SHORT COMMUNICATIONS

Note on the crystal structure of ferroelastic PtGeSe.

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An alternative crystal structure model for PtGeSe to that of Entner & Parthé [*Acta Cryst.* (1973), B29, 1557–1560], in which the identities of the Se and Ge atoms are interchanged, fits the diffraction data as well and gives temperature factors for Pt, Ge and Se that do not differ significantly from the mean of 0.33 Å^2, whereas the original model gives values for Ge and Se that differ by nearly a factor of two. In the alternative model, the average Pt–Ge and Pt–Se distances are 2.466 and 2.554 Å, in agreement with recent determinations that indicate that Pt–Ge may be smaller than Pt–Se and in contrast to expectation based on the sum of Pauling's [*The Nature of the Chemical Bond* (1960), Ithaca: Cornell Univ. Press] tetrahedral covalent radii.

In the course of investigating the ferroelastic properties of the semiconductor PtGeSe* (Abrahams, Bernstein & Buehler, 1976 – hereafter ABB) the possibility arose that the structure determination by Entner & Parthé (1973) – hereafter EP – might have been made on a crystal containing ferroelastically twinned components. Many PtGeSe crystals grown by ABB are twinned and ferroelastically related reflections measured on an automatic diffractometer could appear single: even at high scattering angles, the separation between ferroelastically related reflections is comparable to that caused by the difference between Mo $K\alpha_1$ and α_2 wavelengths. Twinning in the crystal used by EP is, in fact, shown to be unlikely for a difference Fourier series based on EP's model and measured structure factors did not result in positive electron densities at positions corresponding to ferroelastic atomic reorientation.

The uniqueness of EP's model was checked by examining a Fourier series based on phases given only by the Pt atom. Four principal models were identifiable, each of which was subjected to refinement by the method of least squares, using the form factors given in *International Tables for X-ray Crystallography* (1974) including f' and f'', and EP's 1202 structure factors. Weights were taken as $1/\sigma^2 F_{meas}$, where $\sigma F_{meas} = 0.15 F_{meas}$ for $F_{meas} > 0.1 F_{max}$, $F_{max} = 294$; 4.4 for $15 < F_{meas} < 29$; $4.4 + 0.15(15 - F_{meas})$ for $F_{meas} \leq 15$, using the magnitudes of F_{meas} in Table 3 of EP. Models 1 and 2 refined to give the coordinates in Table 1, with respective values of $R = 0.0878$ and 0.0876 based on all 1202 structure factors and values of S close to unity: EP report $R = 0.089$ for coordinates nearly the same as Model 1. Models 3 and 4 both gave $R = 0.129$ and were rejected not only for the poorer fit but also because in both cases the Pt was located in the base of a square pyramid of nearest-neighbor atoms.

The position coordinates of Models 1 and 2 are essentially equivalent except for the interchange of Se and Ge (with atomic numbers 32 and 34 respectively). In Models 1 and 2, the Pt is located in an octahedral environment with three nearest Se and three nearest Ge neighbors. Both Ge and Se

are in tetrahedral environments with three nearest Pt and, respectively, a Se or a Ge neighbor. The arrangement of nearest neighbors in both environments is distorted from geometrical regularity by as much as $9.5°$ in bond angle.

Significant discrimination between Models 1 and 2 is not feasible on the basis of R or wR although a choice may be made on the basis of the temperature factors. In Model 1, the ratio of $B(\text{Se}):B(\text{Ge})$ is 1.77, with $B(\text{Pt})$ nearly the same as $B(\text{Ge})$. In Model 2, no value of B is significantly different from the mean of 0.326 Å. Least-squares refinement of Models 1 and 2 in which each atom is allowed to vibrate anisotropically shows no significant improvement in wR (0.1693 for Model 1, 0.1700 for Model 2). It is a reasonable assumption that all atoms in PtGeSe, a distortion of the pyrite structure, should vibrate equally as found in Model 2 and that, if any of the amplitudes of vibration differ, at least those of Ge and Se should be nearly identical. Model 2 is hence more likely than Model 1.

The principal difference between Models 1 and 2, apart from the amplitudes of vibration, lies in the assignment of Pt–Se and Pt–Ge interatomic distances. In Model 1, the three independent Pt–Se distances are 2.454, 2.456 and

Table 1. *Atomic coordinates and thermal parameters in two models for* PtGeSe

Model 1: $R = 0.0863$, $wR = 0.1716$, $S = 1.050.$*

	x	y	z	B (Å^2)
Pt	0.0081 (1)	0.7422 (1)	0	0.311 (7)
Ge	0.3842 (3)	0.1371 (3)	0.6160 (4)	0.265 (19)
Se	0.6188 (4)	0.3752 (4)	0.3828 (4)	0.469 (21)

Model 2: $R = 0.0861$, $wR = 0.1722$, $S = 1.054.$

	x	y	z	B (Å^2)
Pt	0.0081 (1)	0.7422 (1)	0	0.313 (7)
Ge	0.6190 (4)	0.3751 (4)	0.3830 (4)	0.370 (21)
Se	0.3842 (3)	0.1370 (3)	0.6151 (4)	0.359 (19)

* Space group $Pca2_1$, $a = 6.00984$ (4), $b = 6.06174$ (5), $c = 5.98187$ (5) Å.

* Definitions of R, wR and S are given, for example, by Abrahams & Reddy (1965). R here is for the 1187 $F_{meas} > 0$.

2·490 Å, the corresponding Pt–Ge distances are 2·520, 2·563 and 2·577 Å. In Model 2, the Pt–Se distances are 2·526, 2·563 and 2·573 Å, those of Pt–Ge are 2·452, 2·455 and 2·492 Å. Hence, for either model, the minimum difference between Pt–Se and Pt–Ge interatomic distances is about 0·03 Å with a maximum range of about 0·06 Å in each of the two types of contact, suggestive of near equality between the two bond types. The atomic radii in PtGeSe, based on the average interatomic distances, are Pt 1·275, Ge 1·283, Se 1·191 Å for Model 1 and Pt 1·285, Ge 1·181, Se 1·269 Å for Model 2. Phillips's (1973) rationalized tetrahedral radii for Ge and Se are equal, at 1·225 Å, in contrast to Pauling's (1960) values of 1·22 Å for Ge and 1·14 Å for Se which were initially among EP's criteria (Parthé, 1976) in solving the crystal structure.

The ease with which large atomic displacements are produced in PtGeSe on ferroelastic reorientation together with the low resistivity at room temperature led to the suggestion by ABB that the bonding in PtGeSe tends toward metallic rather than pure covalent. Present bond theory appears unable, in this case, to distinguish between Pt–Se and Pt–Ge interatomic separations.

Experimentally, the Pt–Ge distance has been reported as ranging from 2·480 (6) to 2·656 (5) Å in PtGe by Graeber, Baughman & Morosin (1973), 2·433 (2) Å in cis-(hydroxydiphenylgermanyl)phenylbis(triethylphosphine)platinum(II) by Gee & Powell (1971), and ranging from 2·391 (3) to 2·480 (3) Å in tetramethylammonium pentakis(trichlorogermanyl)platinate(II) by Estes & Hodgson (1973). Heinrich & Schubert (1976) report coordinates for Pt_3Ge_2 that give a range of Pt–Ge distances from 2·535 to 2·690 Å. The only reliable Pt–Se distance found in the literature is the value 2·513 (9) Å reported for $PtSe_2$ by Furuseth, Selte & Kjekshus (1965). The interatomic distances cited for Pt–Se and Pt–Ge are consistent with the values that correspond to Model 2 for PtGeSe. It may be noted, as pointed out by

Parthé (1976), that an attempted distinction between Ge and Se based on neutron scattering will be subject to ambiguities that are similar to those found in the X-ray study, since the neutron scattering amplitudes are 0.819×10^{-12} cm for Ge and 0.80×10^{-12} cm for Se (Bacon, 1972).

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The absolute configuration of apomorphine.

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The absolute configuration of apomorphine was determined with anomalous scattering. 23 Friedel pairs were recorded on film. As has previously been shown with chemical methods it was found that the absolute configuration at the only asymmetric carbon atom is *R*.

Apomorphine is a very important substance in the study of humoural neurotransmission as it acts directly on dopamine receptors. From an inspection of a model of the apomorphine molecule it is immediately evident that the proton of the charged N atom can only be approached from one side of the rather planar molecule. Since this proton presumably plays an important role in the neurotransmission, knowledge of the absolute configuration of apomorphine would indirectly bring information not only about the

receptor, but also about the optimum conformation of related neurotransmitters.

Using chemical methods, Kalvoda, Buchschacher & Jeger (1955) assumed, and Corrodi & Hardegger (1955) confirmed that the configuration of apomorphine is *R* at the only asymmetric carbon atom (6a). Since a suitable crystal was left from a previous investigation (Giesecke, 1973) it was interesting to make a redetermination of the absolute configuration by X-ray methods.