Tin-119 Mössbauer Spectroscopic Study of a Single Crystal of α-SnF₂ and Partially Oriented α-PbSnF₄

By **Thomas Birchall,** * **George Dénès,** and **Krzysztof Ruebenbauer,** Department of Chemistry and Institute for Materials Research, McMaster University, 1280 Main St. W., Hamilton, Ontario L8S 4M1, Canada
Jean Pannetier, Institut Laue-Langevin, 156 X–38042 Grenoble Cedex, France

A [119]Sn Mössbauer study of a single crystal of α-SnF₂ shows that the sign of eQV_{zz} in this compound is positive. Mössbauer data for α-PbSnF₄ are reported. Examination of the spectra from partially oriented crystallites of α-PbSnF₄ show that the sign of eQV_{zz} is also positive.

OVER the years there has been much discussion about the nature of the bonding in compounds of tin(II) [1] and more particularly in SnF₂.[2,3] These discussions have centred upon whether, or not, the dominant contribution to the quadrupole splitting arises from an appreciable p_z character in the non-bonding orbital of tin(II). This difficulty can be solved by determination of the sign of the quadrupole coupling constant. Application of an external magnetic field produces changes in the spectrum which allow the sign of the quadrupole interaction and hence eQV_{zz} to be determined.[4] Using this technique, the sign of eQV_{zz} was concluded to be positive for α-SnF₂.[5,6] Recently, X-ray crystallographic results [7,8] have shown that there are two tin environments in α-SnF₂ so that further confirmation of the sign of eQV_{zz} is called for.

An alternative procedure for determining the sign of the electric field gradient (e.f.g.) is to study the Mössbauer spectrum of an oriented single crystal. In this case, the two lines of a quadrupole doublet show anisotropy depending upon the orientation of the crystal with respect to the γ-ray direction. We report here the results of a study of a single crystal of α-SnF₂ which confirms the findings of Gibb *et al.*[6] that eQV_{zz} is positive in α-SnF₂.

Measurements on partially oriented samples of α-PbSnF₄ are also reported and show that the sign of the quadrupole coupling constant is positive in this compound too.

EXPERIMENTAL

Tin(II) fluoride was supplied by OSI. Single crystals of α-SnF₂ were obtained by cooling an aqueous solution of SnF₂ from 303 to 293 K at a rate of 3 K day⁻¹. The solution was acidified with HF to prevent hydrolysis and maintained in contact with a few pieces of tin metal to prevent oxidation to Sn⁴⁺. A single crystal of dimensions 12 × 8 × 2 mm was polished until it was thin enough to give an acceptable Mössbauer spectrum when it was attached with epoxy-resin to a thin aluminium sheet. The thickness was found to be 0.31(5) mm. The orientation of the single crystal was checked by X-ray diffraction and it was shown that the c* axis was normal to the aluminium sheet which was placed perpendicular to the γ-ray beam so that the γ-ray beam was parallel to c*.

Oriented samples of α-PbSnF₄ were prepared from solution as previously described.[9,10] The white solid was

filtered off by suction, washed with water, then dried under vacuum at room temperature while still on the filter paper. When completely dry the sheet of solid could be removed from the filter paper and cut to the appropriate size. Powder X-ray diffraction data of this sheet showed strong (001) reflections indicating that the crystallites (very thin sheets) were essentially oriented so that their c axes were normal to the plane of the sample and the a and b axes of the tetragonal cell were randomly distributed in the plane of these sheets. Several such sheets of oriented α-PbSnF₄ were stacked together in an aluminium holder having a tightly fitting cap which could be pressed closed. Subsequent X-ray and Mössbauer measurements confirmed that this produced a sample in which the crystallites were almost completely oriented.

After grinding, samples of α-PbSnF₄ showed a much lower degree of ordering of the crystallites than in the sample discussed above. The X-ray patterns of the oriented and random samples are shown in Figure 1. The spectrum of
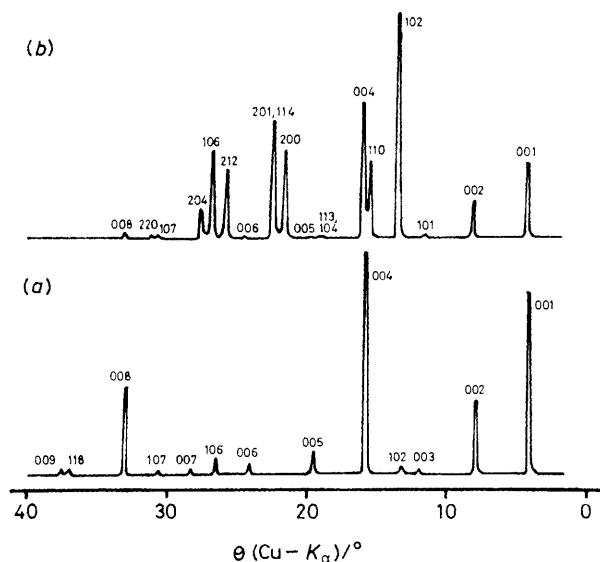

FIGURE 1 X-Ray powder patterns for α-PbSnF₄: (a) oriented sample, (b) after grinding

the oriented sample is dominated by the 00l reflections and only small peaks from the 102, 106, 107, and 118 reflections are visible. After grinding, the 00l reflections are suppressed while the 10l reflections are considerably enhanced in intensity together with many other reflections. However, it is apparent from this pattern that there is still not complete randomisation of the crystallites.

Mössbauer measurements and fitting procedures were made by methods which have already been described.[11,12] The Ca[119m]SnO$_3$ source was supplied by the Spire Corporation and all chemical shifts were measured with respect to CaSnO$_3$ as zero isomer shift. For these measurements the source linewidth and Debye–Waller factors were estimated, using a standard CaSnO$_3$ absorber, as 0.49 mm s^{-1} and 0.175, and these values were fixed in the fitting procedure; all other parameters were allowed to vary.

RESULTS AND DISCUSSION

α-SnF$_2$.—The [119]Sn Mössbauer spectrum of a single crystal of α-SnF$_2$ is shown in Figure 2. An asymmetric

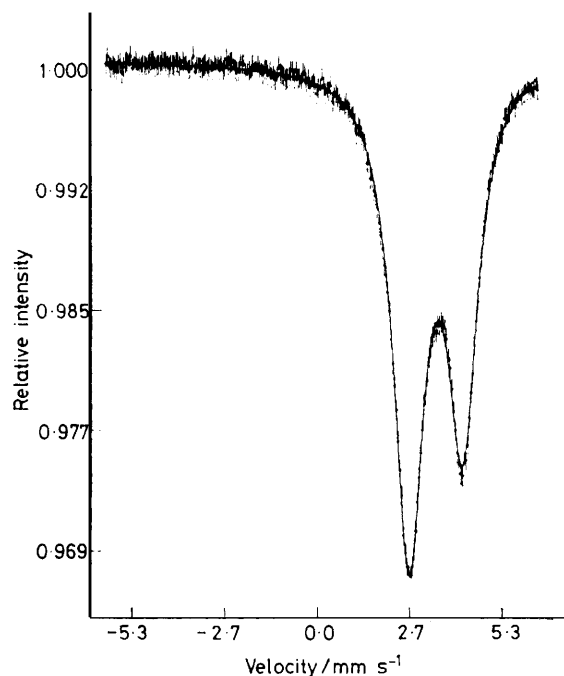**Figure 2** Tin-119 Mössbauer spectrum at 295 K of a single crystal of α-SnF$_2$, $\phi = 0$

quadrupole doublet results since the two transitions, which give rise to this spectrum, are dependent upon the angle θ between the γ-ray direction and V_{zz}, the principal axis of the e.f.g. tensor, which for α-SnF$_2$ is an average

value for the two crystallographically different tin sites that exist in the Sn$_4$F$_8$ unit. The spectrum of a powdered sample of α-SnF$_2$ does in fact show a slight asymmetry in the opposite sense to that for the single-crystal sample.[13] Therefore, it is clear that the asymmetry in the powder spectrum cannot be due to any crystallite orientation. This confirms our earlier conclusions [13] that there is indeed a small Goldanskii–Karyagin effect [14] in α-SnF$_2$.

The data from the computer fitting of the single-crystal spectra obtained from various orientations of the crystal are shown in the Table together with data obtained from a powdered sample for comparison. As the orientation of the c* axis of the single crystal is changed relative to the γ-ray beam, the relative intensities of the lines change in the manner expected, i.e. the line at high velocity increases in intensity relative to that at lower velocity. When the single crystal is placed perpendicular to the counting direction, that is with the c* axis parallel to the γ-ray beam, the computed angle, θ, between the effective V_{zz} and the γ-ray directions is found to be 70°. This calculation is made assuming that η is small and can be neglected. In this crystal orientation, the Sn$_4$F$_8$ ring units, which lie in the ac plane of the crystal, are parallel to the direction of propagation of the γ-rays. One might therefore have expected that the non-bonded electron pairs would be close to the ab plane and that θ would be 90°. However, Dénès et al.[8] have estimated that the non-bonding electron pairs from the two different tin atoms in the tetrameric unit do not lie exactly parallel to the ab plane, but rather make an angle of ca. 5° on both sides of this plane. If V_{zz} was along the axes of the non-bonded electron pairs then one would have perhaps expected that θ would be 90 rather than 70°. The fact that the angle is not far from 90° indicates that V_{zz} lies close to the direction of the non-bonded electron pairs and that they provide the dominant contribution to V_{zz}. The sign of the quadrupole coupling constant is therefore confirmed as being positive with the non-bonded electron pairs having considerable p_z character.

We have already indicated that, as the angle ϕ between the c* axis and the γ-ray direction is increased, the high-

Tin-119 Mössbauer data for α-SnF$_2$ and α-PbSnF$_4$ at 295 K

	δ	Δ	Γ	Ta	$g_{\parallel}$	$\phi^a/°$	$\theta^b/°$	χ^2/degrees of freedom
	mm s^{-1}							
(a) α-SnF$_2$								
Powder	3 430(3)	1.532(2)	0.294(7)	2.70(8)	1.15(2)			0.87
Single crystal	3.452(4)	1.566(6)	0.56(1)	0.70(1)		0	70.0(7)	0.27
	3.521(6)	1.584(6)	0.66(2)	1.10(2)		20	71.2(1.0)	0.76
	3.456(7)	1.572(11)	0.49(2)	0.97(3)		40	65.7(1.1)	0.84
(b) α-PbSnF$_4$								
Powder [c]	3.24(1)	1.56(2)	0.48(3)	0.36(2)	1.67(11)			0.74
[d]	3.24(1)	1.52(3)	0.64(6)	0.32(2)	1.04(9)			0.85
Oriented, not squeezed	3.24(1)	1.56(2)	0.48(3)	0.36(2)		0	42.7(1.4)	0.75
Squeezed	3.22(1)	1.57(2)	0.42(3)	0.86(4)		0	29.2(1.4)	0.84
	3.22(2)	1.59(2)	0.48(4)	0.73(5)		30	40.0(2.0)	0.72
	3.26(2)	1.63(3)	0.39(5)	0.71(7)		45	47.5(2.6)	0.75
	3.17(6)	1.68(12)	0.46(19)	0.12(4)		60	52.0(8.0)	0.80

[a] The angle between the γ-ray direction and the normal to the sample. [b] The angle between the γ-ray direction and V_{zz}. [c] Not mixed with inert material. [d] Ground with sugar.

velocity line in the SnF_2 spectrum increases in intensity relative to that at low velocity. However, the changes in intensity are not as great as would have been expected and it is clear that the computed angle, θ, between the effective V_{zz} and the γ-ray directions does not follow the angle ϕ. This can be accounted for in the following way. When ϕ is $0°$ the directions of the non-bonded electron pairs in the tetrameric unit lie either side of the ab plane and there are only two orientations of these lone pairs. The computed angle of $\theta = 70°$ is then an average angle for the V_{zz} axis with the γ-ray direction. As the crystal is tilted through an angle θ, the two crystallographic tin sites now give rise to four different orientations of the non-bonded electron pairs and the computed angle θ is an average of all of these. The situation is further complicated by the fact that we do not know the orientation of the crystal in the ab plane. If we were in fact rotating the single crystal about the b axis, to which V_{zz} must be almost parallel, then only a minor variation in the computed angle, θ, would be observed. However, changing the orientation of the crystal in the ab plane produced no noticeable difference in the spectra upon rotation of c^* relative to the γ-ray beam. The computer fitting of these relatively thick samples is rather difficult and is further complicated by the fact that there will be a slightly different Debye–Waller factor for each particular lone-pair orientation.

From the measured thickness of the single crystal, 0.31(5) mm, and the computed value for the thickness, Ta, we estimate the recoilless fraction for SnF_2 to be 0.034 at 295 K. This agrees well with the value previously reported.[15]

α-$PbSnF_4$.—It has not been possible, up to the present time, to grow single crystals of α-$PbSnF_4$, but the solid is known to have a tetragonally distorted fluorite structure.[16] The non-cubic environment of the Sn^{II} atom is confirmed by the ^{119}Sn Mössbauer spectrum. The spectrum of a partially oriented sample of α-$PbSnF_4$ appears as an asymmetric doublet having an isomer shift of 3.24 mm s^{-1} and a quadrupole splitting of 1.57 mm s^{-1} (Table). This asymmetry is increased if the sample is squeezed along the γ-ray direction (Figure 3). This behaviour is indicative of a preferred orientation of the crystallites and suggests that V_{zz} lies close to the γ-ray direction; the asymmetry is removed on thorough grinding of the sample with sugar. An angular-dependence study shows that the asymmetry lessens as the plane of the sample is tilted towards the γ-ray direction (Table). At $45°$, the two Mössbauer absorptions are almost of equal intensity and are equal at $60°$. The statistics for this latter spectrum are unfortunately very poor due to the increased thickness of the sample, which attenuates the γ-ray quite severely because of the high percentage of lead in the sample, and also because at this high angle some of the γ-rays do not even pass through the sample.

Computer analysis of the spectra results in a value for θ of $30°$ when the squeezed sample is perpendicular to the γ-ray beam and this value increases as the sample is

tilted out of the horizontal plane. As was noted above for the α-SnF_2 measurements, the change in the angle of orientation of the sample with respect to the γ-ray beam is not exactly reflected in the value for the computed angle θ. For example, a rotation of the sample by $30°$ only produces a change in θ of $11°$. This discrepancy is undoubtedly due to the mosaic nature of the sample since the different layers are not perfectly aligned with one another, and perhaps because the crystallites within
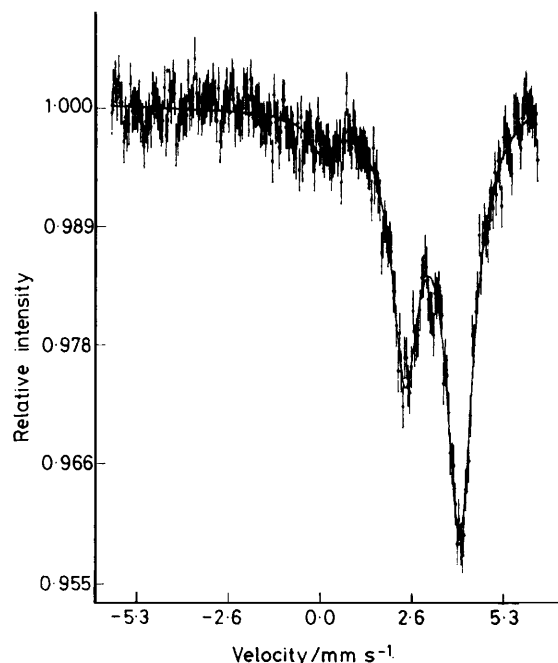

FIGURE 3 Tin-119 Mössbauer spectrum of an oriented sample of squeezed ($\phi = 0$) α-$PbSnF_4$ at 295 K

each layer are also disoriented with respect to one another. Because of the crystal type [16] it is unlikely that there will be more than one orientation of the non-bonded electron pair on tin, although this possibility cannot be ruled out at this stage.

These data, together with the X-ray results presented in the Experimental section, confirm the oriented nature of the sample and show that there is a positive value for the quadrupole coupling constant and, hence, a negative value for V_{zz}, which lies much closer to the γ-ray direction than does V_{zz} in α-SnF_2. On the basis of the crystallographic data [16] we would have expected V_{zz} to be along the c axis, i.e. $\theta = 0$. The fact that the experimental angle is $30°$ rather than 0 can be reconciled by the fact that we were not examining a single crystal, but rather only an assembly of partially oriented crystallites.

There is little that can be said about the magnitudes of the isomer shift and quadrupole coupling constant other than that they are very similar to those found for α-SnF_2. The isomer shift is slightly smaller, indicating a lower s-electon density at the tin nucleus than in α-SnF_2. This suggests a slightly higher participation of the $5s$ non-bonded electron pair in the bonding to the fluorines. One might have expected this to be reflected in an

increase in the quadrupole coupling constant but the opposite effect is noted. Presumably the valence and lattice contributions are in opposition and the structural differences between α-SnF$_2$ and α-PbSnF$_4$ are sufficiently great to negate the increase in valence contribution due to increased p_z character in the non-bonding electron pair discussed above.

It has not been possible to obtain any accurate estimation of the recoilless fraction for α-PbSnF$_4$, but from the computed values of Ta it would appear to be very similar to that for α-SnF$_2$. The rather low value of Ta for the sample oriented at 60° is due to the fact that at this angle some of the γ-rays bypass the sample completely.

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