gènes (2,90 et 2,45 Å). Ce type de coordinence est comparable à celui trouvé notamment dans $NaV_2O_4F\alpha'$ par Carpy & Galy (1971).

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The 4*H* Polytype of Silver Iodide

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Abstract. Hexagonal, $P6_3mc$, $a=4{\cdot}5979$ (4), $c=15{\cdot}029$ (7) Å, $Z=4$, $D_x=5{\cdot}67$ g cm^{-3}. The 4*H* modification of AgI has been studied by conventional three-dimensional techniques using a crystal which had experienced 0·2 GPa hydrostatic pressure. Apart from stacking differences, this polytype is essentially identical to the wurtzite form.

Introduction. A single crystal of AgI grown by the method of Cochrane (1967) was found to exhibit a unit cell unlike any previously reported. This crystal was one of a batch synthesized for high-pressure conductivity studies (Schock & Hinze, 1975). Examination by Weissenberg techniques established it to be a 4*H* polytype of the basic wurtzite structure. This conclusion was confirmed by a complete analysis using diffractometrically acquired data. Subsequently Prager (1974) published evidence for four new polytypes, including this 4*H* form. Since his report is qualitative regarding the structure, we present the results of our three-dimensional analysis.

The high-pressure conductivity studies indicated that a single crystal of AgI underwent an apparently irreversible conductivity change when pressurized beyond 0·1 GPa hydrostatic pressure at temperatures <350 K. To investigate this phenomenon, a first-order hexagonal prism ($0{\cdot}04\times0{\cdot}04\times0{\cdot}3$ mm) was selected to be studied by X-ray techniques before and after the application of 0·2 GPa hydrostatic pressure. Unexpectedly, this crystal exhibited a doubling of the normal wurtzite cell along [001] *before* application of pressure. Since these same prismatic crystals were used in the earlier investigations in which the anomaly was observed, this crystal was subjected to the pressure environment as planned. Upon release of pressure, the crystal was reinspected by Weissenberg techniques whereupon it was established that no significant irreversible modification of the structure had occurred.

It seemed reasonable to conduct a full three-dimensional investigation of the crystal in view of the novel (for AgI) structure. Diffractometrically measured data for 53 nonequivalent reflections were recorded with Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å). The structure, assumed to be 4*H*, refined as shown in Table 1 to a final agreement index of 0·024 provided the 110 reflection was not included. Including this reflection, the index was 0·053. We have not satisfactorily accounted for the disagreement between observed and calculated values for this reflection ($F_o<F_c$); however, since neither final difference Fourier results nor least-squares parameters were materially affected by its presence or absence, we have arbitrarily removed it from consideration for the purposes of the calculations reported here. An absorption correction was not made ($\mu=181$ cm^{-1}); a secondary extinction correction did not affect the agreement of the data and so was not included. No quantitative attempt was made to investigate possible stacking disorder although it was noted that no appreciable streaking was observed on Weissenberg photographs.

Table 1. *Final parameters for* 4*H* AgI

E.s.d.'s are in parentheses. The temperature factor is expressed as $\exp\{-\frac{1}{4}[(h^2a^{*2}+k^2b^{*2}+hka^*b^*)B_{11}+l^2c^{*2}B_{33}]\}$.

	Wyckoff number	x	y	z	B_{11}	B_{33}
Ag(1)	2(*a*)	0	0	$\frac{1}{4}$	6·6 (2) Å^2	6·3 (2) Å^2
Ag(2)	2(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	0	6·6 (2)	6·3 (2)
I(1)	2(*a*)	0	0	0·04384 (4)	4·2 (1)	3·6 (1)
I(2)	2(*b*)	$\frac{1}{3}$	$\frac{2}{3}$	$z-\frac{1}{4}$	4·2 (1)	3·6 (1)

Last shift $<\frac{1}{100}$ e.s.d. and all $\sigma=1$.

The parameters of Table 1 were based on full-matrix least-squares treatment including anomalous dispersion and anisotropic thermal parameters. Atoms of the same species were constrained to move together by varying only the z parameter of iodine and allowing only one thermal description for silver and one for iodine. These constraints are not imposed by the space group ($P6_3mc$) but no significant improvement in agreement of the data occurred when four independent positions were used.*

Discussion. The structure of the normal wurtzite phase has been described by Burley (1963). The present structure of AgI differs in one significant respect. Burley observed equal bond distances (2·814 and 2·813 Å) whereas in the 4*H* polytype there are three Ag–I bond distances of 2·811 (2) and one of 2·832 (6) Å. For both structures the thermal parameters for silver are considerably greater than those of iodine.

Other crystals of a pyramidal morphology were observed in the original preparation. These were found to be of the normal wurtzite type. No significant difference in impurity levels was detected for the two polytypes. Major impurities, as observed by emission spectroscopy analysis, were: Ca (10 p.p.m.), Cu and Si (5 p.p.m.), and Fe and Mg (3 p.p.m.).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30864 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Hexafluoroacetylacetonatothallium(I)

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Abstract. Tl(hfac), triclinic, $P\overline{1}$, $a=9{\cdot}576$ (8), $b=11{\cdot}320$ (8), $c=9{\cdot}445$ (6) Å, $\alpha=103{\cdot}86$ (5), $\beta=107{\cdot}28$ (8), $\gamma=67{\cdot}30$ (8)°. $Z=4$, $D_m=3{\cdot}06$, $D_x=3{\cdot}062$ g cm^{-3}, μ(Mo $K\alpha$) $=182{\cdot}5$ cm^{-1}. The structure consists of polymer chains formed by two different structural units linked by oxygen atoms of hfac anions along the *b* axis. Thallium ions are surrounded by five oxygen atoms. Three of these and the thallium ion lie approximately in a plane and the other two oxygen atoms are on one side of this plane. Tl–O distances range from 2·62 to 3·04 Å.

Introduction. Tl(hfac) is one of the most volatile 1:1 β-diketonato complexes. The crystal structure has been determined in order to gain a greater understanding of the stereochemistry of Tl and to reveal the packing mode of this volatile compound in crystals.

Crystals of Tl(hfac), prepared according to the method described by Hartman, Jacoby & Wojcicki (1970) and grown by sublimation, are thin pale yellow parallelepipeds. Unit-cell dimensions were determined from Weissenberg photographs and were later refined on a diffractometer. The intensities of reflexions were measured on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) monochromated by a graphite plate. A crystal of dimensions $0{\cdot}12\times0{\cdot}15\times0{\cdot}15$ mm was used, coated with polycyanoacrylate resin to prevent sublimation. Out of 3931 accessible reflexions below $2\theta=55°$, 1835 with $|F|>3\sigma$ were used for the refinement. During the data collection, the intensities of standard reflexions decreased exponentially with time to 85% of the initial intensities, owing to sublimation and radiation damage. All the data were corrected for this effect.

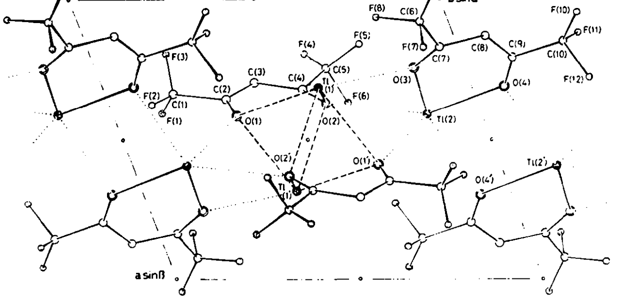

Fig. 1. A projection of the structure along the *c* axis.