THE OCCURRENCE OF AN Ag_6Sb PHASE AT COBALT, ONTARIO

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ABSTRACT

Of the three crystalline phases occurring in the Ag–Sb system, only antimonial silver and dyscrasite (Ag_3Sb) are commonly reported. A mineral equivalent to the synthetic ϵ phase (Ag_6Sb) was long overlooked due to the lack of an accurate phase diagram.

The occurrence of ϵ phase in material from Cobalt, Ontario, was established by *x*-ray powder diffraction. This mineral occurs intimately intergrown with antimonial silver, these phases having exsolved from a high temperature solid solution containing 13.9 weight per cent antimony. Some of the more prominent *x*-ray reflections in this mineral in order of decreasing relative intensity have *d*-values of 2.25, 1.26, 2.38, 2.54, 1.74, 1.47, and 1.35 Å.

INTRODUCTION

A crystalline mineral composed essentially of silver and antimony was known to Rome de L'Isle and to Werner in the eighteenth century. Early named antimonial silver it later received the name 'dyscrasite' (Beudant, 1832) which has been applied to crystallized and massive materials composed of silver with varying proportions of antimony. Andreasberg, in the Harz Mountains, was one of the earliest known locations for dyscrasite. Most of the later investigations of this mineral were conducted on specimens from this area.

The existing analyses of material referred to as 'dyscrasite' (see Table 1) range from about Ag 73, Sb 27 weight per cent, corresponding to Ag_3Sb, to about Ag 84, Sb 16 weight per cent, approximating Ag_6Sb.

DYSCRASITE

Machatschki (1928) investigated a sample of dyscrasite from Andreasberg and concluded that the mineral has a general composition Ag_3Sb. Peacock (1940) studied a crystal of dyscrasite from Andreasberg and concluded it was orthorhombic with the following lattice constants: $a = 2.996$, $b = 5.235$, $c = 4.830$Å*, $Z = 1$. Most workers studying these minerals recognized only the compound Ag_3Sb and grouped the remaining silver antimony compounds either under antimonial silver or a

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*Converted to Ångstroms using the factor 1.002034.

eutectic intergrowth of the two. Schwartz (1928) obtained etch reactions from a specimen showing lamellae which he interpreted as antimonial silver in a matrix of Ag_3Sb.

The silver-cobalt ores at Cobalt, Ontario, include distinctive intergrowths of these Ag–Sb minerals. These often consist of blades or lamellae of a mineral which has been regarded as dyscrasite oriented in the (111) direction of a second mineral which is generally regarded as antimonial silver (Peacock, 1940).

The ϵ Phase*

The ϵ phase is not prevalent. Burrows (reported by Miller, 1910) analyzed a sample from La Rose Mine, Cobalt, Ontario, which gave the general formula Ag_6Sb. Another analysis of this material by N. L. Turner reported by Miller (1910) and by Walker (1921), which is reproduced in Table 1, also yielded the formula Ag_6Sb. Miller termed it 'dyscrasite' but noted that the composition commonly found in other districts was Ag_3Sb. Later, Walker (1921) microscopically examined specimens from the Temiskaming and Kerr Lake Mines and found a fine intergrowth of 'dyscrasite' and native silver. However, all these workers based their interpretations on an incomplete knowledge of the Ag–Sb equilibrium diagram. Early diagrams showed only the α (antimonial silver) and ϵ' (dyscrasite) phases. Carpenter & Fisher (1932), in studying a specimen from Cobalt, Ontario, concluded that if Ag_3Sb was present in the natural intergrowth, it formed the matrix, and the lamellae consisted of antimonial silver. Since this was inconsistent with the equilibrium diagram available to them, they suspected that the diagram was wrong. In fact the existence of a phase intermediate between α and ϵ' had already been established through x-ray diffraction studies by Westgren, Hägg & Eriksson (1929). Edwards (1954, p. 60–62) re-interpreted the observations of Carpenter & Fisher in the light of the phase relations re-determined by Reynolds & Hume-Rothery (1937), Stockdale (1937), and Weibke & Efinger (1940), as either (a) the lamellae consisted of dyscrasite in a matrix of ϵ phase, or (b) the lamellae consisted of antimonial silver in a matrix of ϵ phase. Ramdohr (1960, p. 381–387) observed a mineral in polished sections from the Beaver Mine, Cobalt, Ontario, which he interpreted as ϵ phase and gave the name *allargentum*. However, he did

*The symbols ϵ, ϵ', and α designate the Ag_6Sb phase, synthetic dyscrasite (Ag_3Sb), and the synthetic antimony-bearing silver solid solution. Westgren, Hägg, & Eriksson (1929) introduced this terminology in the first schematic representation of the Ag–Sb phase relations, and its use has been continued to the present by all but a few authors. In this text the Greek symbols for dyscrasite and antimonial silver are used in reference to the synthetic equivalents of these minerals.

TABLE 1. CHEMICAL COMPOSITIONS OF Ag–Sb MINERALS, LOCALITIES, AND THE PROBABLE PHASE(S) TO WHICH EACH BELONGS

Analyses reported by Walker (1921), and Doelter & Leitmeier (1926).

Weight per cent				
Ag	Sb	Total*	Interpreted phase(s)	Locality
84.00	16.0	100	ϵ	Wenzelsgang, Black Forest
84.7	15.0	99.7	ϵ	Andreasberg, Harz Mountains
83.85	15.81	99.66	ϵ	Wenzelsgang
76.0	24.0	100	ϵ'	Wenzelsgang
75.25	24.75	100	ϵ'	Andreasberg
78.00	22.0	100	$\epsilon + \epsilon'$	Andreasberg
77.0	23.0	100	ϵ'	Andreasberg
72.34	27.66	100	ϵ'	Andreasberg
72.36	27.64	100	ϵ'	Andreasberg
72.62	27.88	100	ϵ'	Andreasberg
72.42	25.58	100	ϵ'	Andreasberg
74.67	25.33	100	ϵ'	Andreasberg
75.28	24.72	100	ϵ'	Andreasberg
74.9	24.75	99.65	ϵ'	Andreasberg
75.86	24.3	100.16	ϵ'	Andreasberg
76.83	23.35	100.18	ϵ'	Andreasberg
74.41	25.52	99.93	ϵ'	Andreasberg
75.39	24.63	100.02	ϵ'	Andreasberg
75.13	24.94	100.7	ϵ'	Andreasberg
75.38	24.12	99.5	ϵ'	Andreasberg
71.52	27.2	98.72	ϵ'	Wenzelsgang
76.65	23.06	99.71	ϵ'	Wenzelsgang
76.08	23.92	100	ϵ'	Carrizio in Capiapo', Chile
77.72	22.28	100	$\epsilon + \epsilon'$?	Carrizio in Capiapo', Chile
77.12	22.1	99.22	$\epsilon + \epsilon'$?	Carrizio in Capiapo', Chile
77.58	11.18	99.31	ϵ	Silver Islet Mine, L. Superior
†92.19	6.78	99.42	α	Temiskaming Mine, Cobalt, Ontario
†85.47	12.99	99.58	ϵ	Kerr Lake Mine, Cobalt, Ontario
†93.61	5.89	99.85	α	Buffalo Mine, Cobalt, Ontario
†92.6	6.59	99.75	α	Cobalt, Ontario
†83.9	15.6	99.5	ϵ	La Rose Mine, Cobalt, Ontario

*Excess of the total over the sum of Ag + Sb represents minor elements such as As.
†Walker (1921)

not give x-ray or chemical data to verify its identity or composition. He reported that it had physical properties between those of dyscrasite and antimonial silver. Its reflectivity was slightly more than dyscrasite to which its hardness was nearly equal. A photograph of the polished specimen showed three phases interpreted as antimonial silver, ϵ, and dyscrasite. Since the phase rule precludes the stable coexistence of three condensed phases in a two component system, one may conclude that (a) one of these phases is coexisting metastably, or (b) quite possibly one of the phases lies outside the Ag–Sb system.

A second occurrence of the ϵ phase was reported by Markham & Lawrence (1962) in material from the Consols Mine, Broken Hill, Australia. In polished sections they observed dyscrasite, 'allargentum', and antimonial silver in all possible combinations. One photograph shows dyscrasite exsolution lamellae in 'allargentum' which mass is in turn cut by veinlets or grain boundary exsolutions of antimonial silver plus dyscrasite. The variation in reflectivity between the phases shown in their photographs is surprising since in the Cobalt material the individual phases are almost indistinguishable before etching. They report exsolution intergrowths between dyscrasite and 'allargentum' in all proportions. Regarding the temperature of formation, Markham & Lawrence (1962, p. 73) conclude "There are a few lines of evidence to suggest that the Consols lode minerals have formed at low to moderate temperatures" They note the uncertainties in applying the Ag–Sb phase diagram due to nonequilibrium among the Ag–Sb minerals and further state (p. 77), "If the natural assemblages can be assumed to have crystallized below the ϵ' phase (dyscrasite) transformation, then an upper temperature limit of around 440 °C is indicated. Such an assumption, although probably a reasonable one in this case, is clearly an additional uncertainty in interpretation". There appears to be no justification for making the above assumption, especially since the supposed transition was not found by Somanchi (1966)*. In contrast we suggest that these textures represent exsolutions from solid solutions formed in the 500 to 560 °C range where these phases form an almost continuous solid solution (Somanchi, 1966). Markham & Lawrence do not give *x*-ray or chemical evidence in support of these identifications, but assuming they are correct, it may be concluded that (1) some are disequilibrium assemblages, and (2) possibly the ϵ phase is unstable at 25 °C. However, it is stable down to 300 °C, the lowest temperature at which Somanchi obtained satisfactory rates of reaction in the synthetic system.

RE-INTERPRETATION OF THE CHEMICAL ANALYSES OF Ag–Sb MINERALS

Re-study of the analyses of Ag–Sb minerals from different localities, published by Walker (1921) and Doelter & Leitmeier (1926), in the light of the re-determined phase diagram of Somanchi (1963, 1966) reveals certain interesting features (see table 1—surprisingly, no more recent analyses were found in a search of the literature). All the analyses fall into three distinct groups, with antimony contents in weight per cent varying from 5.89 to 6.78, from 11.18 to 16.17, and from 22.00 to 27.88. These limits correspond remarkably well with the limits of the three solid solution fields in the synthetic system Ag–Sb. It seems clear,

*The phase relations in the Ag–Sb system were recently re-determined and the phase boundaries extended down to 300 °C by Somanchi (1963, 1966) to which the reader is referred for the phase diagram.

therefore, that all three compounds are distinct minerals, and only the lack of a correct phase diagram led the early workers to divide the silver-antimony minerals into only two groups, namely antimonial silver and dyscrasite.

Ag_6Sb FROM THE COBALT DISTRICT

When a specimen from the Cobalt District, Ontario (No. 221–M1, McGill collection, specific locality unknown) was examined under the reflecting microscope, antimonial silver was observed intergrown with a second mineral. As the specimen was too metallic to be ground, fine filings were prepared for *x*-ray study. Portions of the filings were annealed variously for 12 hours at 300 and 415 °C, and for 10 days at 400 °C. The resulting *x*-ray powder diffraction patterns were similar. After annealing at those temperatures, the material was homogeneous and yielded the powder pattern of ϵ phase without extra reflections. The composition of this homogeneous phase, as determined employing the *d* value versus composition curve for the ϵ phase (Somanchi, 1966), was 13.9 weight per cent antimony. This composition lies near the middle of the range of homogeneous ϵ phase solid solutions which, as shown by

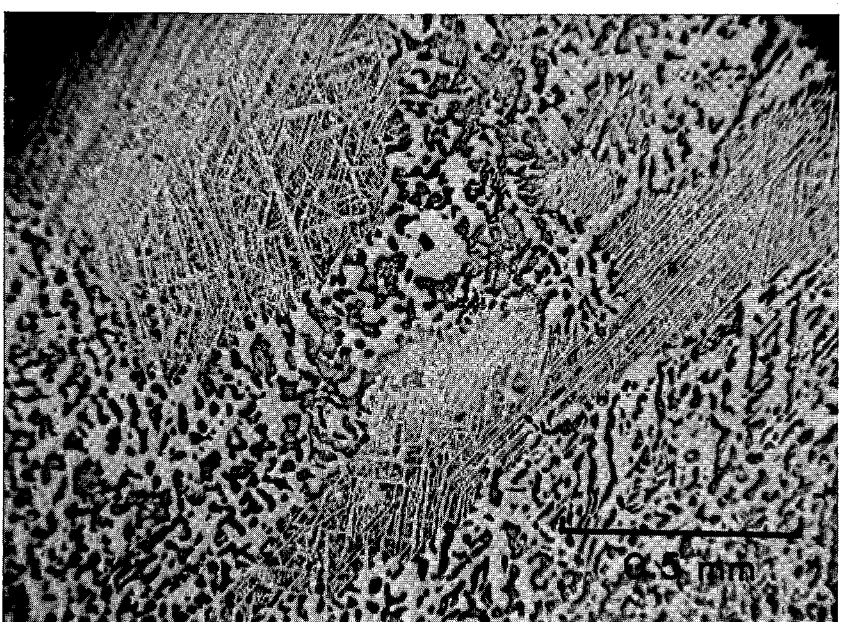

FIG. 1. Exsolution intergrowth of ϵ phase (white) and antimonial silver (dark), etched with HNO_3 and lightly re-polished. Scale bar represents 0.5 mm.

Somanchi (1966), extend from about 10 to 17.7 weight per cent antimony at 400 °C. The implication is that the specimen originally crystallized as a homogeneous phase in the ϵ solid solution field, and as the deposit cooled, antimonial silver was exsolved.

Examination of the specimen under the reflecting microscope revealed both antimonial silver and the ϵ phase as exsolution intergrowths. As shown in Fig. 1, two somewhat different textures were observed. In irregular, approximately 1.5 mm areas the ϵ phase occurs as a complex lattice-work of exsolution lamellae comprising about 60 per cent of the area in a matrix of irregular antimonial silver grains. Between these exsolution areas occurs a more equigranular mosaic containing about 70 per cent ϵ phase and the remainder antimonial silver.

In plain reflected light, the ϵ phase is almost indistinguishable from antimonial silver. The colour is slightly off white relative to the silver, and the ϵ phase exhibits weak anisotropism in contrast to the almost isotropic antimonial silver. Hardnesses are very similar and Vickers hardness of the intergrowth is about 190*. Chemical tests, although a little more vigorous on the antimonial silver, were similar as follows: HNO_3 effervesced rapidly leaving an iridescent tarnish revealing the exsolution texture. Both $FeCl_3$ and $HgCl_2$ rapidly yield iridescent stains and KCN gives a faint brown stain after two minutes. Tests with HCl and KOH were negative. Upon slight polishing after completion of the above tests, most of the stains disappeared. However, in the area etched by HNO_3 the antimonial silver phase retained its black stain whereas the ϵ phase regained its polish providing a ready means to distinguish these phases as shown in Fig. 1.

The ϵ–antimonial silver intergrowth occurs in massive, relatively homogeneous form containing only occasional rounded, irregular grains and knots of niccolite, and safflorite (?), with minor breithauptite and bismuth (?).

The extensive exsolution implies a relatively high temperature of formation and shallower slopes for the solvus curves of both antimonial silver and ϵ phases than are indicated by the experimental work (Somanchi, 1966).

X-ray study of the natural mineral without annealing, clearly shows the presence of antimonial silver (see Fig. 2, film 3). Lines representing the ϵ phase are also present (see also table 2). Peacock (1940), in studying a similar mineral, reported that the *x*-ray powder photographs showed weak reflections corresponding to the strongest lines of pure dyscrasite.

*This is an approximate hardness based on 10 determinations yielding values of 177 using a 200 gram load and 199 with a 100 gram load. No comparison with hardness standards was performed.

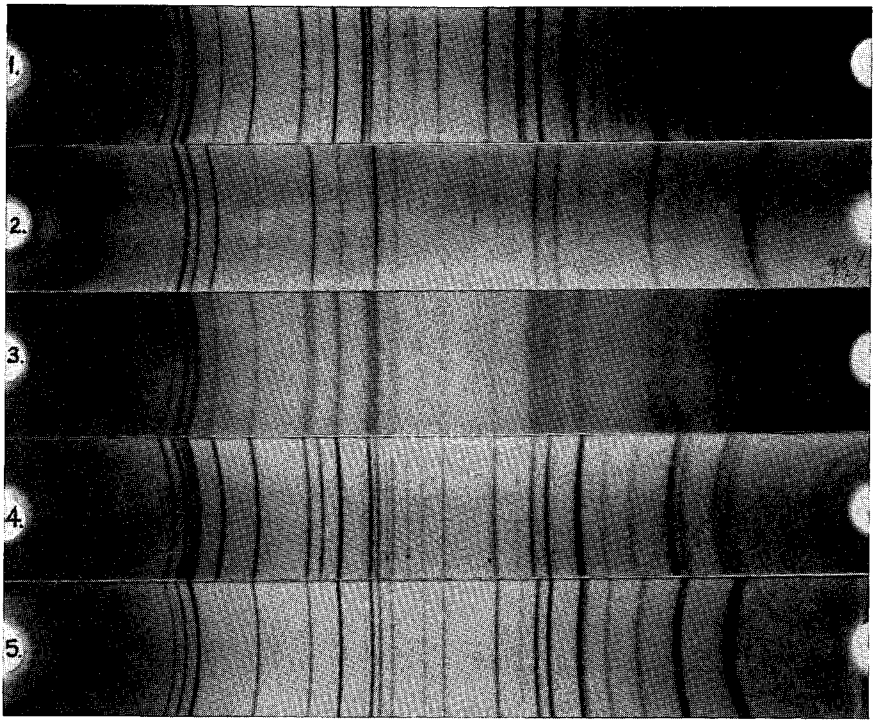

FIG. 2.
1. Synthetic dyscrasite or ϵ' phase (24.01 weight per cent Sb) annealed at 500 °C, 10 days.
2. Synthetic antimonial silver (5.1 weight per cent Sb) annealed at 400 °C, 10 days.
3. Specimen from Cobalt, Ontario (221-M1, McGill collection) containing ϵ phase and antimonial silver. Not annealed.
4. Synthetic ϵ phase (15.97 weight per cent Sb) annealed at 400 °C, 10 days.
5. The same material from Cobalt but annealed at 400 °C for 10 days. Only the reflections for ϵ phase remain.

Note: This is a reproduction of five x-ray powder diffraction films taken using a 114.6 mm diameter Debye-Scherrer camera and Cu-radiation. On films 1 and 4 black dots indicate reflections caused by LiF which was used as an internal standard.

However in x-ray powder diffraction patterns of synthetic dyscrasite (ϵ' phase) and ϵ phase (see films 1 and 4 in Fig. 2), the strongest reflections are sufficiently similar to be readily mistaken. The only distinctive reflections occur at higher 2θ angles, and these lines are always weak (Somanchi, 1966). In the present case, the similarity of reflections in the natural material and those for the synthetic ϵ phase leaves no doubt as to its presence in the sample. It is also probable that the occurrence of this mineral is more widespread than has hitherto been suspected. Table 1 suggests that ϵ phase may occur with about half the frequency of dyscrasite.

TABLE 2. X-RAY POWDER DIFFRACTION PATTERNS OF α, ϵ, ϵ', AND THE NATURALLY OCCURRING INTERGROWTH OF ANTIMONIAL SILVER AND ϵ PHASE FROM COBALT, ONTARIO (NO. 221-M1, MCGILL COLLECTION).

Antimonial Silver[1] (α phase)			Synthetic[2] ϵ Phase			Dyscrasite[3] (ϵ' phase)			No. 211-M1		
d, Å	*hkl*	*I*	*d*, Å	*hkl*	*I*	*d*, Å	*hkl*	*I*	*d*, Å	*I*	Phases indicated
			2.545	100	ms	2.61	020, 110	ms	2.55	s	ϵ
			2.385	002	s	2.42	002	s	2.38	vs	ϵ
2.37	111	vs							2.36	vs	α
			2.248	101	vs	2.29	021, 111	vs	2.24	vs	ϵ
2.059	002	s							2.056	ms	α
			1.743	102	ms	1.771	022, 112	ms	1.747	ms	ϵ
			1.473	110	ms	1.506	130, 220	ms	1.477	ms	ϵ
1.455	022	ms							1.451	ms	α
			1.353	103	ms	1.370	023, 113	s	1.356	ms	ϵ
			1.276		vvw	1.278	132, 202	ms			
			1.256		vs	1.258	041, 221	ms	1.259	ms	ϵ
1.241	113	ms	1.234	201	vw				1.239	ms	α
1.188	222	w				1.207	004	w	1.198	w	α
						1.148	042, 222	w			
			1.127	202	w						
			0.998	023	vw	1.096	024, 114	ms	0.997	vvw	ϵ
						1.012	043, 223	w			
			0.965			0.964	151, 241, 311	w			
0.946	133	ms	0.946	211	vvw	0.942	134, 204	ms	0.943	vvw	α

1. From Berry & Thompson (1962). Natural material from Cobalt, Ontario.
2. Present investigation 14.97 weight per cent Sb.
3. From Berry & Thompson (1962). Natural material from Andreasberg.

ms: medium strong; s: strong; vs: very strong; w: weak; vw: very weak; vvw: very very weak

Summary

In conclusion, the natural occurrence of an Ag_6Sb mineral in material from the Cobalt District, Ontario, has been confirmed by *x*-ray studies and synthesis in the Ag–Sb system. It precipitated as a homogeneous solid solution containing 13.9 weight per cent antimony which on cooling exsolved antimonial silver and a lamellar, more Sb-rich form of the ϵ phase. Phase relations suggest that the original precipitation probably occurred at a temperature well above 400 °C. Assemblages of these minerals plus dyscrasite, described by Markham & Lawrence (1962), suggest the possibility that the Ag_6Sb mineral is unstable at low temperatures. Experimental work shows it is stable down to at least 300 °C.

Acknowledgments

The experimental work was performed using laboratory equipment obtained with funds from the National Research Council (Grant A-1111).

Support was also obtained (S. Somanchi) from Geological Survey of Canada Grant (No. 1-54) held by Drs. J. E. Gill, E. H. Kranck and V. A. Saull, which assistance is gratefully acknowledged. We also acknowledge the assistance of Dr. A. J. Frueh with *x*-ray problems.

References

Berry, L. G. & Thompson, R. M. (1962): *X-ray powder data for ore minerals: The Peacock Atlas, Geol. Soc. Am. Mem.* **85**.

Beudant, F. S. (1832). *Traite elementaire de Mineralogie*, 8Vo, Paris, Second Edition, Vol. 2.

Carpenter, H. C. H. & Fisher, M. S. (1932): A metallographic investigation of native silver, *Trans. Inst. Min. Met., London*, **41**, 382–403.

Doelter, C. & Leitmeier, H. (1926): *Handbuch der Mineral-chemie*, Vol. **4**, Pt. 1, 234–238. Dresden and Leipzig.

Edwards, A. B. (1954): *Texture of the ore minerals and their significance*, Australasian Inst. Min. Met., Melbourne, 2nd ed.

Machatschki, F. (1928): Über die Kristallstruktur des blattrigen Dyskrasites von Andreasberg (Harz) und der künstlich dargestellten Legierung Ag_3Sb. *Zeit. Krist.*, **67**, 169–177.

Markham, N. L. & Lawrence, L. J. (1962): Primary ore minerals of the Consols Lode, Broken Hill, New South Wales, *Australasian Inst. Min. Met. Proc.* No. **201**, 43–80.

Miller, W. G. (1910): The cobalt-nickel arsenides and silver deposits of Temiskaming, *Ont. Bur. Mines Rept.* **19**, Pt. 2, 279 pp.

Peacock, M. A. (1940): On dyscrasite and antimonial silver, *Univ. Toronto Stud., Geol. Ser.*, **44**, 31–46.

Ramdohr, P. (1960): *Die Erzmineralien und ihre Verwachsungen*, Akademie-Verlag, Berlin, 3rd ed.

Reynolds, P. W., & Hume-Rothery, W. (1937): The constitution of silver-rich antimony-silver alloys, *J. Inst. Metals*, **60**, 365–374.

SCHWARTZ, G. M. (1928): Dyscrasite and the silver-antimony constitution diagram, *Am. Min.*, **13**, 495–503.

SOMANCHI, S. (1963): Subsolidus phase relations in the systems Ag–Sb and Ag–Sb–S, *M.Sc. Thesis, Dept. of Geol. Sci. McGill Univ.*, Montreal.

SOMANCHI, S. (1966): Subsolidus phase relations in the system Ag–Sb, *Can. J. Earth Sci.*, **3**, 211–222.

STOCKDALE, D. (1937): Discussion of paper by Reynolds and Hume-Rothery, *J. Inst. Metals*, **60**, 375–377.

SWANSON, H. & TATGE, E. (1953): Standard X-ray diffraction powder patterns, *Nat. Bur. Standards Circular*, **539**, vol. 1.

WALKER, T. L. (1921): Dyscrasite from Cobalt, Ontario, *Univ. of Toronto Studies, Geol. Ser.*, **12**, 20–22.

WEIBKE, F. & EFINGER, I. (1940): Der Aufbau der Legierungen des systems Silber-Antimon, *Z. Elektrochem.*, **46**, 53–60.

WESTGREN, A., HÄGG, G., & ERICKSSON, S. (1929): Röntgenanalyse der Systeme Kupfer-Antimon und Silber-Antimon, *Z. physik. Chem.*, Abt. B, Band **4**, 453–468.

Manuscript submitted by first author August 30, 1965, resubmitted May 19, 1966