On the Structure of Tl_2GeTe_5[1]

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As part of a study on the ternary system Tl–Ge–Te, Abba-Toure *et al.* (*1*) have recently described the synthesis and crystal structure of Tl_2GeTe_5. The authors noted that the crystals appeared to show tetragonal symmetry, with possible space groups $P4_2bc$ or $P4_2/mbc$, but they were apparently unable to derive a satisfactory tetragonal structure and instead described the structure in a doubled orthorhombic cell, space group $Cmmm$, with $a = b = 11.657(5)$ Å, $c = 14.917(5)$ Å.

The $Cmmm$ structure can, in fact, be described—without significant shifts in atom positions—in the tetragonal space group $P4/mbm$. As noted in Ref. (*1*), the tetragonal cell ($a = 8.243$, $c = 14.917$ Å) is defined by the orthorhombic lattice vectors ($\frac{1}{2}$, $\frac{1}{2}$, 0), ($-\frac{1}{2}$, $\frac{1}{2}$, 0), (0, 0, 1); the corresponding coordinate transformations are $x' = x + y$, $y' = -x + y + 0.5$, $z' = z$, where the translation of 0.5 in y is necessary to place the origin at a conventional center of symmetry in $P4/mbm$. After averaging over equivalent atoms, the coordinates in Table I result. The coordinate shifts necessary to satisfy the

higher symmetry of $P4/mbm$ were, on the average, appreciably smaller than the e.s.d.'s given in Table IV of Ref. (*1*); the maximum shifts, of about 2 e.s.d.'s, involved the z coordinates of Te(2) and Te(3). The anisotropic coefficients U_{ij} showed equally satisfactory agreement with the symmetry requirements of $P4/mbm$.

There remains a puzzling question concerning systematic absences. As noted earlier, the original authors (*1*) first noted that the space group might be $P4_2bc$ or $P4_2/mbc$. The corresponding systematic absences would be $0kl$ with k odd (and $h0l$ with h odd) and also hhl with l odd; the first set of absences is satisfied by the revised space group $P4/mbm$, but the second set is not. Indeed, structure–factor calculations based on the revised model (Table I) showed that many intensities in this secondary category—including several $00l$'s with l odd, which are extinguished by a 4_2 axis—would be expected to be large. (Calculations based on the orthorhombic, $Cmmm$ model are, of course, nearly identical. While this space group does not carry any systematic absences other than those related to the C-centering, reflections hhl with h odd all were calculated as very weak, corresponding to

TABLE I

COORDINATES, SPACE GROUP *P4/mbm*, WITH e.s.d's (IN PARENTHESES) AS ESTIMATED FROM THE VALUES
IN TABLE IV OF REF. (*1*).

Atom	Site	x	y	z
Tl(1)	4(*e*)	0.5	0.5	0.1256(3)
Tl(2)	4(*e*)	0.5	0.5	0.3810(2)
Te(1, 8)	4(*g*)	0.1912(5)	0.6912	0.0
Te(2, 3)	4(*f*)	0.5	0.0	0.8732(6)
Te(4, 5)	8(*k*)	0.1827(4)	0.6827	0.2792(3)
Te(6, 7)	4(*h*)	0.3325(5)	0.8325	0.5
Ge(1, 2)	4(*f*)	0.0	0.5	0.3810(7)

Cell dimensions: $a = 8.243(4)$ Å, $c = 14.917(5)$ Å.

the *b*-glide in *P4/mbm*, while those of the types $h0l$ or $0kl$ with l odd calculated to have approximately the same values–sometimes large–as given by the *P4/mbm* model for the hhl's with l odd.) In other words, if the arrangement of atoms proposed in Ref. (*1*) is correct—as seems clearly indicated by the final R value of 0.077–the systematic absences were not consistent with space groups $P4_2bc$ or $P4_2/mbc$, but they are consistent with *P4/mbm*. Unfortunately, the original intensity data, needed for a further check on the situation, apparently are not available; however, it seems likely that this confusion over systematic absences might have been responsible for the original au-

thors' failure to find a satisfactory tetragonal model.

In view of the small shifts in the atom positions, the structure—including the interatomic distances—remains effectively unchanged; only the description is changed.

Acknowledgments

Reference

1. A. ABBA-TOURE, G. KRA, R. EHOLIE, J. OLIVIER-FOURCADE, J.-C. JUMAS, AND M. MAURIN, *J. Solid State Chem.* **84**, 245 (1990).