A Tin-119 Mössbauer Study of the Phase Transitions in SnF_2

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Tin-119 Mössbauer spectra have been recorded for the three known phases of SnF_2. In the monoclinic α phase the two structurally different tin environments have Mössbauer parameters which are indistinguishable from one another (δ = 3.40 mm s^{-1}, Δ = 1.52 mm s^{-1}): a small Goldanskii–Karyagin effect is observed. A discontinuity in the temperature dependences of the Mössbauer parameters occurs at the α ⟶ γ phase transition, *ca.* 425 K. The high-temperature γ phase has δ = 3.15 mm s^{-1} and Δ = 1.95 mm s^{-1}, and exhibits a very large asymmetry in the intensities of the two lines of the quadrupole doublet. There is no such discontinuity at the γ ⇌ β second-order phase transition: progressive changes occur to give parameters for the β phase of δ = 3.11 mm s^{-1} and Δ = 2.10 mm s^{-1}, and a slightly smaller line asymmetry.

TIN-119 Mössbauer data for the common stable phase of tin(II) fluoride, α-SnF_2, have been reported by several groups of workers.[1-3] These data have been interpreted in terms of deviations of the bonding from a sp^3-hybridised tin atom which possesses three fluorines and a 5*s* electron pair in its immediate environment. The sign of eQV_{zz} was determined as positive and it was concluded that the dominant contribution to the electric-field gradient (e.f.g.) is due to appreciable p_z character in the non-bonding orbital of tin(II).[4] Since these measurements were made, *X*-ray analyses of single crystals of α-SnF_2 have been reported.[5,6] It was shown that α-SnF_2 exists in the form of cyclic tetramers, Sn_4F_8, in which there are two different types of tin(II) atoms. The co-ordination of one tin is that of a distorted tetrahedron, SnF_3E, where E represents a non-bonded electron pair, with one fluorine being terminal and the other two bridging: Sn–F 2.057(5), 2.102(5), and 2.156(4) Å. There are three longer Sn–F contacts at distances ranging from 2.671(5) to 3.221(5) Å. The second type of Sn is approximated by SnF_5E, where there is one short axial Sn–F bond [2.048(5) Å], four of intermediate length [2.197(5)—2.494(5) Å], and the sixth position of the octahedron is occupied by the non-bonded electron pair. A still longer contact [3.309(5) Å] is also present. In the light of these findings the previous interpretations of the bonding in α-SnF_2 require re-examination.

Crystallographic data now exist for two new phases of SnF_2, namely the β and γ forms, which have recently been identified.[7,8] The α form is transformed to the γ above *ca.* 425 K and is stable above this temperature to the melting point: it is metastable between 339 and *ca.* 425 K. The γ-SnF_2 phase is converted into the metastable β-SnF_2 phase at 339 K. A variety of methods have been used to investigate these different phases and the transformations that they undergo.[6-10] We present the results of a ^{119}Sn Mössbauer study of all three phases over a range of temperature.

EXPERIMENTAL

Tin(II) fluoride in the stable α, monoclinic, form was used as supplied by O.S.I. Mössbauer spectra were recorded on equipment which has already been described.[11] The measurements at elevated temperatures were carried out using a Ricor vacuum furnace supplied by Elscint Inc. with the samples held in a thin pure copper container. The furnace temperature was monitored and controlled by a Thor Cryogenics temperature controller. The Mössbauer source, $Ca^{119m}SnO_3$ supplied by the Spire Corporation, was maintained at room temperature for all measurements except that at 4.2 K when the source was also at 4.2 K. Spectra were fitted using the computer program of Ruebenbauer and Birchall.[12] For each series of measurements the source linewidth and Debye–Waller factor were estimated using a calibration standard of $CaSnO_3$ and these values (*ca.* 0.49 mm s^{-1}, *ca.* 0.19) were used in the appropriate series of measurements as fixed parameters. All other parameters were allowed to vary and the spectra were fitted using full transmission-integral procedures. The line asymmetry was allowed for in the fitting procedure using a variable parameter g_{11} which has been defined elsewhere.[12]

RESULTS AND DISCUSSION

α-SnF_2.—The ^{119}Sn Mössbauer spectrum of this phase has been recorded many times and a few representative references are listed.[1-3] The spectrum appears as a quadrupole-split doublet showing that there is an appreciable departure from cubic symmetry at the tin nucleus. In view of the recent crystallographic findings[5,6] that there are two tin environments, a closer examination of this material appeared warranted.

In our previous measurements on SnF_2 we have noted that the two components of the quadrupole-split doublet were never quite equal in intensity and better computer fits were obtained when the intensities were allowed to vary. This is illustrated in Figure 1(*b*) and is not a peculiarity of the particular sample; samples from other suppliers show the same feature. Another feature common to all samples examined is the presence of a small tin(IV) impurity. Its intensity (1—2% of the total absorption) is invariant after repeated temperature cycles showing that the tin(IV) contaminant is not being generated in our experiments. The relative Sn^{II} : Sn^{IV} ratios do change slightly with temperature because the Debye temperatures of the two species are not the same:

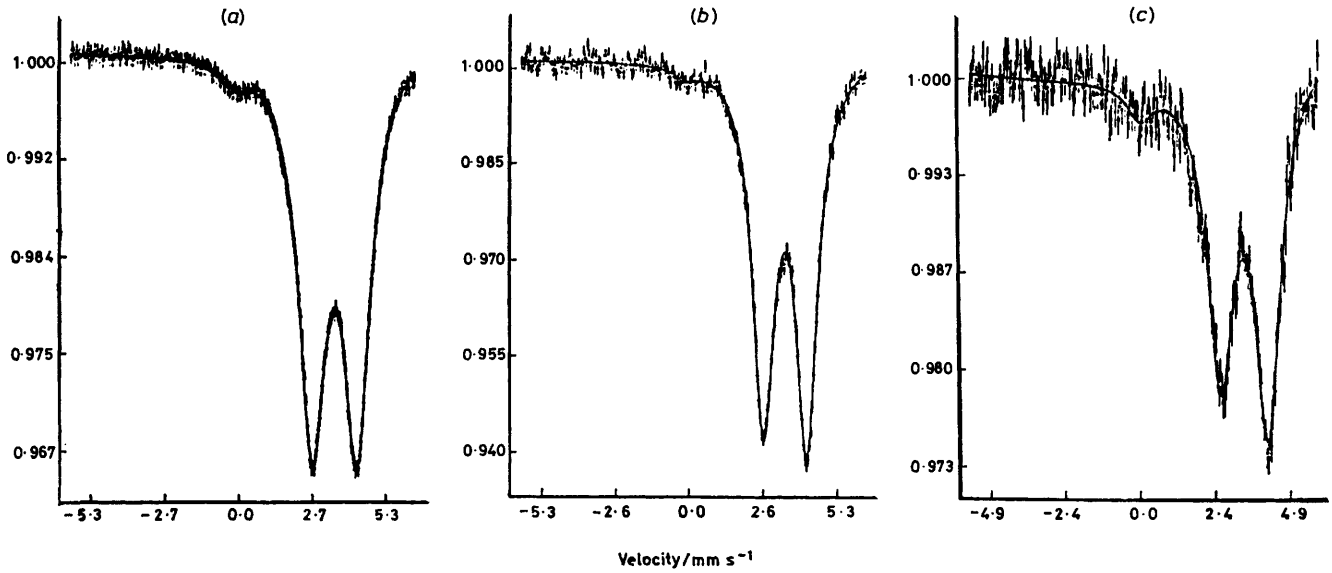


FIGURE 1 Tin-119 Mössbauer spectra of α-SnF_2 at 4.2 (*a*), 295 (*b*), and 398 K (*c*)

the presence of the tin(IV) contaminant is more apparent in the spectra measured at higher temperatures. The doublet asymmetry could arise for a variety of reasons: (*i*) impurities in the sample; (*ii*) two tin(II) sites having slightly different Mössbauer parameters; (*iii*) preferred crystal orientation of the sample in the Mössbauer holder; and (*iv*) the presence of a Goldanskii–Karyagin effect.[13] The only impurity that we have been able to detect is that due to tin(IV) species, probably SnO_2, which has been allowed for in the computer fitting. Since it is the higher velocity line which is the more intense, any other impurity would have to be a tin(II) species with an extremely high isomer shift, a most unlikely situation, and none is detected by other techniques.

It has been shown [5,6] that there are indeed two different tin atoms in the Sn_4F_8 tetrameric units, so that possibility (*ii*) would be a logical explanation for the line asymmetry. Each of the tin environments would be expected to give rise to a characteristic spectrum with slightly different isomer shifts and quadrupole-coupling constants in order for the high-velocity component of the experimental spectrum to be of greater intensity. This would necessitate the lower-velocity line being of greater width than that at higher velocity, and this is not the case. Several attempts were made to fit this spectrum to two overlapping doublets but we were unable to get any of these fits to converge. Our conclusion is that the two tin sites give rise to Mössbauer spectra which are indistinguishable. We will return to this point later.

Preferred crystal orientation is quite a common occurrence in molecular systems, a good example being $[Fe_2(CO)_9]$ where the ^{57}Fe Mössbauer spectrum can be quite asymmetric if suitable precautions are not taken.[14] The Sn_4F_8 tetramers, although not flat units, could perhaps stack in a preferred direction and give rise to the spectral asymmetry observed. Such preferred orientation can be tested in a number of ways. Neither changing the particle size by grinding the sample with a suitable matrix (Al_2O_3, sugar, boron nitride) nor changing the angle between the γ-ray beam and the normal to the absorber plane from 0 to 65° produced a change in the asymmetry, ruling out preferred crystal orientation as the cause of the asymmetry.

The final possibility for such asymmetry is a Goldanskii–Karyagin effect caused by vibrational anistropy in the crystal. This effect is temperature dependent and the spectral asymmetry should be reduced as the temperature is lowered. Figure 1 shows that the asymmetry has virtually disappeared at 4.2 K but increases as the temperature is raised. We conclude that the asymmetric nature of the doublet spectrum from α-SnF_2 is caused by anisotropy of the recoilless fraction. *X*-Ray crystallographic analysis [6] shows that the tin atoms do exhibit some anisotropic thermal vibration. It is interesting to note that the tin atoms are more strongly bound in the lattice along the tin–lone-pair axis as eQV_{zz} has been found to be positive [4] and we observe that g_{11} is greater than one. The relevant Mössbauer data for α-SnF_2 at various temperatures are summarized in the Table (*i*). The small decrease in isomer shift as the temperature is raised is probably associated with the second-order Doppler shift.

Little change in the quadrupole splitting is noted. The dimensionless absorber thickness, T_a, is directly proportional to the recoilless fraction f_a and decreases as the temperature is raised. We have not attempted to normalize all T_a values to the same amount of tin since some samples were mixed with inert material and others were not.

Since the computer analysis of the spectrum for α-SnF_2 only provided a one-doublet fit, when there are two crystallographic tin environments, we conclude that the

Tin-119 Mössbauer data for α-, β-, and γ-SnF_2 with deviations in parentheses.

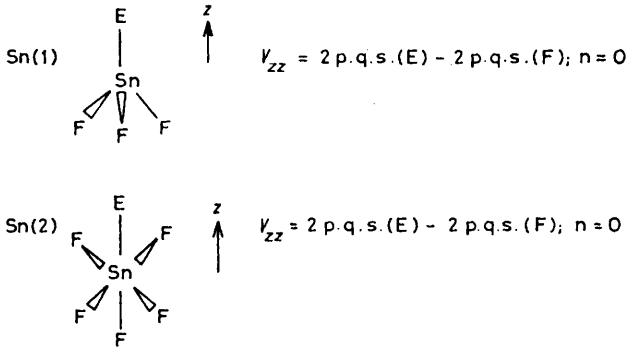
Linewidth Γ is the absorber linewidth (transmission-integral procedure used)

T/K	δ($CaSnO_3$)	Δ	Γ	T_a	χ^2/d.f.[a]	g_{11}
	mm s^{-1}					
(*i*) α-SnF_2						
4.2	3.467(3)	1.627(5)	0.65(1)	0.784(9)	0.219	1.04(2)
295 [b]	3.430(3)	1.532(3)	0.294(7)	2.70(8)	0.873	1.15(2)
323 [b]	3.417(8)	1.554(12)	0.34(2)	1.68(1)	0.778	1.16(6)
348 [b]	3.421(5)	1.530(6)	0.31(1)	1.321(6)	0.781	1.19(4)
373 [b]	3.417(6)	1.518(12)	0.32(2)	0.93(5)	0.658	1.16(4)
398 [b]	3.396(9)	1.530(18)	0.37(3)	0.63(4)	0.816	1.25(7)
295	3.386(8)	1.536(12)	0.55(2)	0.78(3)	0.858	1.07(4) [c]
295	3.413(7)	1.542(12)	0.43(2)	2.01(8)	0.977	1.08(5) [d]
(*ii*) α-, γ- and molten SnF_2						
295	3.451(3)	1.541(5)	0.39(1)	2.16(5)	0.787	1.19(3)
398	3.399(7)	1.536(12)	0.47(2)	0.67(2)	1.074	1.40(6)
433	3.176(7)	1.890(12)	0.61(2)	0.67(2)	1.096	1.62(6)
398	3.168(6)	1.950(12)	0.54(2)	1.20(4)	0.905	1.78(8)
453	3.146(7)	1.944(12)	0.52(2)	0.76(2)	0.791	1.73(8)
398	3.158(4)	1.980(6)	0.54(1)	1.31(2)	1.346	1.48(3)
433	3.146(5)	1.980(6)	0.57(2)	0.93(2)	0.919	1.58(5)
453	3.130(6)	1.968(12)	0.57(2)	0.78(2)	0.886	1.59(5)
453	3.113(7)	1.950(12)	0.59(2)	0.82(2)	0.999	1.55(6)
463	3.094(6)	1.938(12)	0.57(2)	0.64(2)	0.970	1.54(6)
473	3.088(6)	1.926(12)	0.58(2)	0.71(2)	0.881	1.56(6)
483	3.077(8)	1.896(12)	0.75(3)	0.58(1)	0.825	1.38(5)
488	3.093(9)	1.818(12)	1.03(3)	0.52(1)	0.861	1.22(4)
493	3.061(10)	1.776(12)	1.17(4)	0.54(1)	0.984	1.10(4)
503	3.033(12)	1.662(12)	1.29(4)	0.54(1)	0.984	1.00(3)
(*iii*) γ- and β-SnF_2						
343	3.142(5)	2.058(12)	0.65(2)	1.01(2)	0.781	1.46(4)
333	3.101(5)	2.112(12)	0.48(2)	1.65(5)	1.011	1.37(5)
323	3.107(4)	2.100(6)	0.47(1)	1.88(4)	1.069	1.32(3)
313	3.106(5)	2.112(6)	0.49(1)	1.36(5)	1.032	1.31(4)
303	3.114(3)	2.110(4)	0.44(1)	2.30(5)	1.288	1.38(3)
333	3.102(5)	2.094(6)	0.46(2)	1.73(5)	0.890	1.28(4)
294	3.118(3)	2.111(5)	0.430(3)	2.42(5)	1.428	1.27(3)

[a] d.f. = Degrees of freedom. [b] Same sample. [c] Horizontal. [d] 65° between the γ-ray beam and the normal to the absorber plane.

isomer shifts and quadrupole splittings for the two sites are the same within experimental error. The failure of the Mössbauer effect to distinguish between crystallographically distinct tin sites has also been observed in Sn_3BrF_5 [15] and SnI_2.[16] This can probably be accounted for by the presence of the non-bonded electron pairs which have a dominating influence upon the quadrupole splittings of the two tin sites, with the lattice contribution being negligible. This can only occur if there is considerable *p* character to the lone pair and hence an equivalent amount of *s* character to the Sn–F bonds. It is possible to explain qualitatively that both tin sites in SnF_2 have very close quadrupole-coupling constants using what is known as partial quadrupole splitting (p.q.s.) constants.[17] The e.f.g. has been calculated by Sams [18] for various structural models. If we apply these models to α-SnF_2 the result below is obtained where p.q.s. (E) and p.q.s. (F) are the contributions of a lone pair and a fluorine atom, respectively. This simple calculation shows that using the first co-ordination sphere in a point-charge approximation, both tin sites in α-SnF_2 have similar V_{zz} and therefore similar quadrupole-coupling constants.

γ-SnF_2.—Dénès [9] has shown that when α-SnF_2 is heated above 423 K it transforms to the γ form which is stable between the melting point, 488 K, and *ca.* 383 K and metastable between this temperature and 339 K. The Table (*ii*) contains Mössbauer data for a sample of SnF_2 recorded at a number of temperatures, the sequence of measurements being that shown from top to bottom. Heating the sample to 433 K produced significant changes in the spectrum; the isomer shift was reduced, the quadrupole splitting increased, and the spectrum became much more asymmetric. Lowering the temperature gave the same data except that T_a was noticeably increased over that for the α form at 398 K.



The changes that have occurred have clearly resulted in the tin atoms being much more tightly bound in the lattice. The spectra resulting from these two measurements were however not clean, suggesting that conversion was incomplete. Reheating to 453 K gave a much cleaner spectrum, Figure 2(*b*), which was fitted to an asymmetric doublet. While this spectrum is not partial reversion to the α form but this would have been clearly visible in the spectrum and does not show in the computer analysis. In addition, *X*-ray analysis of the β-SnF_2 sample does not show the presence of any other phase. In order to confirm that the asymmetry in the spectrum is indeed due to a Goldanskii–Karyagin effect a sample of β-SnF_2 was oriented at 45° to the γ-ray beam.

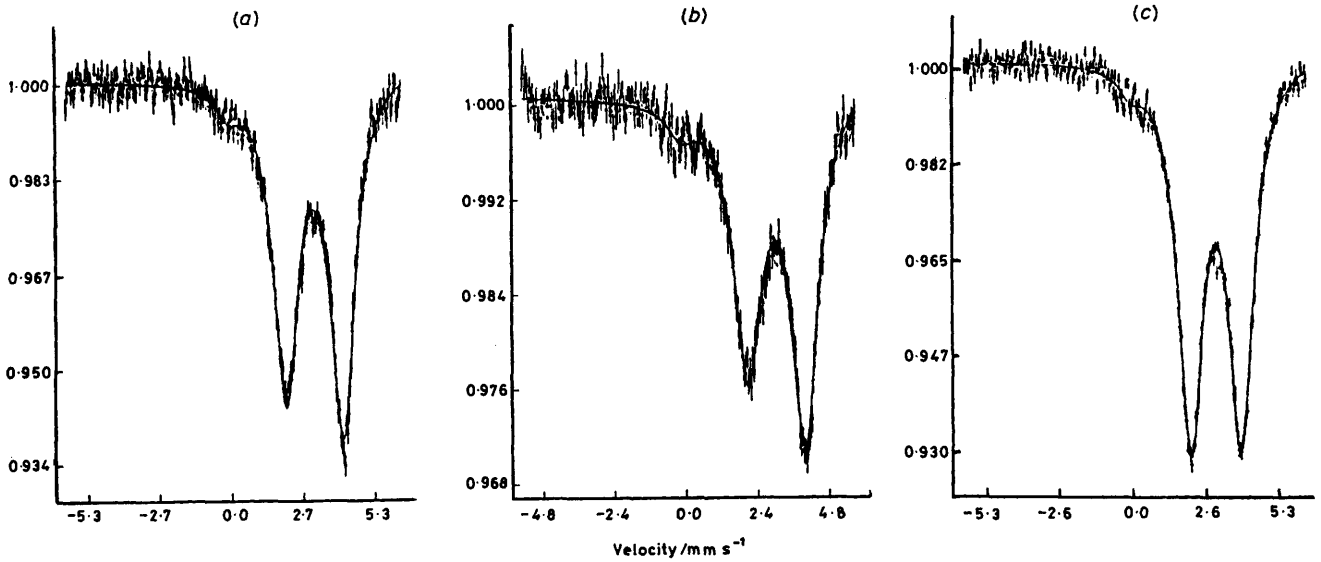


FIGURE 2 Tin-119 Mössbauer spectra of (*a*) β-SnF_2 at 303 K, (*b*) γ-SnF_2 at 453 K, and (*c*) liquid SnF_2 at 493 K

fitted perfectly from a visual point of view, there is no compelling reason to include another doublet due to α-SnF_2. Indeed *X*-ray and neutron-diffraction evidence shows that at this temperature all of the α-SnF_2 is transformed to the γ form.[7-9] Figure 2(*b*), then, is representative of γ-SnF_2. Again, raising the temperature produces the expected changes, *i.e.* the isomer shift, quadrupole splitting, and T_a all decrease. The ' Goldanskii–Karyagin ' g_{11} parameter begins to be reduced as the temperature is raised through the melting point of SnF_2 at 488 K. Surprisingly, 15 °C above the melting point a spectrum is still obtainable, which can be fitted to an equal-intensity doublet [Figure 2 (*c*)]. On cooling the sample after melting, an asymmetric doublet is once again obtained, confirming the absence of preferential orientation in the sample.

β-SnF_2.—At 339 K, γ-SnF_2 undergoes a second-order displacive transition to the β-SnF_2 form which is metastable.[7-9] As expected for this type of transformation, there is no discontinuity in the temperature dependence of the Mössbauer parameters, only a slight increase in isomer shift and quadrupole splitting as the temperature is lowered. The increase in quadrupole splitting presumably reflects the reorientation of the SnF_4E units on going from the γ to the β phase. These changes are summarized in the Table (*iii*).

The spectrum of β-SnF_2, Figure 2(*a*), is still quite asymmetric, although less so than the higher-temperature γ phase. In view of the metastable nature of this phase it is possible that the asymmetry could be caused by

No change in relative intensity of the two peaks was observed. An attempt was made to examine the spectrum at 4.2 K, as was done for the α-SnF_2, and while the peak intensities did become equal a careful examination showed that the quenched sample had been completely transformed to α-SnF_2.

The data for the three different phases are compared in

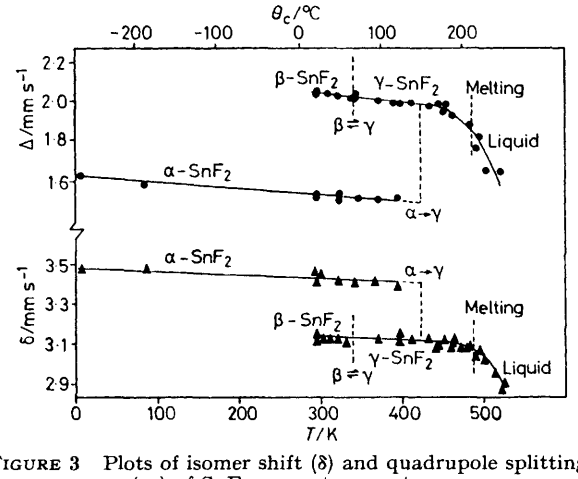
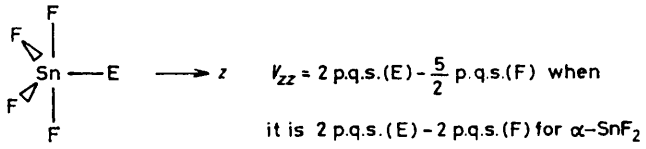


FIGURE 3 Plots of isomer shift (δ) and quadrupole splitting (△) of SnF_2 *versus* temperature

Figures 3—5. The lines drawn have not been least-squares fitted to the data but are included to enable the reader to follow the observed trends. Figure 3 shows the gradual decrease in isomer shift and quadrupole splitting with increasing temperature and illustrates the

dramatic changes which occur on going through the first-order $\alpha \longrightarrow \gamma$ phase transition. The *s*-electron density at the tin nucleus is reduced and the e.f.g., V_{zz}, increases. This indicates that the 5*s* electrons are playing a more active role in the bonds to fluorine and therefore the non-bonding pair of electrons acquires more p_z character. At the $\alpha \longrightarrow \gamma$ transition there is a drastic change, from a structure in which the tin atoms have SnF_3E and SnF_5E environments in a molecular Sn_4F_8 unit with fluorine bridging between units, to one in which the environment of tin is that of a trigonal bipyramid, SnF_4E, similar to that found in TeO_2.[19] The SnF_4E trigonal bipyramids are joined to one another in the form of Sn_6F_6 rings which are linked to give a strong three-dimensional network. The increase in quadrupole splitting at the $\alpha \longrightarrow \gamma$ phase transition can again be qualitatively explained using the models proposed by Sams.[18] On cooling the $\gamma \longrightarrow \beta$



transformation occurs and the SnF_4E trigonal-bipyramidal units rearrange with respect to one another but the polymeric nature of the structure is retained.[7-9] The changes in Mössbauer parameters reflect these progressive structural changes, and any minor changes in Sn–F bonds are compensated for by changes in sp_z character of the non-bonded electron pair.

These progressive changes are also seen in T_a. This parameter is directly related to the recoil-free fraction f_a of the sample which clearly increases (Figure 4) at

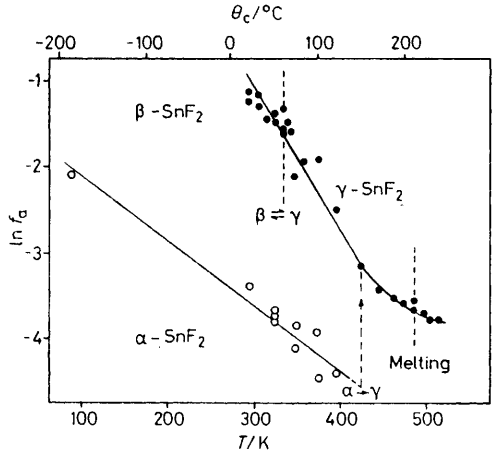


FIGURE 4 Plot of $\ln f_a$ *versus* temperature (f_a is the recoilless fraction for the SnF_2 absorber)

the $\alpha \longrightarrow \gamma$ transition as expected for a change from a molecular to a polymeric system. At structural phase transitions, a dip in the recoilless fraction is often observed which has been interpreted in terms of the existence of a soft lattice mode corresponding to an increase in the mean-square displacement of the atoms.[20]

No discontinuity of f_a is observed at the $\gamma \longrightarrow \beta$ transition of SnF_2 in agreement with our previous ^{119}F n.m.r. and neutron-diffraction results[8] which showed no anomaly in the Debye–Waller factor at the transition. Only a progressive increase of f_a with decreasing temperature is observed, reflecting a strengthening in the cross linking between the Sn_6F_6 rings. The deviation of $\ln f_a = f(T)$ (f_a = recoilless fraction for the SnF_2 absorber) from linearity around the melting point could be attributed to a slow hydrolysis of a part of the sample by traces of water giving black SnO [9] as an impurity which has a higher recoilless fraction,[21] and/or to the anharmonicity of the thermal vibrations which are much more pronounced at high temperature.

Figure 5 summarises all of the data on the asymmetric nature of the spectra that we have shown to be due to the

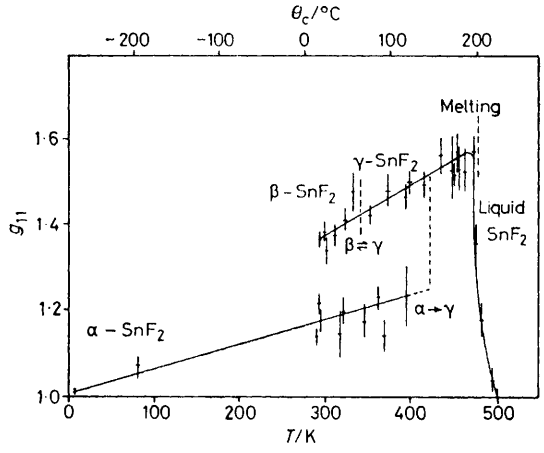


FIGURE 5 Plot of line asymmetry g_{11} of SnF_2 *versus* temperature

presence of a Goldanskii–Karyagin effect. The asymmetry in the case of the β and γ phases is much more pronounced than for α-SnF_2. The evidence appears to favour more pronounced anisotropy in the recoil-free fraction in the β and γ forms. Examination of the structural data[6,8] certainly shows that the near-neighbour bonds in the β and γ forms are more disparate in length than they are for the monoclinic α form. For example, it would be easier for the tin to move in the axial direction than in the equatorial direction of the trigonal-bipyramidal arrangement in γ-SnF_2 since the axial bonds are longer.

A most surprising feature of our investigations is the fact that we were able to get a Mössbauer spectrum of the liquid phase [Figure 2(*c*)]. This must mean that sufficient structure is retained in the liquid to maintain a reasonably high recoil-free fraction. Presumably the polymeric nature of γ-SnF_2 must be largely retained in the liquid phase for this to occur. Certainly it is well known that the vapour pressure of SnF_2 is very low.[22] In fact there is no measureable vapour pressure below 520 K.[23] There is also evidence for the presence of Sn_2F_4 and Sn_3F_6 units at 588 K although their vapour pressures are very low.[22]

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