Mössbauer Effect in Fluorotrimethyltin(IV)

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Synopsis. The angular dependent Mössbauer spectra of ^{119}Sn in needle crystals of fluorotrimethyltin(IV) were studied at 110 K. The principal axis of the electric-field gradient was observed at about 20° from the a axis. ^{19}F NMR spectra of the solid were also studied. From the temperature dependence of the linewidth, the activation energy for the motion of the F atom was estimated to be 6.7 ± 1.3 kJ mol^{-1}.

The X-ray diffraction[1] of fluorotrimethyltin(IV), Me_3SnF, showed that the molecule consists of Me_3Sn groups and F atoms arranged alternately in a chain-like manner along the a axis. Yasuda *et al.*[2] proposed a structure for Me_3SnF on the basis of the X-ray diffraction study. Mössbauer studies[3,4] confirmed a trigonal bipyramidal configuration of the tin atom, and related the intensity asymmetry of the doublet resonance spectrum to the intermolecular bonding, F–Sn···F. ^{1}H NMR study[5] supported the proposed structure from the viewpoint of motions of the Me_3Sn group. The purpose of the present study is to examine the validity of the proposed structure in more detail by means of the angular dependent Mössbauer spectra and ^{19}F NMR of the solid.

Experimental

The angular dependent Mössbauer spectra were obtained from 4—6 mm long needle crystals which were attached in the same direction with nail enamel on an absorber holder and kept at 110 K in a cryostat.

The measurement of the ^{19}F NMR was made at 13.00 MHz by a broad line NMR spectrometer (Japan Electron Optics Lab. Co., Ltd.). The linewidth was measured between maximum and minimum deflection points of the derivative tracing, using an amplitude which was narrow compared to the linewidth. The scanning rate was set to 0.8—2.0 G per second to avoid the saturation broadening.

Results and Discussion

Me_3SnF is an orthorombic crystal, space group Pmcn, with four molecules in a unit cell.[1] If the space group is reasonable, the unit cell comprises two equivalent sites and a 180° rotation about the a axis transforms one into the other. If the areas of the $\sigma(\pm1/2\rightarrow\pm1/2)$ and $\pi(\pm1/2\rightarrow\pm3/2)$ transitions are expressed by A_σ and A_π, and the recoilless fraction is assumed to be isotropic in the first approximation,[6] then, for a single-crystal absorber, the area ratio after Zory[7] is given by Eq. 1 as a function of the polar and azimuthal angles, Θ and Φ, of the incident γ-ray with respect to the crystal axes system O_{bca} (see Fig. 2).

$$\frac{A_\sigma}{A_\pi}=\frac{4\left(1+\frac{1}{3}\eta^2\right)^{1/2}-(3K-1+\eta K')}{4\left(1+\frac{1}{3}\eta^2\right)^{1/2}+(3K-1+\eta K')}, \quad (1)$$

where

$$K=(Z_b^2\cos^2\Phi+Z_c^2\sin^2\Phi)\sin^2\Theta+Z_a^2\cos^2\Theta+Z_bZ_c\sin^2\Theta\sin2\Phi,$$

$$K'=[(X_b^2-Y_b^2)\cos^2\Phi+(X_c^2-Y_c^2)\sin^2\Phi]\sin^2\Theta+(X_a^2-Y_a^2)\cos^2\Theta+(X_bX_c-Y_bY_c)\sin^2\Theta\sin2\Phi.$$

The symbol X_a, for instance, stands for the direction cosine of the angle between the axis of the electric-field gradient (EFG) and the corresponding crystal axis. In the case of needle crystals grown along the a axis, the area ratio is given by integrating Eq. 1 from 0 to 2π on Φ. Expressing each of the direction cosines as a function of the Euler angles (α, β, γ), the resulting area ratio is:

$$\frac{A_\sigma}{A_\pi}=\frac{8\left(1+\frac{1}{3}\eta^2\right)^{1/2}-(3I-2+\eta I')}{8\left(1+\frac{1}{3}\eta^2\right)^{1/2}+(3I-2+\eta I')}, \quad (2)$$

where

$$I=2\cos^2\beta\cos^2\Theta+\sin^2\beta\sin^2\Theta,$$

$$I'=\sin^2\beta\cos2\gamma(2\cos^2\Theta-\sin^2\Theta).$$

In the case of $\eta=0$, this equation becomes equal to that[8] obtained by integrating the transition probabilities.

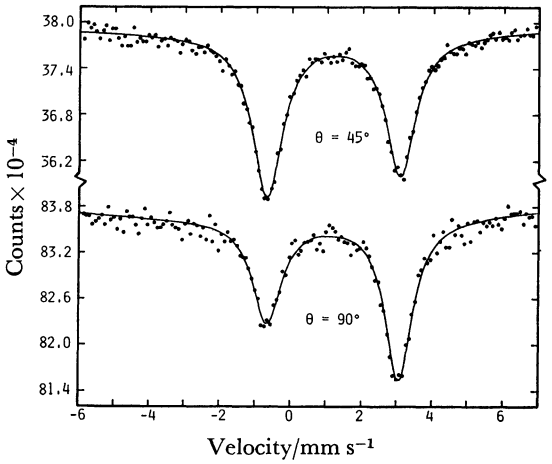

Fig. 1. The Mössbauer absorption spectra of Me_3SnF needle crystals at 110 K.

Figure 1 shows two typical spectra obtained for the γ-ray propagation direction at angles of 45° and 90° from the needle axis. In Fig. 2, the experimental values of the ratio of the high-energy absorption area to the low, A_H/A_L, are plotted against the angle Θ along with the theoretical curves calculated from Eq. 2, assuming that the molecule has C_{3v} symmetry, *i.e.*, $\eta=0$. The experimental points fit closely to the curve of $\beta=20°$.

Figure 3 shows the crystal structure proposed by Yasuda *et al.*[2] The Me_3Sn group forms a planar equilateral triangular structure and is inclined by 21° to the plane perpendicular to the a axis, and the Me_3Sn

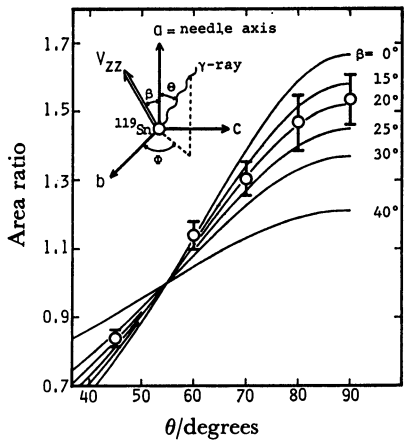

Fig. 2. The angular dependence of the area ratio for Me_3SnF needle crystals at 110 K.

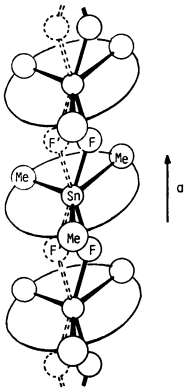

Fig. 3. Arrangement of Me_3SnF molecules.[2] F and F′ indicate the two possible possitions of the fluorine atom.

groups and F atoms are arranged alternately along the a axis. According to this structure, the molecular symmetry about the tin atom is not C_{3v}. However, it is expected that the departure from C_{3v} is not very great, and hence V_{zz} is approximately perpendicular to the plane of the Me_3Sn group, *i.e.*, the angle β is estimated to be about 21°. The value agrees well with our result, and the fact that A_H/A_L is equal to A_σ/A_π means that the σ transition lies at a higher energy than the π transition, *i.e.*, the sign of the principal component of the EFG tensor is positive, $V_{zz}>0$.

In order to explain the anomaly[1] in the electron-density distribution of the F atom, Yasuda *et al.*[2] predicted that the F atom would occupy two positions of minimum potential energy at room temperature, as

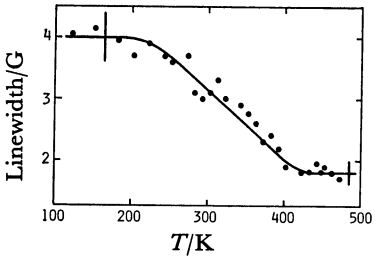

Fig. 4. The ^{19}F NMR linewidth as a function of temperature for Me_3SnF.

seen in Fig. 3. To examine the question of the motion of the F atom, ^{19}F NMR spectra were investigated in the temperature range 123—473 K. The linewidth is plotted as a function of temperature in Fig. 4. Limits of experimental error are shown at low and high temperatures by error bars in the figure. At low temperature the linewidth is constant at 4.0 G, presumably due to the rigid-lattice value. At temperatures around 450 K, the linewidth decreases to 1.8 G. The reduction of the linewidth seems likely to be caused by the switching motion of the F atoms. Accordingly, the molecular symmetry at the tin atom is expected to approach to C_{3v} by such motion. This is reflected also at the IR spectra[4] of the compound: the Sn–C asymmetric streching vibration occurs as a nearly singlet peak in the room-temperature spectrum, whereas in the liquid-nitrogen spectrum it is resolved into a doublet. The activation energy for the motion of the F atom was estimated to be 6.7 ± 1.3 kJ mol^{-1} on the basis of the theory[9] relating linewidth and correlation frequency.

References

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