A Tin-119 Mössbauer Study of Tin(II) Fluoride

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The ^{119}Sn Mössbauer parameters for the β, γ, and liquid phases of tin(II) fluoride previously reported by us are shown to be erroneous; the spectra from which these parameters were obtained were due to a hydrolysis product.

In 1981 we published the results of a tin-119 Mössbauer spectroscopic study of tin(II) fluoride in which we observed a discontinuity in the Mössbauer parameters at the α ⟶ γ phase transition.[1] We attributed the changes that were observed to the different phases of SnF_2 that have been identified by crystallographic means.[2,3] Recently we had occasion to repeat these measurements, and obtained quite different results.

In our earlier measurements the powdered SnF_2 sample was placed, under air, in an open, thin, pure copper container inside a Ricor vacuum furnace which was then connected *via* a rubber hose to an oil-diffusion pump and evacuated: the quality of the vacuum was not monitored. In the present study the sample was contained in a closed Teflon container which was sealed and loaded into the degassed furnace under high-purity dry nitrogen. The furnace was then connected *via* a copper tube to a Pyrex vacuum line where it was evacuated using a two-stage mercury-diffusion pump and a liquid-nitrogen cold trap. The Mössbauer spectra were recorded in the same manner as in our previous paper.[1] Data were obtained at 298, 378, 443, and 473 K but no spectrum could be recorded above the melting point of tin(II) fluoride. The results obtained are summarised in the Table. There are no significant changes in the parameters other than that of the recoilless fraction which undergoes a steady decrease as the temperature is raised. There is no discontinuity in isomer shift, quadrupole splitting, or recoilless fraction, contrary to our earlier claim.

In an attempt to understand the earlier result we repeated the experiment using an open container with a two-stage mechanical pump to evacuate the furnace. The spectra obtained for the α phase were the same as in the closed container but, at the α ⟶ γ phase transition temperature, a dramatic change in the spectrum occurred with a decrease in isomer shift and an increase in the quadrupole splitting. These parameters (Table) are very similar to those reported earlier.[1] On cooling the furnace the sample was found to have acquired a yellow colour and examination by *X*-ray powder diffraction showed it to be identical to Sn_2OF_2.[4] It would appear that, at the α ⟶ γ phase transition, hydrolysis occurs, presumably due to the presence of adsorbed water in the furnace due to inadequate pumping. Such hydrolysis has been observed previously during thermogravimetric analysis.[5] In all earlier experiments the samples were checked by *X*-ray powder diffraction at the end of the heating runs and, although we only detected phases due to tin(II) fluoride, it is now clear from the Mössbauer parameters that species similar to Sn_2OF_2 must have been present and that some hydrolysis had occurred.

Table. ^{119}Sn Mössbauer parameters for SnF_2 and its hydrolysis product

	T/K	δ*	Δ
		mm s^{-1} (±0.01)	
α-SnF_2	298	3.44	1.54
	378	3.42	1.52
γ-SnF_2	443	3.39	1.42
	473	3.39	1.40
SnF_2 hydrolysis product	443	3.04	2.20

* Isomer shift measured against $CaSnO_3$ at room temperature.

Conclusions

The earlier Mössbauer data reported for β, γ, and liquid SnF_2 are incorrect, there is no detectable discontinuity in Mössbauer parameters at the phase transition, and the β and γ phases have parameters which are indistinguishable, within experimental error, from those of α-SnF_2.

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