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PRELIMINARY REPORT ON SUPESTRUCTURING IN MERCURIAN TETRAHEDRITE FROM GANT, TIROL, AUSTRIA

Abstract. Small scale ordering is observed on the electron diffraction and dark-field images of Hg-tetrahedrite. Essentially three types of ordering are observed:

— large rectangular lamellae with the size of 15 × 120 pm (type A),

— thin long needles with the size of 1 × 120 pm located at the edge of lamellae A (type B),

— two types of oblique multiple lamellae with the size of 1.5 × 20 and 0.5 × 20 pm building up lamellae A (type C).

The observed lamellae are probably induced by Sb–As ordering on the M_4^{3+} site, and by $Hg^{2+} - Zn^{2+}$ as well as Hg^{2+}–Cu^{2+} ordering on the M_2^{2+} site in tetrahedrite-tennantite molecule represented by formula $M_{10}^{+} M_2^{2+} M_4^{3+} S_{13}$

Key-words: Hg-tetrahedrite, ordering, lamellae, electron diffraction, dark field.

INTRODUCTION

The limits of metal substitution in natural tetrahedrite-tennantite reveal unsolved problems as to the nature and controls of the elements substitution. The problems is difficult because of the complex chemistry of natural fahlores. The general formula of natural tetrahedrite-tennantite series is $(Cu, Ag)_{10}$ $(Zn, Fe, Cd, Hg, Cu)_2$ $(Sb, As, Bi, Sn, P)_4$ $(S, Te)_{13}$. It may be further generalized as $M_{10}^{+} M_2^{2+} M_4^{3+} S_{13}$.

In nature, the end members, tetrahedrite $Cu_{12}Sb_4S_{13}$ and tennantite Cu_{12} As_4 S_{13}, are rare and appear as minerals replacing other phases. Therefore the presence of M_2^{2+} atoms seems to stabilize the tetrahedrite structure and composition (Pattrick and Hall 1983).

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Hg-rich tetrahedrites have been recorded from many localities. Hg^{2+} substitutes for Cu^{2+} atoms in the 4-fold coordination. Both end members, tetrahedrites and tennantites, with Hg^{2+} are known in nature.

MATERIALS AND METHODS

Electron microscope analyses were made with a JEOL JEM 100C microscope at 100kV. Particles for TEM study were collected under microscopic control from areas previously analysed with microprobe. In this study particles were collected from the microarea No 2222/B2 (Tab. 1).

TABLE 1

Microprobe composition of Hg-tetrahedrite (schwazite), Gant, Tirol (wt.%/ atomic proportions)

SAMPLE →	2222/A3	2222/B2	2222/C2
P	0.10 0.0568	0.12 0.0682	0.08 0.0446
S	23.38 13.0000	23.07 13.0000	23.02 13.0000
Fe	0.14 0.0459	0.16 0.0522	0.30 0.0958
Cu	34.29 9.6205	34.13 9.7034	33.74 9.6133
Zn	0.52 0.1413	0.51 0.1401	0.46 0.1276
As	4.70 1.1181	4.82 1.1633	4.87 1.1778
Ag	0.22 0.0371	0.18 0.0305	0.19 0.0324
Sn	0.08 0.0113	0.06 0.0086	≤0.03
Sb	18.11 2.6519	18.10 2.6861	17.60 2.6171
Hg	18.51 1.6457	18.66 1.6804	18.55 1.6737
Bi	0.05 0.0045	0.07 0.0060	0.45 0.0392
TOTAL	100.01	99.87	99.26

The investigated Hg-tetrahedrite, schwazite, occurs in samples from Gant, Tirol, Austria. The main minerals in the studied sample are: gangue minerals, siderite and schwazite. Schwazite is replaced by malachite and cuprite with simultaneous precipitation of schachnerite $Ag_{1.1}Hg_{0.9}$, moschellandsbergite Ag_5Hg_8 and mercurian silver at the redox interface. The discussed schwazite shows a slight sulphur excess (Tab. 1), which is connected with applied standards rather than with a real sulphur excess.

ELECTRON DIFFRACTION STUDY

Most of the studied schwazite particles shows a composite structure of diffraction dots. They are often double, treble or multiple. The distance between subsidiary nodes increases with an increase of indices (Phot. 1). This may suggest more than one original unit cell or domain structure (Andrews et al. 1967). The 112 diffraction pattern (Phot. 2) shows extra spots at 1/3 of normal distance, which may suggest a supercell 3 times as large as the original tetrahedrite cell. The 210 diffraction pattern shows a composite structure of diffraction dots and anomalously strong $1\,\bar{2}\,\bar{2}$ reflection (Phot. 3). A dark-field image using the $1\,\bar{2}\,\bar{2}$ as a source shows twisted fringes which are probably thickness contours, and white straight continuous or dashed parallel lines. The last feature may be connected with some ordered structures in schwazite.

The most complex diffraction dots appear on the 210 diffraction pattern (Phot. 5). The main diffraction spots are composed of multiple subsidiary nodes. A dark-field image using the $\bar{1}\,2\,\bar{3}$ dot as a source indicates a complex structure of schwazite particle (Fig. 6). Generally four types of ordering may be distinguished:

A) large rectangular lamellae with the size of 15 × 120 pm (Phot. 6),

B) long multiple needles at the edge of lamellae A with the size of about 1 × 120 pm located at the edge of lamellae A (Phots. 6, 7)),

C) two types of multiple oblique lamellae building up lamellae A (Phot. 7). They are piled up at the angle of about 40° to the long axis of lamellae A. The size of the oblique lamellae is 1.5 × 20 pm and 0.5 × 20 pm (Phot. 7),

D) multiple lamellae with the size of 3 × 30 pm composed of needles 0.5 pm thick (Phot. 8).

DISCUSSION

The observed ordering in schwazite may be induced by chemical ordering on the M_2^{2+} and M_4^{3+} sites in mercurian tetrahedrite. It may be tentatively suggested that lamellae A and B result from the ordering on the M_4^{3+} site, where A may be a Sb-rich and B an As-rich unit. Lamellae of the C type may represent either ordering between M_{10}^{+} and M_2^{2+} sites or ordering on the

M_2^{2+} site between Hg–Zn and Hg–Cu^{2+} giving two types of oblique lamellae 1.5 × 20 and 0.5 × 20 pm. Lamellae of the D type may be a variety of oblique lamellae C with fringes 0.5 pm (Phot. 8). Although the proposed interpretation of the ordering in Hg-tetrahedrite seems to be concordat with the observed chemical composition (Tab. 1) further work is necessary to confirm an advanced interpretation. Such a work should include mercurian end members of tetrahedrite.

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Henryk KUCHA, Eugen F. STUMPFL, Władysław OSUCH

NADSTRUKTURY W Hg-TETRAEDRYCIE Z GANT, TYROL, AUSTRIA. KOMUNIKAT WSTĘPNY

Streszczenie

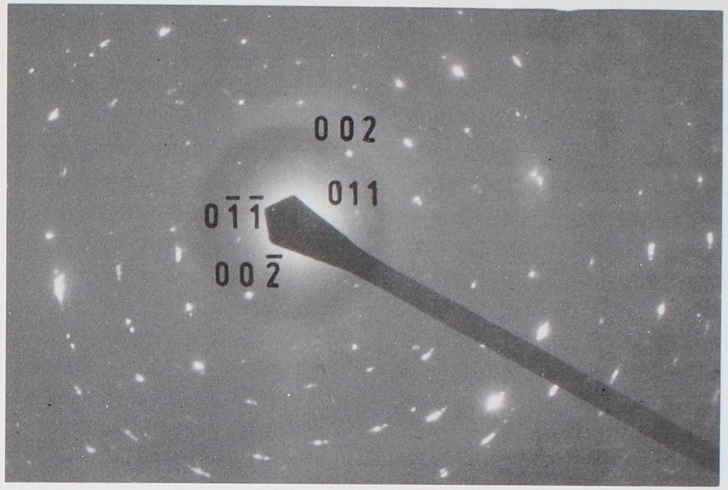
Uporządkowanie w małej skali jest obserwowane na elektrogramach dyfrakcyjnych oraz na obrazach w ciemnym polu otrzymanych z tetraedrytu rtęciowego. Zaobserwowano trzy typy uporządkowania:

— duże prostokątne lamelle o wymiarach 15 × 120 pm (typ A),

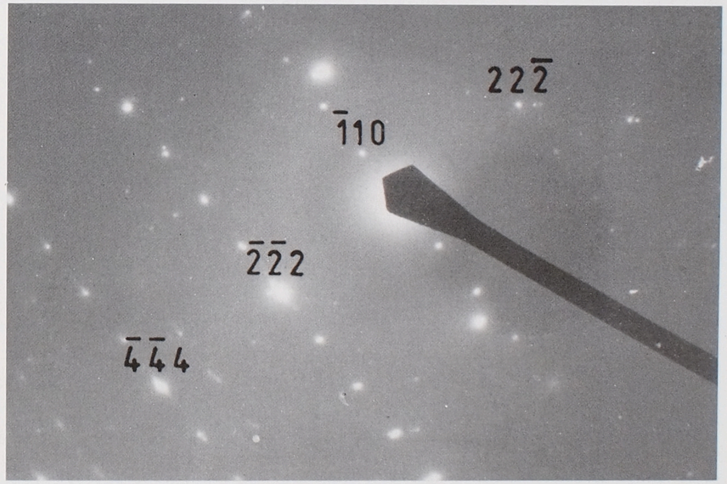
— cienkie wydłużone igły o wymiarach 1 × 120 pm lokujące się na obrzeżach lamelli A (typ B),

— dwa typy ukośnych, polisyntetycznych lamelli o wymiarach 1,5 × 20 i 0,5 × 20 pm budujące lamelle A (typ C).

Obserwowane lamelle są prawdopodobnie wynikiem uporządkowania Sb–As na pozycji M_4^{3+} oraz uporządkowania Hg^{2+}–Zn^{2+} i Hg^{2+}–Cu^{2+} na pozycji M_2^{2+} w tetraedrycie-tennantycie (M_{10}^{+} M_2^{2+} M_4^{3+} S_{13}).

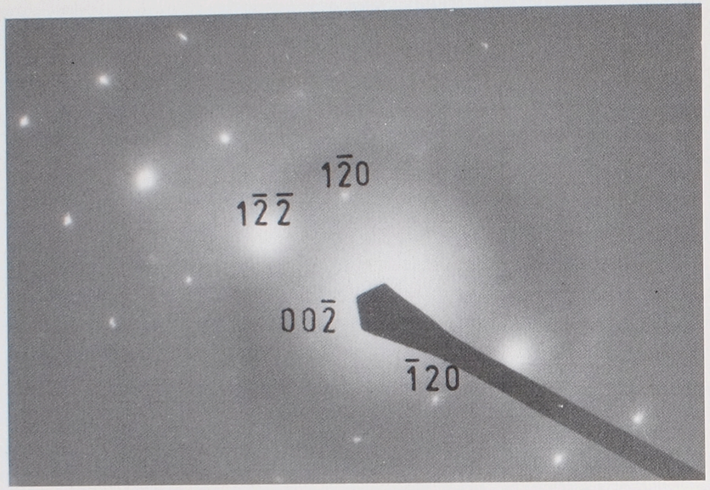


Phot. 1. The 001 electron diffraction pattern of schwazite. Main diffraction dots are composed of two subsidiary nodes. The distance between subsidiary nodes increases with increasing indices, ex. 011, 022, 033, 044

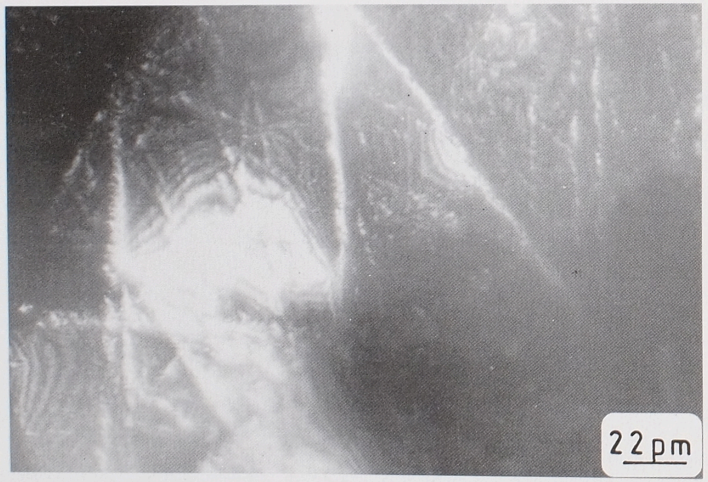


Phot. 2. The 112 electron diffraction pattern of schwazite. Superstructure nodes are visible at fractional distances in front of $\bar{4}\bar{4}4$ and $\bar{6}\bar{6}6$ nodes

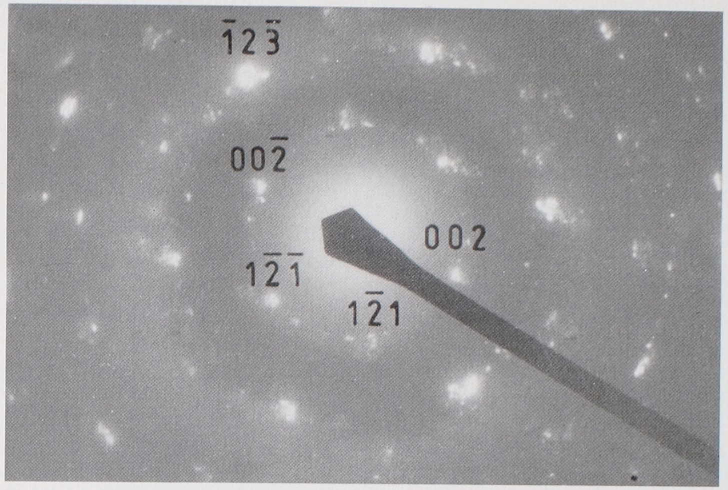
H. KUCHA, E. F. STUMPFL, W. OSUCH — Preliminary report on supestructuring in mercurian tetrahedrite from Gant, Tirol, Austria



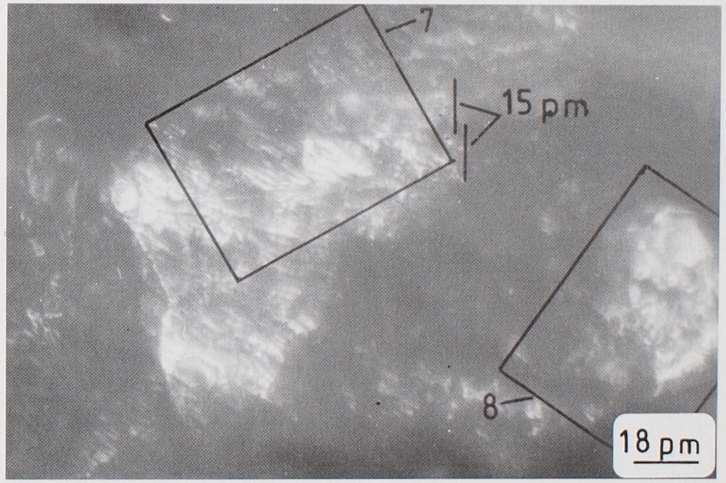
Phot. 3. The 210 electron diffraction pattern of schwazite



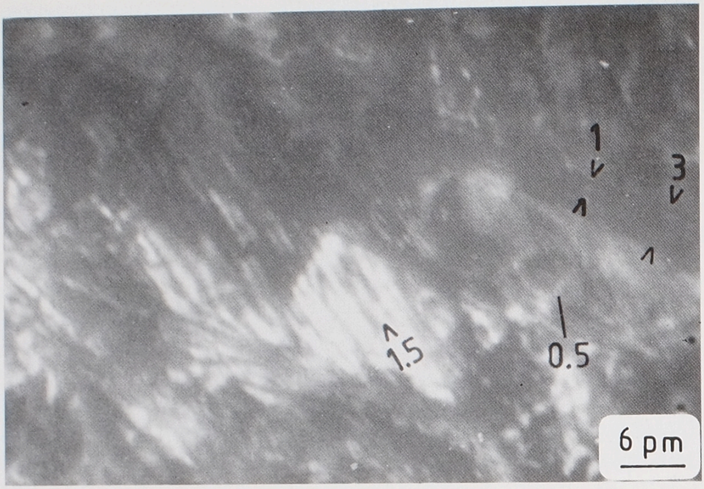
Phot. 4. A dark-field image using the $1\bar{2}\bar{2}$ spot as a source (Phot. 3). The $1\bar{2}\bar{2}$ plane is visible as well as thickness fringes



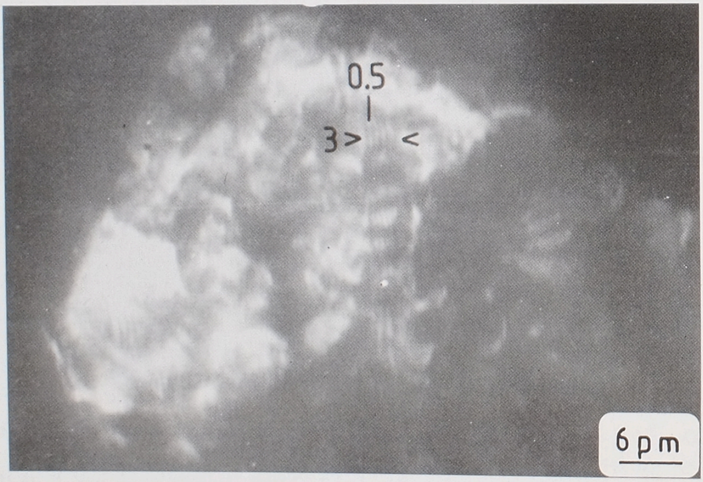
Phot. 5. The 210 electron diffraction pattern of schwazite. A composite structure of diffraction spots is visible



Phot. 6. The $\bar{1}2\bar{3}$ dark-field image (Phot. 5) of schwazite. Three types of lamellae (domains) are revealed: A) large rectangular with the size 15 × 120 pm; B) thin needles with the size 1 × 120 pm located at the edge of lamellae A; C) oblique to lamellae A and B at the angle of about 40° with the size 1.5 × 20 pm. Boxed areas are enlarged on Phot. 7 and 8



Phot. 7. Composite structure of schwazite (boxed area 7 on Phot. 6). Three types of domains are revealed
A) large rectangular of A type seen on Phot. 6; B) thin needles at the edge of domains A with fringes of about 1 pm; C) two types of oblique domains at 40° to the long axis of domains A. One type of oblique domains has size 1.5 × 20 pm, and another one 0.5 × 20 pm



Phot. 8. Composite structure of schwazite (boxed area 8 on Phot. 6). Lamellae with size 3 × 40 pm with fringes 0.5 pm are revealed

H. KUCHA, E. F STUMPFL, W. OSUCH — Preliminary report on supestructuring in mercurian tetrahedrite from Gant, Tirol, Austria