type, designated the α-phase, can be prepared in the range 0 to about 80 molar per cent MnTe. This paper discusses the physical chemistry and phase diagram of these alloys. The results of electrical measurements will be reported in a second paper.

The interest in this system, compared with the HgTe–ZnTe system for example, is the possible influence of the half-filled "*d*" shell of the Mn^{2+} ions on the electrical transport properties. These alloys, HgTe–MnTe, belong to one of the few systems which contain appreciable quantities of paramagnetic ions, and in which high mobilities are observed for either electrons or holes.

The electrical properties of HgTe were first described by NIKOL'SKAYA and REGEL,(1) and later by other authors.(2–6)

HgTe–CdTe alloys have been investigated by LAWSON, NIELSON, PUTLEY and YOUNG,(3) HARMAN *et al.*,(7) and SCHNEIDER and GAVRISHCHAK.(8)

2. PREPARATIVE TECHNIQUE

2.1. *Purity of starting materials*

Manganese was obtained as electrolytic flake of a stated purity of 99·9 per cent, and was melted under hydrogen to remove sulphur. The tellurium was melted in an atmosphere of hydrogen, and zone-refined with ten passes, which gives a purity of at least 99·99 per cent. The major impurities detected spectrographically after the zone-refining process were bismuth, antimony and selenium. The mercury used had been purified by the triple distillation method, which according to LAWSON *et al.*(3) gives a purity of 99·999 per cent.

2.2. *Preparation of Alloys*

Alloys were prepared by sintering powders of HgTe and MnTe together. HgTe was prepared as a cast ingot by melting mercury and tellurium together in an evacuated silica tube. The silica tube was initially heated to 450°C, at which temperature mercury and tellurium react rapidly, and the mass of HgTe which forms can block off unreacted mercury from the remaining tellurium. The tube was therefore slowly heated to 700°C, and continuously rocked to ensure complete mixing of the elements. In this way we avoided the formation of pockets of free mercury which might have caused explosions at the temperatures of the melting points of the alloys. The tube was quenched to 550°C and then slowly cooled to room temperature overnight. The tube was inspected for traces of free mercury before it was opened.

Alternatively, mercury and tellurium powder of less than 250μ size were heated together for one day at 550°C in a hard glass tube. The HgTe which formed was porous, but suitable for milling to a powder.

Manganese and tellurium were separately milled to a particle size of 75μ, and appropriate weights of the mixed powders were placed in silica tubes. The total weight of material used was about 40g. These operations were carried out in an atmosphere of argon. The silica tubes were then evacuated and sealed. The reaction between the elements was initiated by warming one end of the silica tube; the reaction was violent and the heat generated was sufficient to melt the MnTe momentarily. However, the tubes quickly cooled to room temperature. No attack on the silica occurred during the few seconds that the MnTe was molten, and no tube ever cracked or exploded.

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The cast ingots of HgTe and MnTe were separately milled to a particle size of less than 75μ and appropriate quantities weighed out, thoroughly mixed, and pressed into cylinders at a pressure of 5×10^3 kg/cm^2. These operations were also carried out in an atmosphere of argon. The pressed cylinders were sintered in sealed, evacuated hard glass tubes at various temperatures—treatment for three days at 450°C was found to be suitable for most alloy composition. The free space in the tubes was filled by glass discs to minimize the loss of volatile constituents. When an excess or deficiency of tellurium was required, the necessary compositional adjustment was made to the HgTe component of the alloy. The result of the single sintering treatment was in all cases a homogeneous alloy, provided that the alloy was a stable phase. No resintering was necessary, and the sintered cylinders were used for various experiments including preliminary electrical measurements.

3. EXAMINATION OF ALLOYS

3.1. *X-ray examination*

The sintered cylinders were crushed in air to a particle size of 75μ and the powders were annealed at various temperatures for one day in evacuated, sealed tubes in which the free space was kept to a minimum. Hard glass tubes were used up to 550°C, and silica tubes from 550 to 700°C. Since manganese rapidly attacks silica above 700°C, the powders to be annealed above this temperature were placed in small alumina tubes which were sealed inside silica tubes. Samples annealed above 550°C were quenched in water, and those annealed below 550°C were allowed to cool in air after removal from the furnace.

The powders were examined by conventional X-ray powder diffraction techniques, using an 11·46 cm diameter camera and CuKα radiation. The values of $1{\cdot}5405_0$ and $1{\cdot}5443_4$ Å were assumed for the wavelengths of the α_1 and α_2 radiations respectively in calculating the structure-cell dimensions from X-ray patterns of the alloy specimens.

3.2. *Differential thermal analysis* (*DTA*)

The sintered cylinders were crushed to 250μ size and about 12g of powder were packed into a silica tube provided with the usual re-entrant thermocouple well. Temperature differences between the sample and dummy were measured to $\frac{1}{5}$°C, and the absolute temperature was known to 2°C. Heating and cooling rates were 1 to 2°C/min, and little attack took place on the silica during the short time that the samples were molten. The results are summarized in Table 1.

The volume of the sample was only about one half of the volume of the tube after the sample had melted. Therefore some evaporation of mercury from the sample must have taken place to maintain the necessary vapour pressure of mercury. If we assume that the latter is 30 atm over HgTe at the melting point, the loss of mercury is about 2 at. per cent. This is probably an over-estimate for most of our samples, but the point must be considered in discussing the results.

3.3 *Vapour phase equilibration*

The following method was used to explore the tellurium-deficient phase boundary of the α-phase solid solution range.

Samples of $Hg_xMn_{1-x}Te_{1.0}$ were treated at 550°C in a controlled pressure of mercury vapour from a reservoir at 500 or 520°C. The increase in weight of the sample was recorded, and the phases present analyzed by X-ray powder diffraction.

Approximately 2g of sample were used, either as a sintered cylinder or as a powder, and the increase in weight of the sample after treatment was measured to 0·2 mg. The decrease in weight of the mercury in the reservoir was also checked. We believe that the major source of error in experiments such as these is the loss of tellurium from the sample; this tellurium is normally observed as HgTe condensed on the walls of the containing tube. Thus, to minimize the loss of tellurium, heat treatments were carried out for one day only. This treatment was considered to be adequate, since diffusion

Table 1. *Results of DTA runs on* HgTe/MnTe *preparations*

Molar per cent MnTe	Arrest on heating run (°C)	Identification	Arrest on cooling run (°C)	Identification
0	665	m.p.	669	f.p.
5	670	m.p.	680	f.p.
10	677	m.p.	698	f.p.
15	671	m.p.	709	f.p.
17·5	675	m.p.	729	f.p.
20	669	m.p.	775?	f.p.
20	—	—	720	$MnTe_2$ forms
25	650	m.p.	—	No f.p. found
25	—	—	720	$MnTe_2$ forms
35	c.600°C	—	—	No f.p. found*
35	—	—	720	$MnTe_2$ forms

* F.P. is between 850 and 800°C judged by the appearance of the sample after heating runs.

of mercury through the sample is rapid. We assumed that the mercury vapour pressure was high enough to produce a composition in the sample corresponding with that of an α-phase close to the tellurium-deficient phase boundary. The results of our experiments are summarized in Table 2.

Table 2. Results of Mercury vapour equilibration of HgTe/MnTe *preparations, samples at* 550°C

Molar % MnTe	Temperature of reservoir of Hg (°C)	At.% Additional Hg in sample	Phases observed	Lattice parameter of α-phase (Å)	Nominal Composition after Treatment
10	500	3	α (zinc blende type)	—	
25	525	4	α	6·431	$Hg_{0\cdot75}Mn_{0\cdot25}Te_{0\cdot973}$
50	520	10	α	6·406	$Hg_{0\cdot545}Mn_{0\cdot455}Te_{0\cdot91}$
75	520	14	α, $MnTe_2$*	6·373	$Hg_{0\cdot35}Mn_{0\cdot65}Te_{0\cdot87}$
85	500	16	α, $MnTe_2$*, MnTe*	6·367	$Hg_{0\cdot27}Mn_{0\cdot73}Te_{0\cdot86}$
90	500	16	α, $MnTe_2$*, MnTe*	6·362	$Hg_{0\cdot21}Mn_{0\cdot79}Te_{0\cdot88}$

* Traces of these phases were found.

4. DISCUSSION OF RESULTS

4.1. *Binary phase system* Mn–Te

There is little published information on any of the three binary systems involved. The Hg–Mn system does not concern us.

In the Mn–Te system, it is known that only two intermediate phases exist; MnTe with a nickel arsenide type structure, and $MnTe_2$ with a pyrites type structure.

According to FURBERG(9) the phase limits of $MnTe_2$ lie between $MnTe_{1\cdot7}$ and $MnTe_{1\cdot8}$ on the manganese-rich side, and between $MnTe_{1\cdot8}$ and $MnTe_{2\cdot0}$ on the high tellurium side of the phase range. Furberg also reports that the limits of the MnTe phase at 500°C are between $MnTe_{0\cdot8}$ and $MnTe_{0\cdot9}$ on the manganese-rich side, and between $MnTe_{1\cdot0}$ and $MnTe_{1\cdot1}$ on the tellurium-rich side. This agrees with our findings, except that we observe that all our preparations of $MnTe_{1\cdot0}$ at 500°C contain a trace of $MnTe_2$.

The melting point of MnTe is 1167°C(10) and DUDKIN(11) states that $MnTe_2$ decomposes peritectically at 735°C [See Section 4.3].

4.2. *Binary phase system* Hg–Te

Though it is known that HgTe is the only intermediate phase, only a few liquidus points for tellurium-rich compositions have been given.(12) The melting point of HgTe is variously given as 600°C(3) and 675 ± 5°C.(5)

We have determined the main features of the phase diagram near the composition HgTe by DTA and vapour phase equilibration. As was explained in Section 3.2, the actual compositions of the alloys could have been 2 at. per cent deficient in mercury near the melting point compared to the nominal composition, due to the loss of mercury vapour. The temperatures of the arrests were measured to ± 1°C, so that our results are qualitative only, and are shown in the schematic phase diagram (Fig. 1).

The maximum in the liquidus lies on the tellurium-rich side, between 2·5 and 4 at. per cent. The melting point of HgTe is 670 ± 1°C. The solid solubility of mercury in HgTe at 450°C is substantially less than 2 at. per cent and probably approaches 0 per cent; the solid solubility of tellurium in HgTe is appreciable, perhaps 2·5 at. per cent. In agreement with the value quoted by HANSEN,(12) we observed the tellurium–HgTe eutectic at 409 ± 2°C. The lattice parameter of HgTe does not appear to alter appreciably as tellurium is added.

4.3. *The* HgTe–MnTe *section of the ternary phase diagram*

Our results are summarized in Fig. 2. There is no difficulty in preparing single phase alloys containing up to 35 molar per cent MnTe by sintering the components at 450°C, but beyond this composition the α-phase appears to be metastable. All our alloy preparations with more than 35 molar

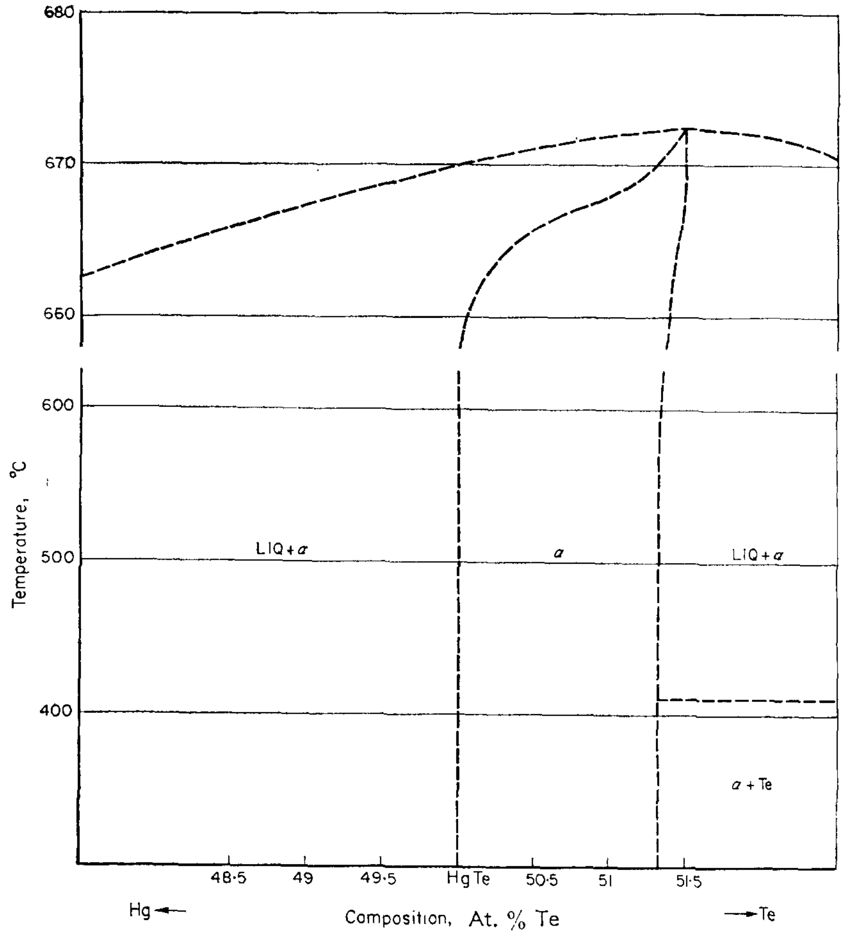

Fig. 1. Schematic phase diagram for the system Hg–Te, at the composition HgTe. *N.B.* Expanded scale used in temperature range 660–670°C.

per cent MnTe contained a trace of $MnTe_2$ after sintering at 450°C for 3 days, the amount observed increasing as the period of heat treatment was extended. It appears that the first product of reaction in this composition range is an α-phase which decomposes slowly into $MnTe_2$ and a mercury-rich α-phase. If free mercury had been present in these alloys, we would have expected to observe traces condensed on the walls of the heat-treatment tube after cooling to room temperature, and we obtained no evidence of this nature for any of our alloy preparations.

We attempted to prepare single phase material of the composition 50 molar per cent MnTe by sintering the components at 250°C, but even after 20 days at this temperature the reaction was not complete. No improvement was observed when a sample sintered at 450°C for 3 days was annealed at 250°C.

The presence of $MnTe_2$ in alloy preparations containing more than 35 molar per cent MnTe accounts for the scatter that we observe in the lattice parameters of the α-phases which are plotted in Fig. 3. Nevertheless, Vegard's Law which is closely obeyed in the composition range 0–35 molar per cent MnTe, still appears to be followed well towards the limiting composition of the α-phase.

During DTA runs we observed only a diffuse arrest for the liquidus when the sample contained

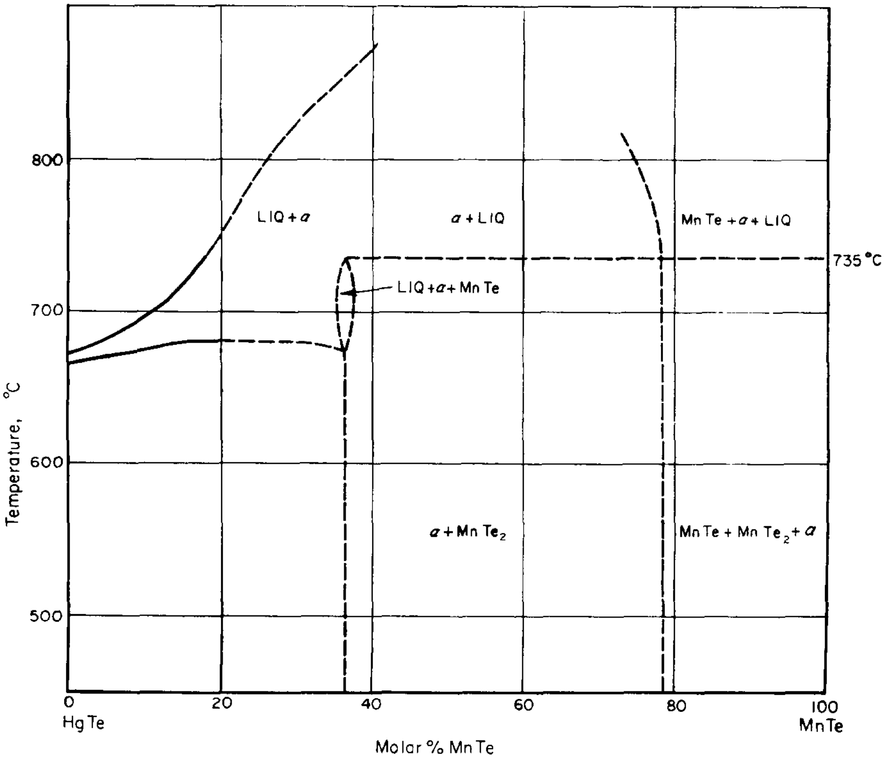

FIG. 2. HgTe–MnTe section of the ternary phase diagram.

10–20 molar per cent MnTe, and failed to observe any arrest for alloys containing more than 20 molar per cent MnTe. Presumably, during the cooling runs the α-phase that first freezes out is appreciably deficient in tellurium compared with the liquid composition, and this accounts for the diffuseness of the arrest. The excess tellurium can then accumulate in the liquid phase, and at 720°C we observe a sharp arrest which we attribute to the formation of $MnTe_2$. DUDKIN[11] states that $MnTe_2$ decomposes peritectically at 735°C.

The materials from the DTA runs were examined by X-ray powder diffraction without further annealing. An inhomogeneous α-phase was observed in each case, the measured range of lattice parameter increasing with increasing manganese content. No trace of $MnTe_2$ was found in any sample. Moreover, during the heating runs on these alloys, no arrest at 720°C could be detected. We conclude, therefore that in our experiments, $MnTe_2$ is not in equilibrium with the α-phase at room temperature, when the concentration of MnTe in the alloys is less than 35 molar per cent. During the cooling runs, mercury from the mercury-rich α-phase which originally solidifies out can diffuse into any $MnTe_2$ formed, to give an α-phase of another composition.

We attempted to determine the phase constitution of alloys in the range 35–70 molar per cent MnTe at temperatures above 720°C. Powders were annealed at 770°C for 1 day and then quenched into water. $MnTe_2$ was observed in some samples, but in randomly varying concentrations, indicating that the high temperature phases were not always retained. A 35 molar per cent MnTe sample contained some free tellurium and an inhomogeneous α-phase. A 50 molar per cent MnTe sample contained MnTe, possibly some free tellurium and an α-phase with a limited range of composition. A sample with 75 molar per

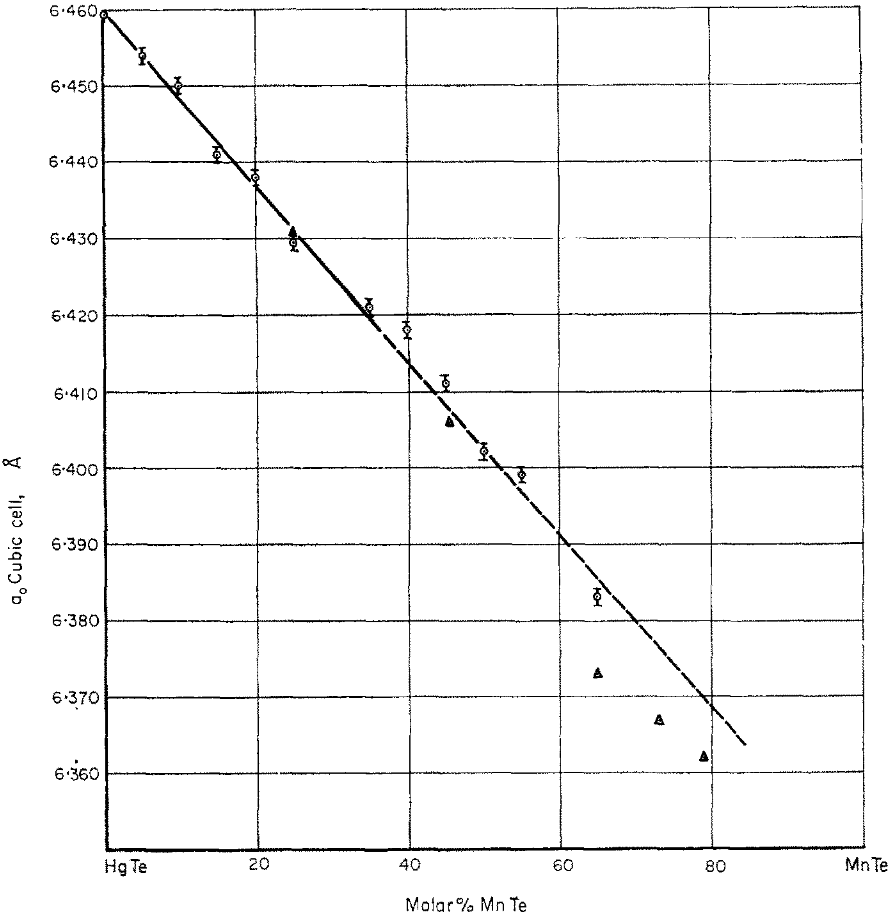

FIG. 3. Variation in structure cell dimensions of α-phases with change in composition.

⊙ As prepared △ Heat-treated in Hg vapour	Values of a_0 obtained from the measurement of one sample only for each alloy composition.

cent MnTe contained MnTe as the major phase, and the percentage of MnTe observed was substantially greater than that in a similar sample annealed at 550°C. It would appear, therefore, that the amount of manganese that the zinc blende type lattice can accommodate decreases with increasing temperature.

4.4 *Tellurium-deficient α-phases* (550°C *isotherm*)

We explored the tellurium-deficient boundary of the α-phase solid solution range at 550°C, by diffusing mercury into $Hg_xMn_{1-x}Te_{1.0}$ alloy samples as described in Section 3.3. Our results are summarized in Table 2 and Fig. 4 which represents the isotherm at 550°C. It can be seen that as the manganese content increases substantial deficiencies of tellurium are observed in the zinc blende type α-phase, reaching a maximum of about 13 per cent.

We have noted that the compound $Hg_{0.5}Mn_{0.5}Te_{0.9}$ is stable up to 770°C, but we have not studied it at higher temperatures.

4.5. *Non-stoichiometric* $Hg_{0\cdot9}Mn_{0\cdot1}Te$ *alloys*

As the mercury-rich end of the α-phase range has the most interesting electrical properties, the alloy $Hg_{0\cdot9}Mn_{0\cdot1}Te$ was studied in further detail. The solubility of excess tellurium in this alloy at 450°C is more than 2·5 at. per cent, and of excess mercury 3 at. per cent. The lattice parameters for alloys containing 2·3 at. per cent excess tellurium and 1·8 at. per cent excess mercury are $6{\cdot}452_5$ and 6·443 Å respectively. The liquidus of this section of the system has a flat maximum at 700°C, occurring at a composition of 1·8 at. per cent excess mercury.

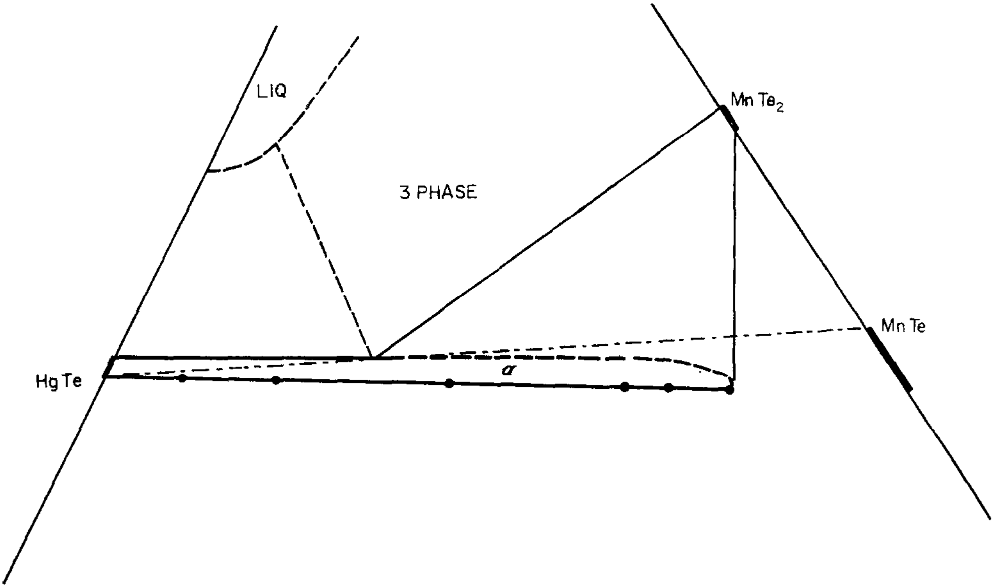

FIG. 4. Ternary isotherm at 550°C showing the α-phase region. —·—·—·— Construction line joining stoichiometric compositions HgTe and MnTe.

4.6. *Other transition metal alloy systems*

In this Section we consider that other alloys might exist which are semiconducting, have a reasonably high mobility, and contain a transition metal with an incompletely filled "*d*" shell.

The close similarity in properties between HgTe and HgSe leads us to predict that HgSe–MnSe alloys will exist, and that their properties will be similar to the HgTe–MnTe alloys described in this present work. It would be interesting to attempt to dissolve transition metals other than manganese in either HgTe or HgSe. We have tried, without success, to dissolve nickel and chromium in HgTe. It is worth noting that MnTe is the only first row transition metal telluride that is semiconducting, all the others being metallic.(13) We suggest, therefore, that only transition metal chalcogenides which are semiconducting will form solid solution alloys with HgS, HgSe and HgTe. In the selenide systems, it is known that MnSe, CrSe and perhaps FeSe are semiconducting, so that these compounds may form zinc blende type solid solutions with HgSe.

Although HgS itself has the cinnabar structure, REGEL(1) reports that solid solutions of HgS with less than 1 per cent HgTe have the zinc blende type structure. CrS, FeS, MnS and possibly NiS and CoS are semiconducting, and these compounds also are likely to form appreciable ranges of zinc blende type solid solutions with HgS containing a little Te. These alloys are being investigated.

We now consider other Group II metal tellurides. JUZA *et al.*(14) report ZnTe–MnTe alloys with the zinc blende type structure and we have prepared CdTe–MnTe alloys containing at least 75 molar per cent MnTe. These alloys are semiconductors with high energy gaps and probably have low mobilities. HARMAN(7) and PUTLEY(3) have shown that $Hg_{0\cdot 9}Cd_{0\cdot 1}Te$ has a mobility of 100,000 cm^2/V sec at 80°K. Alloys of this compound with MnTe should be of interest.

JOHNSTON(10) reports that above 900°C MnTe has the rock salt type structure, and that GeTe–MnTe alloys exist which have this structure at room temperature, and show a wide range of composition. These alloys are of interest as thermoelectric generating materials, but they are unlikely to have high mobilities. We have tried, unsucessfully, to dissolve manganese in PbTe. The large size difference of the Pb^{2+} and Mn^{2+} ions may well account for our failure.

REFERENCES

1. NIKOL'SKAYA E. I. and REGEL A. R., *Zh. tekh. fiz.* **25,** 1352 (1956).
2. BRACH B. Ya, ZHDANOVA V. V. and LEV E. Ya, *Sov. Phys. Solid State* **3,** 571 (1961).
3. LAWSON W. D., NIELSON S., PUTLEY E. H. and YOUNG A. S., *J. Phys. Chem. Solids* **9,** 325 (1959).
4. HARMAN T. C., LOGAN M. J. and GOERING H. L., *J. Phys. Chem. Solids* **7,** 228 (1958).
5. HARMAN T. C. and STRAUSS A. J., *J. appl. Phys.* **32,** 2265 (1961).
6. CARLSON R. O., *Phys. Rev.* **111,** 476 (1958).
7. HARMAN T. C., STRAUSS A. J., DICKEY D. H., DRESSELHAUS M. S., WRIGHT G. B. and MAVROIDES J. G., *Phys. Rev. Letters* **7,** 403 (1961).
8. SCHNEIDER A. D. and GAVRISHCHAK I. V., *Sov. Phys. Solid State* **2,** 1865 (1961).
9. FURBERG S., *Acta Chem. Scand.* **7,** 693 (1953).
10. JOHNSTON W. D. and SETRICH D. E., *J. inorg. nucl. Chem.* **19,** 229 (1961).
11. DUDKIN L. D. and VAIDANICH V. I., *Sov. Phys. Solid State* **2,** 1384 (1961).
12. HANSEN M. and ANDERKO K., *Constitution of Binary Alloys*, p. 840. McGraw-Hill, New York (1958).
13. DUDKIN L. D., *Sov. Phys. Solid State* **2,** 371 (1960).
14. JUZA R., RABENAU A. and PASCHER G., *Z. anorg. Chem.* **285,** 61 (1956).