Synthesis of Pt–Zn and Au–Zn compounds by isopiestic method

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ABSTRACT

This study examined the synthesis of Pt–Zn and Au–Zn compounds by applying Zn vapor. Phases of formed compounds were controlled by an isopiestic method, in which Pt or Au was heated at higher temperature than the Zn vapor source in a reaction container. The result was that γ_1-Pt_3Zn_{10}, r-$PtZn_{1.7}$ and υ-PtZn were synthesized and the activities of Zn in these compounds were obtained. γ_2-$AuZn_3$ and β'-AuZn were synthesized using thermodynamic information previously reported.

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1. Introduction

It is known that dissolution of some precious metals (PMs) into aqueous solution can be enhanced by alloying with other metals [1]. Taking advantage of this phenomenon, an exposure to zinc (Zn) vapor was proposed as a pretreatment for the hydrometallurgical recovery process of platinum group metals [2–5]. As Fig. 1(a) shows, platinum (Pt) forms several kinds of intermetallic compounds with Zn depending on their composition and temperature [6,7]. Because these compounds would behave differently in aqueous solutions, conditions of the vapor pretreatment should be thoroughly considered in order to assure the formation of suitable compounds and optimize the proposed recovery process. Thermodynamic properties of Pt–Zn compounds have not been well studied, however, and conditions for the synthesis of certain compounds remain unclear. Thus in this study, compound formations of Pt–Zn by Zn vapor were examined. An isopiestic method described below was employed to control compositions of the formed compounds. Additionally, gold(Au)–Zn compounds were synthesized by the method because the Zn vapor pretreatment may also be effective for leaching of Au. A phase diagram for the Au–Zn binary system according to Refs. [6,7] is shown in Fig. 1(b).

2. Experimental

An isopiestic method [8–10] was used to examine reactions between Pt or Au and Zn vapor. A schematic illustration of the method is shown in Fig. 2. Sheets of Pt (Tanaka Kikinzoku Kogyo, 99.95%, 0.3 or 0.5 mm thick) or Au (Tanaka Kikinzoku Kogyo, 99.99%, 0.5 mm thick) were cut into rectangles of about 3 mm × 10 mm, and sealed in a quartz tube under vacuum with ca. 4 g of Zn blocks (The Nilaco Co.,

99.5%) and 0.3 g of titanium wires (The Nilaco Co., 1.0 mm in diameter, 99.9%). Pt and Au were supported by a tungsten wire (The Nilaco Co., 0.5 mm in diameter) in the tube. The sealed tube was then heated in an electric furnace with temperature gradients. The furnace has two electric heaters (Kanthal-A1 wire, Kanthal, 800 and 1040 W) with a common mullite tube at each core (Fig. 2(a)). A K-type thermocouple was inserted in the middle part of each heater, and the temperature on the external surface of the mullite tubes was monitored. These temperatures were controlled independently by thermoregulators with PID power controllers. A second mullite tube was inserted in the initial mullite tube with a wire heater twisted around it to control the temperature of the connected region; this temperature became the low point. Temperature distribution in the inner mullite tube was measured with a movable K-type thermocouple before inserting a sealed quartz tube (Fig. 2(b)). Following its insertion, Zn was heated at a temperature (T_1) lower than any other part of the quartz tube. For this purpose, Zn was placed at one end of the quartz tube, and the end was heated at the low point of temperature distribution. Sheets of Pt and Au were placed around the other end and heated at the middle part of one electric heater, where the temperature (T_2) was higher than T_1. Titanium wires were placed in about the middle of the quartz tube and acted as an absorbent of contained oxygen. During the heat treatment, the removable thermocouple was fixed near Zn to monitor T_1 and control it within a deviation of 2 K.

During heating, a partial pressure of Zn inside the sealed tube is maintained at the equilibrium pressure of Zn at T_1, for example, the pressure is 1.5×10^3 Pa at 863 K [8,11]. Meanwhile, Pt and Au have low vapor pressures (1.8×10^{-12} Pa for Pt at 1200 K and 2.9×10^{-10} Pa for Au at 900 K [11]), and thus they react with the Zn vapor virtually without evaporating. Eventually, Pt and Au become compounds, which apparently equilibrate with the gas phase after sufficient reaction time. Eq. (1) represents the activity of Zn in the formed compound ($a_{Zn\ in\ PM–Zn}$), of which the reference state is liquid pure Zn. In the equation, $p_{Zn}(T)$ means equilibrium vapor pressure of pure Zn at T.

$$a_{Zn\ in\ PM–Zn}(T_2) = \frac{p_{Zn}(T_1)}{p_{Zn}(T_2)} \tag{1}$$

This means the activity of Zn can be controlled by regulating the temperature difference in the sealed quartz tube. For Pt–Zn compounds, however, thermodynamic properties have not been known precisely. Thimmaiah et al. reported that they synthesized Pt–Zn compounds of mole fractions of Zn between 80 and 82% [10], but Zn activity in more Pt-rich compounds has not been reported. In this study, conditions for synthesis were determined as shown by Exps. 1–3 in Table 1. After heating, the tube was withdrawn from the furnace and cooled in water in Exp. 1 and 3. Only in

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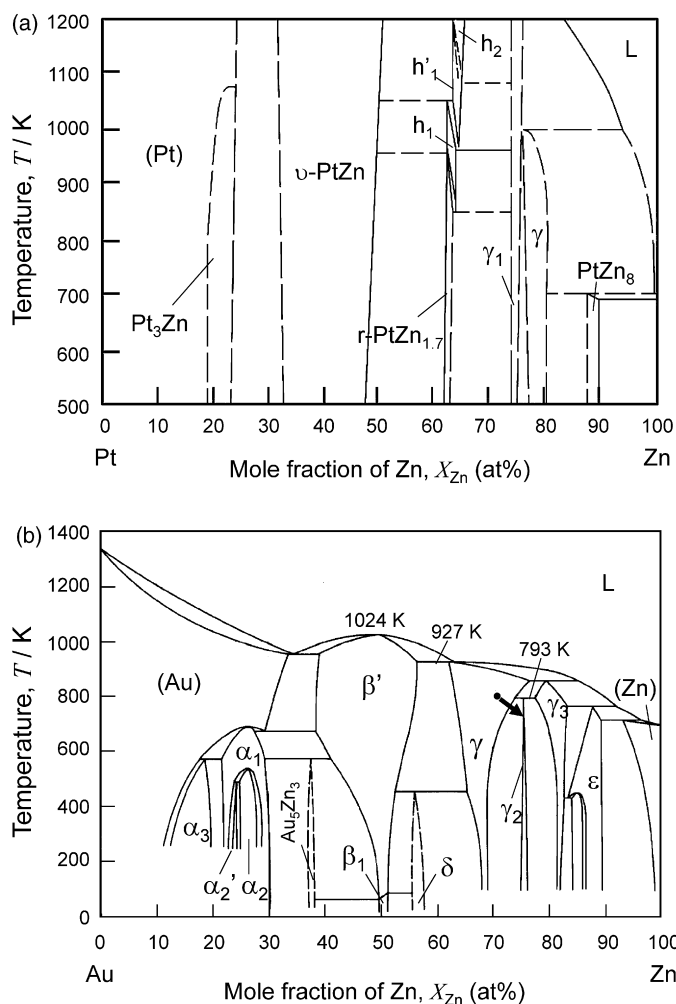 *E-mail address:* hideakis@iis.u-tokyo.ac.jp (H. Sasaki).

Fig. 1. Phase diagrams of (a) Pt–Zn and (b) Au–Zn binary systems [6,7]. Arrow in (b) shows a path of reaction during Exp. 4.

Table 1
Conditions of synthesis of Pt–Zn compounds.

#	T_1 (K)	T_2 (K)	a_{Zn}	Thickness of Pt, l (mm)	Time, t (d)
1	873	973	0.19	0.5	3
2	973	1173	0.086	0.5	4
3	873	1173	0.016	0.3	6

Table 2
Conditions of synthesis of Au–Zn compounds.

#	T_1 (K)	T_2 (K)	a_{Zn}	Time, t (d)
4	803	843	0.43	3
	↓	↓	↓	↓
	719	753	0.40	2
5	873	1173	0.04	4

Exp. 2 was the tube cooled in air. Parts of the experimental results (Exp. 1) were previously reported [12].

Conditions for synthesis of γ_2-AuZn$_3$ and β'-AuZn were determined by reference to thermodynamic activities of Zn in the compounds reported by Liu et al. [13]. Temperatures and heating time are listed in Table 2. According to the phase diagram (Fig. 1(b)), γ_2-AuZn$_3$ is formed below 793 K and the compound has to be made at a temperature lower than this. Compound formations might be slower at lower temperatures, and thus in synthesis of γ_2-AuZn$_3$, a two-step treatment was employed as follows (Exp. 4). First, Zn and Au were heated at 803 and 843 K, respectively, for 3 days. According to the reported activity of Zn, γ phase (Au–70%Zn) forms under this condition. Then these temperatures were changed to heat Zn and Au at 719 and 753 K, where γ_2-AuZn$_3$ was formed. Changes of temperature and composition during the treatment are shown by an arrow in the phase diagram in Fig. 1(b). After maintaining them at these temperatures for 2 days, the tube was cooled in water. On the other hand, β'-AuZn was synthesized by simply heating Zn and Au at 714 and 850 K, respectively, for 4 days followed by cooling in water (Exp. 5).

Formed compounds were observed with a scanning electron microscope (SEM; JEOL Ltd., JSM-5600LV) equipped with an energy dispersive spectroscope (EDS; JEOL Ltd., JED2200). Their crystalline structures were examined by X-ray diffractometer (XRD; Rigaku Co., RINT 2000).

3. Results and discussion

Changes in weight of Pt sheets during reaction are shown in Table 3. In Exp. 1, observation of the cross-sectional surface by SEM-EDS revealed that Zn diffused into the innermost portion of the Pt sheet and a homogeneous compound was formed [12]. The com-
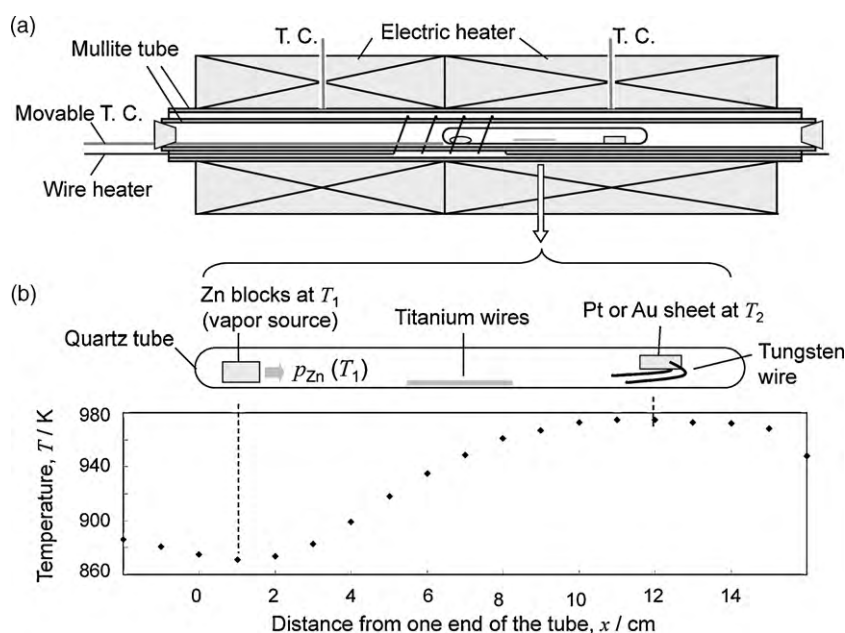

Fig. 2. (a) Schematic illustration of the experimental apparatus for the isopiestic method. (b) Sealed quartz tube containing Pt or Au and Zn. Temperature distribution for Exp. 1 is shown below.

Table 3
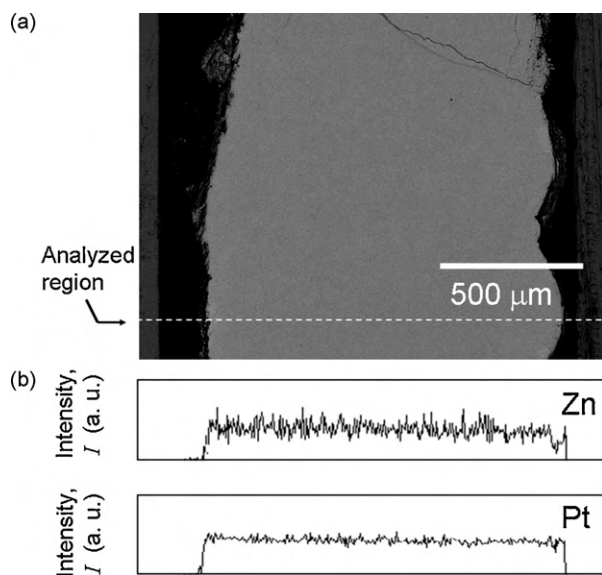Results of synthesis of Pt–Zn compounds.

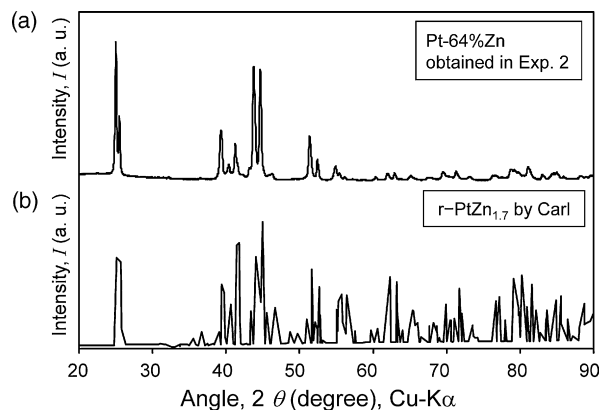| Exp. #	Weight before reaction, w_1 (g)	Weight after reaction, w_2 (g)	Compound formation	Fraction of Zn, X_{Zn} (at%)	Phase
1	0.293	0.587	Completed	75.0	γ_1-Pt$_3$Zn$_{10}$
	0.304	0.608		75.1	
2	0.426	0.677	Completed	63.9	r-PtZn$_{1.7}$
	0.437	0.690		63.5	
3	0.290	0.305	Not completed (only surface)	53.6	υ-PtZn
	0.259	0.273		54.7	
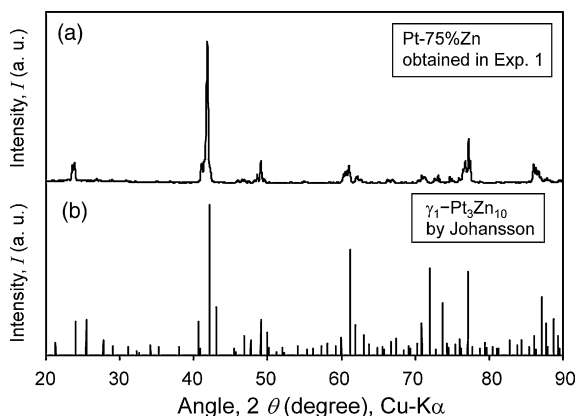
Fig. 3. (a) Powder XRD pattern of the compound obtained in Exp. 1. (b) γ_1-Pt$_3$Zn$_{10}$ by Johansson and Westman [14] with lattice parameter of 1.8165 nm.

position of the formed compound was calculated to be Pt–75%Zn from the change in weight. Powder XRD pattern of the obtained Pt–75%Zn shows formation of γ_1-Pt$_3$Zn$_{10}$, the structure of which was reported by Johansson and Westman [12,14] (Fig. 3). This result disagreed with experiments by Thimmaiah et al., in which the γ_1 phase was not formed in this composition [10,15].

Fig. 4(a) is a SEM image of a cross-sectional surface of a compound synthesized in Exp. 2 with a compositional contrast obtained from reflection electrons. Because there is no shading in the image, formation of a homogeneous compound was visible. An element distribution examined by EDS also confirmed its homogeneity

Fig. 5. (a) Powder XRD pattern of the compound obtained in Exp. 2. (b) r-PtZn$_{1.7}$ by Carl and Schubert [16].

(Fig. 4(b)). From the change in weight during reaction, the composition of the compound was calculated to be Pt–64%Zn (Table 3). The powder XRD pattern indicated the formation of r-PtZn$_{1.7}$ (Fig. 5) [16]. The phase diagram (Fig. 1(a)) shows other phases are stable at elevated temperatures at this composition. Thus, with this synthesis method, the crystallinity of the formed compound may be low because of phase transformations during cooling.

Fig. 6(a) is a SEM image of a cross-section of a Pt sheet after reaction of Exp. 3 with compositional contrast. Below the image, element distributions analyzed with EDS are shown. It is obvious that only the outer layer of the sheet formed a compound with Zn. The
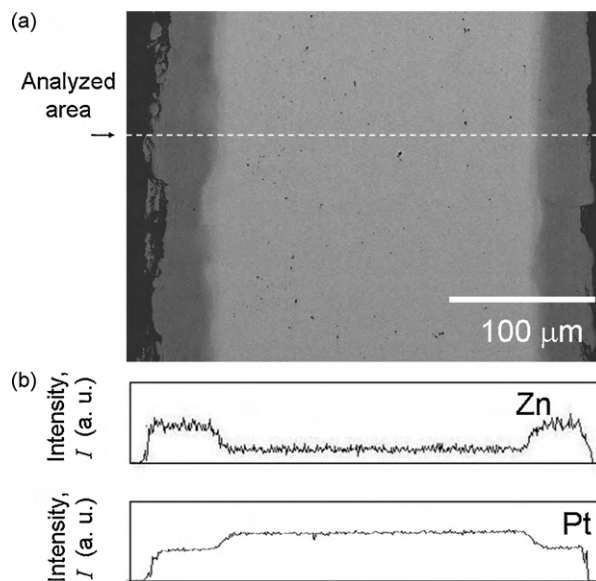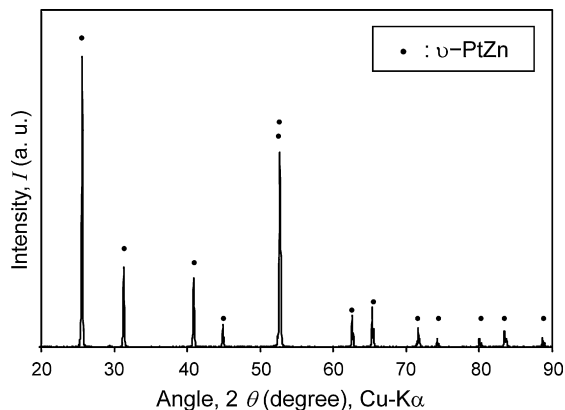

Fig. 4. (a) Cross-sectional surface of Pt sheet after Zn vapor treatment in Exp. 2. The image has compositional contrast. (b) Element distribution examined by EDS along the line indicated in (a).


Fig. 6. (a) Cross-sectional surface of Pt sheet after Zn vapor treatment in Exp. 3. The image has compositional contrast. (b) Element distribution examined by EDS along the line indicated in (a).

Table 4
Results of synthesis of Au–Zn compounds.

Exp. #	Weight before reaction, w_1 (g)	Weight after reaction, w_2 (g)	Compound formation	Fraction of Zn, X_{Zn} (at%)	Phase
4	0.317	0.629	Completed	74.8	γ_2-Pt$_3$Zn$_{10}$
	0.285	0.561		74.4	
5	0.302	0.403	Completed	50.3	β'-AuZn
	0.295	0.395		50.5	

Fig. 7. XRD pattern of the compound surface obtained in Exp. 3. Dots indicate peaks of υ-PtZn reported by Nowotny et al. [17].
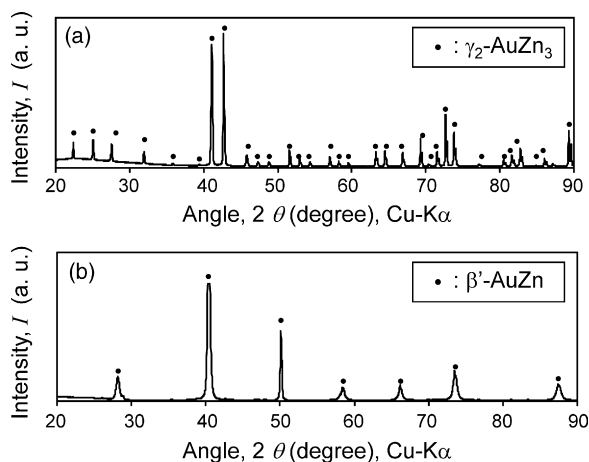
Fig. 8. (a) Powder XRD pattern of Au–75%Zn formed in Exp. 4. Dots indicate peaks of γ_2-AuZn$_3$ [18,19]. (b) XRD pattern of Au–50%Zn formed in Exp. 5. Dots indicate peaks of β'-AuZn [6,19].

thickness of the compound layer was about 40 μm. Assuming there is compositional homogeneity in the layer, the compound formed is 54% Zn. Inter-diffusion in the compound is therefore slow with the low fraction of Zn, and this is why only the outer layer reacted with Zn during a 6-day period. The XRD pattern obtained from the surface indicated a formation of υ-PtZn as Fig. 7 shows [17].

A compound obtained in Exp. 4 was silvery white in appearance, and its homogeneity was confirmed with SEM-EDS. The composition was calculated to be Au–75%Zn as Table 4 shows, and its powder XRD pattern was consistent with that reported for γ_2-AuZn$_3$ (Fig. 8(a)) [18,19]. In Exp. 5, a metallic pink compound was

obtained and its homogeneity was confirmed. The composition was Au–50%Zn, and an XRD pattern obtained from its surface showed a formation of β'-AuZn [6,19] (Fig. 8(b)). Consequently two kinds of expected Au–Zn compounds were successfully synthesized using the isopiestic method.

4. Conclusions

Pt–Zn and Au–Zn compounds were synthesized using an isopiestic method. Homogeneous γ_1-Pt$_3$Zn$_{10}$, r-PtZn$_{1.7}$ and a layer of υ-PtZn were formed and activity of Zn in these compounds was obtained as new information. Homogeneous γ_2-AuZn$_3$ and β'-AuZn were successfully synthesized with reference to reported thermodynamic data. Dissolution behavior of each compound will be reported in future.

References

[1] F. Habashi, Handbook of Extractive Metallurgy, VCH Verlagsgesellschaft-VCH, A Wiley Company, Germany, 1997.
[2] T.H. Okabe, Y. Kayanuma, S. Yamamoto, M. Maeda, Mater. Trans. 44 (2003) 1386.
[3] Y. Kayanuma, T.H. Okabe, Y. Mitsuda, M. Maeda, J. Alloys Compd. 365 (2004) 211.
[4] Y. Kayanuma, T.H. Okabe, M. Maeda, Metall. Mater. Trans. B 35 (2004) 817.
[5] J. Itoh, Y. Kayanuma, M. Miyake, H. Kimura, M. Maeda, Lead & Zinc '05, Proceedings of the International Symposium on Lead and Zinc Processing, Kyoto, Japan, 2005, p. 1157.
[6] B. Predel, in: O. Madelung (Ed.), Phase Equilibria of Binary Alloys, Springer-Verlag, Germany, 2003.
[7] T.B. Massalski, Binary Alloy Phase Diagrams, American Society for Metals, Metals Park, OH, USA, 1986.
[8] S. Kou, Y.A. Chang, Acta Metall. 23 (1975) 1185.
[9] M. Boström, M. Gemmi, K.W. Richter, J. Alloys Compd. 427 (2007) 300.
[10] S. Thimmaiah, K.W. Richter, S. Lee, B. Harbrecht, Solid State Sci. 5 (2003) 1309.
[11] I. Barin, Thermochemical Data of Pure Substances, VCH-Verlagsgesellschaft mbH, Germany, 1989.
[12] H. Sasaki, M. Miyake, M. Maeda, J. Electrochem. Soc. 157 (2010) E82–E87.
[13] H.S. Liu, K. Ishida, Z.P. Jin, Y. Du, Intermetallics 11 (2003) 987.
[14] A. Johansson, S. Westman, Acta Chem. Scand. 24 (1970) 3471.
[15] S. Thimmaiah, M. Conrad, S. Lee, B. Harbrecht, Z. Anorg. Allg. Chem. 630 (2004) 1762.
[16] W. Carl, K. Schubert, J. Less-Common Met. 19 (1969) 279.
[17] H. Nowotny, E. Bauer, A. Stempfl, H. Bittner, Monatsh. Chem. 83 (1952) 221.
[18] E. Günzel, K. Schubert, Z. Metallkd. 49 (1958) 234.
[19] A. Westgren, G. Phragmen, Philos. Mag. 50 (1925) 311.