

## THE CRYSTAL STRUCTURE OF MICHENERITE, PdBiTe \*

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### ABSTRACT

The crystal structure of michenerite, PdBiTe, has been determined by Patterson methods and refined to an  $R$ -value of 0.034 using multiple sets of 4-circle diffractometer data and full-matrix least-squares procedures. Spherical absorption and anomalous dispersion corrections were applied in the refinement. The structure is similar to that of  $P2_13$  ullmannite NiSbS, though there is a greater distortion from the regular octahedral and tetrahedral coordination than in other pyrite-type structures. The atomic separations (Pd-Te = 2.72 Å, Pd-Bi = 2.77 Å, and Te-Bi = 2.91 Å) are in agreement with the sums of the corresponding metallic radii.

### INTRODUCTION

Michenerite is a ternary compound in which tellurium and antimony substitute for bismuth, and platinum substitutes for palladium, over limited compositional ranges. Michenerite has been found in ore deposits at Sudbury, Ontario, and at Monchegorski and Noril'sk, USSR. The mineral was first reported by Michener (1940) as Pd<sub>2</sub>Bi<sub>3</sub> and later re-defined as PdBi<sub>2</sub> by Hawley & Berry (1958). However, a recent re-definition of both natural and synthetic michenerite has shown it to have the stoichiometric formula PdBiTe (Cabri *et al.* 1973).

Synthetic michenerite, PdBiTe, has been described (Hulliger & Müller 1963) as cobaltite-type and a ternary analogue of pyrite, having the general composition  $MXY$ , where  $X$  is one of the elements, P, As, Sb or Bi;  $Y$  is S, Se or Te. When  $M$  is Co, Rh or Ir, the resulting compounds are semi-conducting, and when  $M$  is Ni, Pd or Pt, the compounds are metallic. The latter group results from the presence of excess delocalized valence electrons. Many of the metallic compounds have superconducting properties, as is the case for PdBiTe below  $\sim 1.2^\circ\text{K}$  (Hulliger & Müller 1963).

This study shows that the space group of michenerite is  $P2_13$  and on these grounds its

structural type may be better described as being that of ullmannite, NiSbS, rather than cobaltite, CoAsS. The structures of several ullmannite-type compounds have been determined by x-ray methods (ullmannite: Takeuchi 1957; gersdorffite: Bayliss & Stephenson 1967). The purpose of this study is to provide accurate structural parameters for michenerite and, if possible, to relate them to the observed physical properties.

### EXPERIMENTAL

#### Crystal data

Source: Copper Cliff concentrates, Sudbury, Ontario

Microprobe analysis in weight %: Crystal #3 (Cabri *et al.* 1973) Pd: 24.8(1) Bi: 43.0(1) Sb: 3.3(1) Te: 29.9(1)

Chemical composition: Pd<sub>1.00</sub>(Bi<sub>0.88</sub>Sb<sub>0.11</sub>)Te<sub>1.00</sub>

Space group:  $P2_13$ (No. 198) Cell dimension:  $a = 6.642(1)\text{Å}$   $Z = 4$ ,  $D(\text{calc.}) = 9.84\text{ g/cc}$ ,  $D(\text{meas.}) = \sim 10\text{ g/cc}$

Linear absorption coefficient:  $\mu(\text{MoK}\alpha) = 670.6\text{ cm}^{-1}$

Crystal radius:  $R = 0.046(3)\text{ mm}$ ;  $\mu R = 3.06$   
Intensity data: 849 reflections measured three times.

The large linear absorption coefficient for this material ( $670.6\text{ cm}^{-1}$ ) presented a major difficulty in the accurate determination of the structure. Initial intensity data were collected on an irregularly shaped fragment of michenerite (maximum dimension 0.25 mm). These data proved of limited use because of the lack of correlation between the general absorption corrections and the intensity variations of equivalent reflections. It was not possible using these data to refine the structure below an  $R$ -value of 0.12. When more michenerite became available from the Copper Cliff concentrates, Sudbury, a crystal was ground to a sphere using a high-walled brass grinder, constructed in this laboratory for use with magnetic materials, and fine-grade diamond-impregnated paper. The michenerite crystals have a tendency to shatter and adhere to the walls of a grinder so that considerable care, over a period of several days, was required to

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obtain a sphere of suitable radius. The radius of the sphere, 0.046 mm, represented a compromise between the optimum absorption correction, intensity considerations and the practicality of grinding a small sphere.

Precession photographs of michenerite indicated the presence of cubic symmetry and gave  $h00, 0k0, 00l$  systematic absences of  $h, k, l = 2n + 1$ . This indicated that the space group was  $P2_13$  or  $P4_232$ . Examination of a subsequent Patterson synthesis showed that only the space group  $P2_13$  was consistent both with the vectors occurring in the map and with the unit-cell content expected on the basis of the chemical composition. The space group  $P2_13$  was therefore determined unambiguously for natural michenerite. It should be noted, however, that the powder pattern of synthetic michenerite contains the reflection 100, indexed on the basis of the cubic cell ( $a = 6.6\text{\AA}$ ), and this is only consistent with the space groups  $P23$  or  $Pm3$  (Cabri *et al.* 1973). As a further complication, the powder pattern also shows several weak reflections that cannot be indexed for a cubic cell. This suggests that either synthetic michenerite is a different non-cubic phase, or the powder contains minor impurities of a second phase. The proposal of Bayliss (1969), that the presence of both the 100 and the 011 reflections in cobaltite-type compounds indicates a non-cubic cell with either ordered or disordered atoms, is consistent with the former proposal.

The crystal was mounted in a random orientation on a 4-circle diffractometer and aligned automatically using 20 different reflections. The cell dimensions were determined by a least-squares fit of the diffractometer angles  $2\theta$ ,  $\varphi$ ,  $\chi$  and  $\omega$  for these reflections assuming a triclinic cell. This gave  $a = b = c = 6.642(1)\text{\AA}$  and  $\alpha = \beta = \gamma = 90.00(1)^\circ$ .

The intensities of an asymmetric set of  $hkl$  reflections were measured three times and those of a  $\bar{h}kl$  set once, both to a  $2\theta$ -limit of  $114^\circ$ . The intensity measurements were made on the 4-circle diffractometer using graphite-monochromatized  $\text{MoK}\alpha$  radiation and a  $\theta/2\theta$  scan technique. The scan was adjusted according to the dispersion. Background counts (45 seconds) were measured on each side of a scan (30 seconds per degree  $2\theta$ ). The intensities of three linearly independent reflections were recorded every 50 measurements to monitor crystal alignment and instrument stability.

The three measured sets of  $hkl$  intensity data were compensated for spherical absorption effects and merged into one unique set in two different ways. In the first way, a reflection was considered "observed" at the 10% significance level

( $I(\text{net}) > 1.65\sigma(I)$ ) and "unobserved" intensities were set equal to  $1.65\sigma(I)$ . Using this criterion, 527 of the 849 reflections were considered observed and the average agreement factor ( $\sum \Delta I_{\text{obs}}/I_{\text{obs}}$ ) of any two sets of data and a third was 0.028. In the second way, *all* reflections were considered observed, including the 31 reflections with negative counts which were assigned intensities of zero. The average agreement factor in this case was 0.048. The purpose of considering intensity data in these two ways was to determine what effect the specification of unobserved reflections had on the refinement process and the final atomic parameters.

Because secondary extinction effects are minimized in the grinding of a crystal, no *a priori* corrections of this type were made. Subsequent empirical corrections were found to be negligible. The  $\bar{h}kl$  intensities were reduced to structure factors separately and used later to confirm the correct application of anomalous dispersion corrections.

#### STRUCTURE SOLUTION AND REFINEMENT

A trial structural model was obtained by applying the Patterson method. All of the atoms were located in the special positions  $4a(x, x, x)$  and identified by using the peak heights in a difference synthesis calculated from structure factors where atoms were assumed to be Te only. The Bi site was readily located from electron density considerations but the Pd and Te atoms could not be positively identified on this basis alone. Synthetic work (Cabri *et al.* 1973) on the Pd-Bi-Te system had shown that Te can be substituted for Bi, but not for Pd, over a limited compositional range and this suggested that the Te and Bi atoms had similar chemical environments in the structure. Two of the atomic sites have tetrahedral coordination and the third octahedral. Since Bi was shown to occupy one tetrahedral site, Te could be assigned with some certainty to the second. This conclusion is consistent both with the difference-map peak heights and with atomic radii considerations.

Refinement of the structure was performed using the full-matrix structure factor least-squares program CRYLSQ from the XRAY system of crystallographic programs (Stewart *et al.* 1972) using unit weights. Atomic scattering factors were those of Cromer & Mann (1968), averaged in the case of the Bi site, to account for the partial occupancy by Sb (*i.e.*  $0.88f_{\text{Bi}} + 0.11f_{\text{Sb}}$ ) indicated by the electron probe analysis. After six cycles of isotropic refinement of the trial parameters, the *R*-value dropped to 0.058.

The effect of anomalous dispersion was considered early in this analysis because of the large



## DESCRIPTION OF THE STRUCTURE

Michenerite can be considered as a ternary analogue of the pyrite structure (Elliott 1960). In pyrite, the Fe atom is located at the origin on a three-fold axis of the centrosymmetric space group  $Pa\bar{3}$ . The Fe atom is surrounded by six S atoms forming a distorted octahedron, while each S atom is in a distorted tetrahedral environment of three S atoms and one Fe atom. In michenerite, the Pd atom is located on a three-fold axis, slightly removed from the origin, and surrounded by three Bi and three Te atoms in a distorted octahedral arrangement (Fig. 1 and 2). The Te and Bi atoms are coordinated to three Pd atoms and a Bi or Te atom in a distorted tetrahedral arrangement (Fig. 3). This structure does not show the disorder effects (Bayliss & Stephenson 1968) seen in the structures of other ullmannite-type compounds. The relative atomic separations in michenerite ( $\text{Pd} - \text{Te} = 2.72\text{\AA}$ ,  $\text{Pd} - \text{Bi} = 2.77\text{\AA}$ , and  $\text{Te} - \text{Bi} = 2.91\text{\AA}$ ) are consistent with the corresponding metallic radii of  $r(\text{Pd}) = 1.37\text{\AA}$ ,  $r(\text{Bi}) = 1.54\text{\AA}$  and  $r(\text{Te}) = 1.43\text{\AA}$  (Sutton 1965), as expected with the metallic properties observed for  $\text{PdBiTe}$  (Hulliger & Müller 1963).

The different atom types coordinated about the Pd atom in this structure give rise to a pseudo-centrosymmetric symmetry (Fig. 1) and larger distortions to the regular tetrahedral and octahedral coordination than those observed in the pyrite structure. The tetrahedral angles (Fig.

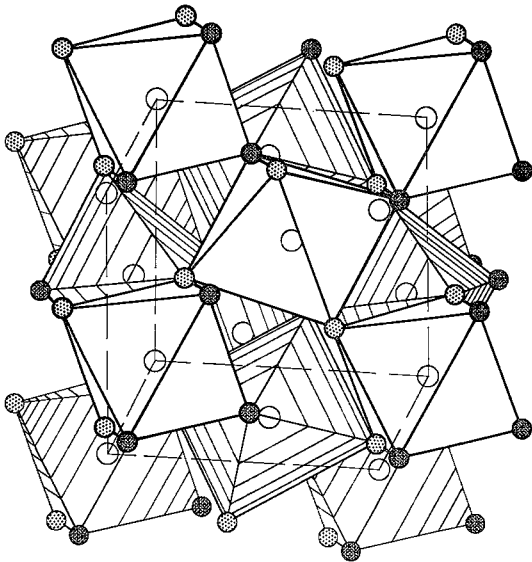


FIG. 1. The crystal-cell model of michenerite showing the octahedral coordination of the Bi atoms (cross-hatched circles) and the Te atoms (dotted circles) about the Pd atoms (open circles).

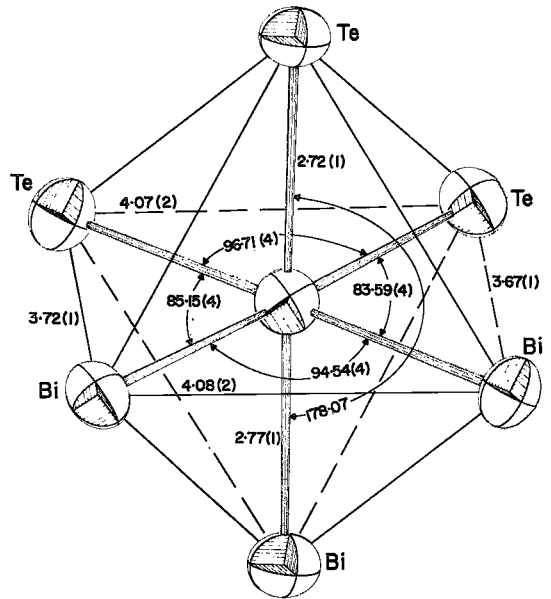


FIG. 2. The octahedral coordination of the Pd atom, showing the interatomic distances in Ångstroms, and angles in degrees. The estimated standard deviations are shown in parentheses. The atoms are plotted as thermal ellipsoids at the 99% probability level (Johnson 1965).

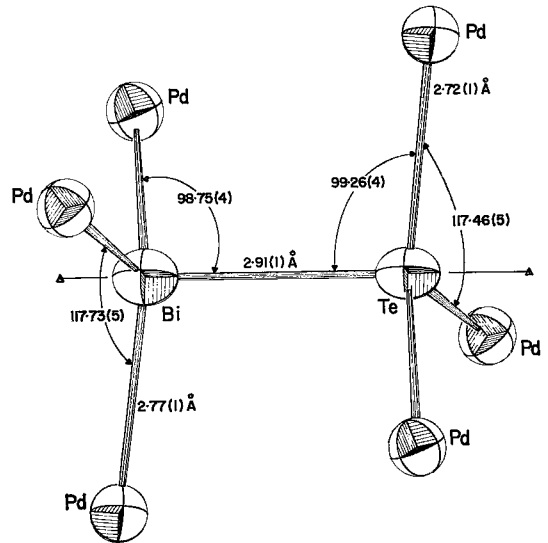


FIG. 3. The tetrahedral coordination about the Bi and Te atoms, showing the interatomic distances in Ångstroms and angles in degrees. The estimated standard deviations are shown in parentheses. The atoms are plotted as thermal ellipsoids at the 99% probability level (Johnson 1965).

3) vary from  $98.8^\circ$  to  $117.7^\circ$  while the corresponding values in pyrite are  $102.1^\circ$  to  $115.7^\circ$  (Elliott 1960). The range of angles (Fig. 2) about the Pd atom of  $83.6^\circ$  to  $95.4^\circ$  is also larger than that in pyrite ( $85.6$  to  $94.9^\circ$ ) and marginally greater than the deviations of  $4^\circ$  to  $5^\circ$  summarized for structures of this type by Hulliger & Mooser (1965). These authors report that the distortions to a regular octahedron are an important indicator to conduction in the pyrite-type compounds, though the electronic configuration of the cation is still the most critical factor. The  $d$ -energy levels are split into three lower and two higher energy levels by the octahedral environment and the degeneracy of the levels is determined by the degree of octahedral distortion. In pyrite, the low-spin  $d^6$  configuration has no unpaired or excess  $d$ -electrons and is thus semi-conducting. In PdBiTe, the low spin  $d^7$  configuration has one unpaired electron and is metallic. In order to explain this, Hulliger & Mooser (1965) suggest that, provided distortion of the regular octahedra is small, the two highest  $d$ -levels are nearly degenerate and, therefore, less than half-filled. This results in the observed metallic properties. While michenerite has a slightly larger (distorted) octahedron than that observed in any of the previously reported pyrite-type structures, it still behaves as a metal and must be considered in this class of compounds.

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