

PHASE RELATIONS IN THE SILVER-TELLURIUM SYSTEM¹

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ABSTRACT

In the Te-Ag₂Te part of the system the liquidus falls from the melting point of Te, 449.8±0.2° C., to an eutectic e₁ at 353.0±0.5° C., 33.3±0.5 at. % Ag, and then rises in several steps to the melting point of Ag₂Te at 960° C. At 420±5° C. the Ag_{5-x}Te₃ compound melts incongruently to crystals of γ -phase and a melt of 44.4±0.5 at. % Ag. Ag_{5-x}Te₃ has a transition at 295±10° C. in the presence of Te and at 265±15° C. in the presence of a more silver-rich phase. This transition has the characteristics of an order-disorder reaction. At 460±5° C. a peritectic reaction occurs, as the incongruently melting γ -phase dissociates into crystals of Ag₂Te and a melt of 48.7±0.5 at. % Ag. γ -phase is not stable below 120±15° C. and has a transition at about 178° C.

In the Ag₂Te-Ag part of the system two immiscible liquids coexist with crystals of Ag₂Te at 881±3° C., the two liquids having the composition 69.6 and 87.5 both ±0.5 at. % Ag; there is an eutectic e₂ of Ag₂Te, Ag, and melt at 869±3° C., 87.5±0.5 at. % Ag.

Ag₂Te has two transitions. The lower transition, monoclinic to face-centred cubic, occurs at 145±3° C. The upper transition, to body-centred cubic, occurs at 689±5° C. on the Te side of Ag₂Te, and at 802±3° C. on the Ag side.

The differential thermal analysis technique has been used to determine the magnitude of the heat effects at some transformations.

INTRODUCTION

This paper has been prepared by Cabri based on an unpublished manuscript by Kracek and Ksanda. Kracek's and Ksanda's experimental work (mostly differential thermal analysis) was performed at the Geophysical Laboratory of the Carnegie Institution, Washington. Cabri's experimental work (high-temperature *x*-ray diffraction and optical and *x*-ray examination of quenched charges) was performed at the Department of Geological Sciences, McGill University, Montreal, Canada. Wherever practicable, Kracek's and Ksanda's original text will be indicated by quotation marks.

This system is of particular interest to mineralogy because the stability fields of reported minerals may be useful in the interpretation of certain ore deposits. The composition of hessite, Ag₂Te, is undisputed. A mineral of approximate composition Ag_{5-x}Te₃ has been widely known as empressite since 1951 (Thompson *et al.*). However, Honea (1964) confirmed that Bradley's (1914) original composition for empressite was AgTe and pro-

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posed naming the $\text{Ag}_{5-x}\text{Te}_3$ mineral stuetzite. Stuetzite was the name given by Shrauf (1878) for a mineral of composition Ag_4Te , but this composition was discredited by Thompson *et al.* (1951). To avoid further confusion in the use of empressite, chemical compositions will be used for AgTe and $\text{Ag}_{5-x}\text{Te}_3$.

PREVIOUS WORK

Previous experimental work in the Ag-Te system indicating only two binary phases has been reviewed by Markham (1960) except for the following. Kiukkola and Wagner (1957) indicated the presence of a phase intermediate between $\text{Ag}_{5-x}\text{Te}_3$ and hessite—the γ -phase—and this has been confirmed (Cabri, 1965a). They showed, by means of solid-state titrations at 250° and 300° C., that there is evidence for the existence of a third phase. The phases were indicated by curves of a plot of the EMF of a cell $\text{Ag}/\text{AgI}/(\text{Ag}, \text{Te})$ vs Ag/Te . The curves were separated by horizontal lines representing two-phase fields. They designated these phases, α , γ and ϵ corresponding to decreasing Ag content. Regarding compositions, they reported (p. 386), "At 300° C. the Ag/Te ratio ranges from 1.99 to 2.00 for the α phase, from 1.88 to 1.91 for the γ phase, and from 1.63 to 1.66 for the ϵ phase." This would correspond to Ag_2Te for α , $\text{Ag}_{1.9}\text{Te}$ for γ , and $\text{Ag}_{5-x}\text{Te}_3$ for ϵ , with x less than 0.11.

Honea (1964) reported that a chemical analysis made on material from the Empress Josephine mine, Colorado, gave the formula AgTe , thus substantiating Bradley's (1914) early analysis. He further made x -ray single crystal and DTA examinations of this material and proposed retaining Bradley's terminology of empressite for the AgTe phase. He was unable to synthesize AgTe and found that it decomposed to $\text{Ag}_{5-x}\text{Te}_3 + \text{Te}$ above 210° C.

At room temperature, hessite is monoclinic (Frueh, 1959), $\text{Ag}_{5-x}\text{Te}_3$ is hexagonal (Thompson *et al.*, 1951), and AgTe is orthorhombic (Honea, 1964).

MATERIALS AND METHODS OF INVESTIGATION

Kracek and Ksanda made mixtures of the desired compositions from silver and tellurium. The silver (999.9₃ fine, as rolled sheet from the U. S. Mint) was cut into 5-mm squares and heated in air to destroy surface sulfide. The tellurium (electrolytic quality) was purified by vacuum distillation in pyrex glass. The distilled metal had a melting point of $449.8 \pm 0.2^\circ$ C. (Kracek, 1941), which agrees well with Machol and Westrum (1958). The mixtures were fused in evacuated pyrex or clear silica glass tubes, cooled, then powdered, repeatedly mixed, and annealed at 300° C. For thermal analysis the prepared mixtures were sealed under

a vacuum in previously described pyrex or silica melting tubes (Kracek, 1930, 1946).

The materials and synthesis used by Cabri have also been described elsewhere (Cabri, 1965b).

Differential thermal analysis. The measurements were made with an electrically shielded Wolff-Feussner potentiometer connected to a galvanometer the sensitivity of which was kept at $1 \mu\text{V}$ per mm. The reading thermocouple was a calibrated Pt vs Pt-10 per cent Rh thermocouple arranged to read the sample temperature; the differential thermocouple was Pt-10 per cent Rh vs Au-40 per cent Pd vs Pt-10 per cent Rh, with one junction in the sample and the other in a neutral body of Pt, or as otherwise required. The furnace arrangements were as previously described by Kracek (1930, 1946).

Thermal calibrations for temperature were made at the melting points of tin (231.9°), zinc (419.4°), antimony (630.5°) and silver (960.5°) on the Day-Sosman scale as tabulated by Adams (1926). The temperatures are given in degrees C. They agree with international temperature scales very closely.

Arrest temperatures were located by plotting the sample temperature vs the differential emf in μV . In taking the measurements, the rise or fall in furnace temperature was controlled by adjusting the resistance of the furnace circuit every half minute using a large 3-decade rheostat.

Furnace calorimetry. Measurements of the heat effect magnitudes at the arrests were carried out by plotting time in minutes vs the differential temperature in μV , and comparing the area under the curve in $\mu\text{V}\cdot\text{min}$ with areas generated by phase reactions of known thermal magnitudes, as originally described by Kracek (1930). The theory of the method has been stated explicitly by Speil (1944), Kerr and Kulp (1948), Wittels (1951) and others. The method was critically examined by White (1929). The apparatus was calibrated for heat effects at the melting points of tin (14.3 cal/g at 231.9°), zinc (25.5 cal/g at 419.4°) and tellurium (33.5 cal/g at 449.8°), using the latent heats quoted by Bichowsky and Rossini (1936). The time-differential emf areas, as plotted, were integrated with a Corradi rolling-sphere planimeter. The calibration is represented by the equation $c = 3.06 + 0.0174 t$, where the thermal equivalent of the apparatus, in calories (cal) per unit area, was plotted vs the temperature of the calibration point. In the absence of suitable calibrating substances for higher and lower temperatures, a straight line was extrapolated down to 100° and up to 470° .

Cabri prepared thirteen charges of different compositions (56.75 to

62.38 wt. % Ag) by heating weighed amounts of Ag and Te in sealed evacuated silica tubes above 950° C. After various heat and grinding treatments, portions of these charges were transferred into silica glass capillaries which were evacuated and sealed for use in the high-temperature x-ray diffraction camera. The heating procedure for this camera is reported elsewhere (Cabri, 1965b).

Another series of experiments to try to synthesize AgTe will be described below.

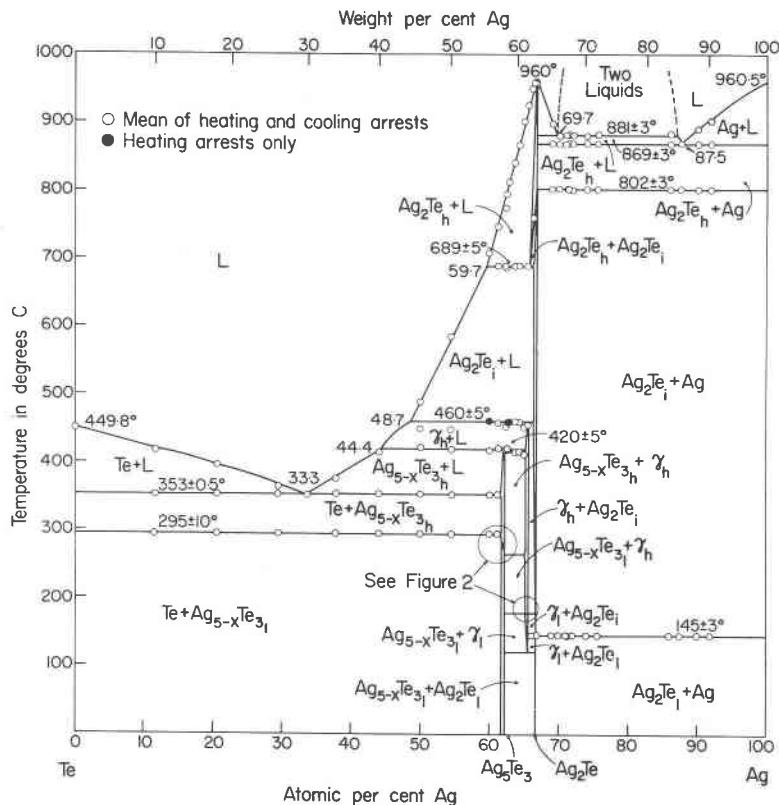


FIG. 1. The phase diagram for the Ag-Te system in the presence of vapor.

EXPERIMENTAL RESULTS

Phase relations in the Ag-Te binary system are shown in Fig. 1 and 2 as temperature-composition diagrams. All temperatures are in degrees Centigrade; compositions are expressed in atomic and/or weight per cent Ag.

“In comparing the results obtained by DTA with those of earlier workers we may note that Chicashige and Saito (1916) and Pellini and Quercigh (1910) employed cooling arrests only. Since some of the phase reactions undercool markedly, the cooling arrest temperatures (c) are correspondingly lower than our average values (m) from heating (h) and cooling arrest temperatures (c) experiments. Our cooling rates were in

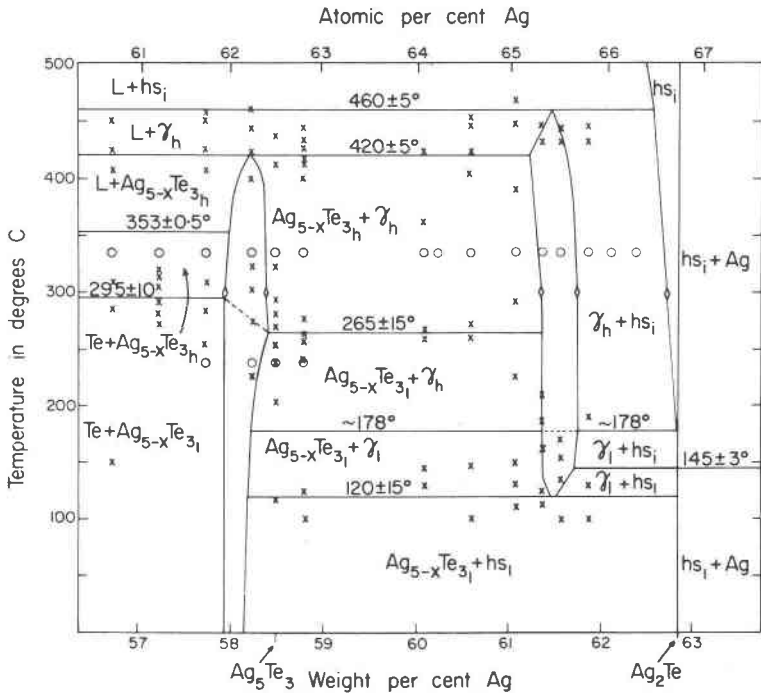


FIG. 2. Portion of the Ag-Te binary phase diagram in the presence of vapor. Crosses represent high-temperature camera data, circles represent quenched runs *x*-rayed with the Guinier camera, and diamonds are the solid solution limits from Kiukkola and Wagner (1957).

the range of 1 to 5 degrees C. per minute. Very few arrests at the phase reactions in the system were actually isothermal. Moreover, because of the low thermal conductivities of some of the mixtures and of the glass or silica containers it is inevitable that the observed beginnings of arrests lay slightly behind the true beginnings of the phase reactions.”

Several anomalous results were ignored in drawing up Fig. 2 from data obtained with the Rigaku-Denki high-temperature diffraction camera. It was established, for example, that reliable data could not be obtained if a capillary was heated up more than once. Heating the same capillary

several times is thought to produce inhomogeneity in the charge. Even with capillaries used only once, several experiments gave anomalous results (*e.g.* the incongruent melting temperature of $\text{Ag}_{5-x}\text{Te}_3$ varied in some experiments up to 445° , the low-to-high transition in Ag-rich $\text{Ag}_{5-x}\text{Te}_3$ occurred as high as 293° in one experiment, and the γ -phase melted incongruently as low as 437° in some experiments).

The binary phase diagram (Fig. 1) at the liquidus may be regarded as composed of two adjoining partial systems a) Te- Ag_2Te , and b) Ag_2Te -Ag.

THE PARTIAL SYSTEM, Te- Ag_2Te

“The liquidus in this portion of the system first descends in a gentle curve from the melting point of Te at $449.8 \pm 0.2^\circ$ (Kracek, 1941) to an eutectic at $353.0 \pm 0.5^\circ$ (m), 33.3 ± 0.5 at. % Ag, and then rises steeply in four steps to the melting point of Ag_2Te at $960 \pm 1^\circ$. Ag_2Te is the primary phase above the peritectic temperature of $460 \pm 5^\circ$,” at which γ -phase dissociates to crystals of Ag_2Te (*i*)¹ and “a liquid of 48.7 ± 0.5 at. % Ag. There is a second break in the slope of the liquidus curve” at $420 \pm 5^\circ$, “ 44.4 ± 0.5 at. % Ag,” at which the primary phase, $\text{Ag}_{5-x}\text{Te}_3$ (*h*), breaks down to crystals of γ -phase plus liquid. “At temperatures above 460° the liquidus of Ag_2Te (*i*) passes through a break at $689 \pm 5^\circ$, 59.7 ± 0.5 at. % Ag, which is due to the newly discovered Ag_2Te (*h*) = Ag_2Te (*i*) transition.”

At subliquidus temperatures the incongruently melting $\text{Ag}_{5-x}\text{Te}_3$ was thought, by Kracek and Ksanda, to undergo a “distributed heat effect” (gradual transition) at $295 \pm 10^\circ$ in the presence of Te and at $252 \pm 13^\circ$ in the presence of a more silver-rich phase. High-temperature *x*-ray powder photographs exhibit perceptible changes in the *x*-ray pattern intensities (Table 1) indicating a reversible, but non-quenchable, polymorphic inversion in $\text{Ag}_{5-x}\text{Te}_3$ above $265 \pm 15^\circ$ on the Ag-rich side and above $295 \pm 10^\circ$ on the Te-rich side. Delineation of the two-phase field ($\text{Ag}_{5-x}\text{Te}_3$ (*l*) + $\text{Ag}_{5-x}\text{Te}_3$ (*h*)) is uncertain and is therefore shown in Fig. 2 as a dashed line.

*The $\text{Ag}_{5-x}\text{Te}_3$ (*l*) = $\text{Ag}_{5-x}\text{Te}_3$ (*h*) transition.* “This transition gave no sharply located arrest, but in compositions richer in Te than Ag_5Te_3 the differential temperature on heating begins to depart gradually from the smooth course previously followed, starting at temperatures as low as

¹ There has been much confusion in the literature in the notation used for polymorphs of silver tellurides. Both Roman numerals and lower case Greek letters have been employed. Throughout this text, the terms low, intermediate, and high, and their abbreviations *l*, *i*, and *h* are used.

230° in some cases; the rounded peak of the effect is not reached until 290° to 306° (h), being then followed by a slow dying out of the differential at still higher temperatures. The characteristics of this effect are reminiscent of a lambda transition rather than of a transition of the first kind, and the phase change appears to be an order-disorder type." This interpretation is confirmed by the high-temperature x-ray patterns, which indicate changes in the intensities of the same reflections for both

TABLE 1. HIGH-TEMPERATURE X-RAY DIFFRACTION PATTERNS FOR γ -PHASE AND $\text{Ag}_{5-x}\text{Te}_3$

γ -phase (61.08 wt. % Ag)				$\text{Ag}_{5-x}\text{Te}_3$ (58.23 wt. % Ag)			
150° C.		227° C.		275° C.		302° C.	
I	d meas.	I	d meas.	I	d meas.	I	d meas.
				w	3.55	w	3.57
				w	3.11	w	3.14
				w	3.03	w	3.02
				w	2.62	vw	2.63
				m	2.57	vw	2.57
vw	2.25	m	2.22	w	2.24	w	2.25
s	2.18	s	2.18	s	2.17	s	2.18
vw	2.11			m	2.13	m	2.15
				w	2.04	w	2.04
				w	1.95	w	1.95
				vw	1.88	w	1.88
				w	1.35	w	1.36

w=weak

vw=very weak

m=medium

s=strong.

forms. "At 62.5 at. % Ag, (Ag_5Te_3), this transition occurs in two well defined steps. On heating, the lower step, characteristic of Ag-rich mixtures, has a rounded maximum at about 265° (h); the upper step, characteristic of Te-rich mixtures, has a sharpish peak at 306° (h). Reversal on cooling through the upper step begins just above 310°, with a peak at about 290° (c); cooling through the lower step yields a wave-like rounded maximum near 240° (c). The mean temperatures are: upper step, characteristic of compositions more Te-rich than Ag_5Te_3 , $295 \pm 10^\circ$ (m), lower step, characteristic of compositions more Ag-rich than Ag_5Te_3 , $252 \pm 13^\circ$ (m); (Note: Cabri has shown those as $295 \pm 10^\circ$ and $265 \pm 15^\circ$ in Fig. 2, from high-temperature diffraction data). At 62.83 at. % Ag, and in more

Ag-rich compositions, only the lower step is observed with a rounded maximum at 260 to 267° (h) and at 238 to 242° (c). The heat effect decreases in magnitude rapidly from Ag_5Te_3 towards Ag_2Te and becomes imperceptible at 66.1 at. % Ag. Note that this transition occurs at lower temperatures in Ag-rich than in Ag-poor $\text{Ag}_{5-x}\text{Te}_3$, this being opposite to the change in the transition temperature in Ag_2Te ."

The gamma-phase. The phase intermediate in composition between $\text{Ag}_{5-x}\text{Te}_3$ and Ag_2Te , termed the γ -phase by Kiukkola and Wagner (1957), is stable between the temperature limits $120 \pm 15^\circ$ and $460 \pm 5^\circ$,

TABLE 2. SELECTED DIFFERENTIAL THERMAL ANALYSIS
DATA FROM KRACEK AND KSANDA

Composition range at. % Ag (wt. % Ag)	Heating arrest	Cooling arrest
62.50 to 65.54 (58.488 to 61.655)	122-138° C.	70-85° C.
65.54 to 66.67 (61.655 to 62.295)	147°	143°
	131-132°	121-123°
		85-110°

Note: $\text{Ag}_2\text{Te} = 66.67$ (62.29)

$\text{Ag}_5\text{Te}_3 = 62.50$ (58.49)

above which it melts to Ag_2Te plus liquid. The compositional range of the γ -phase at 300° is from 61.38 to 61.75 wt. % Ag according to Kiukkola and Wagner. The low-to-high polymorphic inversion, heretofore unreported, occurs at about 178°. No detail was obtained for the narrow field containing both the low and high polymorphs; this field is indicated in Fig. 2 as dashed line. The evidence for this transition is given in Table 1 where the high-temperature x -ray patterns for the two polymorphs are compared.

Kracek and Ksanda had difficulty in interpreting their DTA data in the region between 62.5 and 66.67 at. % Ag and below 150°. Their data are given in Table 2 and can be reinterpreted as follows based on x -ray diffraction analysis.

(1) 62.50 to 65.54 at. % Ag (58.49 to 61.65 wt. % Ag)

The heating arrest represents the formation of γ -phase. The cooling arrest represents the breakdown of γ to $\text{Ag}_{5-x}\text{Te}_3 + \text{Ag}_2\text{Te}$. The larger

divergence between the cooling arrest temperatures and that obtained with the high-temperature camera is not unexpected since the γ -phase can be preserved at room temperature with very rapid cooling.

(2) 65.54 to 66.67 at. % Ag (61.65 to 62.29 wt. % Ag)

The highest heating and cooling arrests correspond very well with the Ag_2Te polymorphic transition (low to intermediate), indicating negligible solid solution in Ag_2Te , as $145 \pm 3^\circ$ is the transition temperature on the Ag-rich side as well. The heating arrest at $131\text{--}132^\circ$ represents the formation of the γ -phase from $\text{Ag}_{5-x}\text{Te}_3 + \text{Ag}_2\text{Te}$. The two cooling arrests may be interpreted in two ways. They could be attributed to a partial, followed by a complete breakdown to $\text{Ag}_{5-x}\text{Te}_3 + \text{Ag}_2\text{Te}$. Alternatively, the highest cooling arrest may be due to a supercooled transition in γ -phase (found at 178°), with the lowest temperature representing the final breakdown to $\text{Ag}_{5-x}\text{Te}_3 + \text{Ag}_2\text{Te}$.

The existence of the γ -phase was confirmed with the high-temperature camera, the Guinier focussing camera, and polished sections. The difficulty of interpreting the two-phase assemblages $\text{Ag}_{5-x}\text{Te}_3 + \gamma$ -phase on high-temperature camera film is readily appreciated by referring to Table 1. However, the change from patterns showing $\text{Ag}_{5-x}\text{Te}_3 + \text{Ag}_2\text{Te}$ to γ -phase only, in preparations of about 61.5 wt. % Ag, above 120° is quite distinct. The Guinier x-ray powder diffraction pattern of the γ -phase at room temperature (Cabri, 1965a) indicates that the pattern is quite distinct from those of $\text{Ag}_{5-x}\text{Te}_3$ and Ag_2Te .

However, Fig. 3, prepared by Kracek and Ksanda, shows further evidence of the presence of the γ -phase. This figure shows estimated values of heat effects of the lower transition in Ag_2Te as a function of the composition. The open circles represent values measured on heating for preparations annealed between 330 and 380° . The straight line indicates that the γ -phase must have decomposed after annealing, i.e., when the measurements were made, and also that this line points to a composition $\text{Ag}_{5-x}\text{Te}_3$ within the error of such experiments. The crosses give values measured on reheating after first cooling through the $\text{Ag}_2\text{Te} (l) = \text{Ag}_2\text{Te} (i)$ transition, and thus represent this readily reversible transition.

Kracek and Ksanda did not comment on the significance of the composition indicated as $\text{Ag}_{1.914}\text{Te}$ and the fact that the crosses on the Te-rich side of this composition do not show evidence of the transition in Ag_2Te . This is readily explained by the presence of the γ -phase. The triangles in Fig. 3 represent values measured after heating to about 500° , that is, above the peritectic of γ -phase, then slowly cooling to room temperature, and reheating, to measure the magnitude of the transition arrest. The increased thermal effect indicates non-equilibrium retention of Ag_2Te in these mixtures.

The peritectic reactions $Ag_{5-x}Te_3$ (h) = γ -phase + liquid, and γ -phase = Ag_2Te (i) + liquid. "Both of these reactions are rapid when initiated, but both had to be superheated and undercooled in (h) and (c) runs, particularly in compositions richer in Te than $Ag_{5-x}Te_3$. A mechanical disturbance, such as lightly tapping the sample container was helpful in starting the reactions. Thus, on cooling, the upper peritectic transforma-

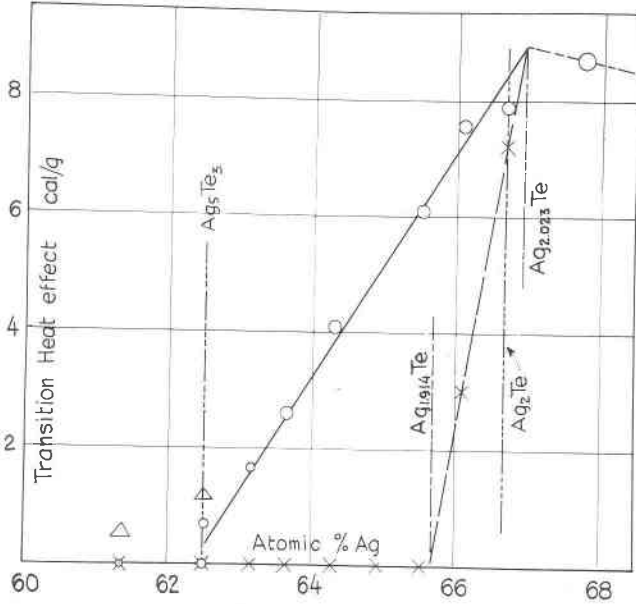


FIG. 3. Heat effect in cal/g for the Ag_2Te (i) = Ag_2Te (l) transition for several compositions. Circles represent heating arrests of material first annealed at 330–380°. Crosses represent heating arrests on second heating cycle after cooling below 145°. Triangles represent heating arrests of material measured after heating to $\sim 500^\circ$ and cooling slowly to room temperature.

tion may be delayed to below 415° (c), to be then followed by the lower peritectic transformation at about 400° (c) or even lower. The superheating tendency on heating is less extreme. The liquidus compositions were 44.4 ± 0.5 at. % Ag at the lower peritectic, and 48.7 ± 0.5 at. % Ag at the upper peritectic."

The Te- $Ag_{5-x}Te_3$ eutectic e_1 . "The eutectic is at $353 \pm 0.5^\circ$ (m), and extends from Te to near Ag_5Te_3 . Koern (1940) observed two phases at 0.5 per cent Ag; accordingly, any solid solution in the Te phase must be of negligible extent. At the other extreme, the eutectic horizontal must terminate, in the absence of solid solution, at the intermediate compound. The thermal

data (Fig. 4) indicate the eutectic heat effect decreasing to zero at about Ag_5Te_3 ."

The AgTe phase. Attempts by Cabri to synthesize this phase, whose presence was recently reported by Honea (1964) in natural ores, were unsuccessful (Cabri, 1965a). It is not included in Figs. 1 and 2 because the stability field of this phase in the synthetic system has not been determined, and for other reasons discussed in Cabri (1965a).

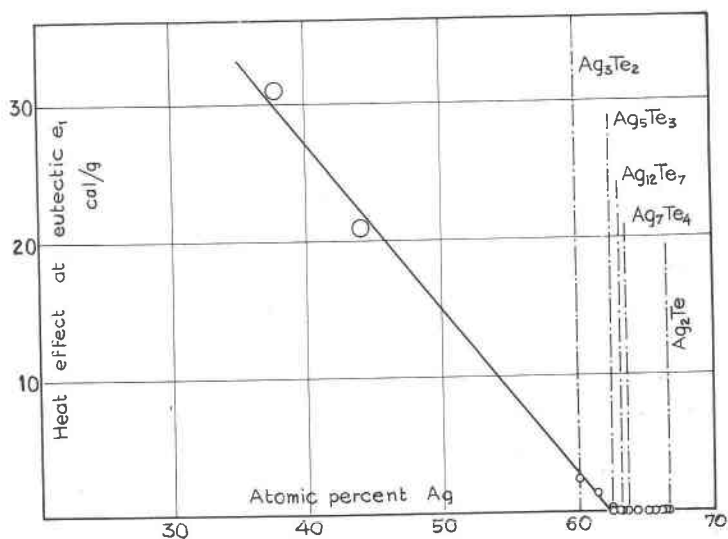


FIG. 4. Heat effect at the eutectic e_1 in cal/g for several compositions.

Composition of $\text{Ag}_{5-x}\text{Te}_3$. The composition of $\text{Ag}_{5-x}\text{Te}_3$ has been confirmed as being close to Ag_5Te_3 by several methods. The thermal analysis results indicate, by the invariability of the eutectic temperature e_1 over its full extent from 0 to 62.5 at. % Ag, that tellurium is an eutectic constituent over this full range. However, quench experiments examined with the Guinier camera indicate that a small solid-solution field exists at 300° , which fits well with Kiukkola and Wagner's data, *i.e.*, from 57.95 to 58.39 wt. % Ag. Kracek and Ksanda's interpretation was that the composition may extend to Ag_5Te_3 .

It is interesting to note the possibility of yet another Ag-Te compound. Luo and Klement (1962), using an extremely rapid quenching technique in air, reported the presence of a simple cubic, metastable, AgTe alloy existing between 20.5 and 30.5 at. % Ag. Between the compositions 33.5 and 50.5 at. % Ag, the x-ray patterns of this cubic phase became progressively weaker and the pattern of an unidentified phase (or phases) be-

came progressively stronger. (A 114.6 mm Debye-Scherrer x-ray film of the 50 at. % Ag-Te alloy, kindly provided to Cabri by H. C. Luo, was examined and identified as $\text{Ag}_{5-x}\text{Te}_3$ + cubic Ag-Te alloy.)

" Ag_2Te exists in three polymorphic forms; neither of the high-temperature forms is quenchable. The temperature of the lower transition, $\text{Ag}_2\text{Te} (l) = \text{Ag}_2\text{Te} (i)$ is $145 \pm 3^\circ$."

THE PARTIAL SYSTEM, Ag_2Te -Ag

"The melting point of Ag_2Te is $960 \pm 1^\circ$ (m) in close agreement with 959° (c) by Pellini and Quercigh (1910). From Ag_2Te the liquidus curve first falls to $881 \pm 3^\circ$, at 69.6 ± 0.5 at. % Ag, and then continues at this temperature to 87.5 ± 0.5 at. % Ag. From about 70 to nearly 90 at. % silver Pellini and Quercigh did not observe the liquidus, but only the eutectic cooling arrest at 872° . Chicashige and Saito (1916), on the other hand, obtained two successive cooling arrests with mixtures in this range of composition, the upper one at 869 – 873° , and the lower one at 847 – 873° . Their conclusion was that the melting relations were simply eutectic, with Ag_2Te and Ag as eutectic constituents, and with the eutectic at 90 at. % silver. The liquidus curve was of an unlikely contour, with a long, nearly horizontal portion, more readily accounted for by liquid immiscibility. To test this, an 80 at. % Ag regulus was prepared, and sectioned for examination. A photomicrograph of the section, Fig. 5, shows separation into two layers. Heating- and cooling-curve measurements on preparations in the region of the horizontal liquidus yielded two arrests, one at $869 \pm 3^\circ$ (m), and the other at $881 \pm 3^\circ$ (m). They are the eutectic and liquid unmixing temperatures, respectively.

"The liquidus curve for silver descends smoothly from 960.5° , the melting point of silver, through 890° at 90.01 at. % Ag. This curve meets the eutectic horizontal of 869° at 87.5 at. % Ag. Only one arrest, at 869° (m) was observed for a preparation of 87.5 ± 0.5 at. % Ag, as the composition of the Ag-rich liquid. Visual evidence of separation into two layers was observed in mixtures between this and 70 at. % Ag. The compositions of the two liquid layers at the liquidus are thus deduced to be 69.6 ± 0.5 and 87.5 ± 0.5 at. % Ag.

"In this part of the system, the temperature of the upper transition, $\text{Ag}_2\text{Te} (i) = \text{Ag}_2\text{Te} (h)$ is $802 \pm 3^\circ$ in contrast with the corresponding temperature in the Te-rich portion of the system, $689 \pm 5^\circ$. The temperature of the lower transition is the same as in the Te-rich part of the system, $145 \pm 3^\circ$."

The $\text{Ag}_2\text{Te} (i) = \text{Ag}_2\text{Te} (h)$ transition. "This transition was found upon a search made to discover the reason for the concavity in the liquidus curve of Ag_2Te apparent in the diagram of Pellini and Quercigh (1910). In mix-

tures from 59.7 at. % Ag, the liquidus composition at the transition, to 66.0 at. % Ag, the transition is located at $689 \pm 5^\circ$ (m), and in those from 66.7 at. % Ag to nearly 100 at. % Ag, at $802 \pm 3^\circ$. The pertinent data are illustrated in Fig. 1. In one composition, 66.1 at. % Ag, the transition proceeded in two steps as the $\text{Ag}_2\text{Te} (i) + \text{Ag}_2\text{Te} (h)$ field is traversed. The

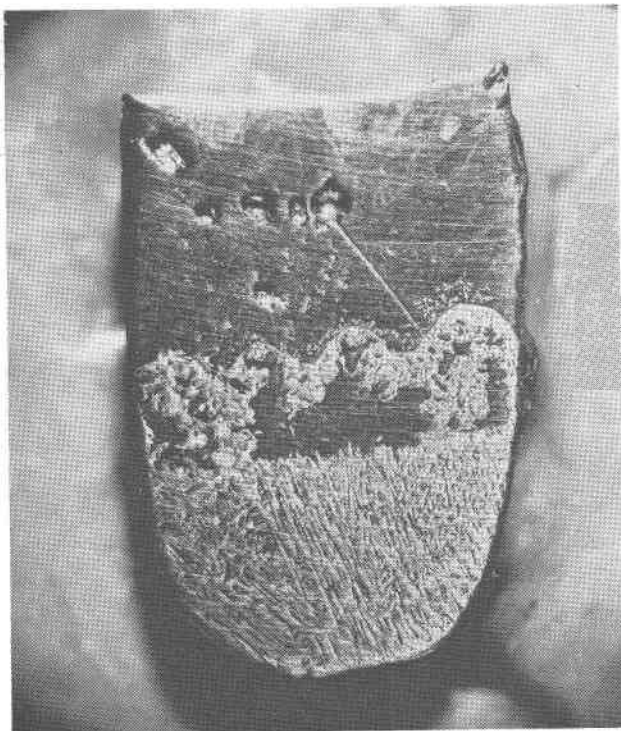


FIG. 5. Photomicrograph of 80 at. % Ag regulus exhibiting separation into two layers.

first heating arrest and the last cooling arrest are typical of this transition, while the second heating arrest and the first cooling arrest are more subdued and might represent metastable phenomena."

Heats of transformations. "The differential thermal analysis technique has been used to determine the magnitude of the heat effects at some transformations with the following results:

- $\text{Ag}_2\text{Te} (l) = \text{Ag}_2\text{Te} (i)$ at 67.75 at. % Ag, 8.5 cal/g;
- $\text{Ag}_{5-x}\text{Te} (h) = \gamma\text{-phase} + \text{liquid}$ at 62.50 at. % Ag, 2.7 cal/g;
- $\gamma\text{-phase} = \text{Ag}_2\text{Te} (i) + \text{liquid}$, 2.4 cal/g;
- $\text{Ag}_{5-x}\text{Te}_3 (h) = \text{Ag}_{5-x}\text{Te}_3 (l)$ at 62.50 at. % Ag, about 2 cal/g."

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