Mössbauer and Other Evidence for the Existence of a New Modification of Tin(II) Fluoride

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DURING recent studies on the solid phases obtained from mixed aqueous solutions of tin(II) fluoride with other metal(II) fluorides, we found that a new crystalline modification of tin(II) fluoride could be obtained by evaporating solutions containing high concentrations of tin(II) fluoride. The known modification of tin(II) fluoride[1] crystallises in the monoclinic system but the form that we report is orthorhombic. All samples of the new modification analysed[2] correctly for SnF_2.

The Table describes the Mössbauer and infrared spectra, and the optical and X-ray-crystallographic data for both forms of tin(II) fluoride.

TABLE

Crystallographic and Spectroscopic Data for Tin(II) Fluorides

		Orthorhombic	Monoclinic
Optics ..		Colourless acicular crystals with straight extinction, low birefringence, positive elongation and $n = 1{\cdot}66$.	Colourless elongated monoclinic crystals with straight extinction, low birefringence, positive elongation and $n = 1{\cdot}70$.
Crystal data ..		$M = 156{\cdot}7$ orthorhombic $a = 15{\cdot}42 \pm 0{\cdot}04$, b $4{\cdot}74 \pm 0{\cdot}02$, $c = 10{\cdot}28 \pm 0{\cdot}02$ Å, U = $751{\cdot}9$ Å^3. $D_m = 5{\cdot}15 \pm 0{\cdot}05$ g./c.c. (by displacement of organic solvents) $Z = 16$, $D_c = 5{\cdot}33$ g./c.c. Space Group, $P2_12_12_1$ (D_2^4, No. 19). Cu–$K\alpha$ radiation single-crystal Weissenberg and rotation photographs about all three axes.	$M = 156{\cdot}7$ monoclinic $a = 13{\cdot}46$, $b = 4{\cdot}92$, $c = 13{\cdot}86$ Å, $\beta = 109{\cdot}5°$, U = $865{\cdot}2$ Å^3 $D_m = 4{\cdot}57$ g./c.c., $Z = 16$. $D_c = 4{\cdot}81$ g./c.c. Space Group $C2/c$ (C_{2h}^6 No. 15). Details from Reference 1.
Infrared Spectra ..		$\nu_1 = 575$ cm.$^{-1}$	$\nu_1 = 446$ cm.$^{-1}$
		$\nu_2 = 370$ cm.$^{-1}$	$\nu_2 = 350$ cm.$^{-1}$
Mössbauer			
δm.m./sec.	tin(IV) oxide source	$+ 1{\cdot}20 \pm 0{\cdot}05$	$+ 1{\cdot}60 \pm 0{\cdot}05$
	β-tin source	$+ 1{\cdot}20 \pm 0{\cdot}05$	$+ 1{\cdot}55 \pm 0{\cdot}05$
Δm.m./sec.	tin(IV) oxide source	$2{\cdot}20 \pm 0{\cdot}05$	$1{\cdot}80 \pm 0{\cdot}05$
	β-tin source	$2{\cdot}15 \pm 0{\cdot}05$	$1{\cdot}75 \pm 0{\cdot}05$

The Mössbauer spectra were obtained at 80°K with the tin(II) fluorides as absorbers and both β-tin and tin(IV) oxide as sources. An effect of about 15% was obtained with both sources and both absorbers. The chemical shifts (δ relative to α-tin) and the quadrupole splitting (Δ) obtained with the two sources are in good agreement for both absorbers. The spectrum of the monoclinic form is in agreement with results already published.[3]

The bonding in α-tin may be regarded as purely covalent bonding based on sp^3-hybridisation of the metal orbitals. Any increase in electrostatic character of the bonds in tin(II) compounds towards an ion of configuration $5s^2$ is shown by a corresponding increase in the positive chemical shift[4,5] of the Mössbauer spectra of the compounds. The smaller positive chemical shift in orthorhombic tin(II) fluoride shows that the tin–fluoride bond in this material is more covalent in character than that in the monoclinic modification. This result is in agreement with the infrared data, because the observed bonds in the infrared spectrum of orthorhombic tin(II) fluoride occur at a higher frequency than the corresponding bonds in the monoclinic form. On the basis of these arguments the orthorhombic form should be the α- and the

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[3] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, *Proc. Phys. Soc.*, 1962, **79**, 416.
[4] V. I. Goldansky, *Atomic Energy Review*, 1963, **1**, 45.
[5] M. Corday-Hayes, *J. Inorg. Nuclear Chem.*, 1964, **26**, 915.

monoclinic form the β-modification of tin(II) fluoride. This is confirmed by the observation that the orthorhombic form can be converted into the monoclinic form by heating.

The quadrupole splitting of the Mössbauer spectra of tin(II) fluorides must be due to the presence of a large electrical field gradient at the tin nucleus. This must be produced by a lowering of the symmetry of the charge distribution of the 5*p*-electrons. The greater quadrupole splitting found in orthorhombic tin(II) fluoride thus suggests that the environment of the tin atom is more distorted in this form than in the monoclinic modification.

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